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Accounts

1-Oxides and 1,1-Dioxides of Thiophenes and Selenophenes and Related Compounds

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The first topic of the present article involves recent advances in the chemistry of thiophene 1-oxides. Next is the chemistry of the parent thiophene 1,1-dioxide, which is followed by that of congested thiophene 1,1-dioxides, where emphasis is placed on their syntheses and synthetic applications. The chemistry of 1-imino, 1,1-diimino, and 1-imino-1-oxo derivatives of thiophenes is then described. Finally, the newborn chemistry of selenophene 1-oxides and 1,1-dioxides is discussed.

Furans **1**, thiophenes **2**, selenophenes **3**, and tellurophenes **4** are typical five-membered, π-electron excessive, heteroaromatic compounds containing one chalcogen atom. Oxidation at the chalcogen atoms of these compounds results theoretically in the formation of the corresponding 1-oxides and 1,1-dioxides. Among them, furan 1-oxides **1-O** and 1,1-dioxides **1-O$_2$** are hypothetical molecules and might be never produced even as transient intermediates. The chemistry of thiophene 1-oxides **2-O** has been attracting much interest recently.[1] Meanwhile, the chemistry of thiophene 1,1-dioxides **2-O$_2$** has been extensively studied both experimentally and theoretically, and is thus well-documented. A recent exhaustive literature survey has revealed that more than three-hundred papers had appeared on the chemistry of **2-O$_2$**.[2] The chemistry of selenophene 1-oxides **3-O** and 1,1-dioxides **3-O$_2$** is a new field in heterocyclic and heteroatom chemistry. When we planned the investigation on **3-O** and **3-O$_2$**, none of monocyclic derivatives of these compounds had been reported. To our knowledge, monocyclic tellurophene 1-oxides **4-O** and 1,1-dioxides **4-O$_2$** have never been synthesized (Chart 1).

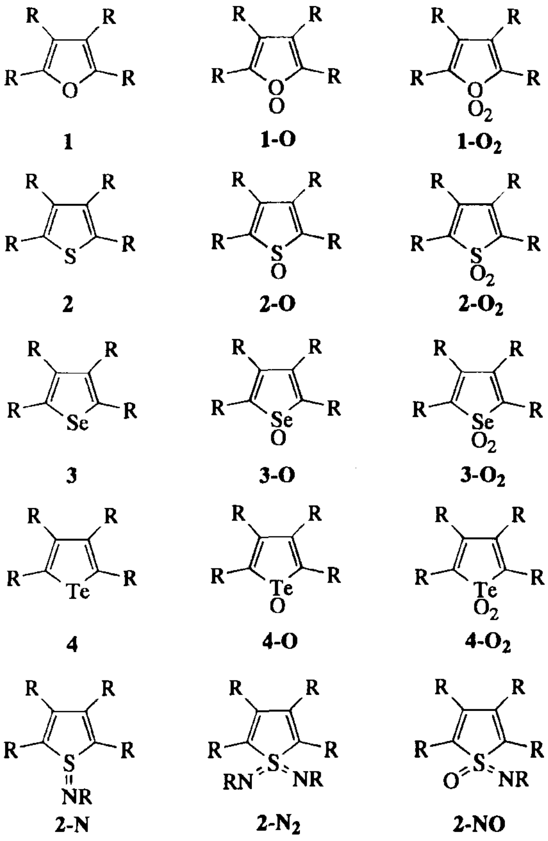


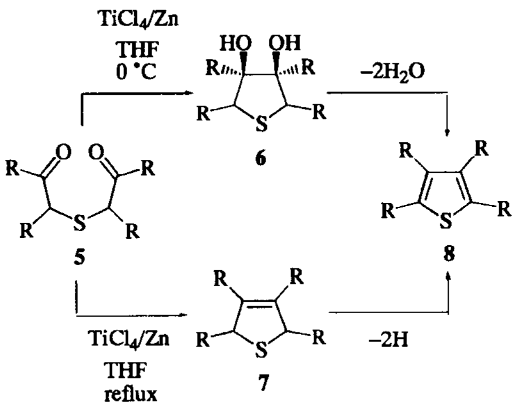
Chart 1.

The first topic of the present article involves recent advances in the chemistry of **2-O**. Next we are concerned with the chemistry of the parent thiophene 1,1-dioxide, which is followed by that of congested thiophene 1,1-dioxides, where emphasis is placed on their synthesis and synthetic applications. Replacement of the oxygen atom(s) of **2-O** and **2-O$_2$** by imino group(s) leads to the imino derivatives **2-N**, **2-N$_2$**, and **2-NO**. The chemistry of these compounds is then described. Finally, the newborn chemistry of **3-O** and **3-O$_2$**, which was initiated by the author's laboratories, is described.

Syntheses of Congested Thiophenes and Selenophenes as Substrates for Oxidation Study

Both 1-oxides and 1,1-dioxides of thiophenes and selenophenes are highly reactive species unless their rings are heavily substituted. Even thiophene 1,1-dioxides, which are the least reactive among these species, require two substituents on the ring to be satisfactorily synthesized and isolated under ordinary conditions. The most straightforward synthesis of these compounds is the oxidation of thiophenes and selenophenes. Therefore, heavily substituted thiophenes and selenophenes must be provided as the starting materials for the synthesis and isolation of these reactive species. These are supplied in the following ways.

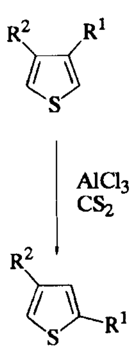
Intramolecular reductive coupling of 3-thiapentane-1,5-diones **5** with a low-valent titanium reagent, prepared from $TiCl_4$ and zinc powder, provides good yields of *cis*-thiolane-3,4-diols **6**[3] or 2,5-dihydrothiophenes **7**[4] depending upon the reaction conditions. Both **6** and **7** are converted to thiophenes **8** in high yields by treatment with an acid catalyst (TsOH) and a dehydrogenation reagent (DDQ), respectively.[3,4] The method is particularly useful for the preparation of 3,4-di-, 2,3,4-tri-, and 2,3,4,5-tetrasubstituted thiophenes which are otherwise difficult to prepare (Scheme 1).[5] Compounds **6** and **7** were also used for preparation of other compounds.[6]



5 6 7 8

Scheme 1.

Application of the above thiophene synthesis enables the easy preparation of a series of congested thiophenes, which possess bulky substituents at the 3- and 4-positions, such as 3,4-di-*t*-butyl-,[7,8] 3-(1-adamantyl)-4-*t*-butyl-,[8] 3,4-di(1-adamantyl)-,[8,9] and 3,4-dineopentylthiophenes[8,10] (**9**, **10**, **11**, and **12**, respectively). When **9** and **11** are treated with $AlCl_3$, they rearrange to thermodynamically more stable thiophenes **13** and **14**, respectively (Scheme 2).[7–9]

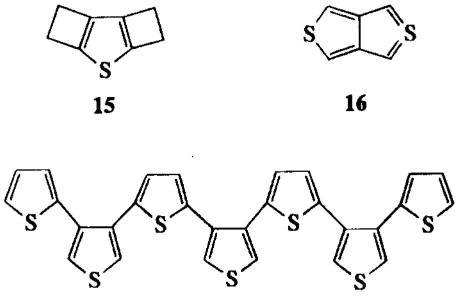


9: $R^1 = R^2 =$ *t*-butyl
10: $R^1 =$ *t*-butyl, $R^2 =$ 1-adamantyl
11: $R^1 = R^2 =$ 1-adamantyl
12: $R^1 = R^2 =$ neopentyl

13: $R^1 = R^2 =$ *t*-butyl
14: $R^1 = R^2 =$ 1-adamantyl

Scheme 2.

The above synthesis is also applied to the preparation of structurally interesting thiophenes such as **15**,[11] **16**,[12] and **17**[13] (Chart 2). Of particular interest is **15**, which undergoes bromine addition and facile Diels-Alder reactions with maleic anhydride and other dienophiles at room temperature because of the decreased aromaticity by angle strains.[11]



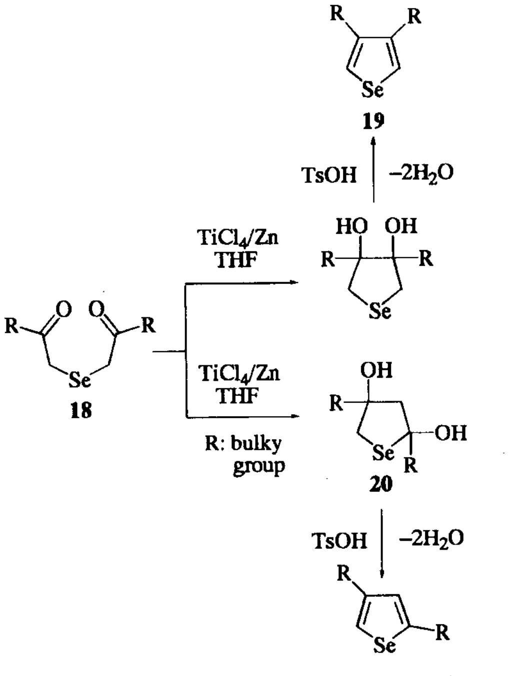
15 16

17

Chart 2.

The synthesis is also applicable to the preparation of selenophenes **19**.[14,15] However, application to congested selenophene synthesis resulted in an interesting rearrangement of unknown mechanism. Thus, treatment of 3-selena-1,5-pentanediones **18**, which possess bulky substituents such as *t*-butyl and 1-adamantyl, with the foregoing low-valent titanium reagent produced selenolane-1,3-diols **20**, which were converted to selenophenes **21** on treatment with TsOH in reasonable overall yields (Scheme 3).[14,16]

The reaction of diarylacetylenes with elemental selenium



19 18 20

21a: R = *t*-butyl
21b: R = 1-adamantyl

Scheme 3.

