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# More than 30 years with organic chemistry of sulfur

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# More than 30 years with organic chemistry of sulfur

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The author has been concerned with the organic chemistry of sulfur for more than thirty years, during which he has written 272 original papers and 22 other scientific articles. These are summarized on the occasion of his retirement from Saitama University.

**Keywords:** 1,3-benzodithioles; 1,3-benzodithiol-2-ylium salt; benzyne; elemental sulfur; thiophene and its oligomers; thiophene 1-oxides and 1,1-dioxides; thiophenetriptycenes; nonclassical thienothiophenes; sulfenic acids; *vic*-disulfoxides; dithiiranes; thiirene 1-oxides; 1,2-dithietes; sulfur monoxide; disulfur monoxide; thiosulfinyl compounds; sterically congested compounds; carbenium dithiocarboxylates



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18. Chemistry of thiosulfinyl compounds
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20. Chemistry of vic-disulfoxides
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## 1. Introduction

Immediately after I had been granted a PhD degree from the University of Tokyo in the early spring of 1974, under the supervision of Professor Osamu Simamura, I was included in the group of Dr Hiroshi Midorikawa of Riken (The Institute of Physical and Chemical Research), who graciously allowed me to have my own project without any restrictions. I decided to investigate the reaction of benzyne with carbon disulfide (*5*) because my PhD thesis was concerned with the chemistry of benzynes (*1–4*, *6*), and I was current on the most recent advances in their chemistry. This was my first encounter with the organic chemistry of sulfur. Since then I have been cultivating a friendship with this partner for more than 30 years. The chemistry of thiophene analogs of triptycene (Section 9) demonstrates the influence of a postdoctoral fellowship appointment with the P.D. Bartlett group in the United States (*25*).

My publications appearing during the period of 1970–2008 are summarized in this article. They include 272 original papers and 22 other scientific publications (accounts, reviews, chapter author of monographs, etc.). More than 20 publications written in Japanese were not included in this article. Each original paper is summarized in a compact way using a graphical abstract. In writing this article, I imagined that my work could be classified into several categories, but before long I discovered that this was not possible. As a result, my work has been divided into 25 smaller categories, contrary to my initial intentions.

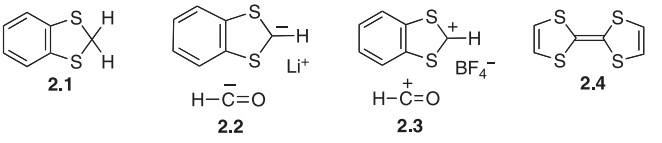
All the literature references of this article were taken from the list of my publications, and therefore publications of other chemists were not included.

The following abbreviations were used throughout this article: DBU for 1,8-diazabicyclo[5.4.0]undec-7-ene; DDQ for 2,3-dichloro-5,6-dicyano-*p*-benzoquinone; DMAD for dimethyl acetylenedicarboxylate; DMD for dimethyldioxirane; DME for dimethoxyethane; DMF for *N*,*N*-dimethylformamide; DMI for 1,3-dimethyl-2-imidazolidinone; LR for Lawesson's reagent [2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide]; MCPBA for *m*-chloroperbenzoic acid; PTAD for 4-phenyl-1,2,4-triazole-3,5(4*H*)-dione; TCNQ for 7,7,8,8-tetracyanoquinodimethane; TMEDA for tetramethylethylenediamine; and TTF for tetrathiafulvalene.

## 2. 1,3-Benzodithioles, 1,3-benzodithiol-2-ylium salts, and related compounds

The methylene hydrogens of 1,3-benzodithiole (**2.1**) are acidic enough to produce the stable carbanion **2.2**, which serves as a masked formyl anion, upon treatment with butyllithium. In addition, **2.1** forms the stable carbenium salt **2.3**, which serves as a masked formyl cation, by treatment with trityl tetrafluoroborate. Furthermore, in 1972 it was found that the charge–transfer salt

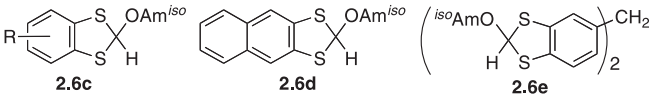
of tetrathiafulvalene (TTF) (**2.4**) with tetracyanoquinodimethane (TCNQ) shows unusually high solid state conductivity. Stimulated by these facts, the chemistry of 1,3-benzodithiole experienced much development in the period of 1975–1985.

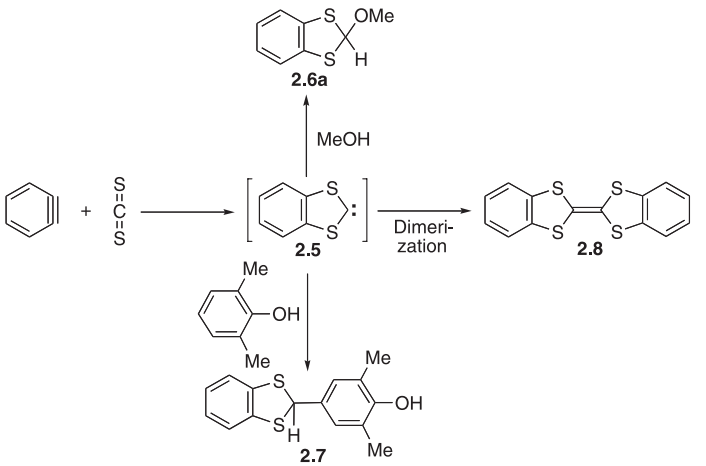



## 2.1. *Preparation of 1,3-benzodithioles*

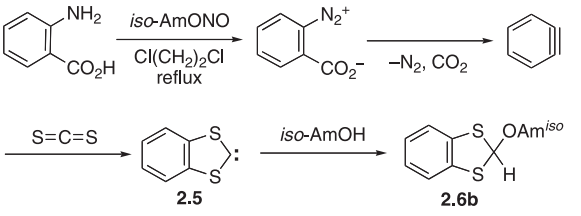
In 1973 the author found that benzyne, generated from a few sources, undergoes a 1,3-dipolar cycloaddition with carbon disulfide to give 1,3-benzodithiol-2-ylidene carbene (**2.5)** in solution (*7*). The carbene **2.5** was captured by a variety of trapping agents. For example, it was trapped by methanol and 2,6-dimethylphenol to yield 2-methoxy-1,3-dibenzothiole (**2.6a**) and 4-(1,3-benzodithiol-2-yl)-2,6-dimethylphenol (**2.7**), whereas, in the absence of a suitable trapping agent, **2.5** was dimerized to give dibenzotetrathiafulvalene (**2.8**) (*5*, *7*) (Scheme 1). A variety of substituted benzynes also underwent 1,3-dipolar cycloadditions with carbon disulfide (*24*, *53*).

Application of the above 1,3-dipolar cycloaddition brought us a one-pot synthesis of 2-alkoxy-1,3-benzodithioles on a 30–40 gram quantity (*8*) (Scheme 2). Thus, aprotic diazotization of anthranilic acid by isoamyl nitrite in boiling 1,2-dichloroethane produced benzenediazonium-2-carboxylate, which immediately decomposed to generate benzyne. Then benzyne reacted with carbon disulfide to give the carbene **2.5**, which was trapped by isoamyl alcohol, either produced from isoamyl nitrite or added beforehand, to give 2-isoamyloxy-1,3-benzodithiole (**2.6b**) in 51% yield (*8*). In this way, a variety of 2-alkoxy-1,3-benzodithioles and the related 1,3-dithioles, such as **2.6c**–**e**, were synthesized in reasonable yields (*24*, *53*).




Scheme 1.




Scheme 2.

## 2.2. *Preparation of 1,3-benzodithiol-2-ylium salts*

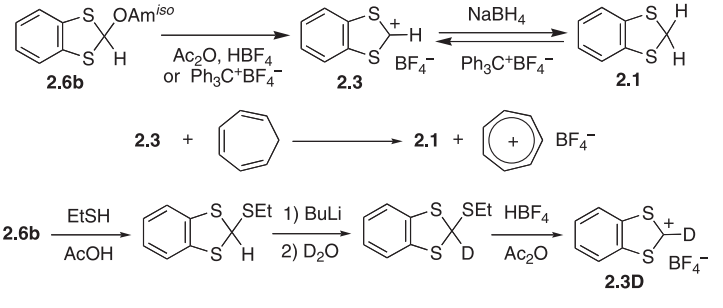
1,3-Benzodithiolylium salt **2.3** was prepared by treating **2.6b** with tetrafluoroboric acid in acetic anhydride (*13*, *16*) or by treating **2.6b** with trityl tetrafluoroborate in high yields (*17*) (Scheme 3) (*27*). Deuterated salt **2.3D** as a synthon for deuterio aldehydes was prepared from **2.6b** in good overall yield (*37*).

The 1,3-dithiol-2-ylium ion is iso-$\pi$-electronic with the tropylium ion and its aromaticity was discussed on the basis of the $^{1}H$ and $^{13}C$ NMR data (*21*). 1,3-Benzodithiole **2.1**, obtainable by reduction of **2.3** with $NaBH_4$, was converted to **2.3** by treatment of trityl salt (Scheme 3). In turn, cycloheptatriene was converted to the tropylium salt by treatment with **2.3** (*16*). Thus, even if the 1,3-dithiol-2-ylium ion is aromatic, its aromaticity is weaker than that of the tropylium ion.

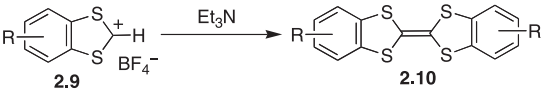
## 2.3. *Syntheses with 1,3-benzodithioles and 1,3-benzodithiol-2-ylium salts*

Dibenzotetrathiafulvalene **2.8** was prepared by thermolysis of the benzodithiole **2.6b** (*9*) and by treatment of the dithiolylium salt **2.3** with triethylamine (*13, 16*). Substituted benzotetrathiafulvalenes **2.10** were also prepared from dithiolylium salts **2.9** (*24*) (Scheme 4).

2-Isoamyloxy-1,3-benzodithiole (**2.6b**) dissociates to the 1,3-benzodithiol-2-ylium ion in acetic acid and reacted with a variety of nucleophiles to serve as its synthetic equivalent (*10*, *11*, *14*, *15*,

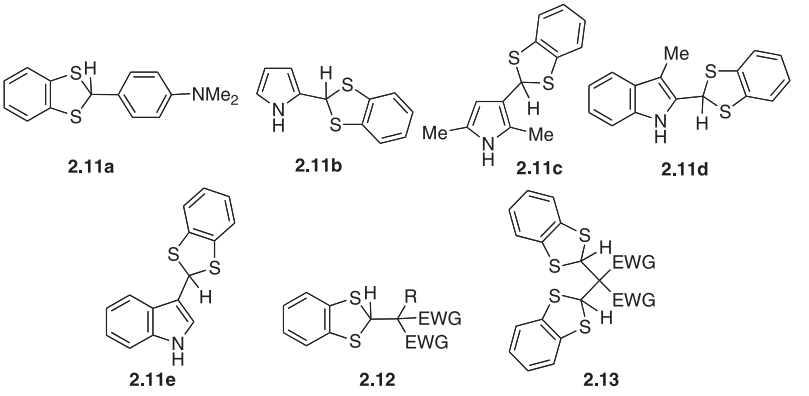



Scheme 3.




Scheme 4.

*18*, *23*, *28*). Thus it reacted with electron-rich aromatic compounds such as *N*,*N*-dimethylaniline, pyrroles, and indoles to give compounds possessing a masked formyl group, such as **2.11a**–**e**, in high yields. It also reacted with active methylene compounds in acetic acid to furnish compounds **2.12** in good yields (*15*). The use of two molar amounts of **2.6b** gave **2.13**.



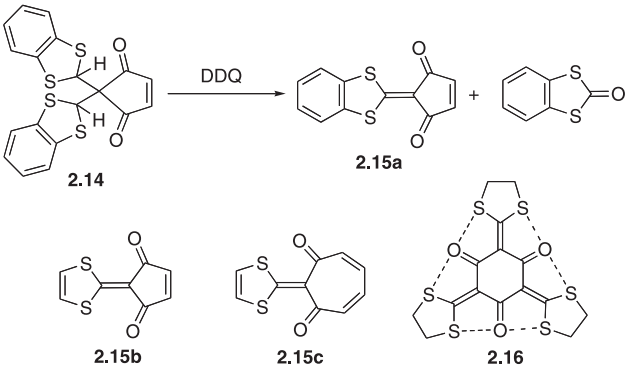

**2.11a** **2.11b** **2.11c** **2.11d** **2.11e** **2.12** **2.13**

Unexpectedly, the oxidation of **2.14** with DDQ gave **2.15a** (*18*) (Scheme 5). A number of related compounds such as **2.15b** and **2.15c** were synthesized (*18*, *19*) and their molecular structure was investigated by X-ray diffraction analysis, which revealed the presence of intramolecular attractive interactions (*31*, *48*) shown by dotted lines in the structure **2.16**.

The reaction of the dithiolylium salt **2.3** with a variety of nucleophiles was investigated (*16*). The reaction of 2,6-disubstituted phenols with an equimolar amount of **2.3** gave **2.17**, whereas the reaction of the phenols with two molar amounts of **2.3** produced **2.18** in high yields (*20*) (Scheme 6). Treatment of **2.18** with triethylamine furnished quinone methides **2.19** quantitatively. Quinone methides **2.20** and **2.21** were prepared in a similar way.

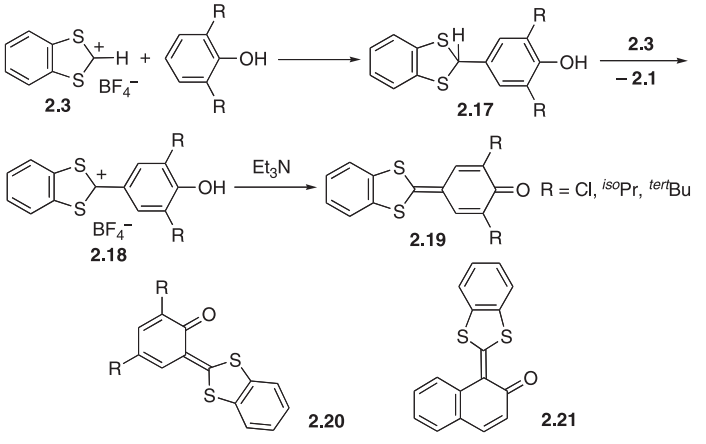
Application of the above synthesis to aromatic amines led to the preparation of quinone methide imines such as **2.23** and **2.24** (*34*) (Scheme 7).

$\alpha$-Oxo ketene dithioacetals **2.27** could be prepared in good yields by reactions of ketones with two molar amounts of **2.3** followed by treatment of the resulting **2.26** with sodium carbonate (*71*) (Scheme 8).

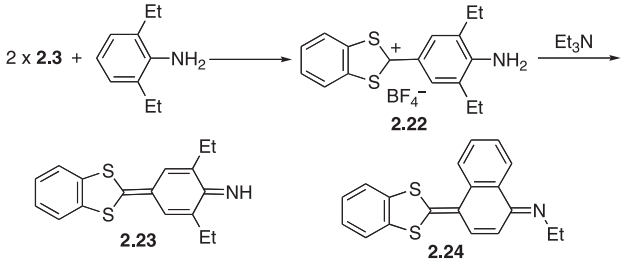



**2.14** **2.15a** **2.15b** **2.15c** **2.16**

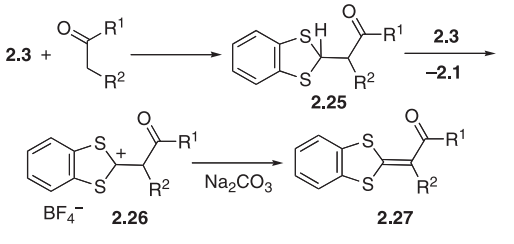
Scheme 5.




Scheme 6.

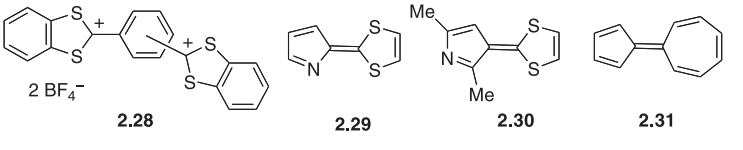



Scheme 7.

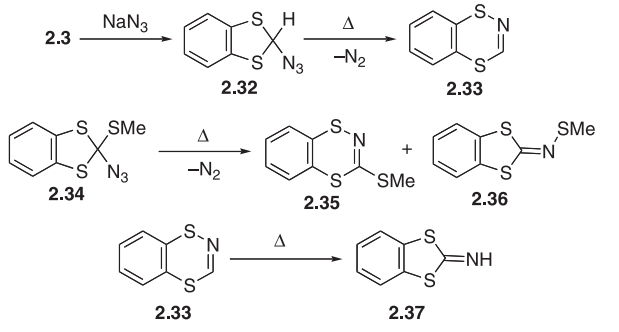



Scheme 8.

Bis(carbenium) salts **2.28** (*o*-, *m*-, and *p*-isomers) were synthesized and characterized (*22*). A range of compounds such as **2.29**, **2.30**, and the related derivatives, which are iso-$\pi$-electronic with sesquifulvalene **2.31**, were synthesized and characterized (*23*, *28*).




Thermolysis of the azide **2.32**, obtainable from **2.3** and sodium azide (*27*), produced benzodithiazine **2.33** in good yield, while that of the azide **2.34** afforded **2.35** (37%) and **2.36** (48%) (*33*, *46*) (Scheme 9). The dithiazine **2.33** underwent thermal rearrangement to 2-imino-1,3-benzodithiole (**2.37**), the rate of which was strongly dependent on the concentration of **2.33** (*47*).



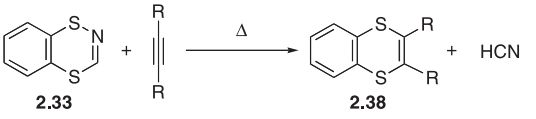
Scheme 9.

The dithiazine **2.33** underwent a sort of addition–elimination to give 1,4-benzodithiins **2.38** on reactions with electrophilic alkynes such as DMAD, ethyl propiolate, and benzyne (*39*) (Scheme 10).

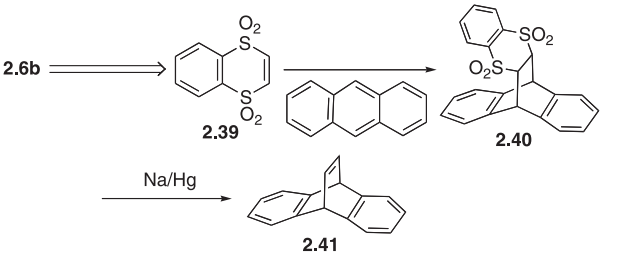
1,4-Benzodithiin tetraoxide **2.39**, prepared by using **2.6b** as the starting material, served as a strong dienophile and underwent Diels–Alder reactions with a variety of dienes. For example, it reacted with anthracene to give **2.40** in 93% yield, which was desulfurized to give dibenzobarrelene **2.41** (*58*) (Scheme 11).

1,3-Benzodithiol-2-ylidene carbenes **2.42**, generated either by thermolysis of benzodithioles **2.6c** or by heating benzodithiolylium salts **2.9** in boiling pyridine, reacted with elemental sulfur or selenium to give 2-thioxo- or 2-selenoxo-1,3-benzodithioles (**2.43** or **2.44**), in good yields, respectively (*44*) (Scheme 12).

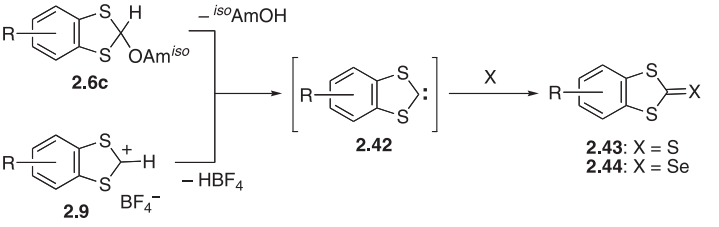
The crystal structure of the charge–transfer complex **2.45** of dibenzotetrathiafulvalene and tetracycanoquinodimethane that showed low electrical conductivity was analyzed by X-ray method (*36*). The reaction of the phosphorus ylide **2.46** with carbon disulfide was examined (*35*).



Scheme 10.

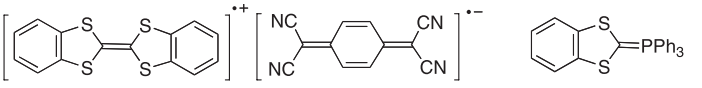


Scheme 11.




Scheme 12.

Base-catalyzed halogen dance of 2-bromotetrathiafulvalene was reported (*63*). The dithiolylium salt **2.3** was used for the oxidation of thiols to produce the corresponding disulfides (*38*).






## 3. Reactions of benzyne with sulfur compounds

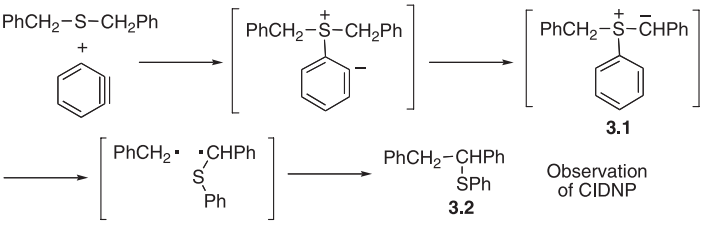
The 1,3-dipolar cycloaddition of benzyne with carbon disulfide and the reaction with benzodithiazine were described in Section 1.

### 3.1. *Reactions with acyclic sulfides*

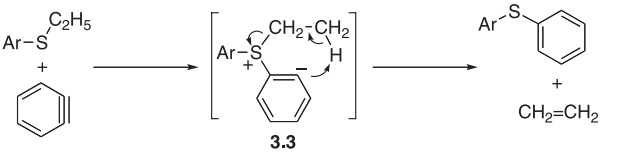
The reaction of benzyne with dibenzyl sulfide afforded sulfide **3.2** through Stevens rearrangement of the ylide intermediate **3.1** (*3*) (Scheme 13). When the reaction was monitored by $^1$H NMR, nuclear spin polarization in **3.2** was observed, thus suggesting that the rearrangement occurs through a radical dissociation–combination mechanism.

Benzyne, generated by aprotic diazotization of anthranilic acid, reacted with a range of aryl ethyl sulfide to give betaine intermediates **3.3**, which eliminated ethylene to furnish aryl phenyl sulfide in excellent yields (*42*) (Scheme 14).

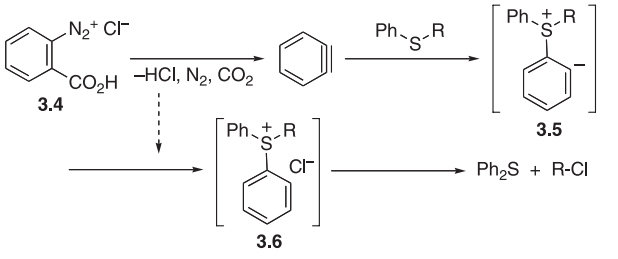
Benzyne, generated from 2-carboxybenzenediazonium chloride (**3.4**), reacted with alkyl phenyl sulfides to give diphenyl sulfide and alkyl chlorides in excellent yields (*59*) (Scheme 15). For this reaction, the initial adducts **3.5** are captured by hydrogen chloride, generated from **3.4**, to yield sulfonium chlorides **3.6**, which decompose to furnish the final products.




Scheme 13.

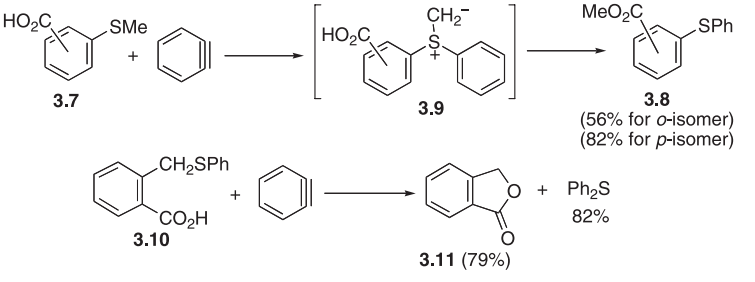



Scheme 14.




Scheme 15.



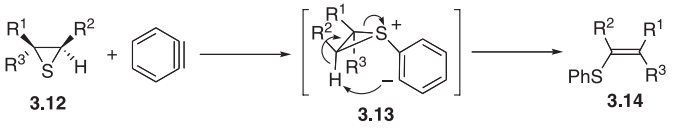



Scheme 16.

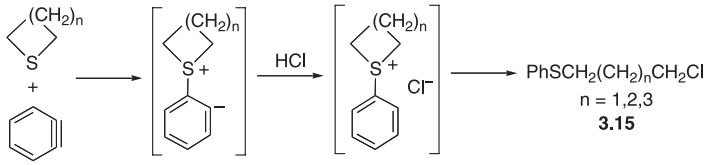
The reactions of benzyne with benzoic acids **3.7** afforded the methyl esters **3.8** probably through methylene transfer to the carboxyl group in the ylide intermediates **3.9** (*40*) (Scheme 16). The reaction with **3.10** produced lactone **3.11** and diphenyl sulfide.

### 3.2. *Reactions with cyclic sulfides*

Benzyne reacted with a series of thiiranes **3.12** to give phenyl vinyl sulfides **3.14** in good yields (*50*) (Scheme 17). The stereochemistry of the thiiranes is retained and the cleavage of the thiirane ring is regioselective. The reaction probably proceeds as shown below through the intermediate **3.13**.




Scheme 17.



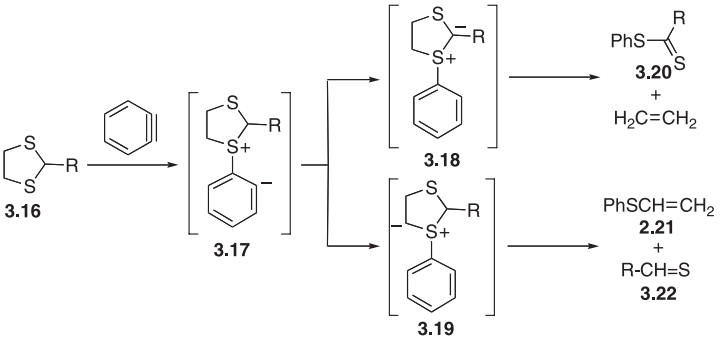

Scheme 18.

The C–S bond cleavage, observed for the reaction of benzyne with alkyl phenyl sulfides (Scheme 15), also took place for the reaction with thietane, thiolane, and thiane to give **3.15** in good yields (*59*) (Scheme 18).

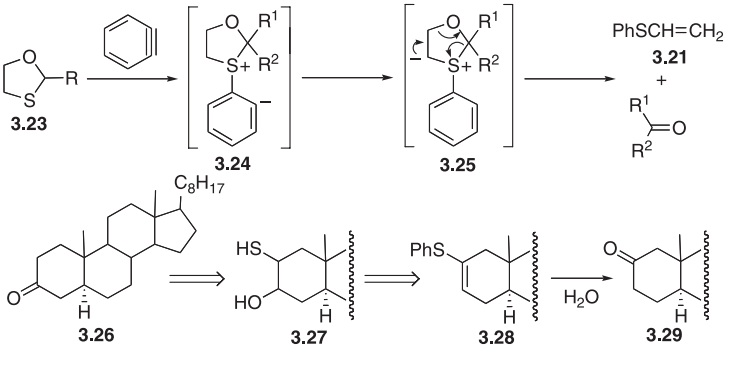
Betaine intermediates **3.17**, formed by reactions of 1,3-dithiolanes **3.16** with benzyne, collapsed in two ways to give ylides **3.18** and **3.19** (*49*) (Scheme 19). The former decomposed to dithioesters **3.20** and ethylene, and the latter to phenyl vinyl sulfide **3.21** and thioaldehydes **3.22**.

On the other hand, betaine intermediates **3.24**, formed by reactions of 1,3-oxathiolanes **3.23**, gave ylides **3.25** exclusively, even when $R^1$ or $R^2$ is hydrogen (*56*). Then **3.25** decomposed to






Scheme 19.




Scheme 20.

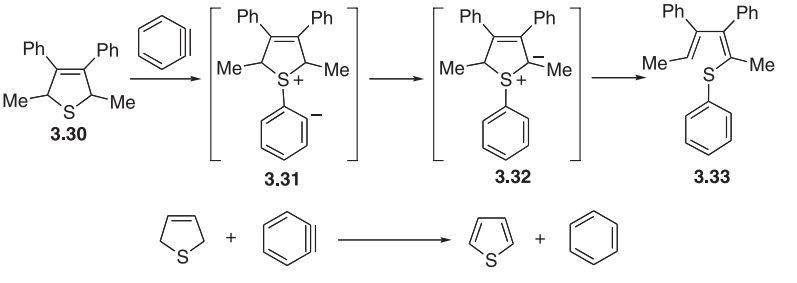
give **3.21** and ketones (Scheme 20). This reaction was applied to 1,2-carbonyl transposition. A representative example is the conversion of chorestan-3-one to chorestan-2-one, where the oxathiolane produced from **3.27** and cyclohexanone reacted with benzyne to give a phenyl vinyl sulfide **3.28** (Scheme 20).

The reaction of dihydrothiophene **3.30** with benzyne gave butadiene **3.33** in 91% yield (*91*) (Scheme 21). The reaction probably proceeds through intermediates **3.31** and **3.32**. The ring-opening of the ylide intermediate **3.32** may take place in a concerted manner. Application of the reactions to other dihydrothiophenes furnished a range of 1-phenylthio-1,3-butadienes in good yields. In all the cases, thiophenes, the dehydrogenation product of dihydrothiophenes, were formed in low yields (6–21%), probably due to the hydrogen transfer to benzyne (Scheme 21).

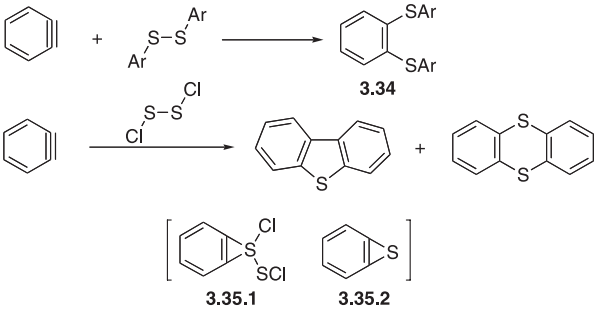
### 3.3. *Reactions with disulfides*

Benzyne inserted into the S–S bond of diaryl disulfides to give **3.34** in low yields (14–30%) (*66*) (Scheme 22). The reaction of benzyne with disulfur dichloride gave dibenzothiophene (8–10%) and thianthrene (26–35%) (*92*). The reaction might involve the initial formation of sulfurane **2.35.1** from which benzothiirene **3.35.2** (or the equivalent) is formed by ligand coupling to give dibenzothiophene and thianthrene by reactions with benzyne and dimerization, respectively (Scheme 22).






Scheme 21.




Scheme 22.

### 3.4. *Reactions with thiophene 1,1-dioxides*

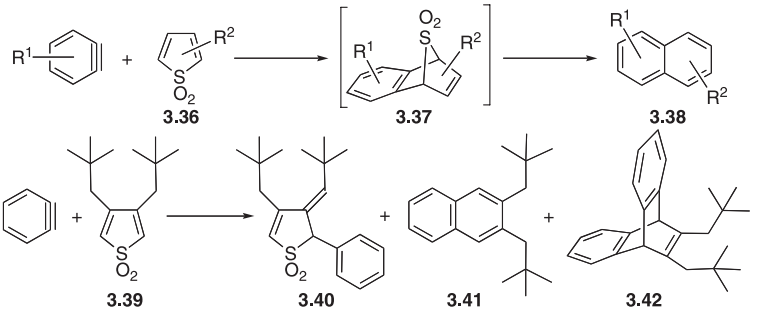
Thiophene 1,1-dioxides **3.36** are no longer aromatic and behave as a typical cyclic diene toward benzyne to give naphthalenes **3.38** by $SO_2$ extrusion in the intermediates **3.37** (*64*) (Scheme 23). Interestingly, the reaction of neopentyl derivative **3.39** gave the *ene*-reaction product **3.40** as the major product (68%), together with Diels–Alder products **3.41** (20%) and **3.42** (7.5%) (*148*) (Scheme 23).

### 3.5. *Reactions with thiocarbonyl compounds*

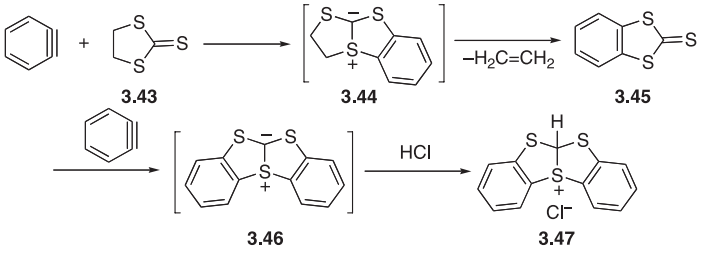
Benzyne undergoes 1,3-dipolar cycloaddition with carbon disulfide as described in Section 1. Benzyne also underwent a 1,3-dipolar cycloaddition with ethylene trithiocarbonate (**3.43**) to give sulfur ylide **3.44**, which decomposed to **3.45** and ethylene by a retro-1,3-dipolar cycloaddition (*160*, *163*) (Scheme 24). Supposedly compound **3.45** will react with benzyne to give another ylide **3.46**. Indeed, when the reaction of **3.45** with benzyne was carried out by using diazonium salt **3.4** as the benzyne source, the hydrogen chloride produced from **3.4** efficiently captured **3.46** to give sulfonium salt **3.47** in 91% yield. The reaction of **3.43** with excess **3.4** gave **3.47** directly in 68% yield.

1,3-Dipolar cycloadditions similar to that of **3.45** with benzyne also took place between **3.48** and diethyl acetylenedicarboxylate and between **3.49** and DMAD (*217*) (Scheme 25). These reactions occurred under high pressure at room temperature to give the same 1,3-dipolar cycloadduct **3.50**, and hence led to the formation of mixtures of **3.48** and **3.49**.

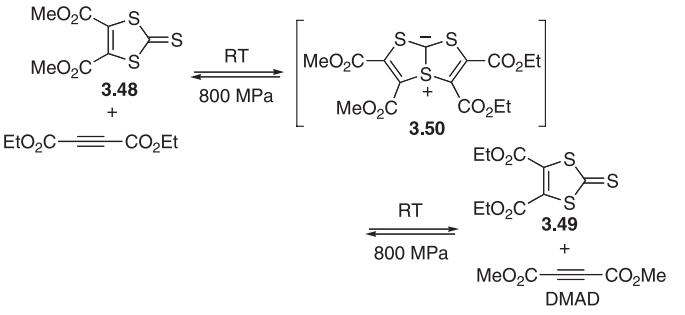





Scheme 23.

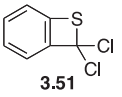



Scheme 24.




Scheme 25.

The reaction of benzyne with thiophosgene afforded three products presumably derived from the initially formed 2+2 cycloadduct **3.51** (*43*).



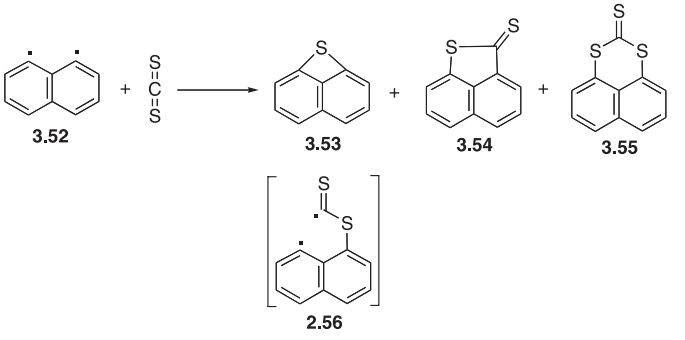

1,8-Dehydronaphthalene **3.52**, a sort of dehydroarene and singlet biradical, reacted with carbon disulfide to give compounds **3.53**, **3.54**, and **3.55**, though in low yields, probably through the biradical intermediate **3.56** (*32*) (Scheme 26).

### 3.6. *Reactions with elemental sulfur*

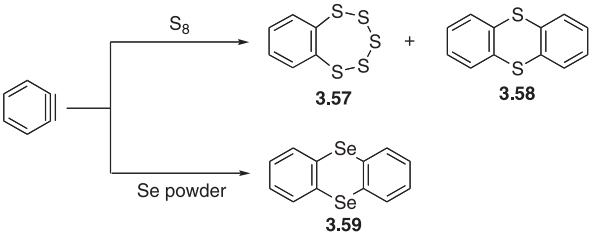
The reaction of benzyne with elemental sulfur gave pentathiepin **3.57** and thianthrene **3.58** in low yields, while the reaction with elemental selenium gave selenanthrene **3.59** in 26% yield (*74*) (Scheme 27).

### 3.7. *Miscellaneous*

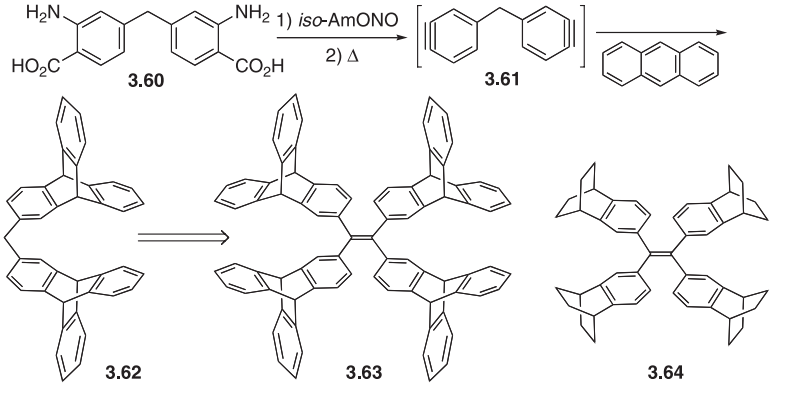
The equivalent of bis(benzyne) **3.61**, produced by aprotic diazotization of **3.60**, reacted with anthracene to furnish bis(triptycene) **3.62** in 46% yield (*53*) (Scheme 28). Alkene **3.63** was prepared from **3.62** to investigate the transannular $\pi$–$\pi$ interactions between the three benzene rings of triptycene (*65*). Compound **3.64** was also synthesized for comparison.




Scheme 26.




Scheme 27.




Scheme 28.



## 4. Organic chemistry of elemental sulfur

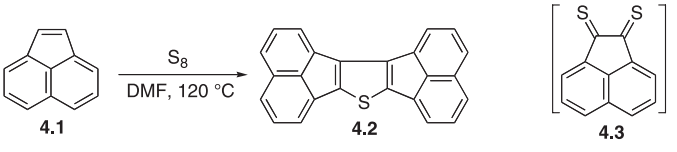
Reactions of 1,3-benzodithiol-2-ylidene carbenes with elemental sulfur and selenium to produce 2-thioxo- and 2-selenoxo-1,3-benzodithioles, respectively, were already taken up in Section 1. The reaction of benzyne with elemental sulfur was also described in Section 2.

### 4.1. *Reactions with alkenes*

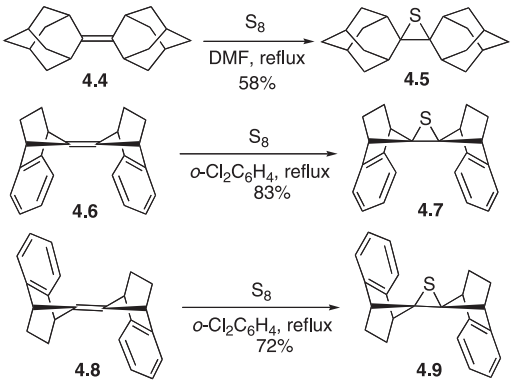
Heating acenaphthylene (**4.1**) with elemental sulfur in DMF gave thiophene **4.2** in 50% yield. The reaction might involve $\alpha$-dithione **4.3** as an intermediate (*94*) (Scheme 29).

Adamantylideneadamantane (**4.4**) reacted with sulfur to give thiirane **4.5** (*119*) (Scheme 30). Similarly, alkenes **4.6** and **4.8** (*216*) reacted with sulfur to give thiiranes **4.7** and **4.9**, respectively (*223*). The latter two reactions are stereospecific with retention of the original stereochemistry of the alkenes (see (*222*) for the stereochemistry of addition of bromine).

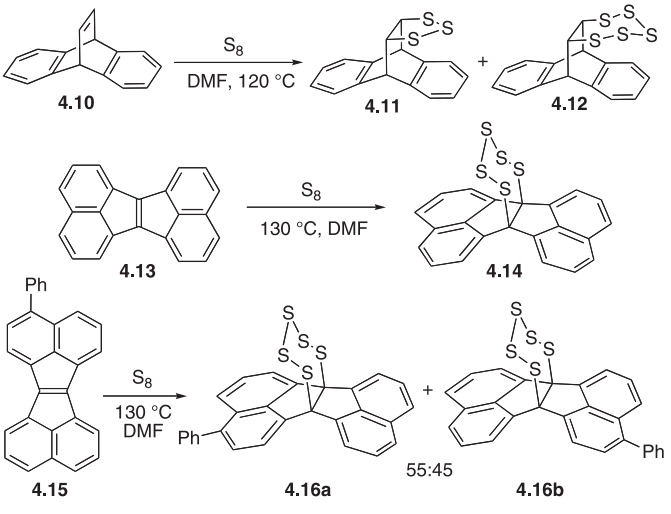
The reaction of benzobarrelene (**4.10**) with sulfur produced trithiolane **4.11** and pentathiepan **4.12** in 33% and 46% yields, respectively (*119*) (Scheme 31). The reaction of acenaphthylene derivative **4.13** with sulfur furnished pentathiepan **4.14** in 88% yield (*188*, *200*, *210*). A dynamic




Scheme 29.




Scheme 30.

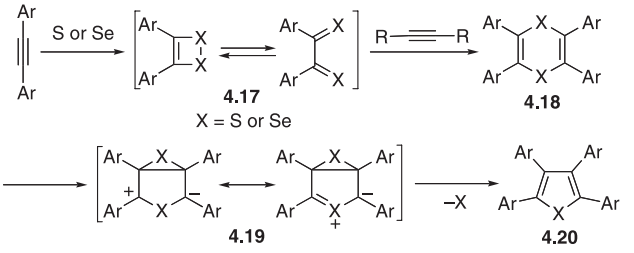



Scheme 31.

NMR analysis of **4.14** revealed that the two naphthalene rings are chemically nonequivalent up to 100°C. The pentathiepan ring of **4.14** adopts a chair conformation both in solution and crystals. In accordance with the above findings, the reaction of **4.15** with sulfur gave a 55:45 isomeric mixture of **4.16a** and **4.16b**, each of which was isolated in pure form.

### 4.2. *Reactions with alkynes*

Reactions of elemental sulfur and selenium with diarylacetylenes provided practical and good yield syntheses of tetraarylthiophenes (4X=S for **4.20**) and tetraarylselenophenes (X=Se for **4.20**), respectively (*75*, *122*, *131*) (Scheme 32). The reactions probably proceed through Diels–Alder reactions of the initially formed $\alpha$-dithione ($\alpha$-diselone) intermediates **4.17** with the starting diarylacetylenes and then sulfur (selenium) extrusion from the resulting 1,4-dithiins (1,4-diselenins) **4.18**. Intermediates **4.17** (X=S; 1,2-dithietes) and **4.18** (X=S; 1,4-dithiins) were isolated in a few cases (*75*, *129*, *133*).




Scheme 32.

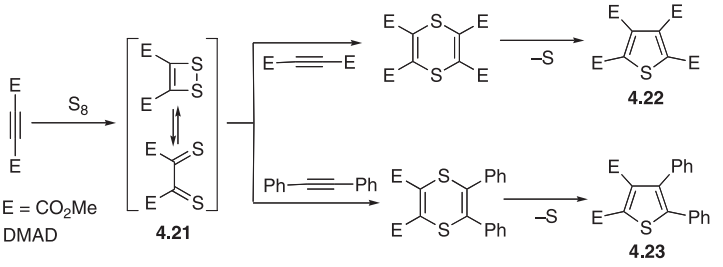
DMAD reacted with elemental sulfur to give thiophene **4.22** in a good yield (*74*) (Scheme 33). When the reaction was carried out in the presence of diphenylacetylene, thiophenes **4.22** and **4.23** were produced because the intermediate **4.21** reacted with both DMAD and diphenylacetylene (*75*).

Acetylenes that possess at least one bulky substituent, such as *tert*-butyl and 1-adamantyl, reacted with elemental sulfur to give thermally stable 1,2-dithietes **4.24** in reasonable yields (*129*, *133*) (Scheme 34). These 1,2-dithietes **4.24** are inert to 1,3-dienes because their double bond is sterically protected, and they also resist reacting with dienophiles because their isomerization to $\alpha$-dithiones are sterically inhibited due to increasing repulsion between substituents.

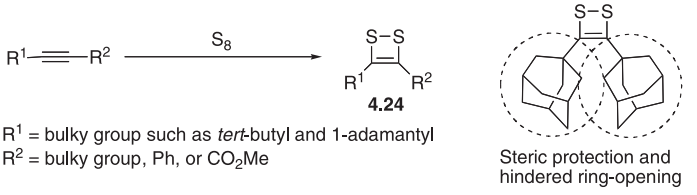
On the other hand, ynamines **4.25** reacted with sulfur to give dithioamides **4.26** in high yields (*133*) (Scheme 35). The diselenoamide **4.27** was also obtained by reaction with selenium and characterized (*145*).

A one-pot synthesis of thieno[3,2-*b*]thiophenes and seleno[3,2-*b*]selenophenes was developed (*144*) (Scheme 36). Preparation of **4.29a** and **4.29b** from **4.28** is a typical example, where **4.30** formed by dehydration of **4.28** is involved as the intermediate.

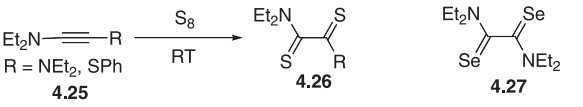




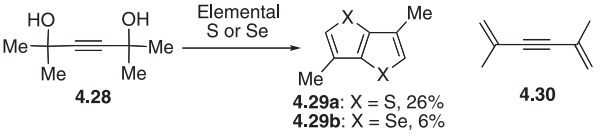

Scheme 33.




Scheme 34.




Scheme 35.




Scheme 36.

### 4.3. *Reactions with electron-rich aromatics*

Aromatics made electron-rich by two dimethylamino groups reacted with sulfur to give *N*,*S*-containing heterocycles (*166*) (Scheme 37). Thus, proton sponge **4.31** gave **4.32** (40%) and **4.33** (31%) when heated with sulfur in boiling *o*-dichlorobenzene.

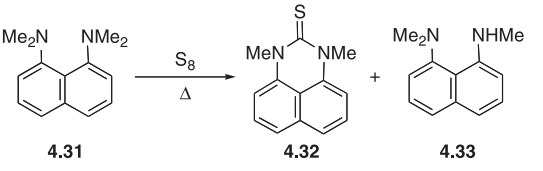
### 4.4. *Reactions with carbenes*

Reactions of 1,3-benzodithiol-2-ylidene carbenes with elemental sulfur and selenium to produce 2-thioxo- and 2-selenoxo-1,3-benzodithioles, respectively, were already taken up in Section 1.

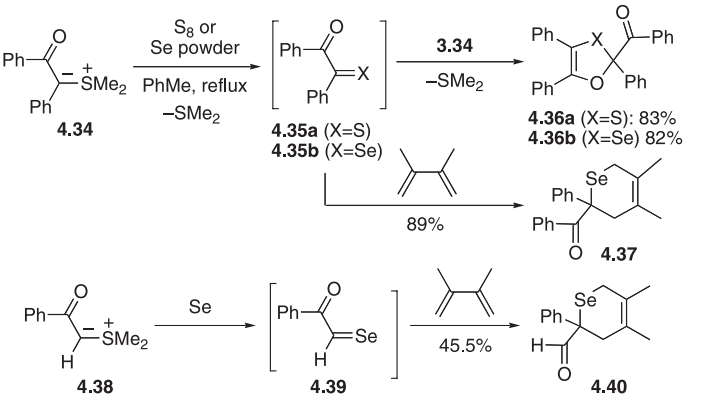
### 4.5. *Reactions with sulfur ylides*

A carbonyl-stabilized ylide **4.34** reacted with elemental sulfur and selenium to give **4.36a** and **4.36b**, respectively, where the initially formed $\alpha$-oxothione **4.35a** and $\alpha$-oxoselone **4.35b** reacted with **4.34** to lead to the final products (*57*) (Scheme 38). Other carbonyl-stabilized ylides reacted similarly. The thione and selenone intermediates were satisfactorily trapped by Diels–Alder reactions with 1,3-dienes. For example, selenoketone **4.36b** and selenoaldehyde **4.39** (produced from **4.38)** were trapped by 2,3-dimethyl-1,3-butadiene to give **4.37** and **4.40**, respectively (*78*) (Scheme 38).

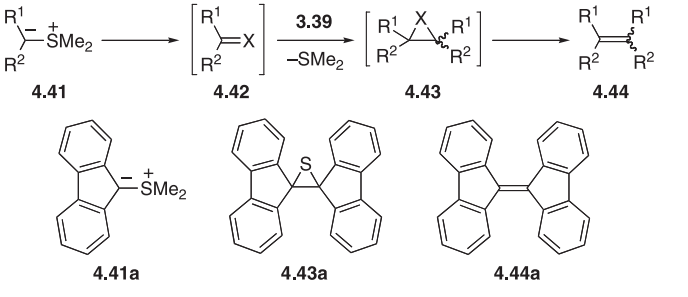
Other stable sulfur ylides **4.41** underwent both sulfur- and selenium-catalyzed decomposition to give alkenes **4.44** (*81*) (Scheme 39). The reaction involves **4.42** and **4.43** as the intermediates. In the case of ylide **4.41a**, thiirane **4.43a** was isolated in 67% yield in addition to alkene **4.44a** in 26% yield.




Scheme 37.




Scheme 38.

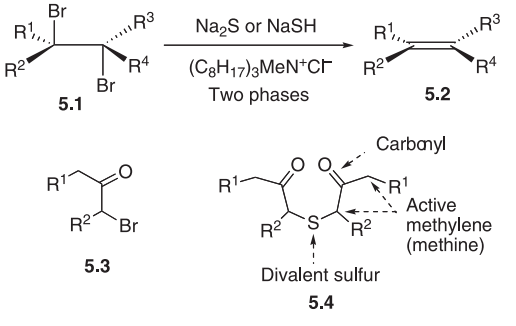



Scheme 39.

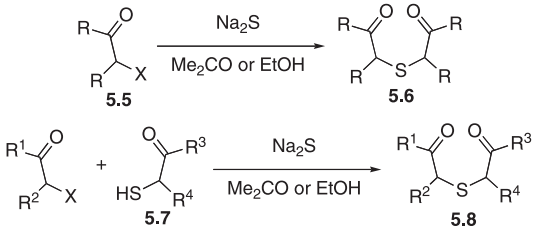


## 5. Diketo sulfides and synthetic applications

In 1983 we found that *vic*-dibromides **5.1** are debrominated to furnish the corresponding alkenes **5.2** by aqueous sodium sulfide using trioctylmethylammonium chloride as the phase transfer agent in a two-phase mixture (*45*) (Scheme 40). When the present system was applied to the debromination of $\alpha$-bromoketones **5.3**, diketo sulfides **5.4** were produced in most cases, whereas the expected reduction took place only when $R^2$ is phenyl (Scheme 40). The diketo sulfides **5.4**, accidentally obtained in this way, possess the three functional groups; carbonyl, active methylene (methine), and divalent sulfur. In addition, these are suitably arranged for the intramolecular transformations. Thus we started projects that use **5.4** as the starting materials for organic syntheses.