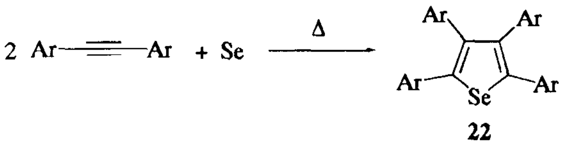
provides a convenient synthesis of tetraarylselenophenes **22**, which were also used in the oxidation study (Scheme 4).[17] For example, heating diphenylacetylene (35.7 g) with elemental selenium (11.9 g) at 230—240 °C for 24 h furnishes tetraphenylselenophene (32.9 g) by simple crystallization workup.

Thiophene 1-Oxides

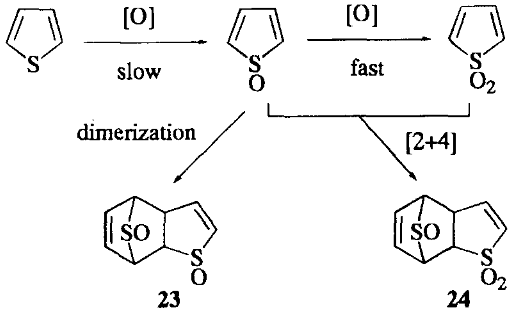
The oxidation of thiophenes, which seemingly provides the most straightforward way to thiophene 1-oxides, has been impeded by two factors.[1] The first one is that oxidation of thiophenes to thiophene 1-oxides, which is a process of the loss of aromaticity of thiophenes, is generally much slower than oxidation of thiophene 1-oxides to thiophene 1,1-dioxides. This renders quenching of the oxidation at the 1-oxide stage very difficult. The other factor is that thiophene 1-oxides are kinetically very reactive species. Particularly, when the double bonds of thiophene ring are not placed under steric protection, rapid cyclodimerization, which is often faster than oxidation to thiophene 1,1-dioxides, might take place to lead to dimeric products such as **23**. In addition, reaction of 1-oxides with 1,1-dioxides may result in adduct formations such as **24** (Scheme 5).

Many efforts were devoted to generate the parent thiophene 1-oxide as a transient intermediate and to trap it chemically.[18] However, it still eludes structure elucidation by spectroscopic means. The first synthesis of an isolable, monocyclic thiophene 1-oxide was carried out by *m*-chloroperbenzoic acid (MCPBA) oxidation of 2,5-di-*t*-butylthiophene.[19] The oxidation with an equimolar amount of MCPBA gave, in addition to 2,5-di-*t*-butylthiophene 1,1-dioxide (**26**) and some other products, approximately a 5% yield of 2,5-di-*t*-butylthiophene 1-oxide (**25**) (Scheme 6). In this case, the bulky *t*-butyl groups not only slow down further oxidation of **25** to **26** but also protect the ring double bonds from dimerization, thus making **25** stable enough to be isolated.

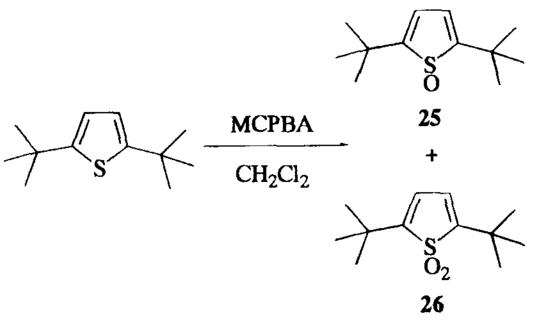
Recently, breakthroughs in the inconvenience described above were brought about by two groups. Furukawa et al. developed the oxidation in the presence of $BF_3 \cdot Et_2O$; the oxidation of 2,5-bis(trimethylsilyl)thiophene and related thiophenes with MCPBA in the presence of $BF_3 \cdot Et_2O$ provided the corresponding thiophene 1-oxides **27** in moderate yields.[20a] In this case, formation of adducts **28** with BF_3 prevents further oxidation to 1,1-dioxides.[20b] On the other hand, Mansuy and Dansette group developed the oxidation in CF_3CO_2H.[21] The oxidation of 2,5-diphenylthiophene in CF_3CO_2H–CH_2Cl_2 (1 : 2) with H_2O_2 afforded 2,5-diphenylthiophene 1-oxide (**29**) in 25% yield, which is stable at −25 °C. Protonation of **29** by CF_3CO_2H will prevent further oxidation to the 1,1-dioxide (Scheme 7).



Scheme 4.



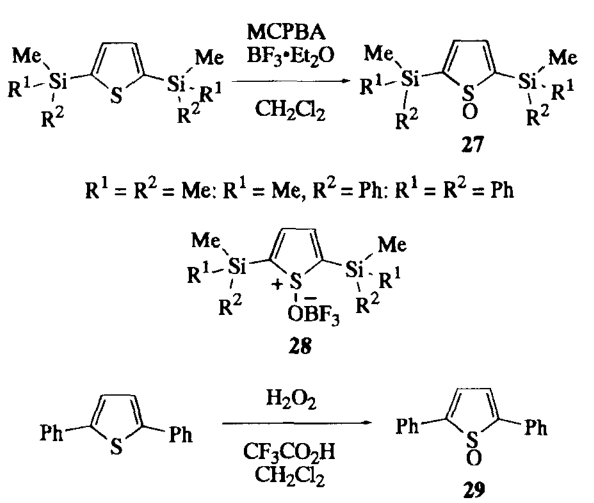
Scheme 5.



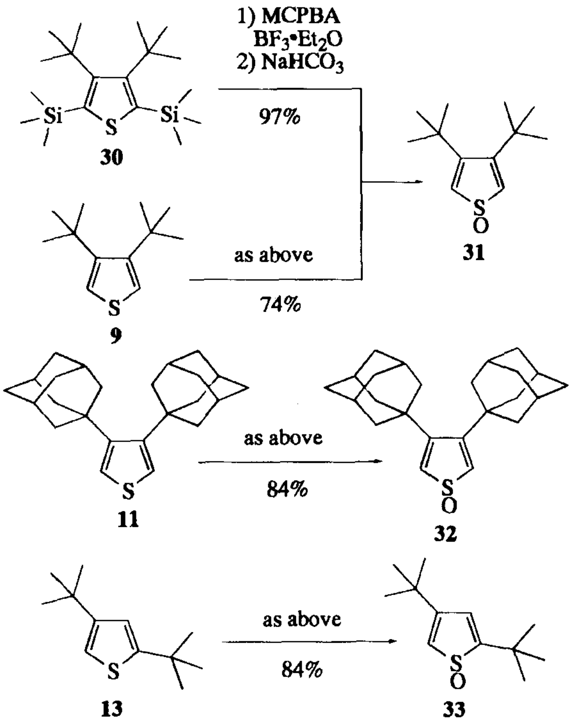
Scheme 6.

In our continuing interest in the chemistry of congested thiophenes, the oxidation of thiophene **30**[22] with an equimolar amount of MCPBA was examined in the presence of $BF_3 \cdot Et_2O$. The reaction, with unexpected concomitant desilylation, gave thiophene 1-oxide **31** in 97% yield.[23] The 1-oxide **31** is thermally unusually stable, and was recovered, even on prolonged heating in refluxing chlorobenzene, in 90% yield. This prompted us to examine oxidation of other congested thiophenes under the same conditions. Thus, oxidation of thiophenes **9**, **11**, and **13** gave the corresponding 1-oxides **31**, **32**, and **33**, respectively, in good yields (Scheme 8).[23]

Figure 1 shows a part of the molecular structure of the parent thiophene 1-oxide obtained by ab initio calculations,[24] while Fig. 2 shows that of the thiophene 1-oxide **31** which was determined by X-ray crystallographic analysis.[23] The



Scheme 7.



Scheme 8.

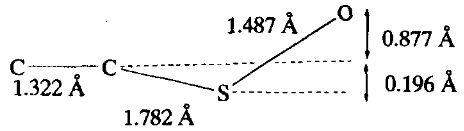


Fig. 1. Molecular structure of thiophene 1-oxide obtained using the STO-3G* basis set.

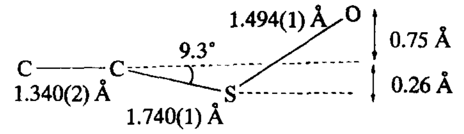


Fig. 2. Molecular structure of 3,4-di-*t*-butylthiophene 1-oxide (X-ray).

molecular structure of **29** was also determined by X-ray crystallographic analysis.[21] The results of X-ray crystallographic analyses and those of calculations are basically in good agreement.

The above results show that the sulfur atom of thiophene 1-oxides adopts a pyramidal configuration in crystals. The geminal methylene hydrogens of thiophene 1-oxide **34** appear nonequivalent in the ^{1}H NMR spectrum at −10 °C because of the anisotropy of the sulfoxide functionality, which in turn reveals the pyramidal configuration of the sulfur atom also in solution (Chart 3).[19] The $\Delta G^{\neq}_{26}$ of the pyramidal inversion at the sulfur atom of **34**, obtained from the coalescence temperature (26 °C), is 14.8 kcal mol^{-1}. The barrier to the pyramidal inversion for 2,5-dimethylthiophene 1-oxide (**35**) was estimated to be 13.3 kcal mol^{-1} by CNDO/2 semi-empirical calculations.[25] In harmony with these results, attempted separation of the enantiomers of **33** was fruitless despite the chirality of the sulfur atom.[26] The ca. 20 kcal mol^{-1} lowering of the inversion barrier of thiophene 1-oxides, relative to that of common sulfoxides, might be ascribed to the delocalization energy of the planar thiophene 1-oxides in the transition state.