Scheme 40.




Scheme 41.

Incidentally, the preparation of diketo sulfides does not require the use of phase transfer agents. Thus symmetrically substituted derivatives **5.6** were easily obtained by treatment of $\alpha$-haloketones **5.5** with sodium sulfide in aqueous acetone or ethanol (*54*) (Scheme 41). Preparation of unsymmetrically substituted ones **5.8** were rather troublesome since it required unstable $\alpha$-mercaptoketones **5.7** as one of the starting materials.

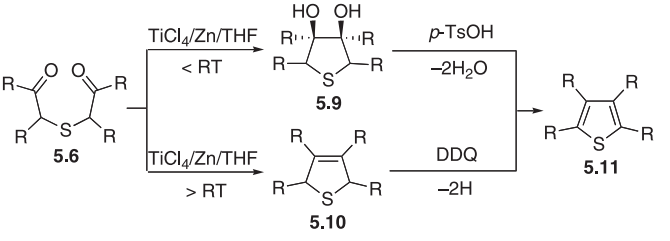


### 5.1. *New thiophene synthesis*

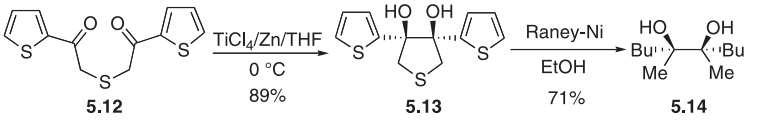
A newly developed thiophene synthesis with diketo sulfides **5.6** as the starting material is shown in Scheme 42. Treatment of **5.6** with a low valent titanium reagent prepared from $TiCl_4$ and Zn afforded thiolanediols **5.9** in good yields when the reaction was carried out around 0 °C (*55*), while it afforded more reduced dihydrothiophenes **5.10** when done at room temperature or higher temperatures (*54*). Both **5.9** and **5.10** were converted to thiophenes **5.11** by acid-catalyzed dehydration and DDQ oxidation, respectively. This new thiophene synthesis is particularly useful to prepare 3,4-disubstituted derivatives that are otherwise difficult to prepare, as described in Section 10.

The two hydroxyl groups of the thiolanediols **5.9**, prepared from **5.6**, are *cis* to each other without any exception (*55*, *70*). The findings were applied to the stereoselective synthesis of a range of 1,2-diols (*70*). One example is given in Scheme 43.

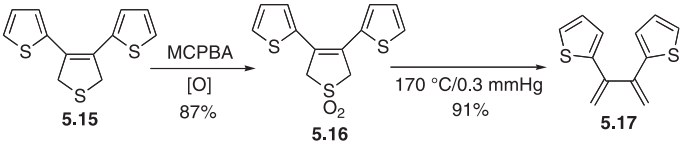
The reaction of dihydrothiophenes **5.10** with benzyne that gave 1,3-dienes was described in Section 3. Dihydrothiophenes **5.10** were also converted to a series of 1,3-dienes through oxidation




Scheme 42.




Scheme 43.




Scheme 44.

and thermolysis (*61*). For example, thermolysis of the sulfolene **5.16**, obtainable from **5.15** by MCPBA oxidation, furnished the diene **5.17** (Scheme 44).

### 5.2. *New 1,4-dithiin synthesis*

Thionation of the diketo sulfides **5.6** with $P_4S_{10}$ or LR gave 1,4-dithiins **5.19** in 40–80% yields through dehydration of the thioketone intermediates **5.18** (*51*; see also *89*) (Scheme 45). Among 1,4-dithiins synthesized, 2,6-diphenyl-1,4-dithiin was found to exist in two polymorphic forms (*259*).

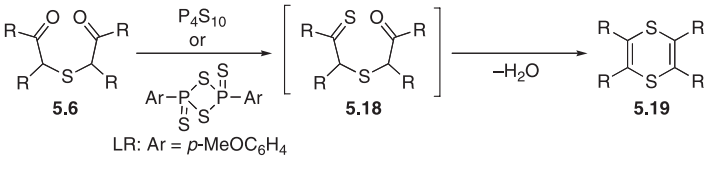


### 5.3. *Synthesis of pyridazines*

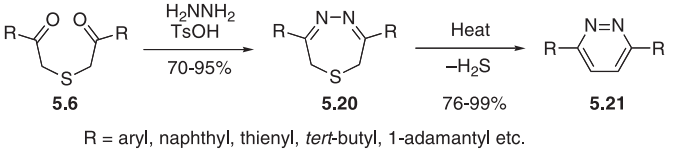
Diketo sulfides **5.6** condensed with hydrazine to give **5.20**, which gave pyridazines **5.21** by extrusion of hydrogen sulfide when heated in boiling diethylene glycol (*95*) (Scheme 46).

### 5.4. *Intramolecular condensation*

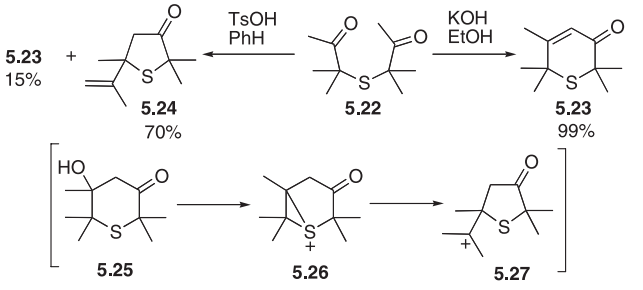
Diketo sulfides such as **5.22** undergo intramolecular aldol condensation (*72*) (Scheme 47). Thus, the KOH-catalyzed aldol condensation of **5.22** gave thiopyranone **5.23**, while the TsOH-catalyzed condensation afforded thiolanone **5.24**, in addition to **5.23**, through intermediates **5.25**, **5.26**, and **5.27**.




Scheme 45.




Scheme 46.




Scheme 47.

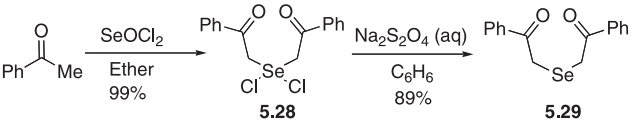
## 5.5. *Diketo selenides and the syntheses*

Diketo selenides are also easily obtainable (*68*). For example, the selenide **5.29** could be prepared by the reaction of acetophenone with commercially available selenium oxychlorde, followed by reduction of the resulting selenurane **5.28** in good overall yield (Scheme 48).

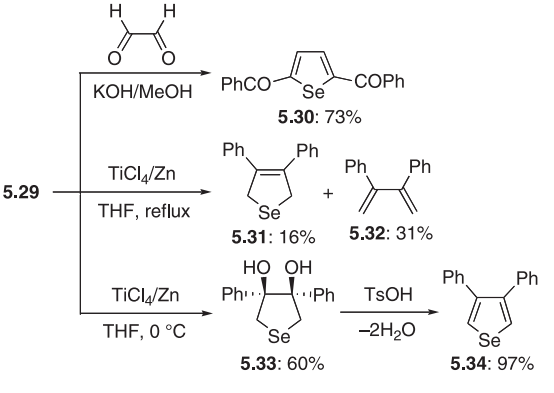
Condensation of the selenide **5.29** with glyoxal afforded selenophene **5.30** (*68*) (Scheme 49). Treatment of **5.29** with the low valent titanium reagent in boiling THF furnished dihydroselenophene **5.31** and diene **5.32** (*77*), whereas the reaction at 0 °C produced selenolanediol **5.33** from which selenophene **5.34** was derived by dehydration (*80*).

The selenide **5.29** underwent the C–Se bond cleavage to generate selenoaldehyde **5.35**, which was trapped by dimethylbutadiene to give **5.36** (*82*) (Scheme 50). Selenurane **5.28** underwent a seleno Pummerer reaction to give **5.38** probably through selenium ylide **5.37** when heated or treated with $Et_3N$ (*83*).

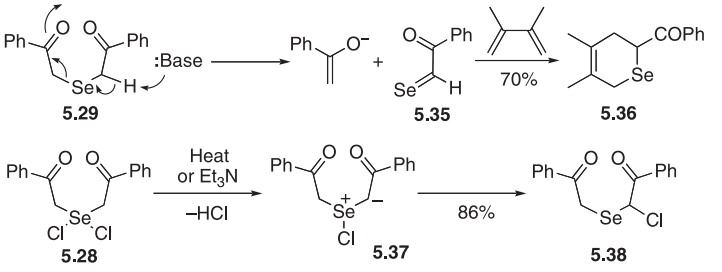
Diketo telluride **5.40** was obtained as yellow crystals from acetophenone (*96*) (Scheme 51). The C–Te bond of **5.40** was sensitive to light, acids, and bases, and hence easily cleaved.



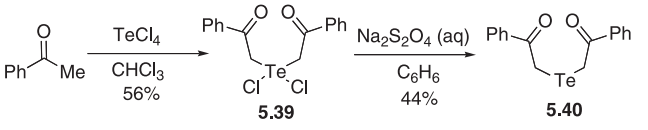

Scheme 48.




Scheme 49.




Scheme 50.




Scheme 51.



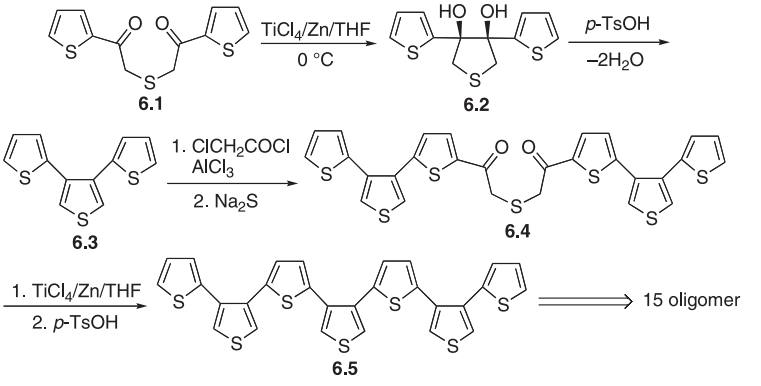
## 6. Chemistry of thiophene oligomers

### 6.1. *α, β-Type thiophene oligomers*

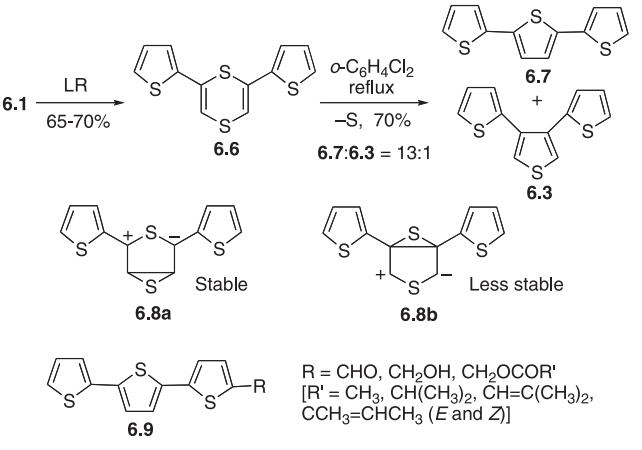
$\alpha$, $\beta$-Type thiophene oligomers composed of odd numbers of thiophene rings were prepared (*76*) (Scheme 52) by application of the new thiophene synthesis described in Section 5. Thus, terthiophene **6.3** was prepared in an excellent overall yield by intramolecular reductive coupling of **6.1** that was derived from 2-acetylthiophene. Chloroacetylation of **6.3** followed by reaction with $Na_2S$ furnished diketo sulfide **6.4**, from which septithiophene **6.5** was easily derived. Repetition of this procedure allowed the preparation of pentadecathiophene oligomer (unpublished results).

### 6.2. *α-Oligothiophenes*

Dithiin **6.6** was also prepared from **6.1** by application of the new 1,4-dithiin synthesis described in Section 5. Thermal sulfur extrusion of **6.6** afforded a 13:1 isomeric mixture of terthiophenes **6.7** and **6.3** (*60*, *69*) (Scheme 53). Terthiophene **6.7**, less soluble in organic solvents than **6.3**, was easily isolated in pure form by a single recrystallization. The sulfur extrusion probably proceeds




Scheme 52.




Scheme 53.

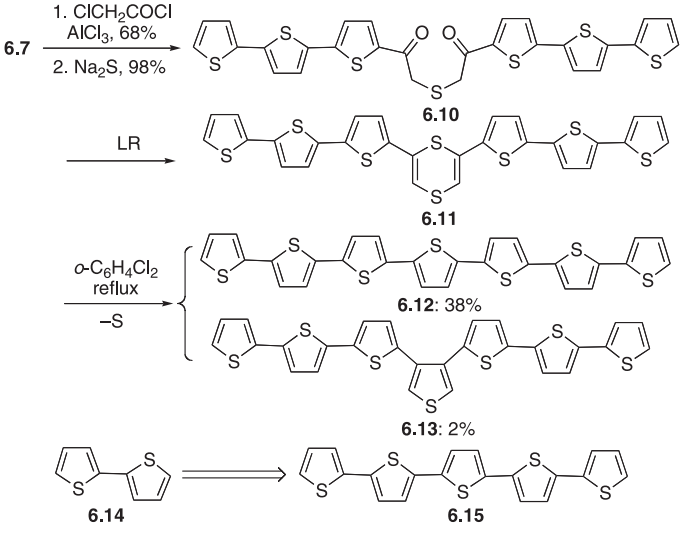


through intermediates **6.8a** and **6.8b**. **6.8a** is more stable than **6.8b**, therefore, **6.7** is formed preferentially (*60*). Naturally occurring terthiophenes **6.9**, isolated from *Eclipta erecta* L., were synthesized from **6.7** that had become readily obtainable in the above way (*62*).

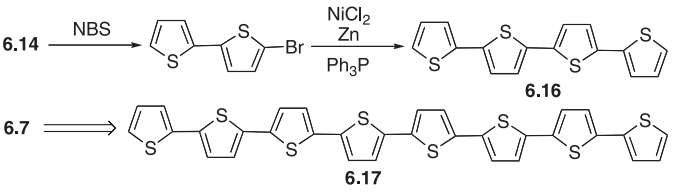
Application of the same procedure to terthiophene **6.7** allowed the preparation of the septithiophene **6.12** (*69*) (Scheme 54). Quinquethiophene **6.15** was also prepared from bithiophene **6.14** in a similar way.

Oligothiophenes composed of even numbers of thiophene rings cannot be synthesized by the above method. They were prepared in the following ways (*73*) (Scheme 55). Thus, quaterthiophene **6.16** was prepared from bithiophene **6.14**. In turn octithiophene **6.17** was prepared from **6.16**. At that time **5-15** had been the largest thiophene oligomer ever synthesized.

Physico-chemical studies of the $\alpha$-oligothiophenes synthesized above were reported in many papers (*84*, *85*, *98*, *103*, *130*, *149*).




Scheme 54.




Scheme 55.

The tetraarylthiophene and tetrarylselenophene syntheses described in Section 4 which utilize elemental sulfur and selenium, respectively, as chalcogen sources made it possible to prepare oligothiophenes **6.19a** and **6.19b** (*122*) (Scheme 56).

An orthogonally bisected terthiophene system **6.22** was built by reaction of cyclopentanone **6.20** with cerium reagent **6.21** followed by dehydration of the resulting alcohol (*116*) (Scheme 57).

Lithiation of **6.23** with BuLi (4 molar amounts) and reaction of the resulting lithiated **6.23** with **6.24** (4 molar amounts) gave organosilicon dendrimer **6.28**, composed of sixteen thiophene rings, in addition to compounds **6.25**, **6.25**, and **6.27** (*179*) (Scheme 58).

A system **6.30**, in which two $\alpha$-oligothiophene units are cofacially oriented, was built up starting from **6.29** (*125*, *139*) (Scheme 59). Also synthesized were **6.32** and the related compounds, where three $\alpha$-oligothiophene units are cofacially oriented (*147*). The structure of these oligomers was examined by X-ray diffraction analysis and the structure of their radical cation was also discussed based on oxidation potential data (*139*, *147*).

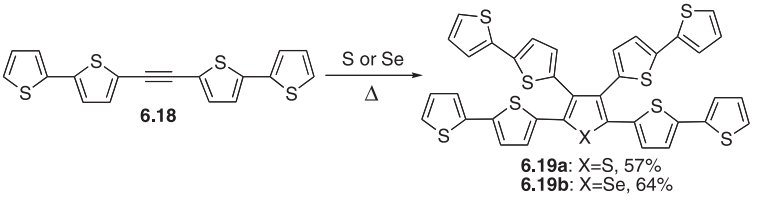


### 6.3. *Thieno[3,2-b]thiophene and seleno[3,2-b]selenophene oligomers*

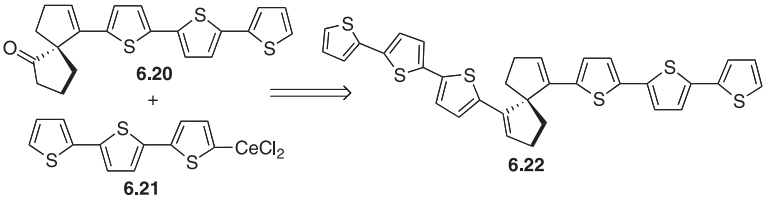
A one-pot synthesis of thieno[3,2-*b*]thiophene **6.33a** and seleno[3,2-*b*]selenophene **6.33b** was described in Section 4. Their tetramers **6.34a** and **6.34b** were synthesized from **6.33** (*159*) (Scheme 60). The dimers and trimers were also synthesized. Redox property of the Pt(II) complex of **6.33a** was examined (*240*).

### 6.4. *2,5-Bis(diarylmethylene)-2,5-dihydrothiophenes*

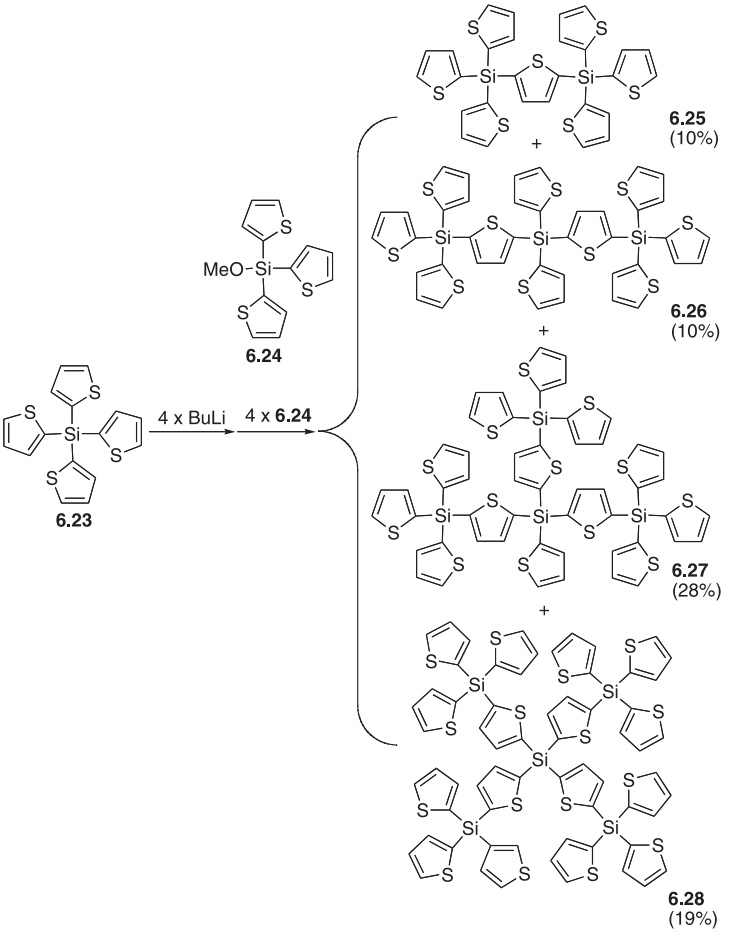
2,5-Bis(diarylmethylene)-2,5-dihydrothiophenes **6.37**, important as electron-donor and acceptor compounds, were synthesized (*114*) (Scheme 61). A representative example is **6.37a**.




Scheme 56.




Scheme 57.

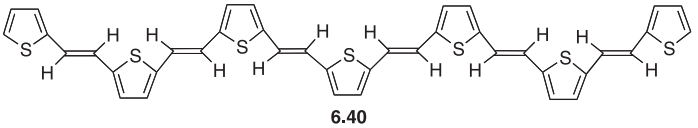



Scheme 58.

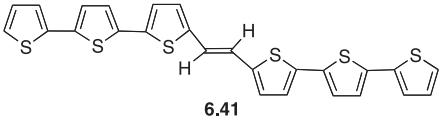
Furan, selenophene, and *N*-methylpyrrole analogs **6.38** were also synthesized. Mono- and multilayers of novel molecular complex of **6.37a** with TCNQ **6.39** were constructed and their properties examined (*134*).

### 6.5. *Oligo[thiophene-2,5-diyl]vinylenes, oligo(thio-2,5-thienylenes), and sulfur-bridged [1.$_n$](2,5)thiophenophanes*

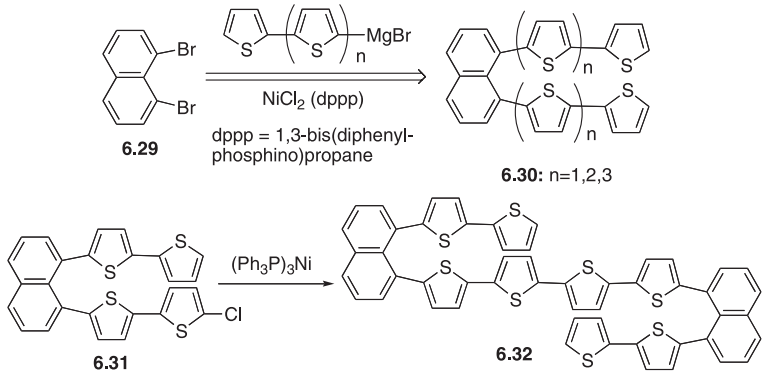
A series of oligo[thiophene-2,5-diyl]vinylenes including **6.40** were prepared and their properties were examined (*111*). Terthienyl substituted ethylene **6.41** was also synthesized (*67*).



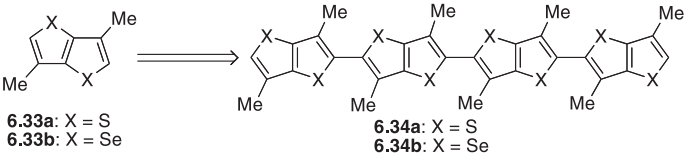
**6.40**



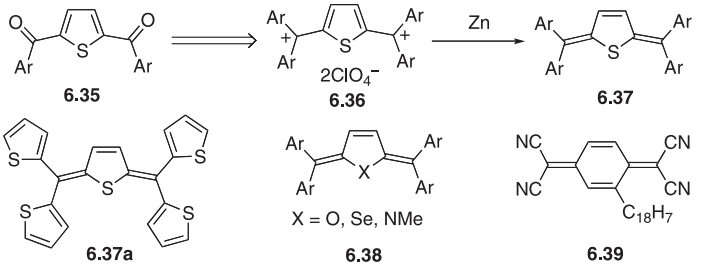
**6.41**




Scheme 59.




Scheme 60.

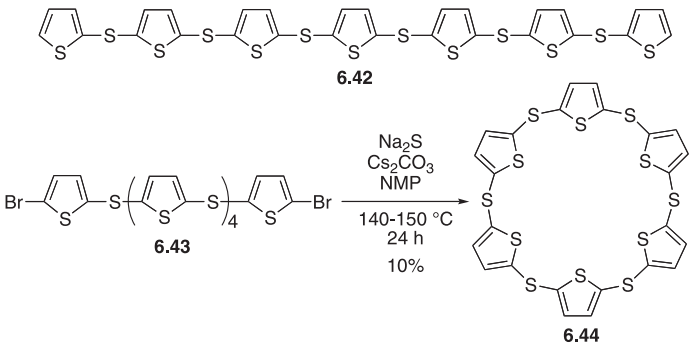



Scheme 61.

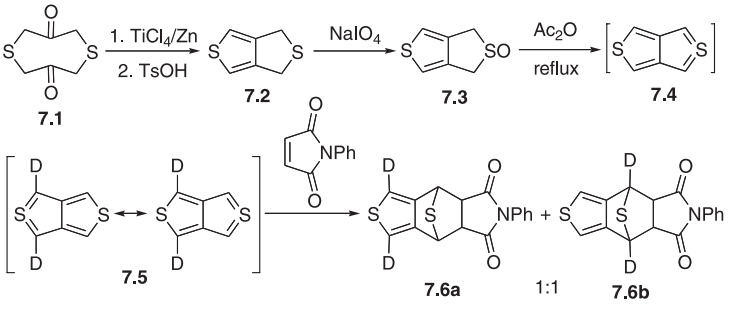
Oligo(thio-2,5-thienylenes) such as **6.42** were synthesized (*165*). Their cyclized analog, sulfur-bridged [1.$_n$](2,5)thiophenophanes such as **6.44** were also synthesized, and their structure investigated by X-ray diffraction analysis (*180*, *194*) (Scheme 62). **6.44** formed a self-assembled mono-molecular layer on polycrystalline gold, and it regulated an electrochemical electron transfer by the host–guest interaction between the cavity and reactants (*211*).

## 7. Chemistry of "non-classical" thienothiophenes

Thiophene **7.2** was prepared from **7.1** by the thiophene synthesis described in Section 5 (Scheme 63). Pummerer dehydration of the sulfoxide **7.3** brought about the efficient generation of the parent non-classical thiophene ($2\lambda^4\delta^2$-thieno[3,4-*c*]thiophene) **7.4**, which acted as a diene to afford Diels–Alder adducts in good yields upon reactions with dienophiles (*86*). The D-labeled species **7.5** was generated and trapped with *N*-phenylmaleimide, which gave a 1:1 mixture of **7.6a** and **7.6b**, thus revealing that the both thiophene rings of **7.5** are chemically equivalent.



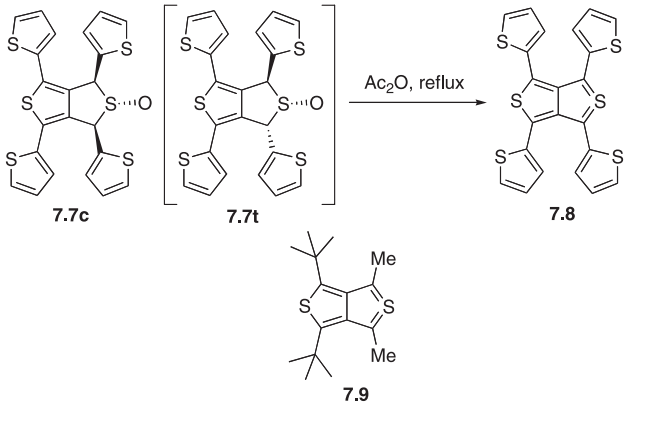

Scheme 62.




Scheme 63.



Tetrathienyl derivative **7.8** was prepared by dehydration of **7.7c** or of a mixture of **7.7c** and **7.7t** in good yield as dark purple crystals and was fully characterized (*109*) (Scheme 64). Although *tert*-butyl derivative **7.9** was also prepared by Pummerer dehydration, it was not stable enough to be isolated (*126*).




Scheme 64.

## 8. Chemistry of tri-2-thienylmethyl radical, cation, and anion

### 8.1. *Tri-2-thienylmethyl radical*

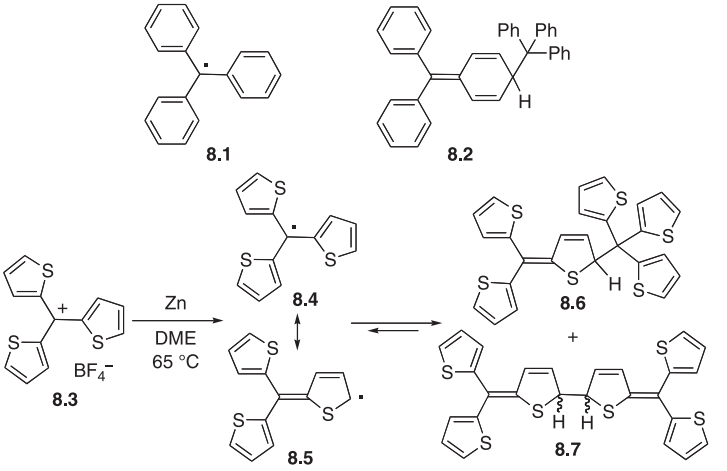
In 1968, the dimer of the triphenylmethyl radical **8.1** was shown to have the quinonoid structure **8.2** and not the hexaphenylethane structure. Then what dimer is produced from the tri-2-thienylmethyl radical **8.4**? In order to answer this question, carbenium salt **8.3** was reduced by zinc powder in DME to generate **8.4** (*101*). The reaction gave an isomeric mixture of the two dimers **8.6** and **8.7** (Scheme 65). The former dimer is produced by coupling between canonical structures **8.4** and **8.5**, and the latter by self-coupling of **8.5**. Both the isomers are isolable, but they isomerize to each other when heated through dissociation to **8.4**, whereas the formation of **8.6** is kinetically favored.

The diphenyl-2-thienylmethyl radical **8.8** dimerized to give **8.9**, along with a small amount of **8.10** (*108*) (Scheme 66).

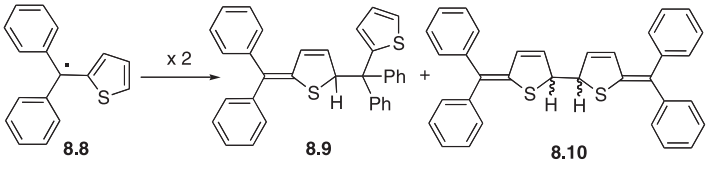
### 8.2. *Tri-2-thienylmethylcarbenium ion*

The positive charge of the tri-2-thienylmethylcarbenium ion is also delocalized over all three thiophene rings (Scheme 67). Thus, reduction of the perchlorate salt **8.11** with $LiAlH_4$ produced a mixture of **8.12** (55%) and **8.13** (32%) (*102*). The addition of MeMgBr to **8.11** gave the three isomers **8.14** (54%), **8.15** (11%), and **8.16** (26%). The additions of EtMgBr, *iso*-PrMgBr, *tert*-BuMgBr also gave three isomers corresponding to **8.14**–**8.16**, while that of ArMgBr afforded the two isomers corresponding to **8.15** and **8.16**.

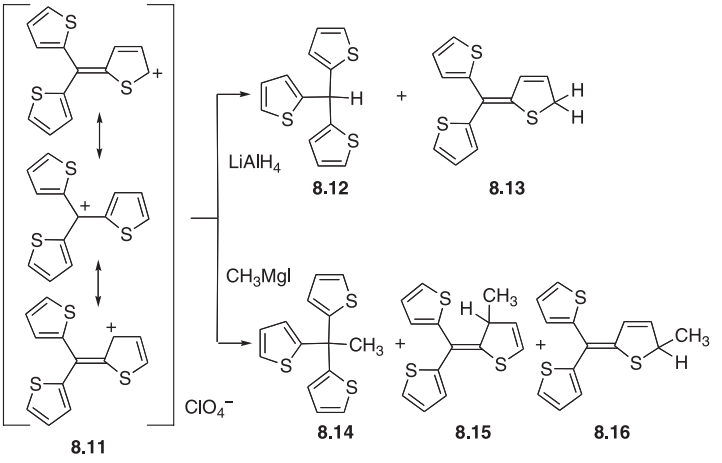





Scheme 65.




Scheme 66.



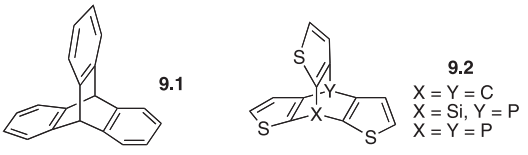

Scheme 67.

### 8.3. *Tri-2-thienylmethylcarbanion*

Tri-2-thienylmethyllithium **8.17**, prepared from **8.12**, reacted with primary alkyl halides to give **8.18** in high yields, while it reacted with secondary and tertiary alkyl halides to give mixtures of **8.18** and **8.19** (*121*) (Scheme 68). The formation of adducts **8.20** was never observed.

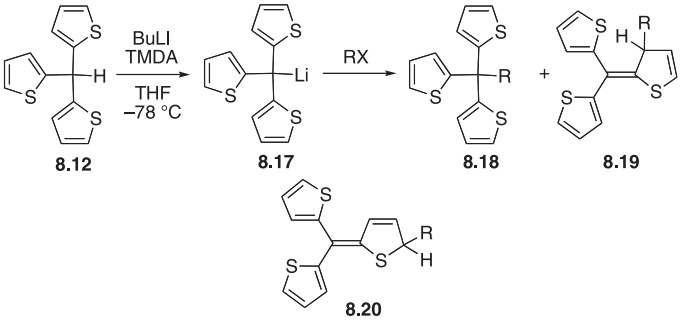
## 9. Chemistry of thiophenetriptycenes

Synthesis and properties of thiophenetriptycenes **9.2** (X=Y=C), where the benzene rings of triptycene (**9.1**) are replaced by thiophene rings, were investigated. Heterothiophenetriptycenes **9.2** (X=Y=P or X=Si, Y=P) were also investigated.

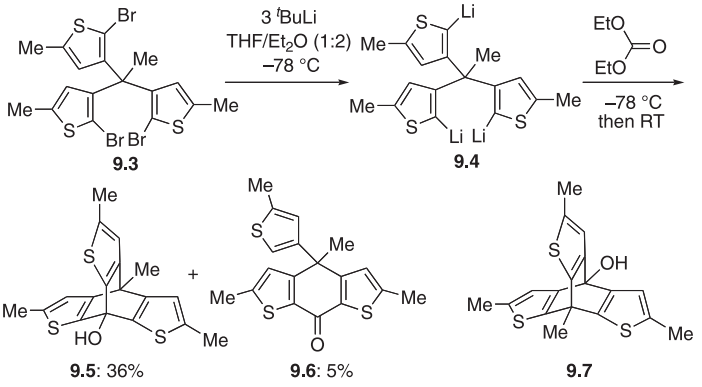



### 9.1. *Thiophenetriptycenes*

Trilithiation of tribromide **9.3** and then treatment of the resulting **9.4** with diethyl carbonate furnished the expected thiophenetriptycene **9.5** together with a small amount of **9.6** (*115*, *161*) (Scheme 69). The isomeric compound **9.7** was prepared in a similar way (*161*).




Scheme 68.



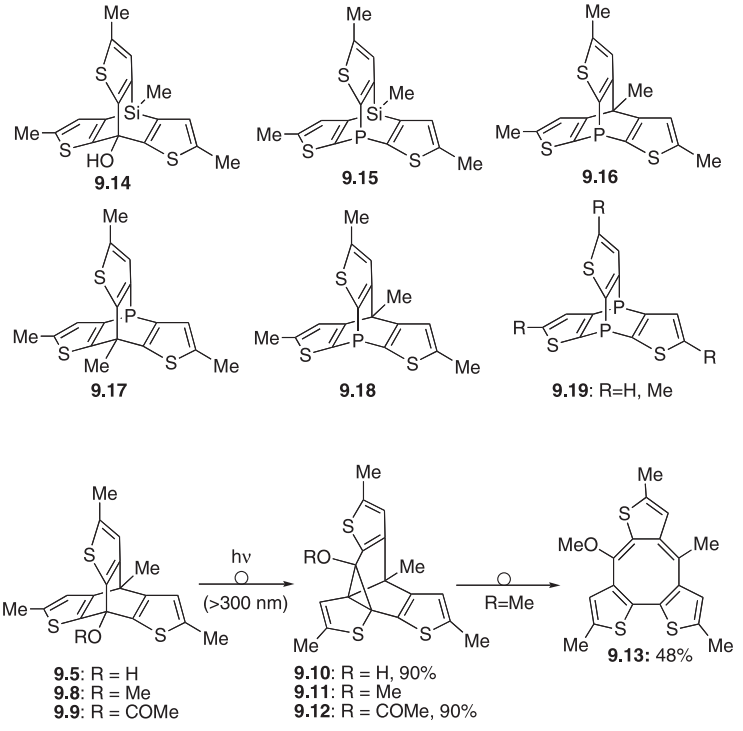

Scheme 69.

Chemical properties of **9.5** and **9.7** were examined (*132*, *161*). Di-$\pi$-methane rearrangement of **9.5** is of particular interest (*132*). Photoirradiation of **9.5** and its derivatives **9.8** and **9.9** gave rearrangement products, semibullvalenes **9.10**–**9.12**, in high yields (Scheme 70). **9.11** is thermally unstable and rearranged immediately at room temperature to give **9.13**.



## 9.2. *Heterothiophenetriptycenes*

Heterothiophenetriptycenes **9.14**–**9.19** were synthesized and their properties were investigated (*135*, *142*, *143*).




Scheme 70.

## 10. Sterically congested thiophenes

The new thiophene synthesis developed in Section 5 enabled us to prepare congested thiophenes carrying bulky substituents at the 3- and 4-positions (*79*, *104*, *110*, *148*, *190*) (Scheme 71). Thus, 3,4-di-*tert*-butyl-, 3,4-di(1-adamantyl)-, and 3,4-dineopentylthiophenes (**10.3a**–**c**) were synthesized from **10.1a**–**c**. Unsymmetrically substituted **10.3d** was also prepared.

Congested heteroaromatics, 3,4-di-*tert*-butylpyrrole (**10.4**), 3,4-di-*tert*-butylfuran (**10.5**), and 3,4-di-*tert*-butylselenophene (**10.6**) were derived from **10.3a**, though in low yields (*105*) (Scheme 72).

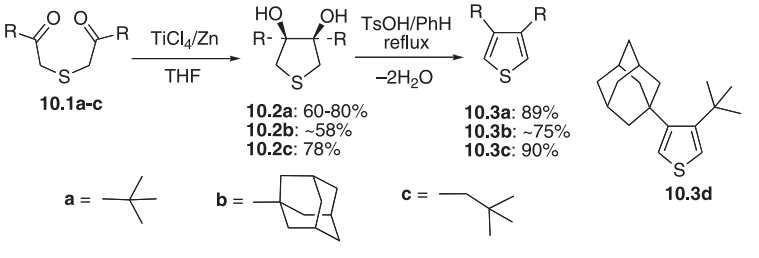
Scheme 73 shows the derivation of other congested thiophenes from **10.3a**. Dilithiation of thiophene **10.7** quantitatively obtainable from **10.3a** and treatment of the resulting **10.8** with triisopropylsilyl chloride furnished highly congested, nonplanar thiophene **10.9** (*177*). The Pd-catalyzed coupling of bromide **10.10** with Grignard reagent **10.11** afforded bithiophene **10.12**, in which two thiophene rings are perpendicular to each other (*171*).

Dithiete **10.13** reacted with DMAD under forcing conditions to give thiophenes **10.14** and **10.15** in a low combined yield (*97*) (Scheme 74). 2,3-Di-*tert*-butylthiophene (**10.16**) was derived from **10.15** by hydrolysis and decarboxylation.

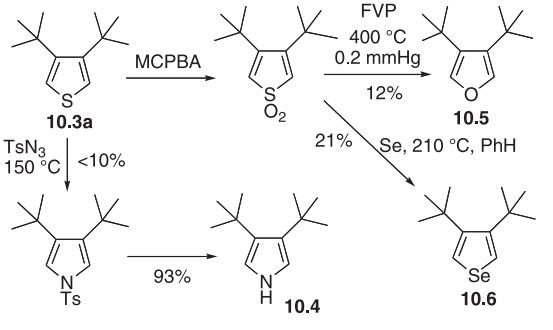


## 11. Angle-strained thiophene and miscellaneous works on thiophenes

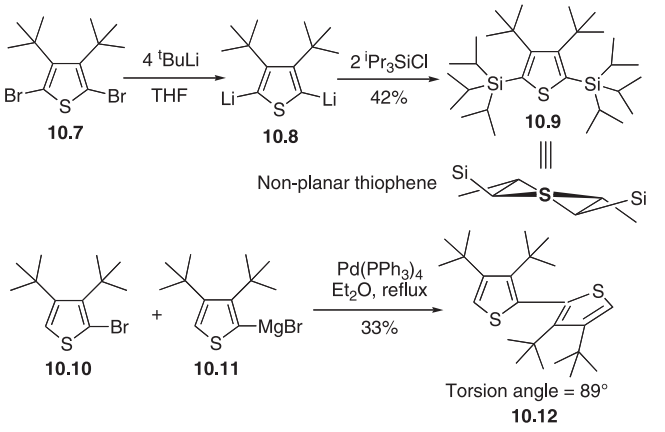
The new thiophene synthesis developed in Section 5 also enabled us to prepare angle-strained dicyclobuta[*b*, *d*]thiophene **11.4** starting from cyclobutanone (*136*) (Scheme 75). In this case, thiolanediol **11.2** resisted acid-catalyzed dehydration that gives **11.4**. Therefore **11.2** was methanesulfonated and then treated with *tert*-BuOK to give **11.4** quantitatively as a crystalline solid.



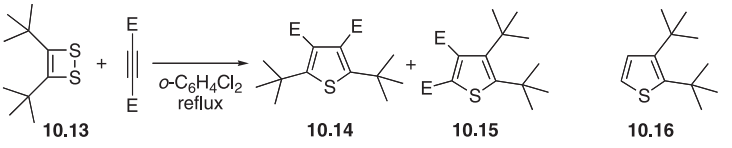

Scheme 71.



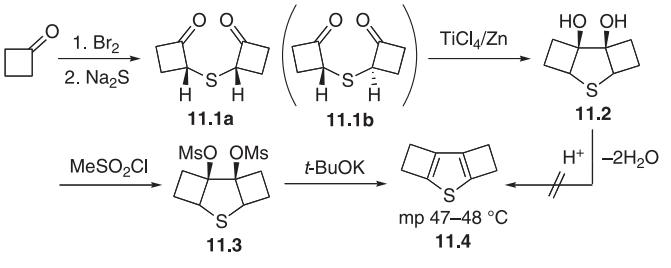

Scheme 72.




Scheme 73.




Scheme 74.



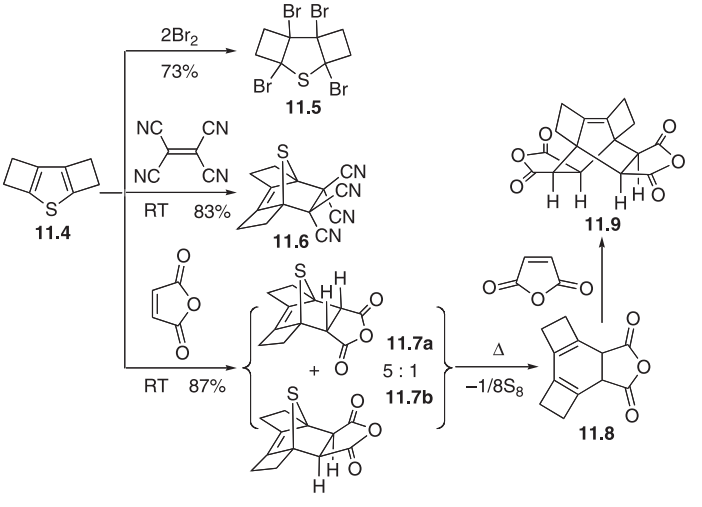

Scheme 75.

The highly angle-strained thiophene **11.4** shows diene-like properties (*136*) (Scheme 76). Thus, bromine added **11.4** to give tetrabromide **11.5**. It reacted with tetracyanoethylene at room temperature to give Diels–Alder adduct **11.6**. The reaction of **11.4** with an equimolar amount of maleic anhydride afforded a 5:1 mixture of adducts **11.7a** and **11.7b**. These adducts extruded sulfur to give **11.8** when heated. Thus, heating **11.4** with excess maleic anhydride in boiling benzene gave structurally interesting bis-adduct **11.9** through **11.8** in 84% yield.

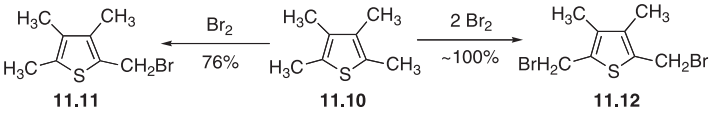
Uncatalyzed side-chain halogenation took place regioselectively at the $\alpha$-methyl of polymethyl-substituted thiophenes (*140*) (Scheme 77). Thus, the reaction of thiophene **11.10** with an equimolar amount of bromine gave **11.11**, while the reaction with two molar amounts of bromine afforded **11.12**.

Heating thiophene **11.13** with *p*-toluenesulfonic acid in toluene brought about an intramolecular disproportionatin to give **11.14** (*202*) (Scheme 78).

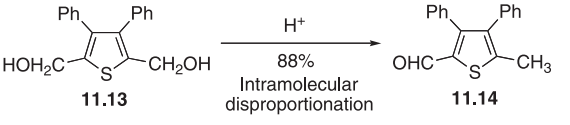
Diformylation of bithiophene and terthiophene was reported (*100*) (Scheme 79).



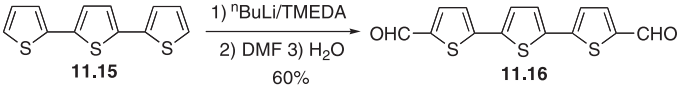

Scheme 76.




Scheme 77.

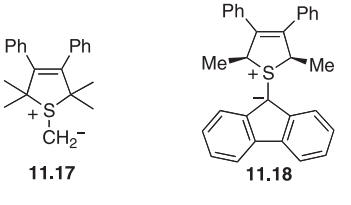



Scheme 78.




Scheme 79.

Thermolysis of dihydrothiophenium ylides such as **11.17** and **11.18** was investigated (*90*).

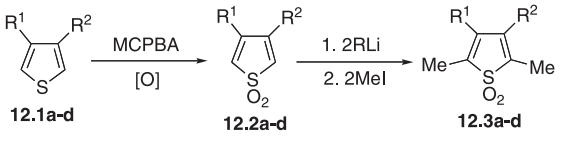


## 12. Preparation of congested compounds with 3,4-di-*tert*-butylthiophene 1,1-dioxide and related compounds

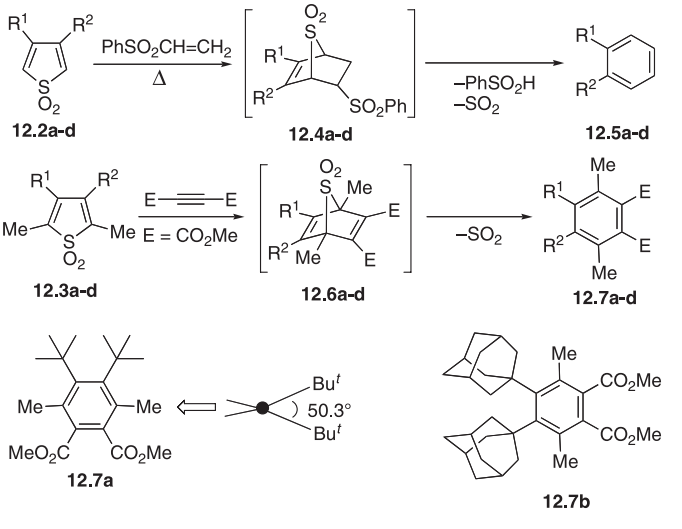
Sterically congested thiophenes **12.1a–d** were easily oxidized by MCPBA to give the corresponding thiophene 1,1-dioxides **12.2a–d** in good yields (Scheme 80). Although the thiophene **12.1a** resisted lithiation with alkyllithiums and lithium diisopropylamide (LDA), probably because of steric hindrance (*79*), **12.2a–d** were easily dilithiated due to the increased acidity (*124*, *141*, *190*). This enabled us to prepare more congested dimethyl derivatives **12.3a–d** through lithiation followed by treatment with methyl iodide.

Thiophene 1,1-dioxides are not aromatic any longer and hence generally reactive. Although **12.2a–d** and **12.3a–d** are thermally stable because of the inhibited self-dimerization by steric hindrance, they are still reactive toward simple dienophiles. Thus, **12.2a–d** reacted with phenyl vinyl sulfoxide to give Diels–Alder adducts **12.4a–d**, which spontaneously extruded benzenesulfinic acid and sulfur dioxide to furnish **12.5a–d** in high yields (*87*, *104*, *148*, *190*) (Scheme 81). Other dienophiles also reacted with **12.2a** to give the corresponding *o*-di-*tert*-butylbenzene derivatives in good yields (*87*). Dimethyl derivatives **12.3a–d** reacted with DMAD to give **12.7a–d** through sulfur dioxide extrusion of the intermediates **12.6a–d** (*190*). Preparation of *o*-di-*tert*-butyl- and *o*-dineopentyl benzenes had required tedious multistep reactions. Preparation of *o*-di(1-adamantyl)benzene and its derivatives had never been reported before us. The method described above provided the most convenient synthesis of such compounds. **12.7a** and **12.7b** are the examples of the most congested compounds synthesized by us (*190*). X-ray diffraction and temperature-dependent NMR analyses of these congested compounds were investigated (*110*, *190*).

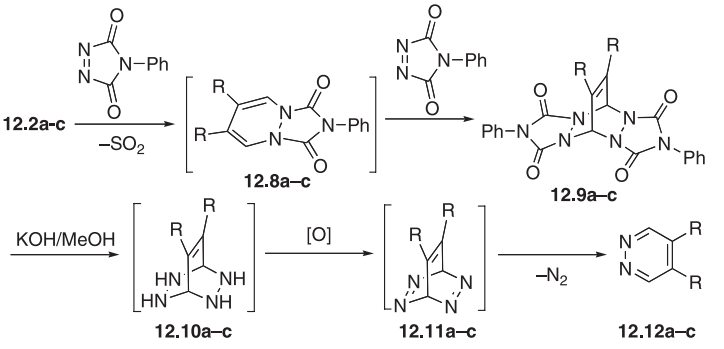





Scheme 80.




Scheme 81.




Scheme 82.

The reactions of **12.2a–c** with two molar amounts of PTAD afforded bis-adducts **12.9a–c** in excellent yields through Diels–Alder reactions of **12.8a–c** that are formed by sulfur extrusion of the initial Diels–Alder adducts (*93*, *104*, *148*, *190*) (Scheme 82). Unexpectedly, treatment of **12.9a–c** with KOH in methanol provided pyridazine **12.12a–c** directly in high yields. This new pyridazine formation probably involves **12.10a–c** and **12.11a–c** as intermediates.

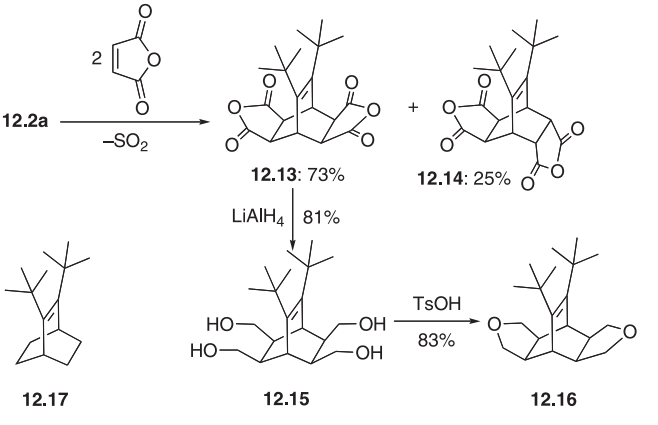
The same Diels–Alder reaction also took place between **12.2a** and maleic anhydride to afford an isomeric mixture of the bis-adducts **12.13** and **12.14**, each of which was easily isolated in pure form (*107*) (Scheme 83). Treatment of **12.13** with $LiAlH_4$ and dehydration of the resulting tetraol **12.15** led to highly congested alkene **12.16** that possesses the framework of 2,3-di-*tert*-butylbicyclo[2.2.2]oct-2-ene (**12.17**).