Recent development of synthetic methods for thiophene 1-oxides has just enabled us to investigate their chemical reactivities both on the sulfur atom and double bonds.[20b,26—28] In addition, biological studies have shown that thiophenes and benzo[*b*]thiophenes can be oxidized enzymatically in vivo and in vitro into the corresponding thiophene 1-oxides.[29] The chemistry of thiophene 1-oxides will therefore grow in the near future into an important field in heterocyclic and heteroatom chemistry.

Thiophene 1,1-Dioxides

Parent and Monosubstituted Thiophene 1,1-Dioxides. Thiophene 1,1-dioxides, which are no longer aromatic and hence undergo a wide variety of reactions as unsaturated cyclic sulfones, have attracted much attention from synthetic as well as theoretical chemists.[2] They are generally highly reactive, and only those which have more than two substituents on the thiophene ring are stable enough to be isolated under ordinary conditions. Although the parent thiophene 1,1-dioxide (**36**) also had been a molecule of keen interest, it eluded isolation and full characterization.[30] We have recently succeeded in these experiments.[31,32]

Previously the 1,1-dioxide **36** was generated by elimination reactions of precursor compounds such as **37** and **38** (Chart 4).[30] Evidence for the generation of **36** was provided by the formation of its [4+2] self-dimerization product and also by adduct formations with some reagents. Determination of ^{1}H and ^{13}C NMR and UV/vis spectra were also claimed.[30] Many calculation studies have been also reported.[30]

Oxidation of the parent thiophene, the most general way to thiophene 1,1-dioxides, produces the sesquioxide **24**.[33] In our study, dimethyldioxirane (DMD), which is a strong but neutral oxidant and would be capable of oxidation of thiophene at lower temperatures, was employed for the purpose of isolation of **36**. Thus, thiophene was oxidized with three molar amounts of DMD in acetone at −20 °C, and the solvent and volatile materials were evaporated at −40 °C. This furnished practically pure 1,1-dioxide **36** as colorless crystals, which

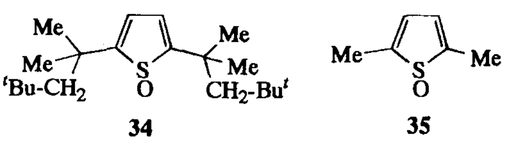


Chart 3.

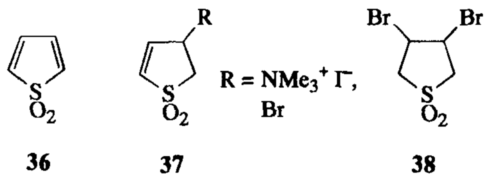


Chart 4.

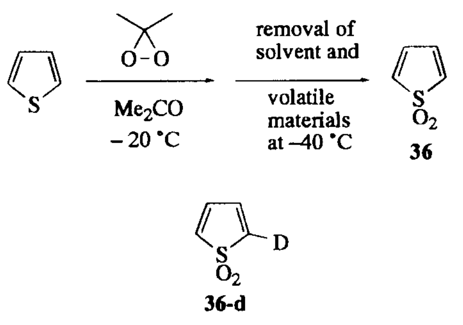
melted at about 6 °C with decomposition (Scheme 9).[31,32]

The ^{1}H NMR spectrum of **36** showed multiplets typical of an AA′BB′ pattern at δ = 6.53—6.61 and 6.75—6.83 (each 2H), where the up-field multiplet was assigned to the α-hydrogens and the down-field one to the β-hydrogens with $^3J_{2,3}$ = 6.7, $^4J_{2,4}$ = 1.1, $^5J_{2,5}$ = 2.5, and $^3J_{3,4}$ = 4.0 Hz. This assignment was made unambiguous by comparison with the spectrum of 2-deuteriothiophene 1,1-dioxide (**36-d**), which was prepared by oxidation of 2-deuteriothiophene. The ^{13}C NMR spectrum of **36** showed only two peaks at δ = 129.3 and 131.1 as expected from its structure. The signal at δ = 131.1 was assigned to the α-carbons and that at δ = 129.3 to the β-carbons by C-H COSY NMR analysis.[31,32]

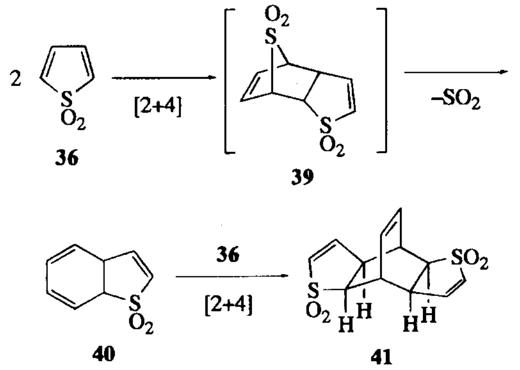
The IR spectrum showed very strong absorptions due to ν_{SO_2} asymmetric and symmetric stretching vibrations at 1306 and 1152 cm^{-1}, respectively. Also in the Raman spectrum, the corresponding Raman bands were observed at 1305 and 1151 cm^{-1}; the C=C stretching vibration, which was very weak in the IR spectrum (1530 cm^{-1}), was observed as an intense and sharp signal at 1530 cm^{-1}. The UV/vis spectrum in CHCl$_3$ showed two absorption maxima at 245 (ε 870) and 288 nm (1070). The GC/MS showed the molecular ion peak at the correct position of *m*/*z* 116; the most intense peak, which corresponds to the furan radical cation, appeared at *m*/*z* 68.[31,32]

The 1,1-dioxide **36** decomposes to give a trimeric product **41** in addition to a dimeric product **40** (Scheme 10). The ratio of **41** to **40** depends on the concentration of **36** in solution; the ratio of **41** increases with increasing concentration. The formation of **40** is explained by [2+4] cyclodimerization of **36**, followed by loss of SO$_2$ from the adduct **39**. The formation and stereochemistry of **41** reveals that [4+2] cycloaddition between **40** and **36** took place in an endo mode, as was true in most Diels–Alder reactions, and that in a head-to-tail manner.[31,32]

Figure 3 shows the ^{1}H NMR spectrum of a nearly pure sample of **36** and its time course ^{1}H NMR spectra which exhibit the way of decomposition of **36** (0.12 M CDCl$_3$ solution, M = mol dm^{-3}).[31,32] After 17 h, six multiplets due to the six olefinic hydrogens of **40** appear, and then new multiplets due to the trimeric product **41** begin to appear. The half-life of **36** is 137 min in a 0.12 M CDCl$_3$ solution, while it is as long as 747 min in a dilute solution of 0.025 M. Kinetics of the decomposition of **36** was determined by using a dilute CDCl$_3$ solution of 0.024 M, where the trimerization is negligibly small at the early stage of the reaction. The second order rate constants in **36** are 1.65×10^{-3}, 2.49×10^{-3}, 3.78×10^{-3}, and 5.21×10^{-3} M^{-1}s^{-1} at 303, 308, 313, and



Scheme 9.



Scheme 10.

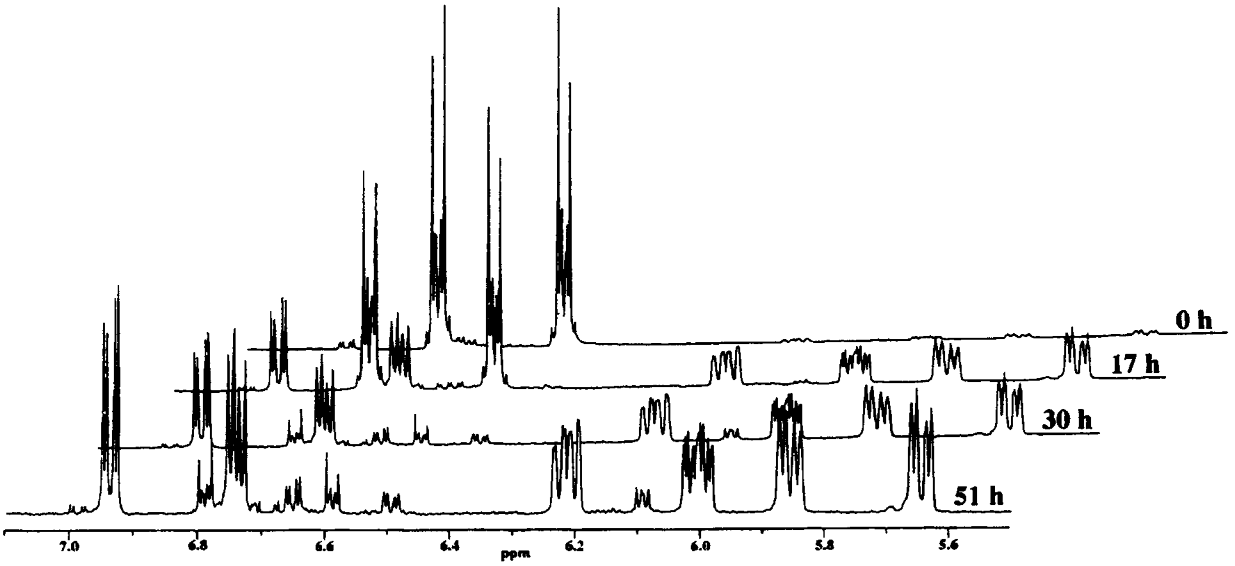


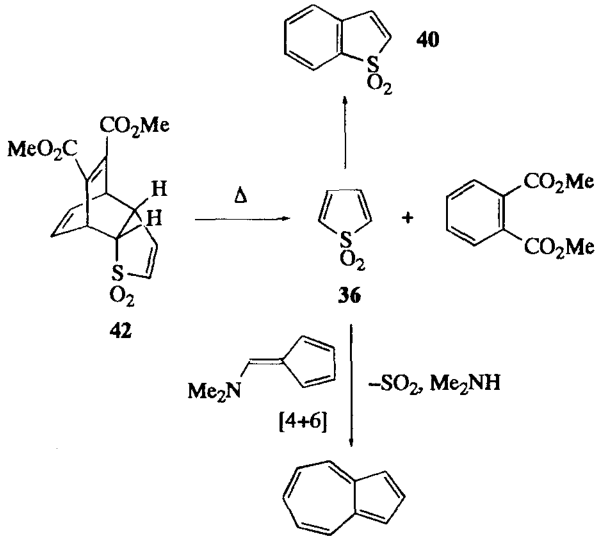
Fig. 3. Time course ^{1}H NMR spectra of **36** at 298 K for a 0.12 M CDCl$_3$ solution; from the top, after 0, 17, 30, and 51 h, respectively.