Thiolanediol **12.19**, prepared from diketo sulfide **12.18**, underwent pinacol rearrangement to give **12.20** together with a minor amount of **12.21** (*117*) (Scheme 84). The sterically protected carbonyl group of **12.20** is unreactive toward a series of nucleophiles.

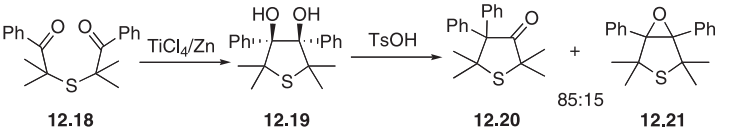


## 13. Synthesis and characterization of the parent thiophene 1,1-dioxide

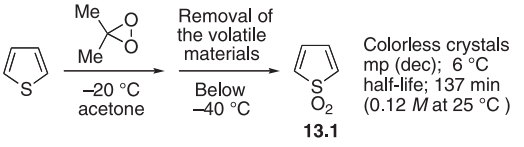
The oxidation of thiophene with dimethyldioxirane (DMD) in acetone at −20 °C and the removal of the volatile materials below −40 °C allowed the first synthesis and isolation of the parent



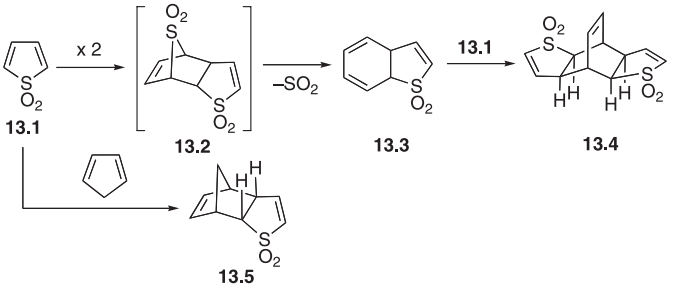

Scheme 83.




Scheme 84.




Scheme 85.




Scheme 86.



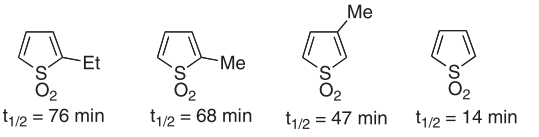
thiophene 1,1-dioxide **13.1** as colorless crystals that melted at 6 °C with decomposition (*182*, *206*) (Scheme 85). The half-life of **13.1** in solution depends on concentration, and was 137 min at 25 °C for a 0.12 *M* $CDCl_3$ solution.

Dioxides **13.1** collapsed through [2 + 4] self-dimerization to give **13.2**, which extruded sulfur dioxides to yield the dimer **13.3** as the final product (*182*, *206*) (Scheme 86). The further Diels–Alder reaction of **13.3** with **13.1** increased with increasing concentration of **13.1** to produce the trimer **13.4**. Since the above dimerization occurred rapidly, many attempted reactions of **13.1** with dienophiles were fruitless. The only successful example is the reaction with cyclopentadiene, where **13.1** served as a dienophile to furnish **13.5** in 25% yield.

The 1,1-dioxides of six monosubstituted thiophenes were synthesized and their properties were fully characterized. Half-lives of the representative compounds are summarized in Scheme 87 (*212*).

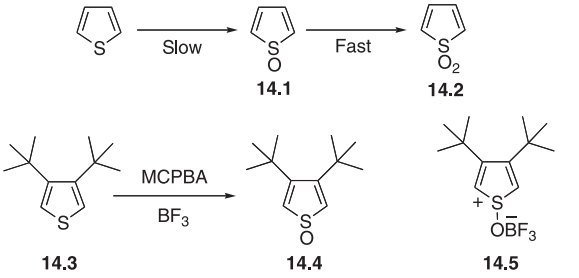
## 14. 3,4-Di-*tert*-butylthiophene 1-oxide and the $\pi$-face-selective reactions

Oxidation of thiophene 1-oxide (**14.1**) to 1,1-dioxide **14.2** is faster than the oxidation of thiophene to the 1-oxide **14.1** (Scheme 88). Therefore, the oxidation of thiophenes could not be stopped at the 1-oxide stage under usual conditions. However, in the presence of $BF_3$ etherate, complexation of the resulting 1-oxide with $BF_3$ prevents further oxidation. Thus, the oxidation of thiophene **14.3** with MCBA in the presence of $BF_3$ etherate furnished thiophene 1-oxide **14.4** in good yield (*175*). Further oxidation of **14.4** is inhibited by formation of **14.5**. Incidentally **14.5**, which is stable




Half-lives of monosubstituted thiophene 1,1-dioxides at 40 ¡C for 0.32 M $CDCl_3$ solutions

Scheme 87.




Scheme 88.



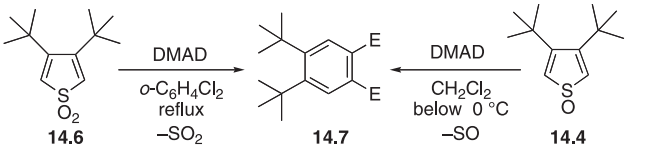
enough to be isolated, was prepared by mixing **14.4** and $BF_3$ etherate in $CH_2Cl_2$ (unpublished results).

### 14.1. *Diels–Alder reaction*

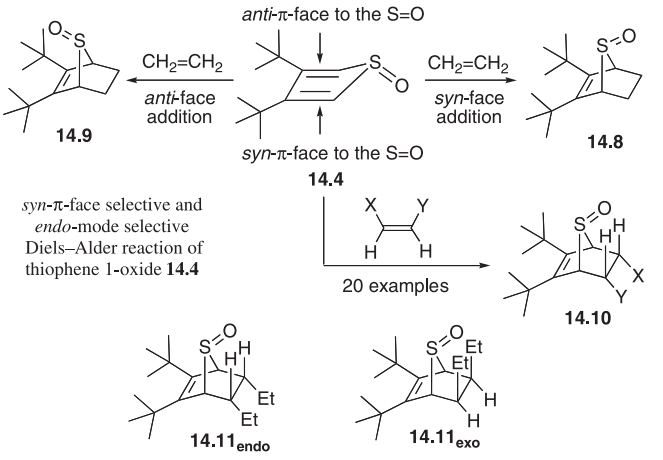
Thiophene 1-oxide is far more reactive as a diene than is the corresponding 1,1-dioxide. Thus, the Diels–Alder reaction of 1-oxide **14.4** with DMAD that affords **14.7** through sulfur monoxide extrusion of the initial adduct occurred even below 0 °C (*248*), whereas the same reaction of 1,1-dioxide **14.6** took place when heated in boiling *o*-dichlorobenzene (*87*, *190*) (Scheme 89).

The structure of thiophene 1-oxide **14.4**, given in Scheme 90, reveals that it has two $\pi$-faces, *anti*- and *syn*-$\pi$-faces, with respect to the S=O bond. This is also true for other thiophene 1-oxides. Thus, if its reaction with ethylene took place, either a mixture of *anti*- and *syn*-$\pi$-adducts is formed, or one of them is formed selectively. We had examined the stereochemistry of the Diels–Alder reaction of **14.4** in detail (*248*, *249*, *263*). As a result, it became clear that a wide variety of dienophiles (angle-strained, electron-rich, and electron-deficient dienophiles, and even simple cyclic and acylic alkenes) all undergo Diels–Alder reactions with **14.4** under mild conditions, and the reactions take place exclusively on the *syn*-$\pi$-face *syn* to the S=O bond and in the *endo* mode (*264*). The only exception is the reaction with *cis*-2-hexene that gave a mixture of *endo*-adduct $\mathbf{14.11_{endo}}$ (60%) and *exo*-adduct $\mathbf{14.11_{exo}}$ (36%).

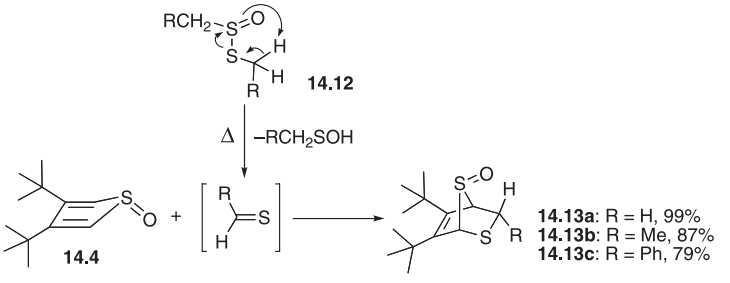
1-Oxide **14.4** reacted with unstable, transient thioaldehydes to furnish Diels–Alder adducts **14.13** in excellent yields (*249*) (Scheme 91). The reaction was carried out by heating an equimolar




Scheme 89.




Scheme 90.



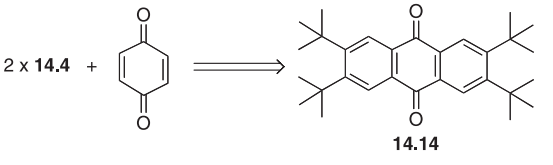

Scheme 91.



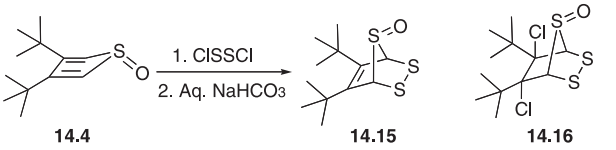
mixture of **14.4** and thioaldehyde precursor **14.12** in boiling toluene. It is worthy to note that thioformaldehyde adduct **14.13a** was obtained in 99% yield.

Sterically congested anthraquinone **14.14** was prepared through Diels–Alder reaction of **14.4** with *p*-benzoquinone (*269*, for the related paper, see also *272*) (Scheme 92). The Diels–Alder reaction of **14.14** with tetrachlorocyclopropene was reported (*262*).

When 1-oxide **14.4** was allowed to react with disulfur dichloride ($S_2Cl_2$) and the resulting mixture was treated with aq. $NaHCO_3$, cyclic disulfide **14.15**, in which the disulfide bond is *syn* to the S=O, was formed exclusively in good yield (*258*) (Scheme 93). The reaction formally corresponds to the stereospecific [2 + 4] addition of diatomic sulfur ($S_2$) to **14.4**. The mechanism of the reaction is not clear, except for the probable formation of the initial adduct **14.16**.




Scheme 92.




Scheme 93.

### 14.2. *1,3-Dipolar cycloaddition*

1-Oxide **14.4** served as a 1,3-dipolarophile to a range of 1,3-dipoles. The 1,3-dipolar cycloadditions of **14.4** also took place on the *syn*-$\pi$-face *syn* to the S=O bond, though not exclusively (*258*, *271*) (Scheme 94). For example, although the reactions with acetonitrile oxide and diazomethane took place exclusively at the *syn*-face to give **14.17** and **14.19**, respectively, the reaction with benzonitrile oxide gave the *anti*-product **14.18$_{anti}$**, though in a small amount, in addition to the *syn*-product **14.18$_{syn}$**. In the course of this study, it was found that tetracyanoethylene oxide not only oxidizes sulfides to sulfoxides but also reduces sulfoxides to sulfides, with generation of two molecules of carbonyl cyanide (*261*).

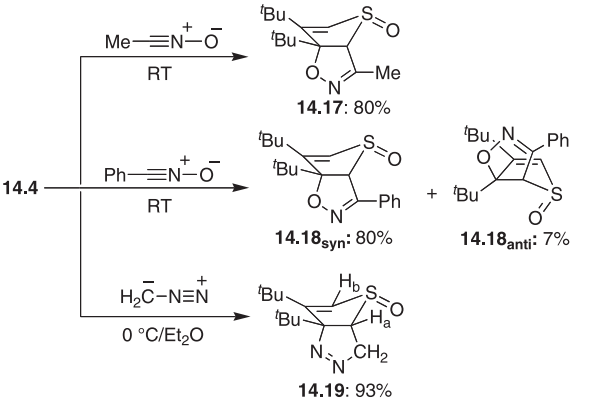


### 14.3. *Electrophilic addition (addition of bromine)*

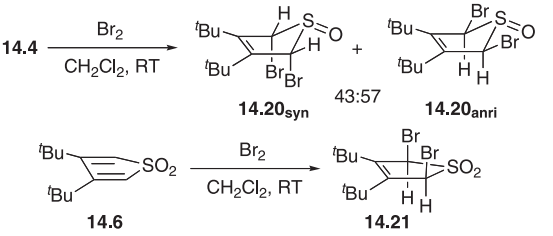
Bromine underwent exclusive 1,4-addition to **14.4** to produce a 43:57 mixture of **14.20$_{syn}$** and **14.20$_{anti}$** without $\pi$-face selectivity (*247*) (Scheme 95). Incidentally, bromine added to 1,1-dioxide **14.6** also to give 1,4-adduct **14.21** exclusively.

### 14.4. *Nucleophilic addition (Michael addition)*

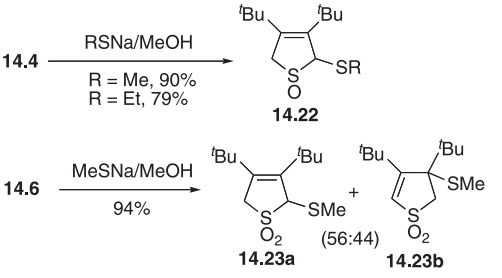
The reactions of methane- and ethanethiolate with **14.4** at room temperature gave Michael adducts **14.22** selectively, whereas the reaction of **14.6** with methanethiolate afforded a 56:44 mixture of **14.23a** and **14.23b** (*215*) (Scheme 96).




Scheme 94.




Scheme 95.

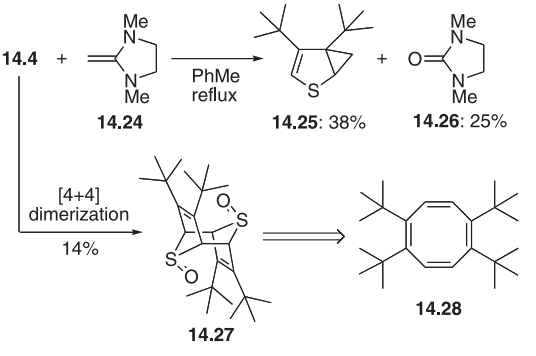



Scheme 96.



### 14.5. *Oxygen–methylene exchange*

When **14.4** was heated with 2-methylene-1,3-dimethylimidazolidine (**14.24**) in refluxing toluene, two unexpected reactions were observed (*232*) (Scheme 97). One is an oxygen-methylene exchange which produced **14.25** and **14.26** in moderate yields, and the other is [4 + 4] dimerization of **14.4**, which resulted in the formation of **14.27** in low yield. When **14.4** was placed under rather forcing conditions in other cases, **14.27** was also formed in low yield. Tetra-*tert*-butylcyclooctatetraene (**14.28**) was derived from **14.27** (*253*).




Scheme 97.

## 15. Chemistry of 1-imino, 1,1-diimino, and 1-imino-1-oxo derivatives of 3,4-di-*tert*-butylthiophene

### 15.1. *Synthesis*

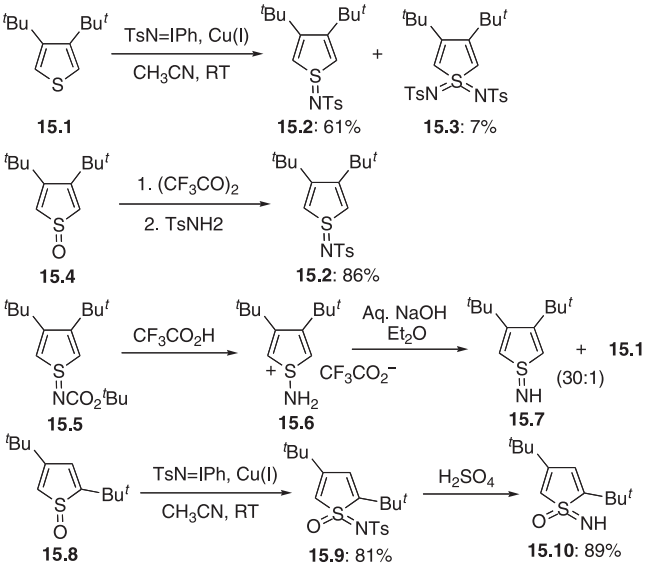
The reaction of thiophene **15.1** with iodinane (TsN=IPh) in the presence of $Cu(MeCN)_4PF_6$ furnished 1-imino- and 1,1-diimino derivatives, **15.2** (23–61%) and **15.3** (7–18%), together with three other products in low yields (*204*, *229*) (Scheme 98). 1-Imino derivative **15.2** was prepared in a better yield by treatment of thiophene 1-oxide **15.4** with trifluoroacetic acid anhydride and then with *p*-toluenesulfonamide (*221*, *229*). A range of 1-imino derivatives were prepared by this method (*221*, *229*). Compound **15.5** as a representative of these 1-imino derivatives obtained in this way generated a sulfonium salt **15.6** by treatment with trifluoroacetic acid. The latter was converted to labile *N*-unsubstitited derivative **15.7**. Treatment of thiophene 1-oxide **15.8** with TsN=IPh in the presence of $Cu(MeCN)_4PF_6$ gave 1-imino-1-oxo derivative **15.9**, hydrolysis of which provided the *N*-unsubstituted compound **15.10** (*203*, *229*). The sulfur atom of **15.9** is chiral and HPLC on a chiral column allowed separation of a pair of the enantiomers, whose absolute configuration was determined by X-ray diffraction analysis.



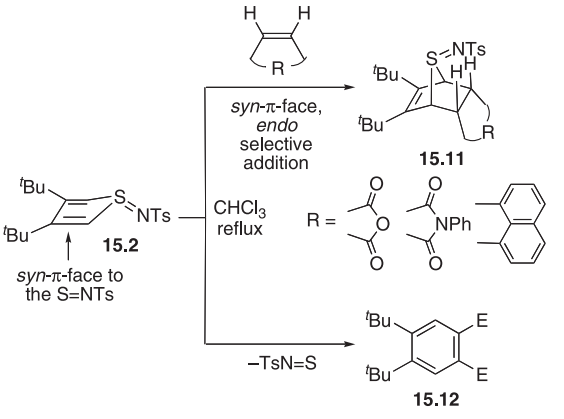
### 15.2. *Reaction*

The stereostructure of thiophene 1-imino derivatives is similar to that of thiophene 1-oxides (*229*). Thus, **15.2** also possesses two $\pi$-faces with respect to the S=NTs bond. The Diels–Alder reaction of **15.2** was also *syn*-$\pi$-face and *endo* selective, and afforded adducts **15.11** in high yields, while the reaction with DMAD gave **15.12** with extrusion of a thionitroso compound (TsN=S) from the initial adduct (*248*) (Scheme 99). **15.2** is less reactive than 1-oxide **15.4**, and therefore, the Diels–Alder reactions took place when heated in refluxing chloroform.

1-Imino derivative **15.2** reacted with oxygen and sulfur nucleophiles to provide thiophenes **15.13** and **15.14**, respectively, with loss of *p*-toluenesulfonamide (*215*) (Scheme 100). *N*-Unsubstituted **15.7** was easily hydrolyzed to give **15.1** (*229*).




Scheme 98.




Scheme 99.

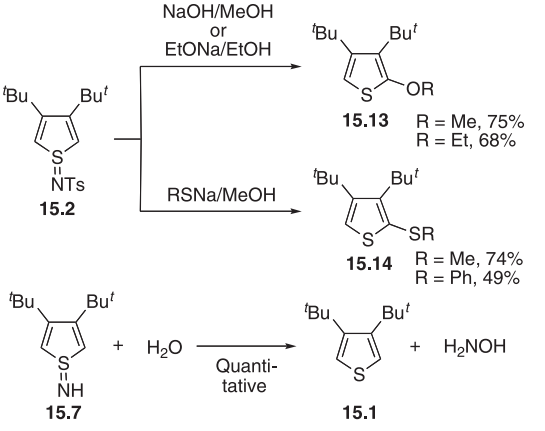
Bromine underwent *cis*-1,4-addition to 1-imino-1-oxo derivative **15.15** to give a 33:67 mixture of **15.16a** and **15.16b**, whereas the reaction with **15.2** gave a number of bromination products of the thiophene nucleus with loss of *p*-toluenesulfonamide (*247*) (Scheme 101).



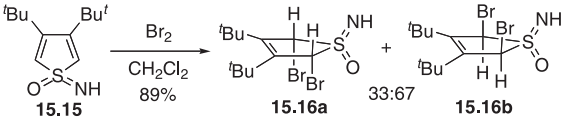
## 16. Chemistry of selenophene 1-oxides and 1,1-dioxides

### 16.1. *Synthesis*

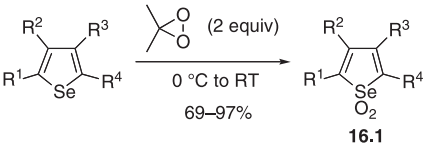
Seven selenophene 1,1-dioxides **16.1** were prepared by oxidation of the corresponding selenophenes with two molar amounts of dimethyldioxirane (DMD) in 69–97% yields (*158*, *169*) (Scheme 102).



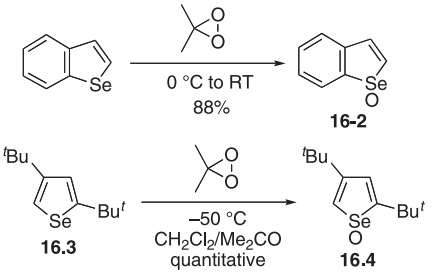

Scheme 100.




Scheme 101.




Scheme 102.




Scheme 103.

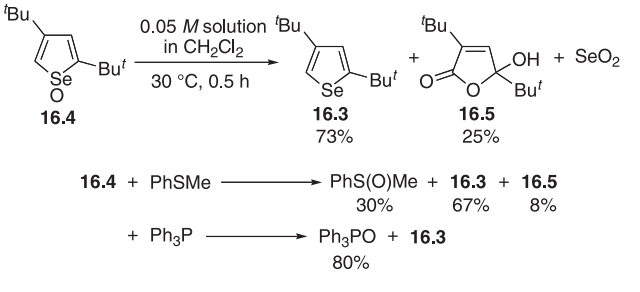


Benzo[*b*]selnophene 1-oxide (**16.2**) was obtained by DMD oxidation of benzo[*b*]selenophene (*158*, *169*) (Scheme 103). DMD oxidation of selenophene **16.3** at −50 °C and removal of the volatile materials at the same temperature gave the colorless crystals of monocyclic selenophene 1-oxide **16.4** quantitatively (*195*).

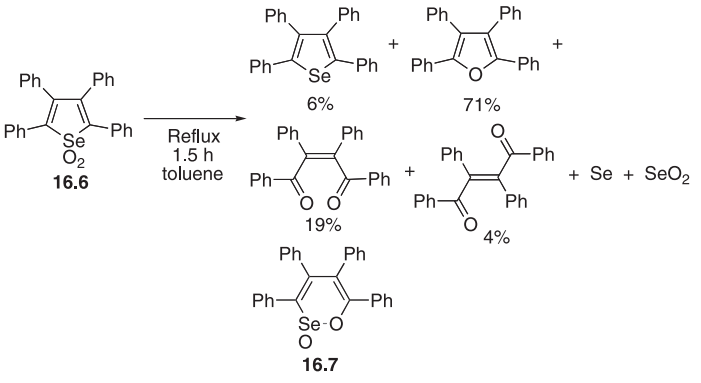
## 16.2. *Properties*

Interestingly, both selenophene 1-oxides **16.2** and **16.4** are easily soluble in water although they possess hydrophobic benzene ring and *tert*-butyl groups, respectively (*158*, *169*, *195*). **16.4** is far less stable than the corresponding thiophene 1-oxide and the half-life is only 42 min for a 0.018 *M* $CDCl_3$ solution at 30 °C (*195*). A 0.05 *M* $CH_2Cl_2$ solution of **16.4** on standing for 30 min resulted in decomposition that yielded selenophene **16.3**, furanone **16.5**, and $SeO_2$ (Scheme 104). **16.4** oxidized thioanisole and triphenylphosphine to give the corresponding oxides.

Thermolysis of selenophene 1,1-dioxides was investigated. For example, thermolysis of 1,1-dioxide **16.6** in refluxing toluene gave the results shown in Scheme 105 (*184*). The reaction probably involves **16.7** as the intermediate that was formed by homolytic C–Se bond cleavage, followed by recyclization.




Scheme 104.




Scheme 105.

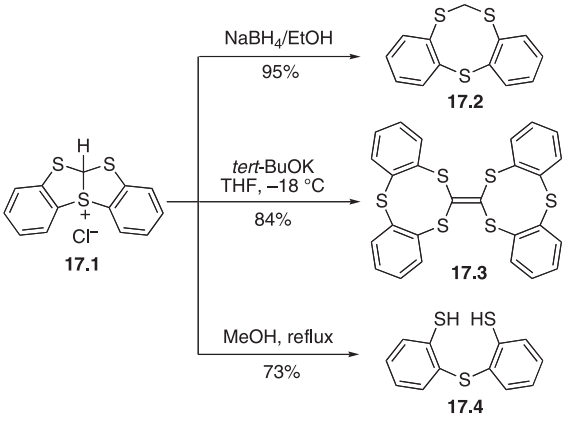
## 17. Macrocycles containing mutiple sulfur atoms

One-pot synthesis of sulfonium salt **17.1** was developed in 1996 (*160*, *163*), as described in Section 3. The sulfonium salt **17.1** serves as useful starting material for the preparation of a number of heterocycles containing multiple sulfur atoms. Thus, reduction of **17.1** with $NaBH_4$ afforded trithiocin **17.2**, while treatment with *tert*-BuOK furnished bitrithiocinylidene **17.3**, a higher analog of TTF (*163*) (Scheme 106). Unexpectedly, heating **17.1** in refluxing methanol produced a new dithiol **17.4** (*187*).

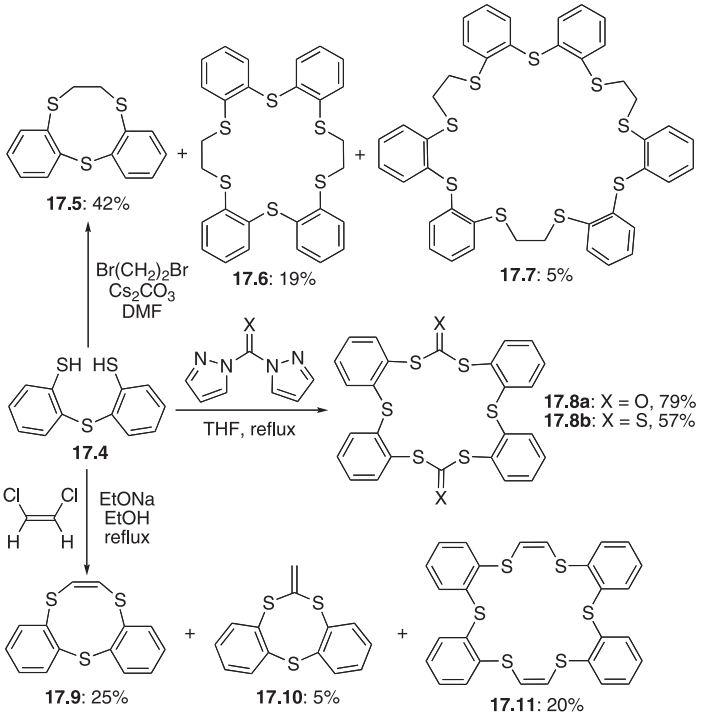
A series of macrocycles containing multiple sulfur atoms were derived from the dithiol **17.4**. Three examples that demonstrate the usefulness of **17.4** are given in Scheme 107 (*198*, *207*).

## 18. Chemistry of thiosulfinyl compounds

Treatment of the thiolanediol **18.1** with four molar amounts of 1,1'-thiobis(1*H*-benzimidazole) furnished an 82:18 mixture of two diastereomers (**18.2** and **18.3**) of the cyclic thionosulfite, with different configurations at the pseudo-tetrahedral center of the thiosulfinyl (>S=S) group (*251*, *264*) (Scheme 108). The configuration of the S=S group of the major diastereomer (isolated in 45% yield) was established to be *syn* to the thiolane ring, while that of the minor diastereomer




Scheme 106.

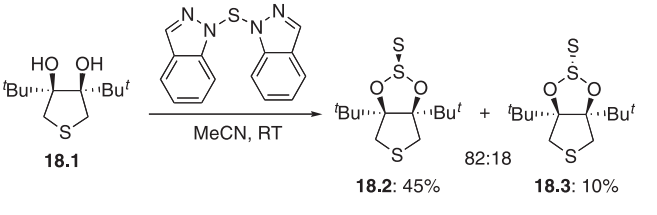



Scheme 107.



(isolated in 10% yield) was *anti* by X-ray diffraction analysis. $^1$H NMR spectroscopic analysis clarified that the shielding and deshielding zones of the S=S group are similar to those of the well-documented S=O group (Figure 1).

Dilithiation of **18.4** followed by treatment with disulfur dichloride afforded a thiosulfinyl compound **18.6**, which is unstable both thermally and kinetically and thus could not be isolated in pure form (*267*) (Scheme 109). On the other hand, the same treatment of **18.5** furnished a new heterocyclic compound **18.7**.




Scheme 108.

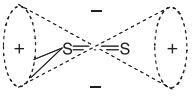
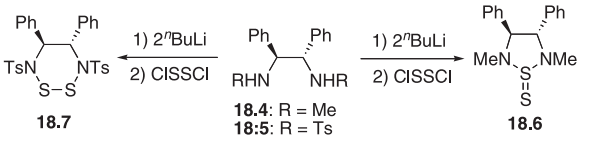
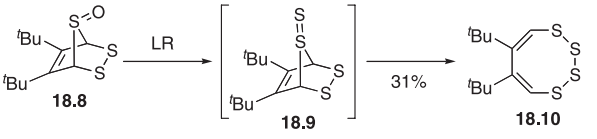


Figure 1. Magnetic-shielding (+) and -deshielding (−) zones of the S=S group.




Scheme 109.




Scheme 110.

Treatment of **18.8**, preparation of which was described in Section 14, with LR afforded tetrathiocin **18.10** along with other products. The reaction probably involves the thiosulfinyl intermediate **18.9** (*258*) (Scheme 110).



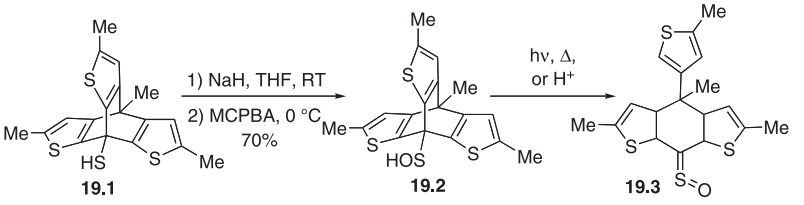
## 19. Sulfenic and selenenic acids and related compounds

Treatment of a sterically hindered thiol **19.1** with NaH and oxidation of the resulting thiolate furnished sulfenic acid **19.2** as a pale yellow, crystalline compound (*167*) (Scheme 111). Its structure was unambiguously determined by X-ray diffraction analysis. **19.2** is stable for a long time in the dark, but is light-sensitive and isomerized to the sulfine **19.3** in solution or even in the solid state when exposed to the light.

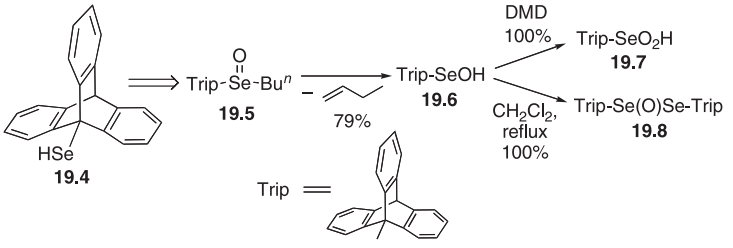
Thermally labile selenoxide **19.5** derived from selenol **19.4** decomposed at room temperature in solution to give selenenic acid **19.6** and 1-butene (*201*) (Scheme 112). Pale yellow crystalline **19.6** was easily oxidized to the selenic acid **19.7** and underwent a self-condensation to give **19.8** when heated in boiling $CH_2Cl_2$.

Acid-hydrolysis of the ester **19.9** provided thioselenenic acid **19.10** as a pale yellow crystalline compound (*242*) (Scheme 113). The sulfur atom of **19.10** was easily desulfurized by triphenylphosphine to give selenol **19.11**.

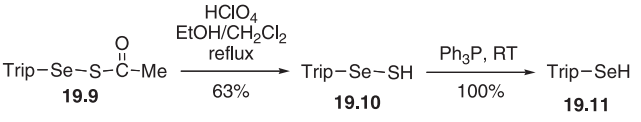
Hydrolysis of the selenoseleninate **19.8** was studied in some detail (*228*) (Scheme 114). Acid hydrolysis gave selenenic acid **19.6** as the principal product, whereas alkaline hydrolysis yielded diselenide **19.12** and seleninic acid **19.13**.



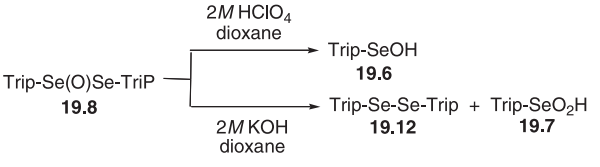

Scheme 111.




Scheme 112.




Scheme 113.




Scheme 114.



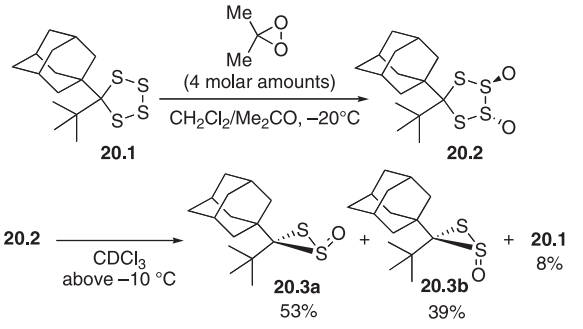
## 20. Chemistry of *vic*-disulfoxides

*vic*-Disulfoxides had been thought to be formed by stepwise oxidation of disulfides through thiosulfinates as the intermediate. However, most of *vic*-disulfoxides were elusive and their existence was only detected in a few cases by NMR spectroscopy.

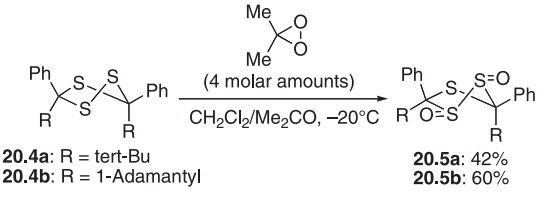
In 1999 we succeeded in the first synthesis and isolation of a *vic*-disulfoxide. The oxidation of tetrathiolane **20.1** by DMD yielded *vic*-disulfoxide **20.2**, which was isolated in pure form by removal of the volatile materials from the reaction mixture at −20 °C *in vacuo* and crystallization of the remaining solid from $CH_2Cl_2$/hexane at the same temperature (*208, 219*) (Scheme 115). The *vic*-disulfoxide **20.2** was stable even at room temperature in the crystalline state, but decomposed above −10 °C in solution with extrusion of disulfur monoxide ($S_2O$) to give an isomeric mixture of dithiiranes **20.3a** and **20.3b** in addition to **20.1**. The chemistry of disulfur monoxide will be discussed in Section 25.

Oxidation of trithiolanes **20.4a** and **20.4b** at −20 °C also furnished *vic*-disulfoxides **20.5a** and **20.5b**, respectively (*241*, *254*) (Scheme 116). Stereochemistry of the above oxidation and properties of the resulting disulfoxides were examined in detail.

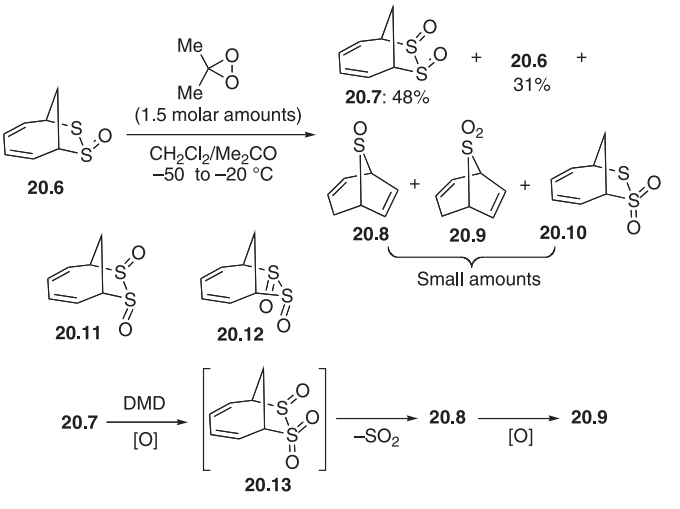
Oxidation of cyclic thiosulfinate **20.6** resulted in the stereospecific formation of *vic*-disulfoxide **20.7** in which two S=O groups exist in the eclipsed configuration (*260*) (Scheme 117). Compounds **20.8–20.10** were formed in small amounts, but no stereoisomers **20.11** and **20.12** were formed. **20.8** and **20.9** were probably formed through further oxidation of **20.7** that afforded **20.13**.




Scheme 115.



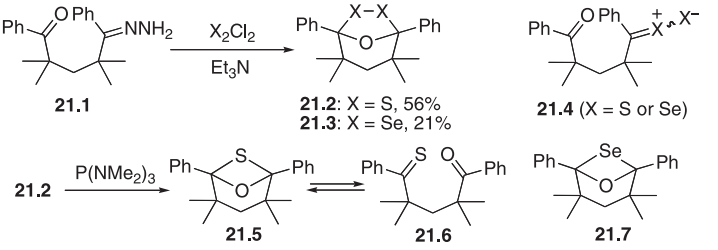

Scheme 116.



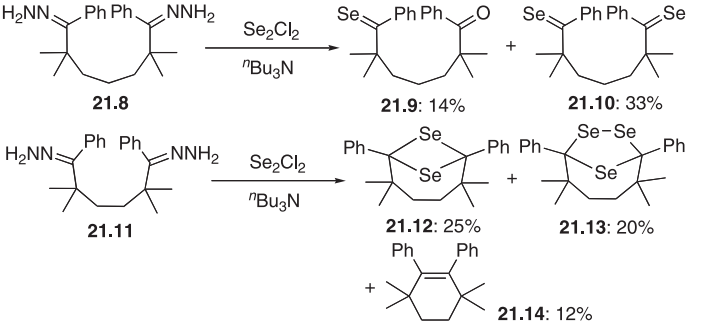

Scheme 117.

## 21. Syntheses with reactions of hydrazones with disulfur dichloride and diselenium dichloride

The reaction of hydrazone **21.1** with disulfur dichloride in the presence of $Et_3N$ furnished a novel heterocycle, 1,3,4-oxadithiolane **21.2**, that corresponds to the intramolecular 1,3-dipolar cycloadduct of thiosulfine intermediate **21.4** (X=S) (*118*, *138*) (Scheme 118). The same reaction worked to give oxadiselenolane **21.3** by use of diselenium dichloride. Desulfurization of **21.2** with $P(NMe_2)_3$ gave an inseparable mixture of 1,3-oxathietane **21.3** and thione **21.6**, which are in




Scheme 118.




Scheme 119.



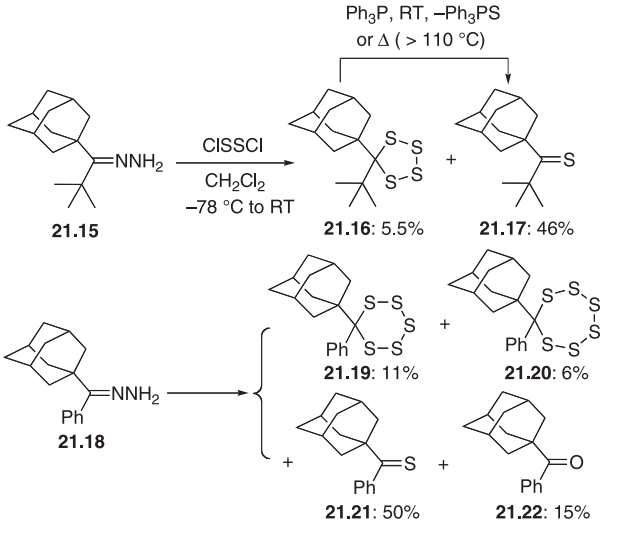
equilibrium with each other in solution. In the selenium case, oxaselenetane **21.7**, the deslenation product of **21.3**, did not show such an equilibrium and was isolated as a pure species.

The reaction of dihydrazone **21.8** with diselenium dichloride produced selones **21.9** and **21.10**, while the same reaction of **21.11** gave new heterocycles **21.12** and **21.13**, together with cyclohexene derivative **21.14** (*128*) (Scheme 119).

The reaction of hydrazone **21.15** with disulfur dichloride led to the preparation of the first compound **21.16** that possesses a tetrathiolane ring system (*168*) (Scheme 120). Yellow crystalline **21.16** is thermally unstable and decomposed to give thione **21.17**. On the other hand, the same reaction of hydrazone **21.18** gave pentathiane **21.19** and hexathiepane **21.20** together with **21.21** and **21.22** (*172*).

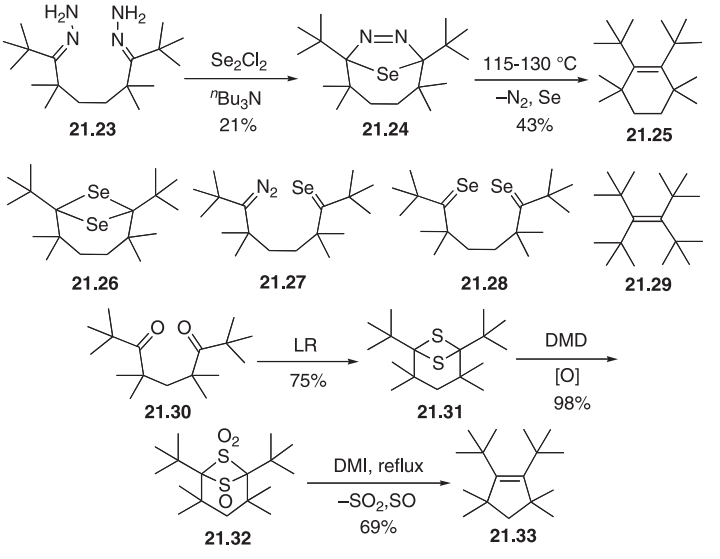
Treatment of dihydrazone **21.23** with diselenium dichloride in the presence of tributylamine produced selenadiazoline **21.24** together with other compounds such as diselenetane **21.26** (*214*) (Scheme 121). Compounds **21.24** and **21.26** correspond to the intramolecular [2+3] cyclization product of **21.27** and [2+2] cyclization product of **21.28**, respectively. Light- and heat-sensitive **21.24** gave cyclohexene derivative **21.25** on thermolysis. The cyclohexene **21.25** is a tied-back tetra-*tert*-butylethylene and is one of the compounds that came closest to tetra-*tert*-butylethylene **21.29**. Highly congested cyclopentene **21.33** was prepared from **21.30** as the starting material via sulfurization with Lawesson' reagent, oxidation of dithietane **21.31**, and thermolysis of the resulting **21.32**.

Diazo-compound **21.34**, obtained by nickel peroxide oxidation of hydrazone **21.23**, reacted with elemental selenium and sulfur in the presence of DBU to give diselenocane **21.35** and dithiocane **21.36**, respectively (*239*) (Scheme 122). In the selenium case, the cyclohexene **21.25** was formed as the major product probably through intermediary formation of **21.27**.




Scheme 120.



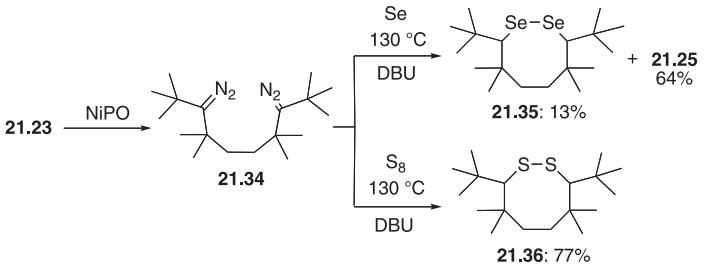



Scheme 121.

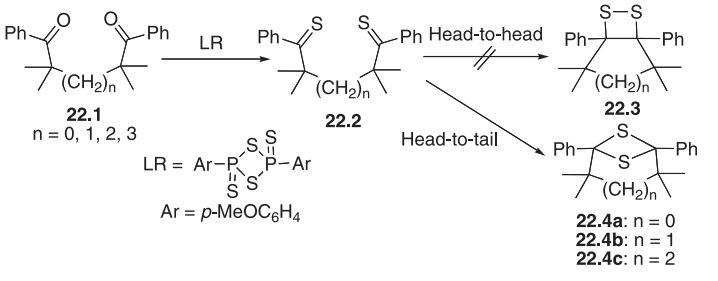
## 22. Sulfurization of nonenolizable diketones and some related works

The most remarkable achievement, developed from the sulfurization study of nonenolizable diketones, is the successful synthesis of dithiiranes, whose chemistry is described in Section 23. Some related works are summarized here.

Sulfurization of diketones **22.1** by Lawesson's reagent (LR) was examined in detail with the expectation that the resulting dithiones **22.2** might undergo [2+2] intramolecular head-to-head dimerization to furnish 1,2-dithietanes **22.3** (*99*) (Scheme 123). However, the reaction did work in the expected way, but it gave head-to-tail dimerization product, 1,3-dithietanes **22.4**, when $n = 0$, 1, 2. Dithiones **22.2** were obtained as the major product when $n = 2$, 3.




Scheme 122.



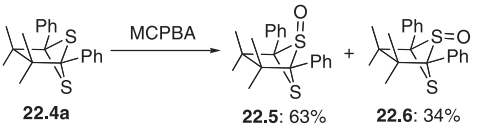

Scheme 123.

Oxidation of **22.4a** with MCPBA gave *endo*-sulfoxide **22.5** and *exo*-sulfoxide **22.6** (*127*) (Scheme 124). Further oxidation of **22.5** and **22.6** took place much slower for **22.5**, which was ascribed to the existence of a 1,3-transannular interaction that lowers the electron density of the sulfide sulfur for **22.5** (Figure 2).

Treatment of **22.7**, prepared by oxidation of **22.4b**, with Montmorillonite K10 resulted in the rearrangement to **22.8** in 11% yield with 87% recovery of **22.7**, while treatment of **22.8** under the same conditions gave **22.7** in 89% yield with 9% recovery of **22.8** (*151*) (Scheme 125).

Lithiation of **22.11**, prepared from **22.9**, led to the discovery of an interesting rearrangement (*209*) (Scheme 126). Thus, treatment of **22.11** with LDA at −78 °C followed by alkylation with methyl iodide gave **22.12**, while alkylation with isopropyl bromide afforded **22.13**.

Oxidation of dithietane **22.14**, obtained by desulfurization of **22.10** with $P(NMe_2)_3$, produced tetrathiane **22.15** as a 1:1 mixture of *cis-trans* isomers in 72% combined yield (*213*) (Scheme 127).




Scheme 124.

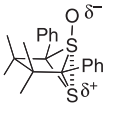
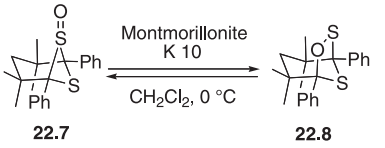
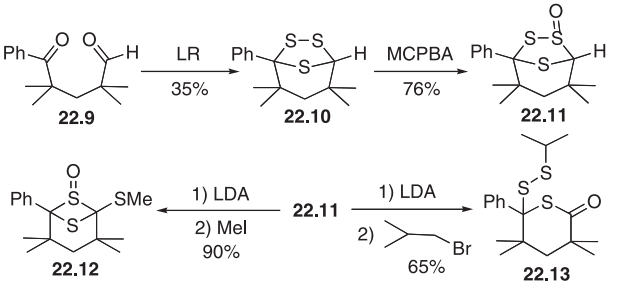


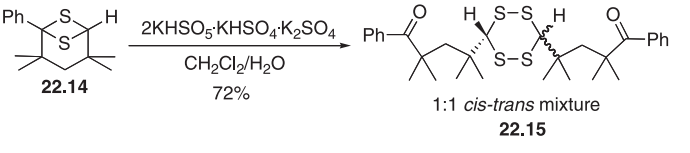
Figure 2. Transannular interaction in **22.5**.




Scheme 125.




Scheme 126.




Scheme 127.



## 23. Chemistry of three-membered ring compounds

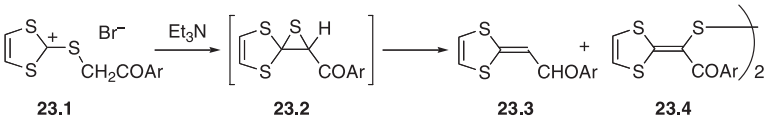
### 23.1. *Thiiranes*

Reactions of thiiranes with benzyne that produce phenylthio-substituted alkenes were described in Section 3. Preparation of thiiranes by reactions of adamantylideneadamantane and related compounds with elemental sulfur were also described in Section 4. Probable formation of thiiranes by reactions of sulfur ylides with sulfur was introduced in Section 4.

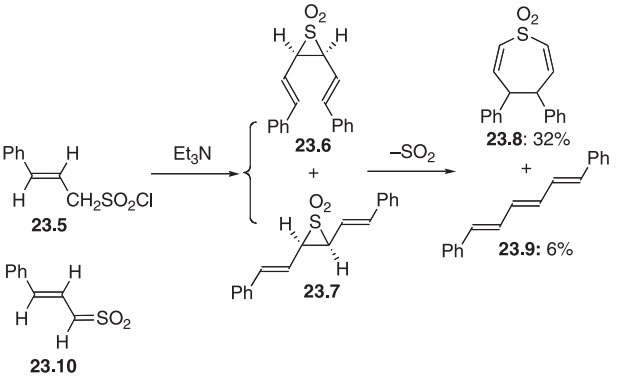
Treatment of dithiolylium salts **23.1** with $Et_3N$ afforded compounds **23.3** and **23.4** in good combined yield through thiiranes **23.2**, cyclization products of the initially-formed sulfur ylide intermediate (*29*) (Scheme 128).

Treatment of the sulfonyl chloride **23.5** with $Et_3N$ resulted in the probable formation of episulfones **23.6** and **23.7** through intermediary sulfene **23.10** (*52*) (Scheme 129). Then $SO_2$ extrusion of **23.6** and **23.7** gave thiepine **23.8** and triene **23.9**, respectively, as the final products.

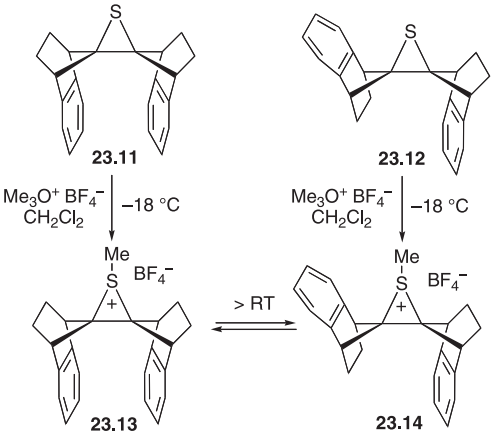
Preparation of thiiranes **23.11** and **23.12** was described in Section 4. These were methylated at −18 °C to give the sulfonium salts **23.13** and **23.14**, respectively (*234*) (Scheme 130). Interestingly,




Scheme 128.




Scheme 129.




Scheme 130.