318 K, respectively, thus furnishing the following activation parameters: $E_a = 64.4\ (\pm 0.3)\ \mathrm{kJ\,mol^{-1}}$, $\Delta H^{\neq} = 62.0\ (\pm 0.3)\ \mathrm{kJ\,mol^{-1}}$, and $\Delta S^{\neq} = -59.8\ (\pm 1.0)\ \mathrm{J\,K^{-1}\,mol^{-1}}$. The E_a value of the dimerization of cyclopentadiene was reported to be 68.5 kJ mol^{-1} both in benzene and ethanol,[34] which is 4.1 kJ mol^{-1} larger than that of **36**. The relatively large negative value of $\Delta S^{\neq}$ reveals that the [4+2] dimerization of **36** takes place in a concerted Diels–Alder mode and the extrusion of SO_2 from the intermediate **39** is sufficiently fast and is not involved in the rate-determining step.

Reportedly, the 1,1-dioxide **36** acted as a dienophile or a diene towards 2π-, 4π-, and 6π-components such as diethyl acetylenedicarboxylate, cyclooctyne, 1-bromo-2-chlorocyclopropene, indene, 1,2-bis(methylene)cyclohexane, and 6-(dimethylamino)fulvene.[30] In our experiments, however, **36** failed to react with electron-deficient dienophiles, dimethyl acetylenedicarboxylate (DMAD), 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (PTAD), and *p*-benzoquinone, angle-strained alkenes, norbornene and acenaphthylene, and an electron-rich alkyne, bis(diethylamino)acetylene.[31,32] In the case of DMAD and PTAD, compounds **42** and **43** (Chart 5), which correspond to the Diels–Alder adducts of the dimer **39** with DMAD and PTAD, were obtained in good yields. In the other cases, the sole product was the dimer **40**, indicating that the dimerization of **36** is much faster than reactions with these dienophiles. Cyclopentadiene is the only compound that was able to react with **36** to give the Diels–Alder adduct **44**. 2,3-Dimethyl-1,3-butadiene, though used in large excess, failed to react with **36**. Consequently, the previous results, which claimed that **36**, generated in situ, could be trapped with a series of substrates,[30] might require reconsideration.

Interestingly, the adduct **42** undergoes a retro Diels–Alder reaction to give **36** and dimethyl phthalate.[31,32] Thus, heating **42** in boiling 1,2-dichloroethane provided **40** and dimethyl phthalate in 85 and 95% yields, respectively, suggesting the efficient formation of **36**. Trapping reactions of **36**, generated in this way, were also examined in some detail. For example, the thermolysis of **42** in the presence of 6-(dimethylamino)fulvene afforded azulene in a moderate yield through [4+6] cycloaddition followed by elimination of SO_2 and Me_2NH of the resulting adduct (Scheme 11).

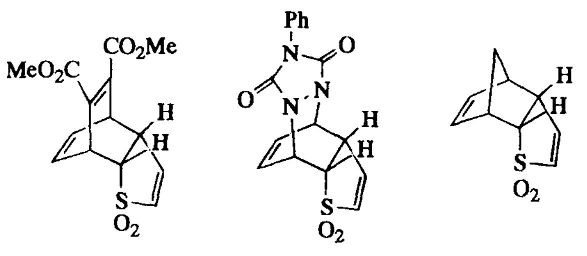
Even monosubstituted thiophene 1,1-dioxides had been neither isolated nor characterized. 2-Methyl-, 3-methyl-, 2-ethyl-, and 2-bromothiophene 1,1-dioxides (**45a**—**d**) were satisfactorily synthesized and isolated in pure form by oxidizing the corresponding thiophenes with DMD at −20 °C in acetone and then by removing the solvent and volatile materials at −40 °C (Scheme 12).[35] These were characterized by ^{1}H and ^{13}C NMR, IR, UV/vis, and MS spectroscopies. The half-lives of the parent compound **36** and the monosubstituted derivatives **45b**, **45a**, and **45c** were determined to be 14, 47, 68, and 76 min, respectively, at 313 K (40 °C) in 0.32 M $CDCl_3$ solutions, thus allowing the direct comparison of the dimerization rate of these compounds. Thus, the ethyl group is more effective in suppressing the dimerization than is the methyl group, and the methyl group at the 2-position is more effective than that at the 3-position.



Scheme 11.

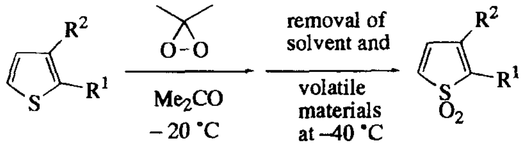
The 1,1-dioxide **45a** underwent a [4+2] cyclodimerization in which one molecule of **45a** acted as a diene and the other as a dienophile to provide two regioisomeric products: **46a** (major) and **46b** (minor). In addition, the trimeric product **47** was formed by further [4+2] cycloaddition of the major isomer **46a** with **45a**, which took place in an endo and head-to-head mode, whereas trimerization of **36** leading to **41** occurred in a head-to-tail mode. Dimeric and trimeric product formations were also observed on the decomposition of **45b** and **45c**, whereas **45d** underwent only dimerization (Scheme 13).[35]

Sterically Congested Thiophene 1,1-Dioxides and Their Synthetic Applications. Sterically congested thiophenes **9**—**12** are oxidized by *m*-chloroperbenzoic acid (MCBA) to the corresponding thiophene 1,1-dioxides **48**—**51** in good



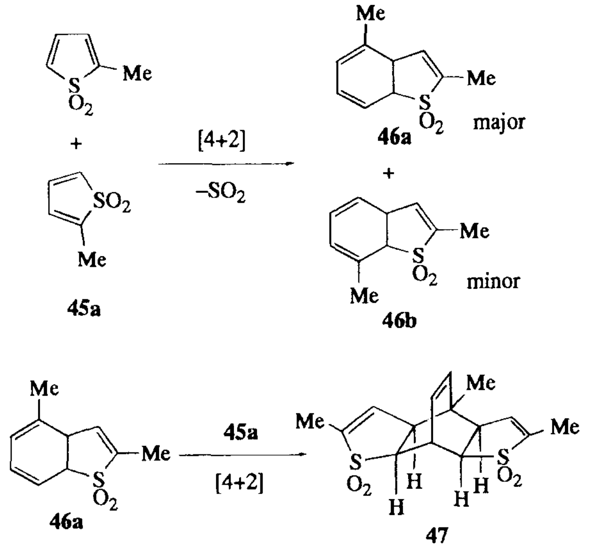
42 43 44

Chart 5.

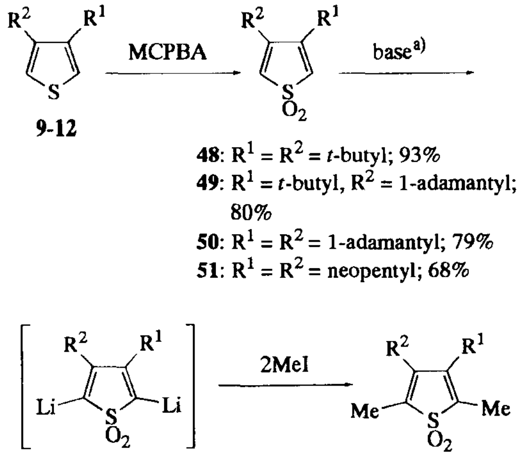


45a: R^1 = Me, R^2 = H
45b: R^1 = H, R^2 = Me
45c: R^1 = Et, R^2 = H
45d: R^1 = Br, R^2 = H

Scheme 12.



Scheme 13.



48: $R^1 = R^2 =$ *t*-butyl; 93%
49: $R^1 =$ *t*-butyl, $R^2 =$ 1-adamantyl; 80%
50: $R^1 = R^2 =$ 1-adamantyl; 79%
51: $R^1 = R^2 =$ neopentyl; 68%

52: $R^1 = R^2 =$ *t*-butyl; 67%
53: $R^1 =$ *t*-butyl, $R^2 =$ 1-adamantyl; 37%
54: $R^1 = R^2 =$ 1-adamantyl; 61%
55: $R^1 = R^2 =$ neopentyl; 87%

a) Lithiation of **48**: lithium diisopropylamide; lithiation of **49** and **50**, lithium 2,2,6,6-tetramethylpiperidide; lithiation of **51**, *n*-BuLi

Scheme 14.

yields.[7—10] In these cases, the initially-formed thiophene 1-oxides do not suffer from self-dimerization and other side reactions because their double bonds are sterically protected, and thus they are efficiently oxidized to afford the 1,1-dioxides. Although it is well documented that the α-hydrogens of thiophene and its simple derivatives are sufficiently acidic to be lithiated by organolithium reagents, **9** resisted such lithiation, probably because of steric reasons.[36] Oxidation of **9**—**12** to 1,1-dioxides makes the α-hydrogens more acidic, thus permitting dilithiation by appropriate organolithium reagents. Thus, **48**—**51** were dimethylated via dilithiation to give more congested 1,1-dioxides **52**—**55** in reasonable yields (Scheme 14).[8—10]

The thiophene 1,1-dioxide that was most extensively studied is tetrachlorothiophene 1,1-dioxide (**56**), which is an extremely versatile, reactive but stable, cheletropic reagent. It undergoes [4+2] cycloaddition with a variety of inactivated double bonds, followed by extrusion of SO_2.[37] Congested thiophene 1,1-dioxides **48**—**51** also behave as 4π-components (dienes) toward a variety of dienophiles.[8—10,38] A remarkable example is provided by the reaction with phenyl vinyl sulfone, which directly furnished congested benzenes **58**—**61** in high yields through simultaneous elimination of benzenesulfinic acid and SO_2 of the initial adducts **57** (Scheme 15). Compound **60** is the first congested molecule that possesses two 1-adamantyl groups at ortho positions of the benzene ring. Incidentally, the 1-adamantyl group, which is composed of a rigid σ-framework, behaves as a more bulky substituent than does the *t*-butyl group, when placed in a sterically congested system. Dimethyl acetylenedicarboxylate (DMAD) also reacted with **48**, **50**, and **51** to give dimethyl phthalates **63**, **64**, and **65**, respectively, in excellent yields, by loss of SO_2 from the initial adducts **62**.