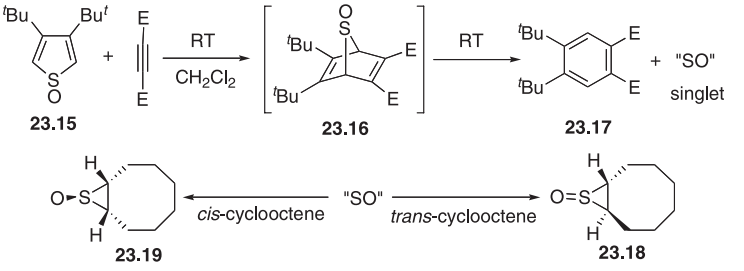
these sulfonium salts underwent mutual isomerization at room temperature. Thus the methylation at room temperature gave 1:4 equilibrium mixtures of **23.13** and **23.14**, irrespective of the starting sulfides.

The Diels–Alder reaction of thiophene 1-oxide **23.15** with DMAD takes place at room temperature and the resulting adduct **23.16** spontaneously extrudes sulfur monoxide "SO" (*248*) (Scheme 131). If these two reactions are concerted, the SO formed would be singlet. Attempted trapping of the SO with *cis*- and *trans*-cyclooctenes gave thiirane oxides **23.18** and **23.19**, respectively, though in low yields, with retention of the stereochemistry of the alkenes (*266*) (Scheme 131). The SO could be trapped by other angle-strained alkenes.

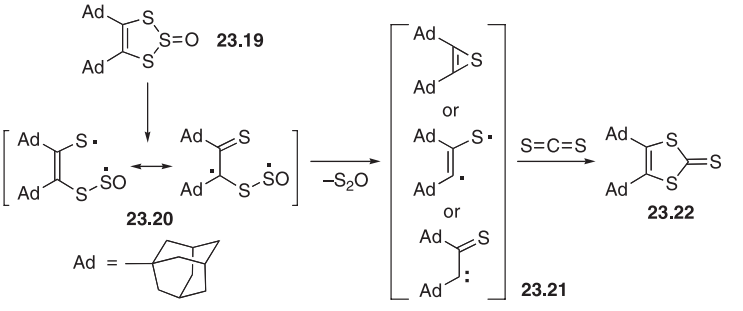
## 23.2. *Thiirenes and their S-oxides*

The reaction of benzyne with disulfur dichloride may involve benzothiirene as the intermediate, which leads to the final products (Section 3).

Thermolysis of trithiole **23.19** affords thiirene **23.21** or the equivalent with extrusion of disulfur monoxide "$S_2O$" (*186*) (Scheme 132). Thus, thermolysis in carbon disulfide at 120 °C in a sealed tube gave dithiole **23.22** in 70% yield, which corresponds to the adduct of **23.21** with carbon disulfide. Preparation of **23.19** and chemistry of "$S_2O$" will be described later.




Scheme 131.



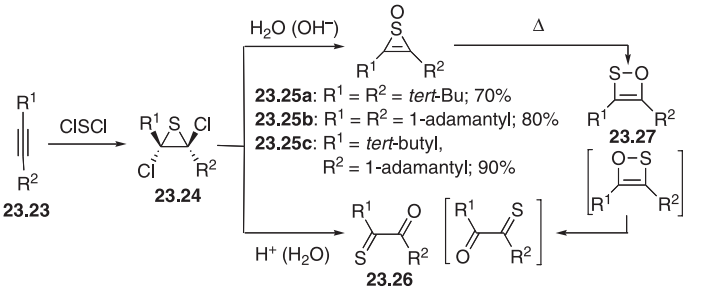

Scheme 132.

Sulfur dichloride added to acetylenes that possess bulky substituents to furnish thiiranes **23.23** quantitatively (*220, 231, 238*) (Scheme 133). Alkaline hydrolysis of **23.24** provided thiirene oxides **23.25**, while acid hydrolysis gave $\alpha$-oxothioketones **23.26**, thus providing new syntheses of thiirene oxides and $\alpha$-oxothioketones, respectively. Thermolysis of **23.25** in refluxing toluene resulted in the isomerization to **23.26** in excellent yields probably via oxathietes **23.27**.

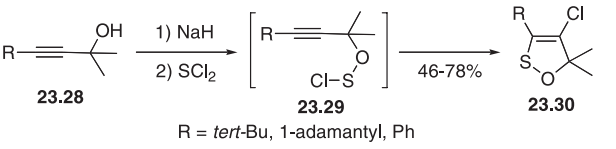
Incidentally, treatment of the sodium salt of propargyl alcohols **23.28** with $SCl_2$ gave oxathioles **23.30** through the initial adducts **23.29** (*246*) (Scheme 134).

Most surprisingly, the "SO" extruded from **23.16** (adduct of **23.24** and DMAD) added to alkynes to furnish thiirene 1-oxides **23.31** in 5–20% yields (*266*) (Scheme 135). The reaction could be carried out under mild conditions and thus allowed the preparation of hitherto unknown structurally simple thiirene 1-oxides such as **22.31a–c**.

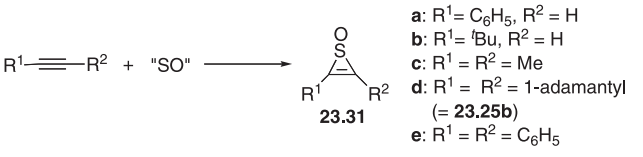
With expectation of obtaining *S*-unoxidized thiirene **23.34** by elimination of sulfur from **23.33**, thiirene 1-oxides **23.25a** and **23.25b** were treated with LR (Lawesson's reagent) (*252*) (Scheme 136). The reaction most unexpectedly afforded $\alpha$-dithiones **23.32a** and **23.32b**,



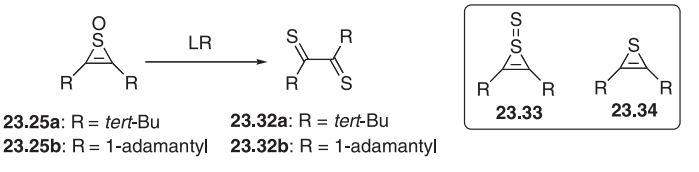

Scheme 133.




Scheme 134.




Scheme 135.



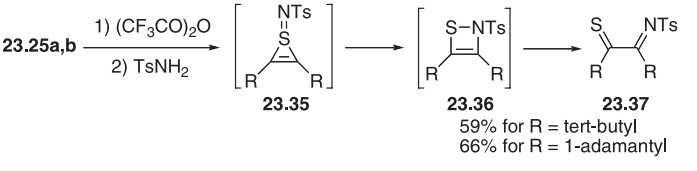

Scheme 136.



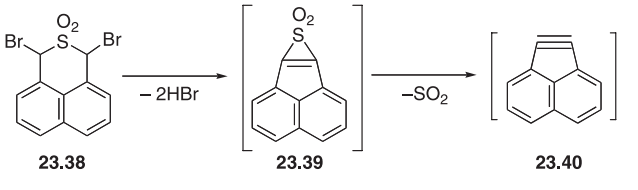
respectively. These are the first examples of aliphatic $\alpha$-dithiones that were synthesized and characterized.

Treatment of **23.25a,b** with trifluoroacetic acid anhydride and then with *p*-toluenesulfonamide afforded $\alpha$-iminothioketones **23.37** via intermediates **23.35** and **23.36** (*236*) (Scheme 137).

Highly strained alkyne **23.40** could be generated by the Ramberg–Backlund reaction of **23.38** through $SO_2$ extrusion of thiirene dioxide **23.39** (*41*) (Scheme 138).




Scheme 137.




Scheme 138.

## 23.3. *Dithiiranes*

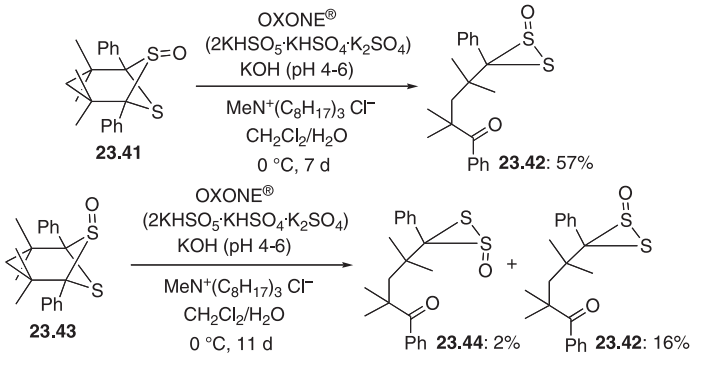
### 23.3.1. *Preparation*

Dithiiranes, the smallest cyclic disulfide, had been known only as an elusive intermediate until 1993. In that year, we reported the synthesis, isolation, structure, and reactions of dithiiranes (*137*, *173*) (Scheme 139). Thus, oxidation of **23.41** with OXONE® under carefully controlled conditions furnished dithiirane oxide **23.42**, along with two other compounds. Oxidation of **23.43** gave a mixture of **23.44** and **23.42**. The structure of **23.42** was determined unambiguously by X-ray diffraction analysis.

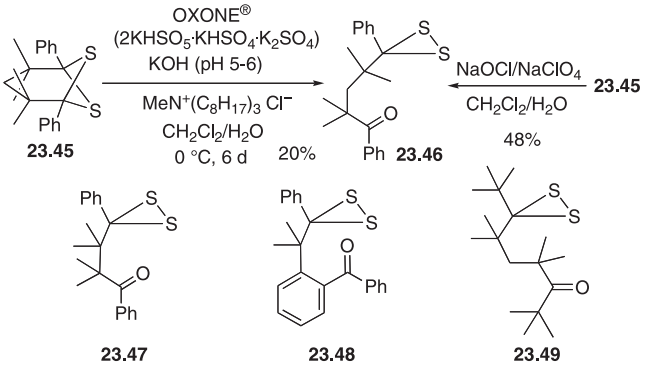
Oxidation of the *S*-unoxidized starting material **23.45** under the same conditions furnished *S*-unoxidized dithiirane **23.46** (*146*, *173*) (Scheme 140). Later it was shown that oxidation of **23.45** by a $NaOCl/NaClO_4$ system afforded **23.46** in a better yield (*153*, *173*). Preparation of other *S*-unoxidized dithiiranes such as **23.47**–**23.49** was also reported (*173*, *174*).

Furthermore, two new methods were developed for preparation of *S*-oxidized dithiiranes. Oxidation of tetrathiolane **23.50a** with dimethyldioxirane (DMD) at −78 °C afforded thermally unstable terathiolane 2,3-dioxide **23.51**, which extruded disulfur monoxide ($S_2O$) on being warmed to room temperature, to give a mixture of dithiirane oxides **23.52** and **23.53** in almost equal amounts (*189*, *208*, *219*) (Scheme 141). In a similar way, **23.54** was obtained from **23.50b**. Compounds **22.55** were by-products of these reactions.

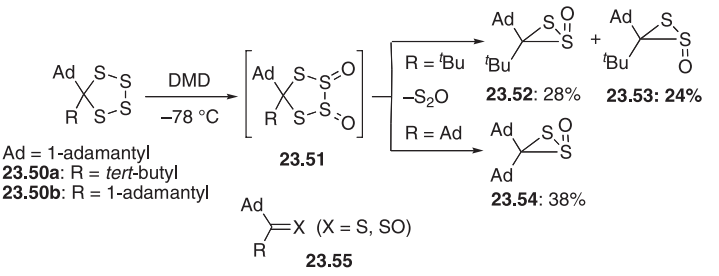




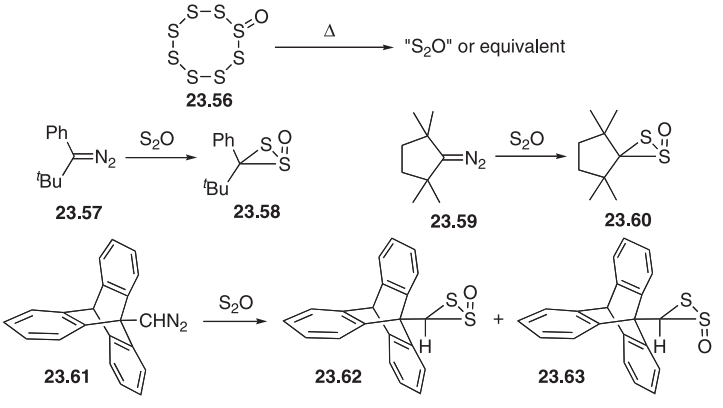

Scheme 139.




Scheme 140.




Scheme 141.




Scheme 142.



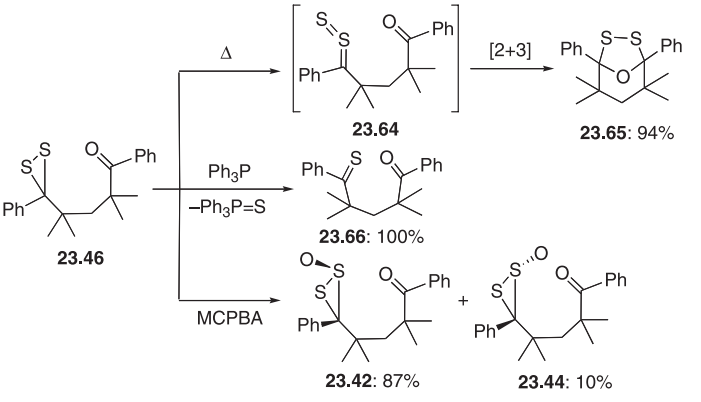
It was found that octasulfur monoxide ($S_8O$) **23.56** serves as a disulfur monoxide equivalent. Thus, heating diazoalkanes **23.57** and **23.59** with **23.56** resulted in the replacement of $N_2$ by $S_2O$ to give **23.58** and **23.60**, respectively, in reasonable yields (*227*) (Scheme 142). From **23.61**, *cis*- and *trans*-dithiirane oxide isomers **23.62** and **23.63** were obtained in 8% and 10% yields, respectively, along with three other products (*265*).

### 23.3.2. *Chemical properties*

Dithiirane **23.46** is a red crystalline compound that decomposes at 68–75 °C and shows an absorption maximum at 452 nm ($\varepsilon$ 104) in $CH_2Cl_2$ (*146*, *173*). Heating a dilute solution of **23.46** in dichloethane brought about isomerization to thiosulfine **23.64**, which then underwent an intramolecular 1,3-dipolar cycloaddition to yield **23.65** as the final product (Scheme 143). Treatment of **23.46** with triphenylphosphine gave desulfurized product **23.66** quantitatively. Oxidation of **23.46** with MCPBA produced a mixture of oxidized dithiiranes **23.42** and **23.44**.

Dithiirane 1-oxides have two asymmetric centers if two substituents on the carbon are not the same (*176*) (Figure 3). Optical resolution of **23.42** and **23.44** was carried out and absolute configuration of the enantiomers was determined by X-ray crystallographic analyses. The thermal racemization (oxygen migration) between (1*S*,3*R*)- and (1*R*, 3*S*)-dithiirane oxides, which obeyed reversible first-order kinetics, was investigated with HPLC.

The divalent sulfur of **23.42** was easily removed by triphenylphosphine to give **23.67** (*137*, *173*) (Scheme 144). Heating **23.42** in refluxing toluene yielded **23.66** and **23.67** with extrusion of sulfur monoxide and sulfur, respectively, in addition to diketone **23.68**, which was probably derived from **23.66** and/or **23.67**.




Scheme 143.

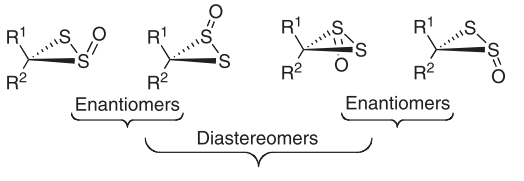
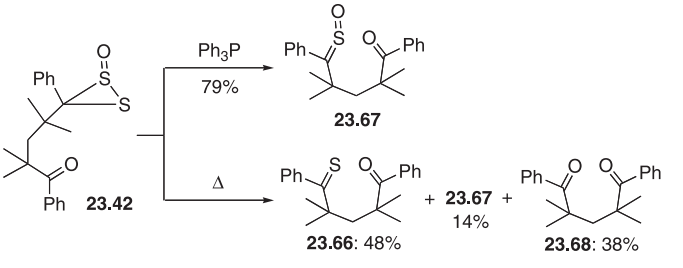


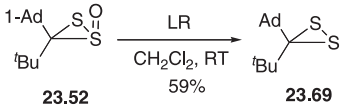

Figure 3. Diasteromers and enantiomers of dithiirane 1-oxides.



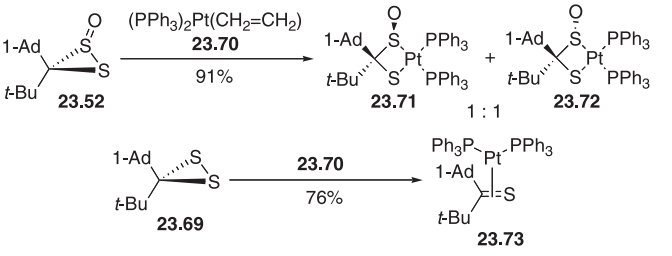

Scheme 144.

Dithiirane 1-oxides were deoxygenated by LR to give *S*-unoxidized compounds (*245*). A typical example is given in Scheme 145.

Treatment of **23.52** with platinum(II) complex **23.70** gave a 1:1 mixture of **23.71** and **23.72**, while the reaction of **23.69** with **23.70** gave **23.73** (*237*) (Scheme 146).




Scheme 145.




Scheme 146.

### 23.4. *Miscellaneous*

A series of di-, tri-, and tetra-substituted *N*-tosylaziridines underwent a $BF_3$-catalyzed rearrangement (aza-pinacol rearrangement) under mild conditions to give the corresponding *N*-tosylimines in satisfactorily yields (*244*). A representative example is given in Scheme 147.

Cyclopropanes **23.76** and **23.77** were prepared and their oxidation was investigated (*113*) (Scheme 148).



## 24. Chemistry of four-membered ring compounds

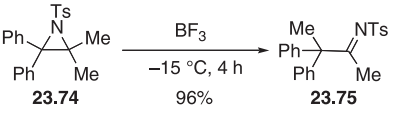
### 24.1. *1,3-Dithietane*

Formation of 1,3-oxathietanes, 1,3-dithietanes, 1,3-oxaselenetanes, and 1,3-diselenetanes by [2+2] intramolecular cycloaddition was described in Sections 21 and 22.

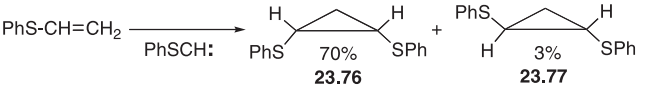
The reaction of ynamine **24.1** with carbon disulfide under 800 MPa at 70 °C furnished diethietane **24.2** quantitatively (*155*) (Scheme 149).

### 24.2. *1,2-Thiazetidine*

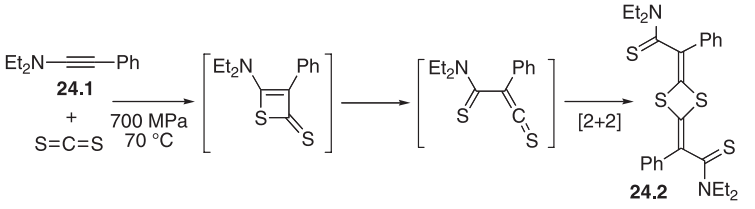
Preparation of thiophene 1-imides **24.3** and **24.6** was described in Section 15. The Diels–Alder reaction of **24.3** with PTAD in refluxing $CH_2Cl_2$ unexpectedly furnished a 1,2-thiazetidine **24.5** through the initial adduct **24.4**, whereas in the case of **24.6**, the initially formed thiazetidine **24.7** underwent a ring-expansion to give **24.8** (*248*) (Scheme 150). This provided the first successful synthesis of 1,2-thiazetidine.



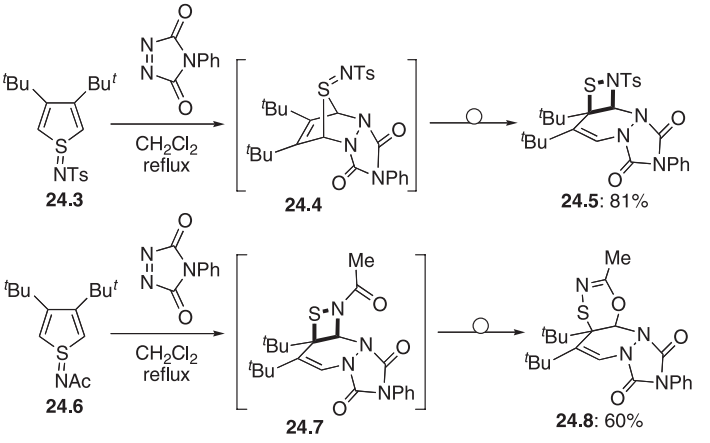

Scheme 147.




Scheme 148.



Scheme 149.



Scheme 150.



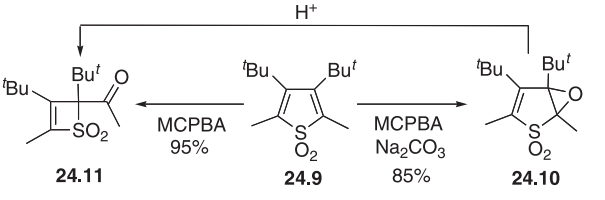
### 24.3. *Thiete*

Highly congested thiophene 1,1-dioxides afforded the corresponding epoxides by MCPBA oxidation in the presence of $Na_2CO_3$, whereas the oxidation in the absence of $Na_2CO_3$ produced the ring-contracted thiete 1,1-dioxides. Thus, **24.9** gave **24.10** or **24.11** depending upon the reaction conditions (*124, 141*, see also *232*) (Scheme 151).

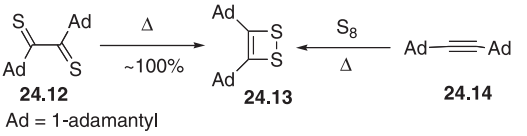
### 24.4. *1,2-Dithiete*

Dithiete **24.13** was prepared by reaction of acetylene **24.14** with sulfur, as described in Section 4. It was also formed by thermal isomerization of dithione **24.12** (*252*) (Scheme 152).

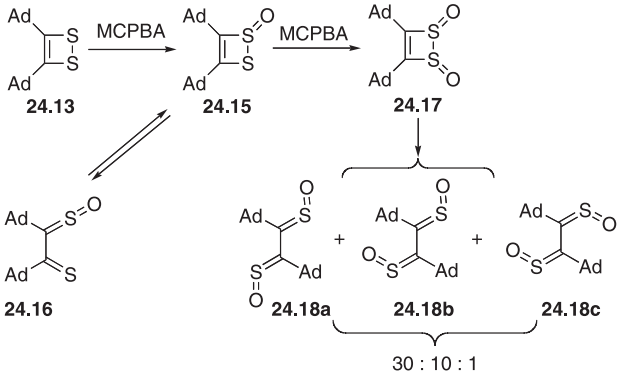
Oxidation of dithiete **24.13** with MCPBA (1 equiv.) yielded **24.15**, which, when heated in toluene, formed a mixture of **24.15** and sulfine **24.16** ($\lambda_{max}$ 576 nm) in the ratio 1:7 (*156*) (Scheme 153). Further oxidation of **24.15** gave a 30:10:1 isomeric mixture of $\alpha$-disulfines **24.18a–c**, where the major isomer **24.18a** was isolated in 65–70% yield.



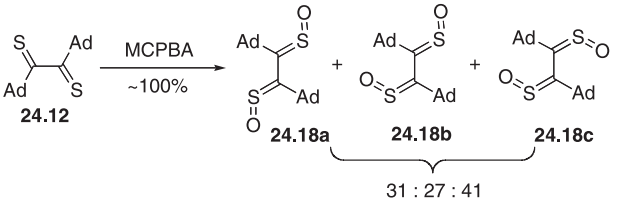
Scheme 151.




Scheme 152.




Scheme 153.




Scheme 154.



MCPBA oxidation of **24.12** also gave an isomeric mixture of **24.18a–c** in the different ratio of 31:27:41 (*252*) (Scheme 154).

Many compounds, such as **24.19**–**24.23**, some of which possess two *cis*-configured 1-adamantyl groups at the vicinal position, could be derived from dithiete **24.13** (*186*) (Scheme 155).

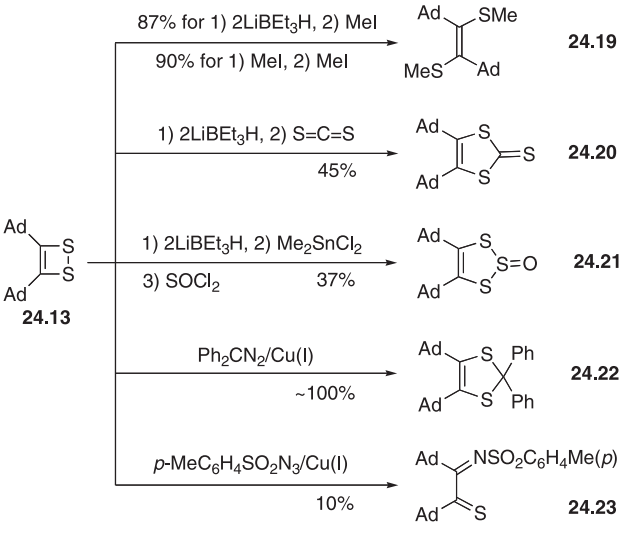
### 24.5. *Sulfur-peribridged naphthalenes*

The photolysis of thiadiazine **24.25**, prepared by aprotic diazotization of **24.24**, furnished sulfur-peribridged naphthalene **24.26** quantitatively (*26*). The oxidation of **24.25** with MCPBA gave thiadiazine *S*-oxide **24.27**, which spontaneously extruded $N_2$ to give sulfoxide **24.28** in 71% yield together with sulfone **24.29** in 4% yield (Scheme 156).