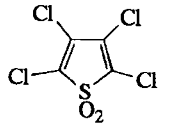
Even more congested thiophene 1,1-dioxides **52**, **54**, and **55** are capable of cycloaddition with DMAD, though rather forcing conditions are required, to provide the corresponding highly congested hexasubstituted benzene derivatives **66** (67%), **67** (56%), and **68** (86%), respectively (Chart 6).[8—10] The benzene ring of these compounds is neither equilateral-hexagonal nor planar because of extreme steric congestion. The internal rotation barrier of the bulky substituents in **66**—**68** were studied by variable temperature ^{1}H and ^{13}C NMR spectroscopies.[8,10]

An exceptional reactivity of **51** as a diene was provided by reaction with benzyne, which produced an ene reaction product **69** in 68% yield in addition to **70** (expected [4+2] adduct) (20%) and **71** (adduct of **70** with benzyne) (7%) (Scheme 16).[8,10]

Reactions of congested thiophene 1,1-dioxides **48**, **50**, and **51** with PTAD provide a new pyridazine synthesis.[8,9,39,40] These dioxides reacted with two molar amounts of PTAD to give bis-adducts **73** in good yields. Treatment of **73** with KOH in MeOH at room temperature directly afforded, with evolution of nitrogen, congested pyridazines **76** in good yields, probably through intermediates **74** and **75** (Scheme 17).

The 1,1-dioxide **48** reacted with two molar amounts of maleic anhydride to afford two isomeric bis-adducts, **77** and **78**.[40] Reduction of the major endo-endo adduct **77** with $LiAlH_4$, followed by dehydration of the resulting tetraol with TsOH, provided the alkene **79** in good overall yield (Scheme 18). The double bond of **79**, which is sterically heavily protected, is inert to hydroboration and also oxidation with singlet oxygen and peracid.

Sterically congested 3,4-di-*t*-butylfuran (**80**), selenophene (**81**), and pyrrole (**83**) (Scheme 19), which had not been obtained by other methods, could be also derived from the thiophene **9** or its dioxide **48** as the starting materials, though



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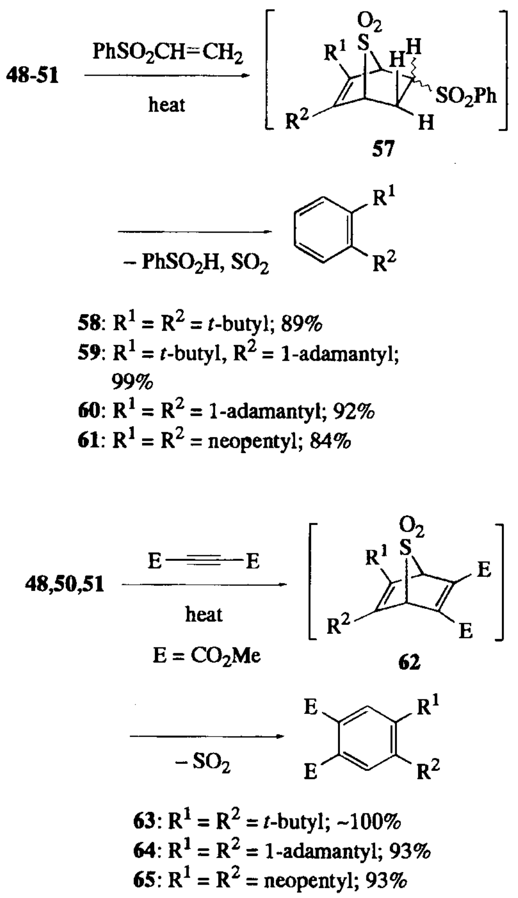
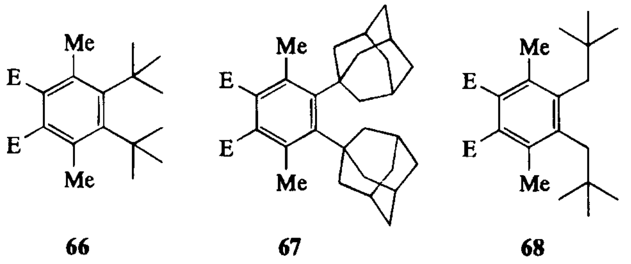


58: $R^1 = R^2 =$ *t*-butyl; 89%
59: $R^1 =$ *t*-butyl, $R^2 =$ 1-adamantyl; 99%
60: $R^1 = R^2 =$ 1-adamantyl; 92%
61: $R^1 = R^2 =$ neopentyl; 84%

63: $R^1 = R^2 =$ *t*-butyl; ~100%
64: $R^1 = R^2 =$ 1-adamantyl; 93%
65: $R^1 = R^2 =$ neopentyl; 93%

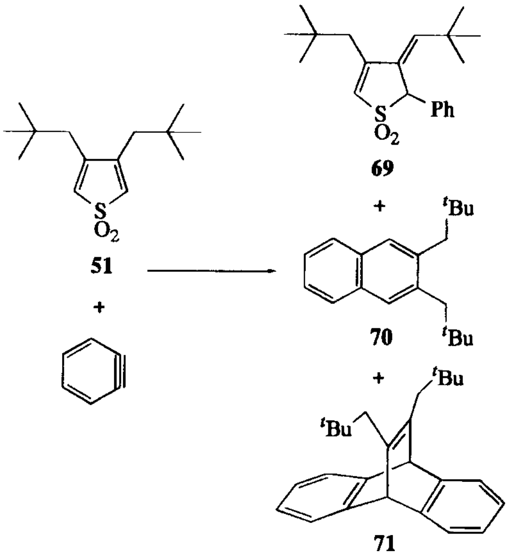
Scheme 15.



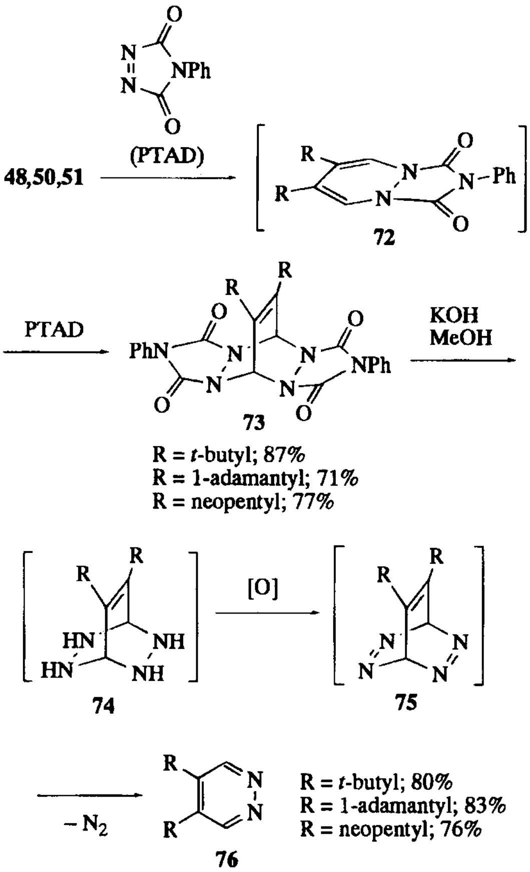
66 **67** **68**

E = CO_2Me

Chart 6.



Scheme 16.



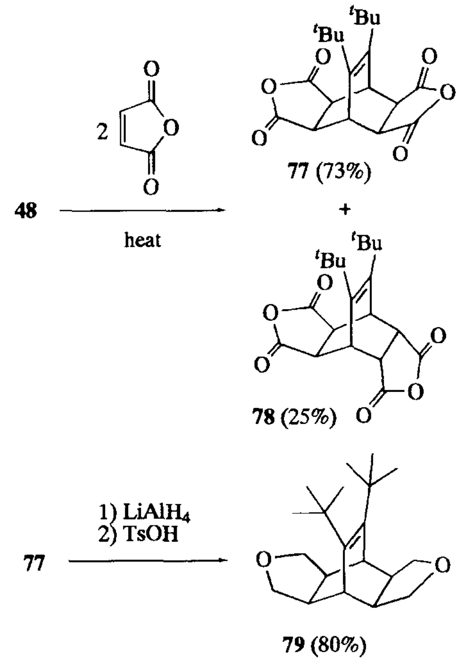
R = *t*-butyl; 87%
R = 1-adamantyl; 71%
R = neopentyl; 77%

R = *t*-butyl; 80%
R = 1-adamantyl; 83%
R = neopentyl; 76%

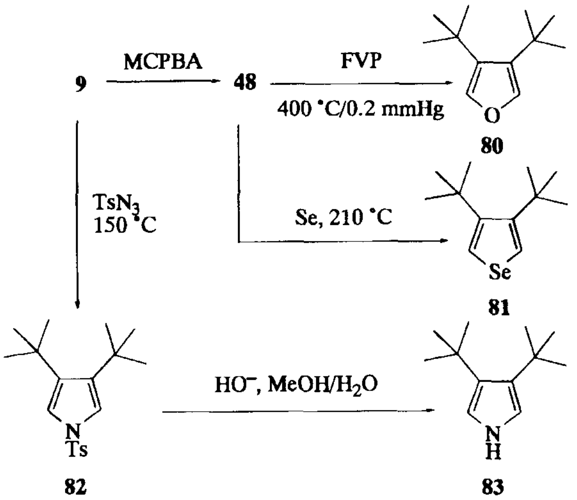
Scheme 17.

the yield of each conversion was low.[41] The formation of the furan **80** by thermolysis of **48** is consistent with the appearance of the furan radical cation peak as the most intense peak in the mass spectrum of the parent compound **36**,[31,32] while that of the selenophene **81** by reaction of **48** with selenium is unprecedented.

Further oxidation of the thiophene 1,1-dioxide **48**, though slow, produced epoxide **84** in high yield along with a small amount of thiete 1,1-dioxide **85** that was formed by rearrangement of the former.[42,43] Interestingly, the oxidation of more congested thiophene 1,1-dioxides **52** and **54** took place more rapidly, despite the expected severe steric hindrance, to furnish thiete 1,1-dioxides **86** and (**87**) nearly quantitatively through spontaneous rearrangement of the resulting epoxides (Scheme 20). Excessive steric congestion in these dioxides probably facilitates the epoxidation by destablization of the HOMO level, i.e., activation of the double bonds. Steric con-



Scheme 18.

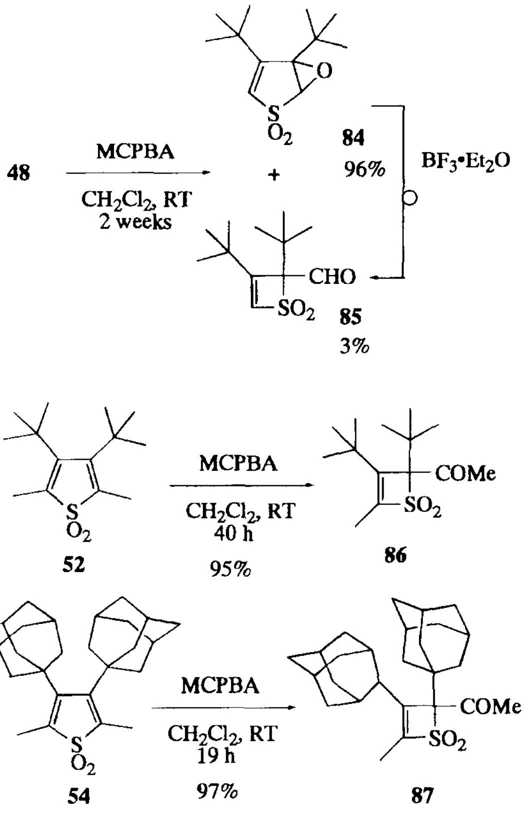


Scheme 19.

gestion will also facilitate the rearrangement of the epoxides to **86** and **87**. Incidentally, the oxidation of tetramethylthiophene 1,1-dioxide takes place much more slowly.

1-Imino, 1,1-Diimino, and 1-Imino-1-oxo Derivatives of Thiophenes

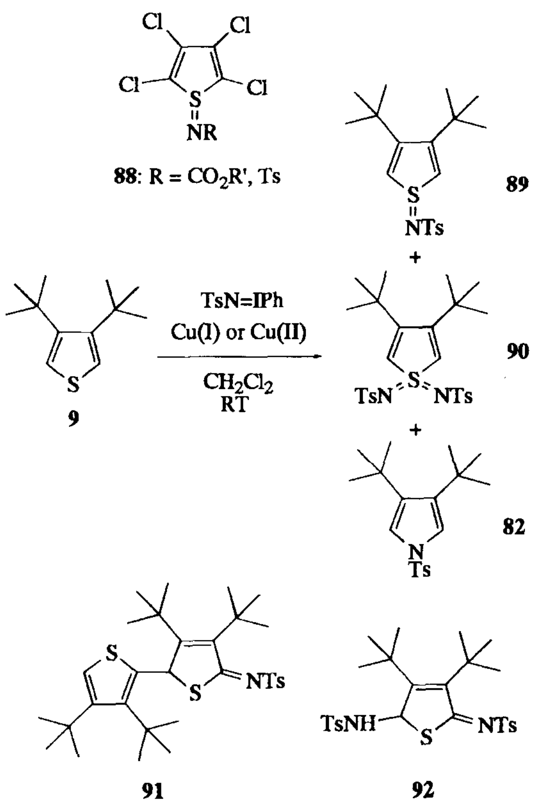
Sulfilimines, where the oxygen atom of sulfoxides is replaced by an imino group, sulfone diimines, where both oxygen atoms of sulfones are replaced by two imino groups, and sulfoximines, where one of the two oxygen atoms of sulfones is replaced by an imino group, have been extensively studied from a variety of points of view. The chemistry of thiophene analogs of these compounds is described.



Scheme 20.

The chemistries of 1-imino and 1,1-diimino derivatives of thiophenes (sulfilimine and sulfone diimine derivatives, respectively) have been rarely studied. Particularly, the latter species still remains unknown. 1-Imino derivatives **88**, which were obtained by thermolyses of azides in tetrachlorothiophene,[44] are the only reported example of sulfilimines derived from monocyclic thiophenes. The successful synthesis of **88** is seemingly exceptional: other thermolysis studies of azides in thiophenes all failed to give sulfilimines.[41,44,45] This would be attributed to the probable thermal instability of the sulfilimines, which renders survival of these compounds very difficult under thermolytic conditions of azides (130—150 °C). Both sulfilimines and sulfone diimines of thiophenes would be stabilized by introduction of bulky substituents into the ring, as were thiophene 1-oxides and 1,1-dioxides.

Taking these into account, we investigated the reaction of sterically congested thiophene **9** with [(*p*-tolylsulfonyl)imino]phenyl-λ^3-iodinane (TsN=IPh), which generates the tosyl nitrene or its equivalent at lower temperature in the presence of a Cu(I or II) catalyst.[46] Thus, varying ratios of **9** and TsN=IPh were allowed to react in the presence of 5 mol% of [Cu(CH$_3$CN)$_4$]PF$_6$[(Cu(I)] or Cu(OTf)$_2$[Cu(II)] in MeCN. The reaction gave the expected sulfilimine **89** with unexpected formation of sulfone diimine **90** and the pyrrole **82**. Compounds **91**, **92**, and TsNH$_2$ were also isolated in small amounts (Scheme 21). Better results were attained by using the Cu(I) as the catalyst rather than the Cu(II). The yield of **89** increased with an increasing molar ratio of **9**; a satisfactory yield of 61% was attained by use of 20 molar amounts of **9**. Most probably, the sulfone diimine **90** would be formed by further reaction of **89** with TsN=IPh. However,



Scheme 21.

a separate reaction of **89** with TsN=IPh in the presence of 5 mol% of the Cu(I) gave **90** only in low yield (10%) with recovery of **89** in 48% yield. Both **89** and **90** are thermally stable, probably because of steric protection, and melted at 130.0—131.0 and 155.0—155.5 °C, respectively, without decomposition.

ORTEP drawing structures of **89** and **90** are given in Figs. 4 and 5[47] along with the relevant bond lengths and angles data.[46]

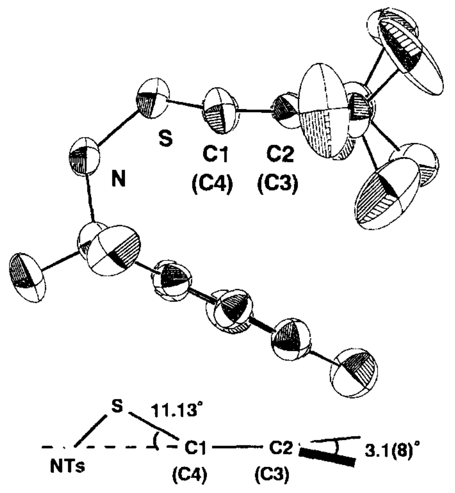


Fig. 4. ORTEP diagram of **89**. Selected bond lengths: S–N, 1.595(7); S–C1, 1.744(7); S–C4, 1.742(8); C1–C2, 1.332(11); C2–C3, 1.535(10); C3–C4, 1.329(10) Å. Bond angles: C1–S–C4, 90.7(4); S–C1–C2, 113.6(6); C1–C2–C3, 109.9(7); C2–C3–C4, 111.7(7); C3–C4–S, 112.6(6)°.