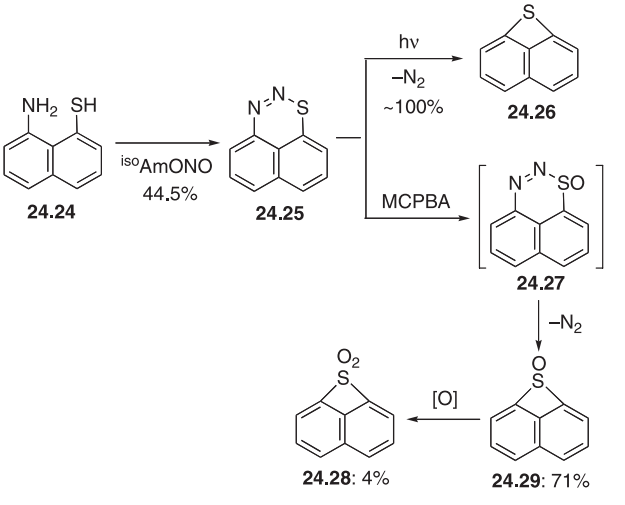
## 25. Chemistry of small molecules of sulfur: SO, $S_2O$, and $S_3$

### 25.1. *Sulfur monoxide (SO)*

As was described in Section 23, the Diels–Alder adduct **25.2**, produced from **25.1** and DMAD, split into **25.3** and sulfur monoxide (SO) spontaneously, and the SO thus formed added to alkynes and




Scheme 155.

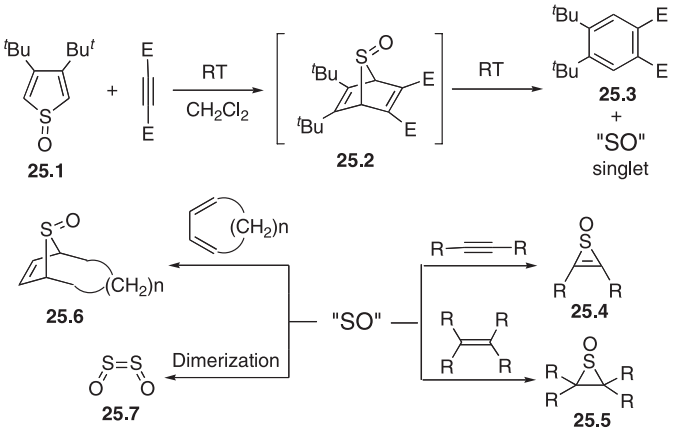



Scheme 156.

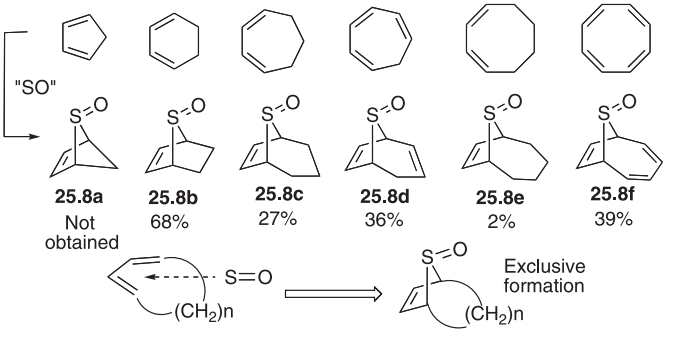
alkenes to furnish thiirene 1-oxides **25.4** and thiirane oxides **25.5**, respectively (*266*) (Scheme 157). The SO was also trapped by cyclic dienes (polyenes) to give bicyclic sulfoxides **25.6**. It was also trapped by a range of acylic dienes. Seemingly, the SO dimerized to give disulfur dioxide **25.7**.

The SO underwent a [1+4] addition to a series of cyclic dienes (polyenes) to furnish sulfoxides **25.8a**–**f** (*266*) (Scheme 158). The reaction is stereospecific, thereby yielding the adducts in which the S=O group is *anti* to the newly formed double bond, that is, the SO approaches to the diene part from the direction shown in Scheme 158.

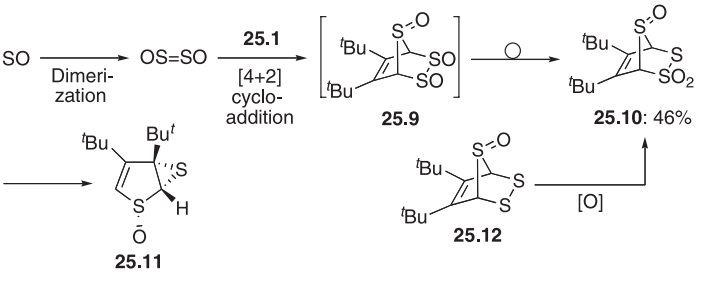
The reaction of **25.1** with DMAD, when carried out in the absence of a suitable trapping agent, afforded **25.10** in low yield, in addition to **25.3** as the major product. The yield of **25.10** increased up to 46% when **25.1** and DMAD were rapidly mixed up in the molar ratio 2:1. The formation of **25.10** is best explained by assuming dimerization of the SO, Diels–Alder reaction of the resulting OS=SO with **25.1**, and 1,2-rearrangement of the *vic*-disulfoxide **25.9** (*266*) (Scheme 159). **25.10**




Scheme 157.




Scheme 158.

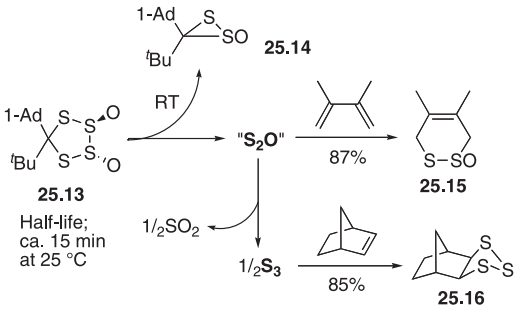



Scheme 159.

was independently prepared by oxidation of **25.12**, and was thermally unstable and decomposed to give **25.11**.

### 25.2. *Disulfur monoxide (dithioozone, $S_2O$), and triatomic sulfur (trithioozone, $S_3$)*

As was described in Section 20, thermolysis of tetrathiolane 2,3-dioxide **25.13** furnished dithiirane oxide **25.14**, thereby at the same time providing a new method for the generation of disulfur monoxide, "$S_2O$" (*208*, *219*) (Scheme 160). The $S_2O$ formed underwent a [2+4] cycloaddition with 2,3-dimethyl-1,3-butadiene to give **25.15**. In the absence of a suitable trapping agent, it




Scheme 160.

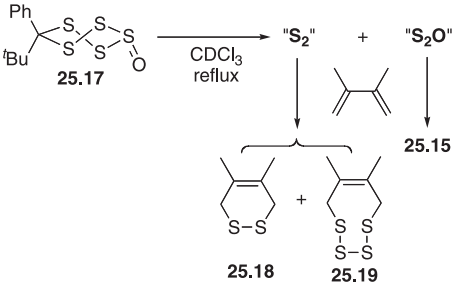
disproportionated to $SO_2$ and triatomic sulfur "$S_3$". The latter could be trapped by norbornene to give **25.16**.

Thermolysis of pentathiane oxide **25.17** probably generates both diatomic sulfur $S_2$ and disulfur monoxide $S_2O$ (*226*) (Scheme 161). Thus, the thermolysis of **25.17** in the presence of 2,3-dimethyl-1,3-butadiene afforded **25.14**, **25.18**, and **25.19**, together with a few products that were produced from the organic counterparts.

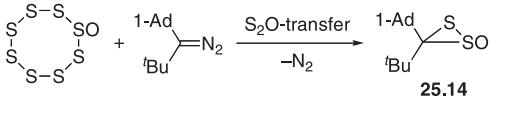
Octasulfur monoxide $S_8O$ serves as the $S_2O$ equivalent. Thus, thermolysis of $S_8O$ in the presence of diazoalkane provided a new synthesis for dithiirane oxide, as described in Section 23. A typical example is the preparation of **25.14** (*227*) (Scheme 162).

DMD oxidation of **25.12**, prepared by addition of $S_2Cl_2$ to **25.1**, gave a 7:1 isomeric mixture of **25.20a** and **25.20b** (*258*) (Scheme 163). Both isomers are thermally labile and begin to dissociate into **25.1** and $S_2O$ in a reversible way above room temperature. The process of the dissociation could be observed by $^1$H NMR spectroscopy. The $S_2O$ formed was trapped by 2,3-dimethyl-1,3-butadiene and disproportionated to $S_3$ and $SO_2$ in the absence of a suitable trapping agent.

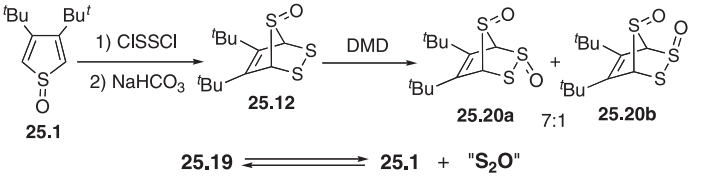
As is expected from the fact that **25.20** dissociated into **25.1** and $S_2O$, the adduct **25.21** of cyclopentadiene and $S_2O$ also might dissociate into the starting materials (*258*) (Scheme 164). Thus, even if the generated $S_2O$ was trapped by cyclopentadiene, the final destination of $S_2O$ would be $S_3$ and $SO_2$ via disproportionation. Indeed, the $S_3$ was formed in this way and underwent a [2+3] cycloaddition with cyclopentadiene to give **25.22**.



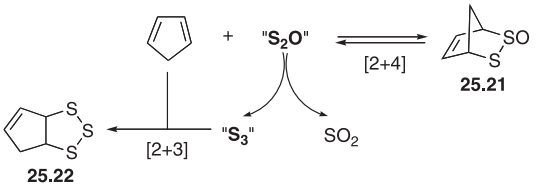

Scheme 161.



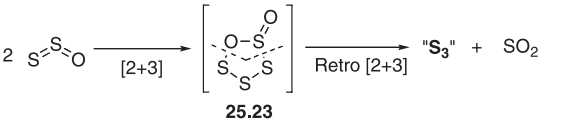

Scheme 162.




Scheme 163.




Scheme 164.




Scheme 165.

The mechanism that involves [2+3] and retro [2+3] cycloadditions was proposed for the disproportionation of $S_2O$ based on DFT calculations (*258*) (Scheme 165).



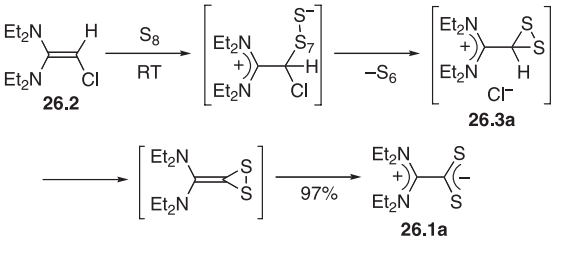
## 26. Carbenium dithiocarboxylates and the related compounds

### 26.1. *Carbenium dithiocarboxylates: inner salts composed of $(R_2N)_2C^+$– and $–CS_2^-$ ions*

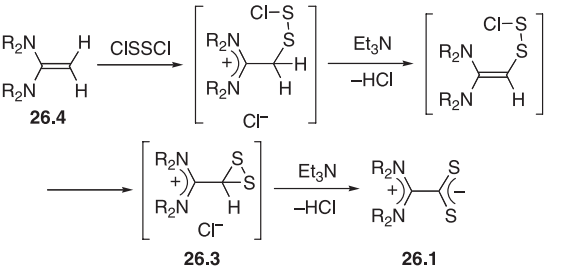
Carbenium dithiocarboxylates **26.1** are the inner salt that is composed of $(R_2N)_2C^+$– and $–CS_2^-$ ions.

#### 26.1.1. *Synthesis*

In 1992, a sort of serendipity led us to a new synthesis of the inner salt **26.1a** by reaction of **26.2** with elemental sulfur (*123*, *150*) (Scheme 166).




Scheme 166.




Scheme 167.

The mechanism shown in Scheme 166 was proposed for the formation of **26.1a**. If this mechanism is operative, the reaction of enamines **26.4** with disulfur dichloride also should lead to the formation of the inner salts **26.1**, because addition of disulfur dichloride to **26.4** would lead to the formation of carbenium ions **26.3** that correspond to the intermediate **26.3a** (Scheme 167). Indeed, the intended reaction worked cleanly to furnish a series of **26.1** (*183*).



### 26.1.2. *Structure*

The most characteristic structural feature of the inner salt is that the two planes given by the carbenium and dithiocarboxylate ions are nearly perpendicular to each other, where the formally vacant carbon p-orbital and the negatively charged sulfur atoms are placed in the same plane (*150*, *218*, *243*; see *196* for the structure of a dinucler Pt(II) complex) (Figure 4). Thus the thermal stability of **26.1** would originate from the attractive coulombic interactions between the positive and negative centers.

### 26.1.3. *Reactions*

**26**.**1**.**3a** *Nucleophilic reactions.* The sulfur atoms of **26.1** are highly nucleophilic, and therefore **26.1a** was easily methylated to give **26.5** (*150*) (Scheme 168). An application of this reactivity is the reaction of **26.6** with six molar amounts of **26.1a** that furnished a huge molecule **26.7**, which has six carbenium carbons and is soluble in water (*230*).

The formal addition of tosyl nitrene to **26.1a** took place to furnish a new sort of inner salt **26.8** when **26.1a** was allowed to react with PhI=NTs without use of any catalysts (*224*) (Scheme 169).

**26**.**1**.**3b** *Electrophilic reaction.* A range of Grignard and organolithium reagents added to the negatively charged sulfur atom of **26.1a**, despite the presence of the positively charged carbon atom, to give enethiolates **26.9**, which were methylated to give **26.10** as the final products (*185*; see *178* for the reaction of **26.5** with nucleophiles) (Scheme 170). A mechanism involving a single-electron-transfer process from nucleophiles to **26.1a** was presented for this anomalous thiophilic addition.

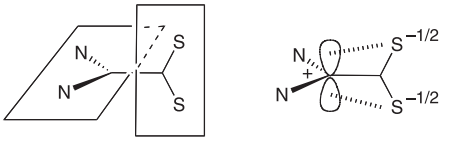
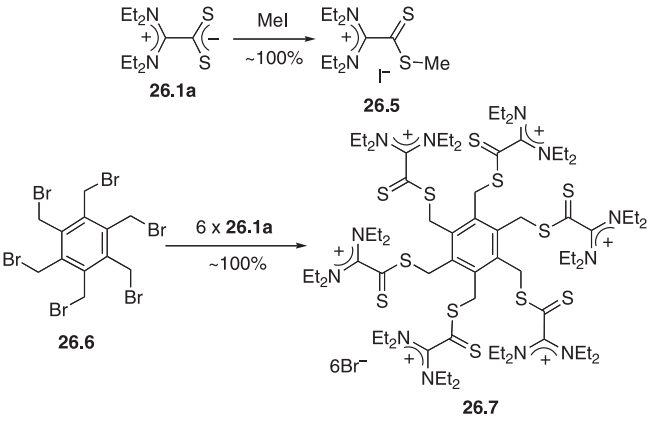
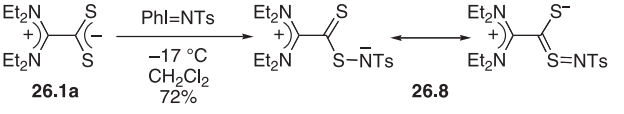


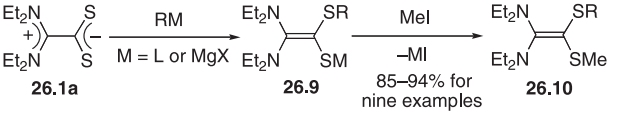

Figure 4. Structure of the inner salt **26.1**.




Scheme 168.




Scheme 169.

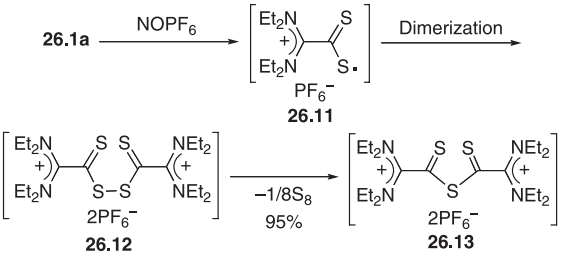



Scheme 170.

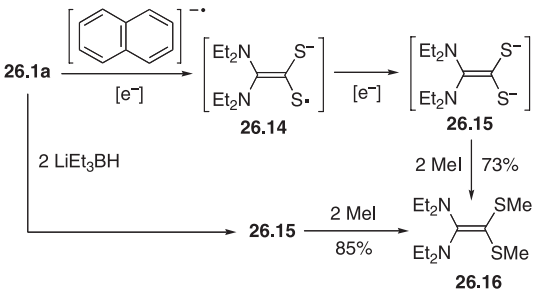


**26**.**1**.**3c** *Oxidation and reduction.* Oxidation of **26.1a** with $NOPF_6$ gave bis(carbenium) salt **26.13** via formation of radical cation **26.11** by a single-electron-transfer process (*197*) (Scheme 171).

On the other hand, reduction of **26.1a** with naphthalene anion radical furnished enedithiolate **26.15** through single-electron-transfer processes to give **26.16** by treatment with methyl iodide (*197*) (Scheme 172). The same compound was obtained by reduction with $LiEt_3BH$ and then methylation with methyl iodide.




Scheme 171.



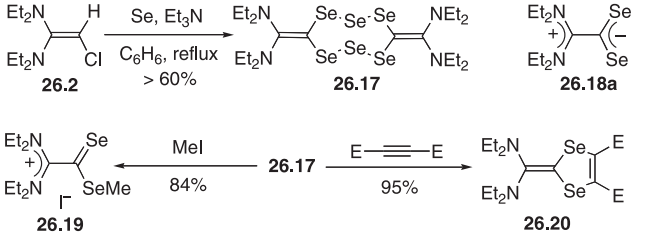

Scheme 172.

## 26.2. *Carbenium diselenocarboxylates: inner salts composed of $(R_2N)_2C^+$– and –$CSe_2^-$ ions*

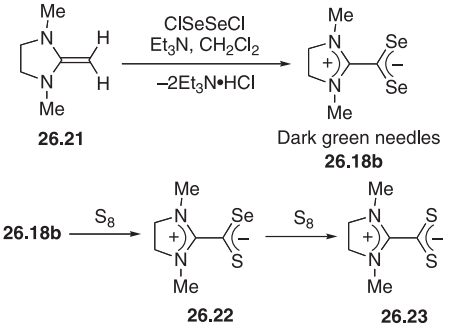
The reaction of **26.2** with elemental selenium furnished red solid compound **26.17**, whose crystalline state structure was determined by X-ray diffraction analysis (*193*) (Scheme 173). None of the expected carbenium diselenocarboxylate **26.18a** was formed. Compound **26.17** showed highly complex $^1$H and $^{13}$C NMR behavior in solution and served as the equivalent of inner salt **26.18a**, thus giving **26.19** and **26.20** by reactions with methyl iodide and DMAD, respectively.

The genuine inner salt **26.18b** was obtained as dark green crystals by reaction of **26.21** with diselenium dichloride (*218*) (Scheme 174). When **26.18b** was treated with elemental sulfur, its selenium atoms were replaced by sulfur atoms to give **26.22** and then **26.23**.

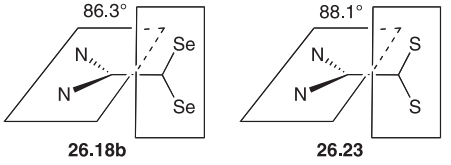
The two planes of **26.18b** given by the carbenium and diselenocarboxylate ions are nearly perpendicular (86.3°) to each other (*218*) (Figure 5). The structure of **26.23** was given for comparison.




Scheme 173.




Scheme 174.




**26.18b** **26.23**

Figure 5. Structure of the inner salt **26.18b** and **26.23**.

## 26.3. *Carbenium dithiocarboxylates: inner salts composed of $(R_2N)_2C^+$– and $–CS_2^-$ ions insulated by $sp^3$ carbon*

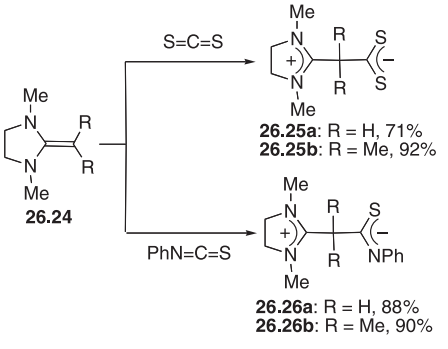
Inner salts **26.25**, which are composed of $(R_2N)_2C^+$– and $–CS_2^-$ ions insulated by one $sp^3$ carbon, were prepared by addition of carbon disulfide to enamines **26.24** (*191*) (Scheme 175). Inner salts **26.26** were prepared by addition of phenyl isothiocyanate to **26.24**.

When there exists at least one hydrogen atom on the $sp^3$ carbon, the inner salts isomerize to the corresponding dithiocarboxylic acids. Thus, the adduct of carbon disulfide to **26.27** existed as an equilibrium mixture of **26.28** and **26.29** in the ratio 9:1 in $CDCl_3$ at 22 °C (*170*) (Scheme 176).

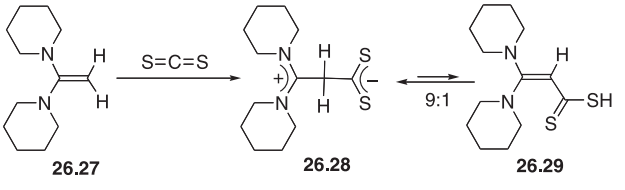
Although both **26.25** and **26.26** were expected to serve as 1,4-dipoles, only **26.26** worked so (Scheme 177). Thus, **26.25b** reacted with two molecules of DMAD to give **26.30** with probable extrusion of **26.31** (*191*), while the reaction of **26.26b** with DMAD furnished 1,4-dipolar cycloadduct **26.33** (*192*). The former reaction might involve the initial formation of **26.32**.

## 26.4. *Miscellaneous*

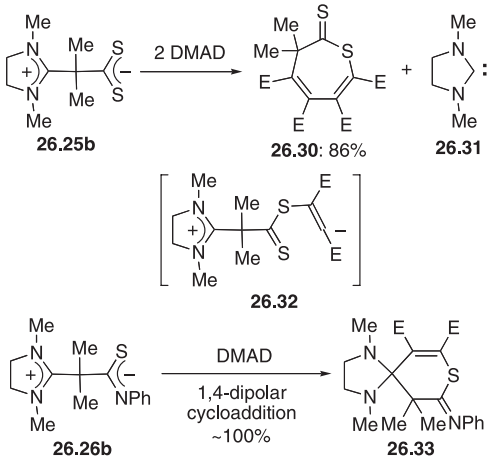
A new inner salt **26.34** was prepared by reaction of ethylenetrithiocarbonate with PTAD (*225*) (Scheme 178). Similarly, **26.35** was obtained from 2-thioxo-1,3-dithiole.




Scheme 175.




Scheme 176.



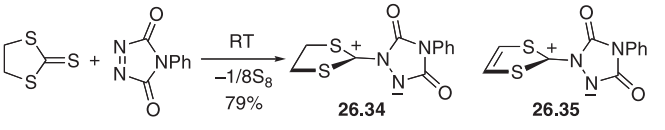

Scheme 177.



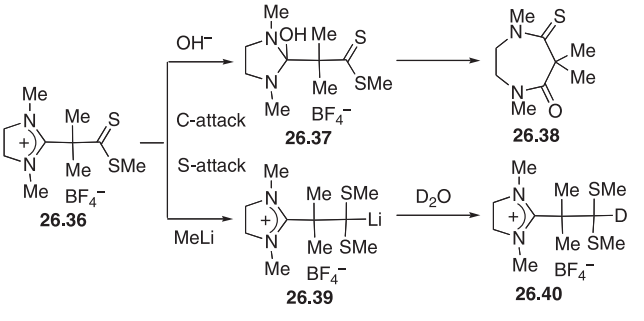
Carbenium salt **26.36**, derived from **26.25b**, reacted with $OH^-$ at the carbenium carbon to give **26.38** via ring expansion of **26.37**, whereas it reacted with MeLi to give **26.40** via hydrolysis of **26.39** (*199*) (Scheme 179).

Dithioesters **26.41** and **26.42** were prepared by alkylation of **26.29**. The reaction of **26.41** with propyl iodide gave a 94:4 mixture of **26.43** and **26.44**, and the reaction of **26.42** with methyl iodide afforded a 3:97 mixture of **26.43** and **26.44** (*181*) (Scheme 180).

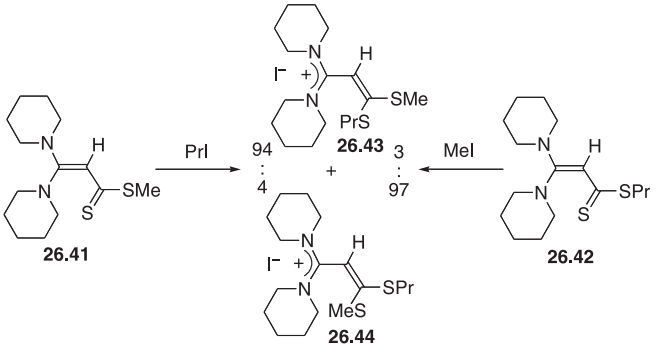
Disulfide **26.45**, obtained by reaction of **26.2** with carbon disulfide (*157*), reacted with DMAD to furnish thiopyran-2-thione **26.46** (*162*) (Scheme 181).



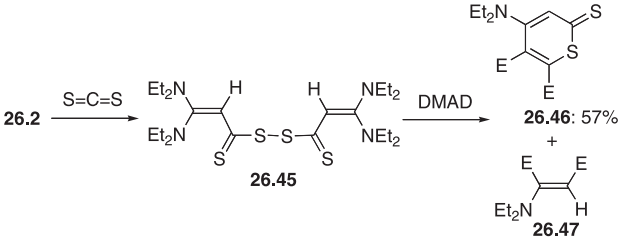

Scheme 178.




Scheme 179.




Scheme 180.




Scheme 181.



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