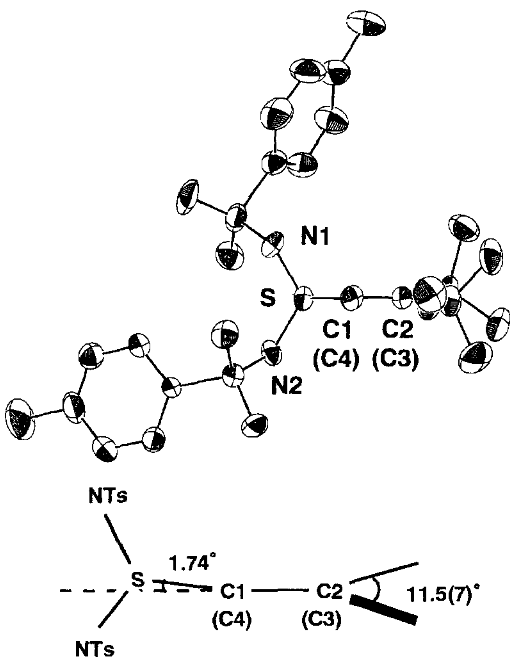
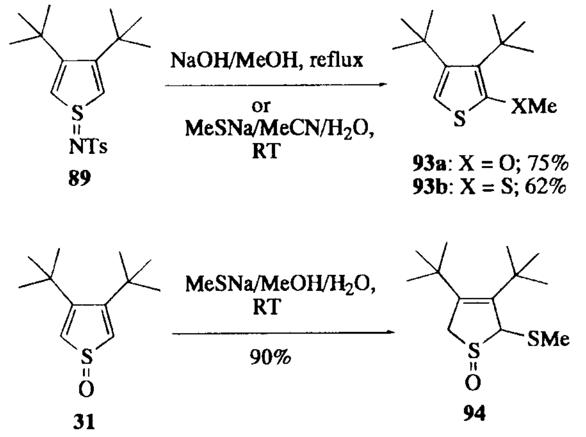


Fig. 5. ORTEP diagram of **90**. Selected bond lengths: S–N1, 1.551(6); S–N2, 1.557(5); S–C1, 1.737(7); S–C4, 1.728(7); C1–C2, 1.339(10); C2–C3, 1.524(11); C3–C4, 1.343(9) Å. Bond angles: N1–S–N2, 121.5(3); C1–S–C4, 93.1(4); S–C1–C2, 111.7(5); C2–C3–C4, 111.7(6); C3–C4–S, 111.7(5)°.

In both compounds, although the four carbon atoms of the thiophene ring form a quasi-plane, their C2–C3 (1.53—1.54 Å) and C1–C2 (C3–C4) bond lengths (1.33—1.34 Å) are almost equal to the common single and double bond lengths, respectively, indicating the presence of bond alternation, that is, the loss of the aromaticity of the thiophene ring. The geometry of sulfilimine **89** is, on the whole, similar to that of thiophene 1-oxides with a pyramidal configuration at the sulfur atom and with the S–N bond length of 1.60 Å (see Fig. 2). The pyramidal sulfur geometry and the bond lengths data lead to the conclusion that **89** is not aromatic. On the other hand, for the sulfone diimine **90**, the thiophene ring is nearly planar as for most thiophene 1,1-dioxides. The S–N1 and S–N2 bond lengths of **90** are 1.55 Å and are nearly equal to the bond length (1.54 Å) of the common S–N bonds that are conventionally expressed by a double bond.

Treatment of **89** with NaOH in boiling MeOH afforded an unexpected product **93a** in 75% yield probably through a Pummerer-like reaction.[48] The same reaction took place with MeSNa at room temperature to give **93b** in 62% yield. In contrast, the 1-oxide **31** gave a simple Michael adduct **94** in 90% yield on reaction with MeSNa (Scheme 22).

To our knowledge, the sulfoximine **95**, which was obtained by MCPBA oxidation of the sulfilimine **88** (R = CO$_2$Et), is the only known monocyclic sulfoximine derivative of a thiophene.[44,49] The lack of suitable precursors is most likely responsible for the inaccessibility of sulfoximines. The author's group has succeeded in derivation of sulfoximines from thiophene 1-oxides **31** and **33**, optical resolution

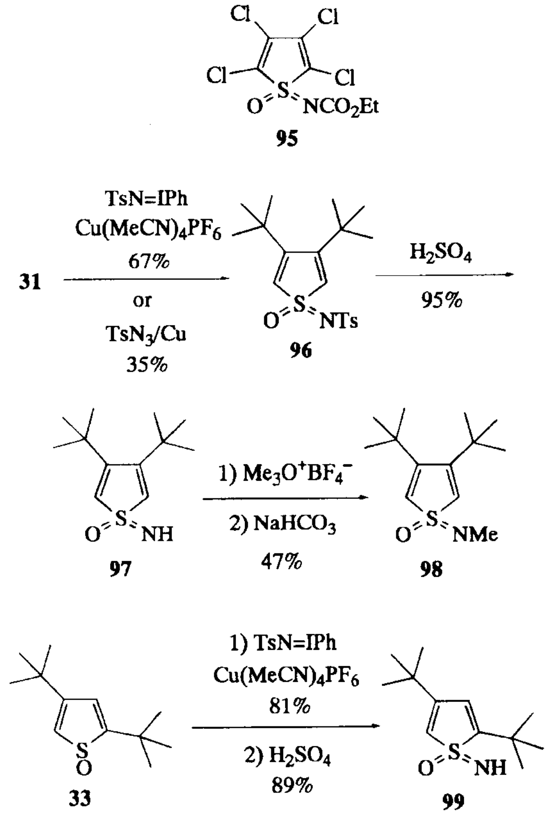


Scheme 22.

of a pair of enantiomers of the sulfoximine derived from **33**, and determination of the absolute configuration of the enantiomers.[26]

The reaction of the 1-oxide **31** with 1.2 molar amounts of TsN=IPh proceeded smoothly in the presence of [Cu-(MeCN)$_4$]PF$_6$ in MeCN at room temperature to provide the expected thiophene sulfoximine **96** in 67% yield. A conventional method, which employs three molar amounts of *p*-toluenesulfonyl azide in the presence of activated copper powder in refluxing MeOH, worked, only sluggishly, to produce **96** in a moderate yield of 35%. Hydrolysis of **96** with concentrated H_2SO_4 afforded the parent sulfoximine **97** in 95% yield. Treatment of **97** with $Me_3O^+BF_4^-$ gave the *N*-methylated compound **98** in 47% yield with recovery of **97** in 44% yield. Similarly, treatment of the unsymmetrically substituted thiophene 1-oxide **33** with TsN=IPh, followed by hydrolysis of the resulting sulfoximine, provided the parent sulfoximine **99** in a good overall yield (Scheme 23).[26] Both **97** and **99** are thermally labile; **99** decomposed completely when heated in boiling toluene for several hours.

The tetra-coordinated sulfur atom of **99** is chiral, and the enatiomers of **99** were isolated in pure form by HPLC on a chiral column.[26] Both enantiomers, on slow evaporation of a hexane solution, provided good crystals for an X-ray crystallographic analysis. The analysis disclosed that the second-eluted enantiomer with HPLC has an (*S*)-configuration. (*R*)-Configuration is therefore assigned to the first-eluted enantiomer. An ORTEP diagram of (*S*)-**99** is given in Fig. 6[47] along with the relevant bond lengths and bond angles data. The thiophene ring of (*S*)-**99** is planar as were those of **31**, **89**, **90**, and many thiophene 1,1-dioxides. The bond length data (1.32 Å for C2–C3 and C4–C5, 1.49 Å for C3–C4) are indicative of bond fixing, that is, nonaromaticity of the thiophene ring. The S–O and S–N bond lengths are 1.45 and 1.54 Å, respectively, and are comparable with those of other sulfoximines. The O–S–N bond angle of 119° is larger than those of acyclic sulfoximines.



Scheme 23.

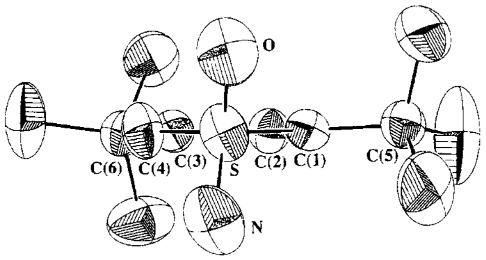


Fig. 6. ORTEP diagram of (+)-(*S*)-**99**. Selected bond lengths: S–O, 1.445(3); S–N, 1.536(3); S–C1, 1.796(3); S–C4, 1.739(3); C1–C2, 1.321(3); C2–C3, 1.492(3); C3–C4, 1.319(4); C1–C5, 1.520(4); C3–C6, 1.507(4) Å. Bond angles: O–S–N, 119.3(2); C1–S–C4, 92.9(2); S–C1–C2, 107.3; C1–C2–C3, 116.4(2); C2–C3–C4, 111.5(3); C3–C4–S, 111.9(2); S–C1–C5, 123.2(2); C2–C3–C6, 121.5(2)°.

Both (*R*)-**99** and (*S*)-**99** had the same melting point of 114—115 °C, which is much higher than that of the racemate **99** (mp 82.5—83.5 °C), and showed specific rotations of −48.6° and +48.6° (*c* 0.10 g/100 ml, $CHCl_3$, 26 °C), respectively.[26] The UV/vis spectrum of the racemate **99** showed absorption maxima at ca. 315 (sh), 279, and 245 nm. Thus, (−)-(*R*)-**99** showed the negative first Cotton effect at 315, the positive second one at 279, and the negative third one at 236 nm in the circular dichroism (CD) spectrum, while (+)-(*S*)-**99** gave the quite reverse pattern. The results given here provide the first example where the chirality was introduced to the sulfur atom of the thiophene ring, and optical resolution and determination of the absolute configuration of a pair of enantiomers were accomplished.

The present study, which has developed fairly simple syntheses of 1-imino, 1,1-diimino, and 1-imino-1-oxo derivatives of thiophenes, would hopefully contribute to open a new branch of heteroatom and heterocyclic chemisty.

Selenophene 1-Oxides

When we initiated selenophene 1-oxide and 1,1-dioxide chemistry several years ago, dibenzoselenophene 5-oxides **100** and **101** had been the only known oxides of selenophenes (Chart 7).[50] After a number of attempts, we have succeeded in the preparation of a series of monocyclic selenophene 1,1-dioxides, which are stabilized electronically or sterically, by oxidation of selenophenes with DMD as described later. However, despite many efforts, selenophene 1-oxides, intermediates leading to the former dioxides, have never been isolated in pure form.

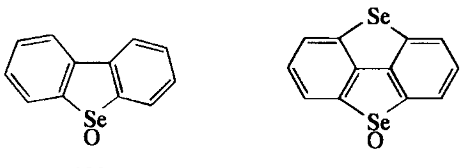
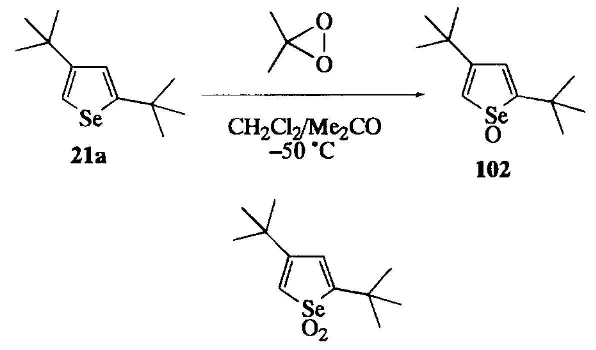


Chart 7.

2,4-Di-*t*-butylselenophene 1,1-dioxide (**103**) is the most thermally stable of the synthetically available selenophene 1,1-dioxides because of steric protection.[51,52] Since this should also be true for selenophene 1-oxides, 2,4-di-*t*-butylselenophene (**21a**) was chosen as the substrate of the oxidation study to obtain selenophene 1-oxide stable enough to be isolated. Thus, a solution of an equimolar amount of DMD in Me_2CO was added to a solution of **21a** in CH_2Cl_2 at −50 °C, which resulted in the consumption of **21a**. The solvent and volatile materials were removed from the mixture under vacuum below −50 °C. The resulting colorless crystals were washed with a small amount of pentane at the same temperature to leave pure 2,4-di-*t*-butylselenophene 1-oxide (**102**) nearly quantitatively (Scheme 24).[16] No formation of the 1,1-dioxide **103** was observed. The 1-oxide **102** is highly hygroscopic and deliquesced on exposure to moist air. It decomposed on warming, to liquefy at about 54—55 °C. NMR data of **102** are summarized in Table 1 together with those of **21a**, **103**, and a range of compounds derived from **102**. The ^{1}H NMR chemical shift values of **102** fall in between those of **21a** and **103**. The same trend is also observed with a thiophene series. The ^{77}Se NMR spectrum showed the only one signal at δ = 986, which is lower than chemical shift values of the common selenoxides. The IR spectrum showed the Se–O stretching vibration at 798 cm^{-1}. This assignment was supported by the Raman spectrum in which a strong band appeared at 788 cm^{-1}.



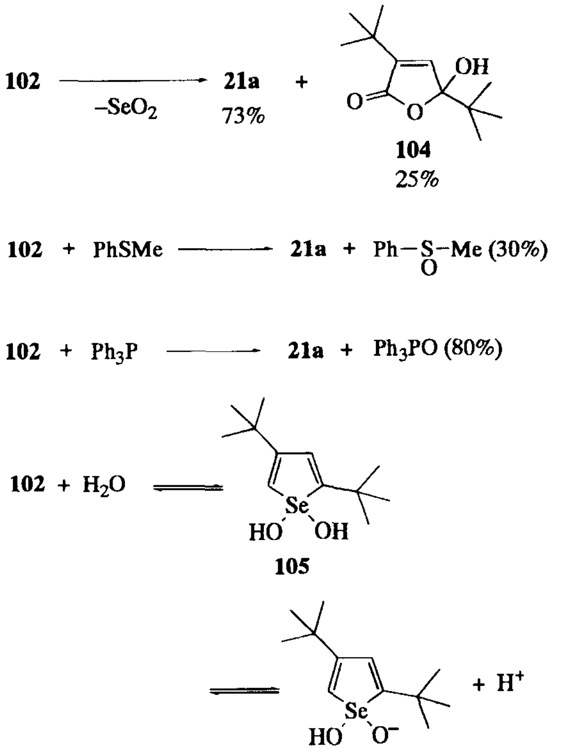
Scheme 24.

The 1-oxide **102** is far less stable than the corresponding thiophene 1-oxide **33** and selenophene 1,1-dioxide **103**; it decomposed at 20 °C with half-lives of 42 and 34 min in 0.018 and 0.036 M $CDCl_3$ solutions, respectively.[16] A 0.05 M solution of **102** in CH_2Cl_2 standing at 30 °C for 0.5 h gave **21a** (73%), furanone **104** (25%), and SeO_2 by an unknown process; kinetics of the decomposition fitted neither first- nor second order in **102** (Scheme 25). As is expected from the formation of **21a**, **102** functions as an oxidizing agent. Standing a 1 : 1 mixture of **102** and PhSMe in CH_2Cl_2 gave PhS(O)Me in 30% yield along with **21a** (67%) and **104** (8%). Ph_3P was also oxidized by an equimolar amount of **102** to give Ph_3PO in 80% yield. Surprisingly, **102** is readily soluble in water, despite the presence of two hydrophobic *t*-butyl groups, to give an acidic solution (pH 6.6 for 5.7×10^{-2} M solution) (also easily soluble in MeOH). In addition, it is stabilized by water and persisted in D_2O without marked decomposition at least for 24 h at room temperature. These observations indicate that the Se–O bond is highly polarized, as supported by the foregoing deshielded ^{77}Se chemical shift value, is solvated in water. The acidity of **102** is suggestive

Table 1. ^{1}H NMR,[a] ^{13}C NMR,[b] and ^{77}Se NMR[c] Data (δ) of **102** and Related Compounds

Compounds	**21a**	**102**	**102**[d]	**102**[g]	**103**[h]	**106**	**107**	**108**		**109**
C3–H	6.99	6.67	6.93[e]	6.92	6.57	6.81	6.72	6.75,	6.77	6.72
C5–H	7.31	6.83	6.94	6.97	6.75	6.98	7.07	7.21,	7.32	6.79
C-2	164.5	170.1	171.2[e]	170.8	157.6	169.7	168.7	164.0,	164.3	163.8
C-3	123.1	128.1	133.8	130.8	121.2	132.4	128.8	132.4,	132.5	130.9
C-4	153.9	163.1	169.8	166.1	155.6	164.6	164.4	168.55,	168.57	165.7
C-5	118.2	127.3	128.5	128.2	119.0	121.5	125.6	124.8,	124.9	118.0
^{77}Se	552	986	965[f]		1054[i]	953—955	959[j]	957,	959	610

a) In $CDCl_3$ with TMS as the internal standard at 233 K, unless otherwise stated (400 MHz). b) In $CDCl_3$ with $CDCl_3$ (δ = 77.0) as the internal standard at 233 K, unless otherwise stated (100 MHz). c) In $CDCl_3$ with the parent selenophene (δ = 608.6) as the external standard at 233 K, unless otherwise stated (76 MHz). d) In D_2O. e) DSS as the internal standard at 297 K. f) At 278 K. g) In CD_3OD with TMS as the internal standard at 297 K. h) At 297 K. i) In $CDCl_3$ with D_2SeO_3 (δ = 1282) as the external standard. j) In CD_3CN at 248 K.



Scheme 25.

of the presence of an equilibrium involving a λ^4-selane **105**, which lies to the selenoxide side.

The 1-oxide **102** quantitatively forms a 1 : 1 adduct **106**[20b] with BF_3 when treated with $BF_3 \cdot Et_2O$ at −40 °C (Table 1).[16] The 1-oxide **102** also quantitatively gave a 1 : 1 adduct **107** with *p*-toluenesulfonic acid at −40 °C, similar in structure to the adduct reportedly formed with dibenzyl selenoxide (Chart 8).[53] Since the selenium atom of **102** is chiral, optical resolution should be possible provided the inversion on the selenium atom and the well-known racemization process through hydration is slow.[54] As an approach to this goal, **102** was treated with (1*S*)-(+)-10-camphorsulfonic acid. The ^{1}H NMR of the resulting 1 : 1 adduct **108** showed a pair of signals of equal intensities due to the α- and β-hydrogens, revealing the formation of a pair of diastereomers. This conclusion was also supported by ^{13}C and ^{77}Se NMR (observations of two signals at δ = 957 and 959) spectra (Table 1), although separation of the diastereomers was impeded by instability of the adduct. Treatment of **102** with malononitrile at −40 °C gave the selenonium ylide **109** quantitatively, thus providing a new route to selenophenium ylides.[55]

Similar oxidation of 2,4-di(1-adamantyl)selenophene (**21b**) and tetraphenylselenophene (**112a**) also gave the corresponding 1-oxides **110** and **113** nearly quantitatively.[16] The 1-oxide **110**, which deliquesces on exposure to air and is slightly soluble in water, quickly decomposed at 30 °C in CH_2Cl_2 to give **21b** (85%) and furanone **111** (12%), while **113** gave **112a** (73%) and *cis*-butenedione **114** (25%) under the same conditions (Chart 9).

Selenophene 1,1-Dioxides

Thiophene 1,1-dioxides have been supplying a rich field of heteroatom and heterocyclic chemistry.[2] If selenophene 1,1-dioxides became readily available, their chemistry would develop into a new branch of heteteroatom and heterocyclic chemistry. However, when we initiated the present study, none of selenophene 1,1-dioxides had been known. In addition, although the oxidation of selenophenes would be the most straightforward way to this species, it has never been examined in any detail.

The oxidation of selenophenes with several oxidation reagents was investigated by using the selenophene **112a** as the substrate.[51,52] This revealed that DMD as the oxidant affords the best results. The oxidation with an equimolar amount of DMD at 0 °C in Me_2CO immediately resulted in nearly complete consumption of **112a**. At that time, however, the expected 1-oxide **113** could not be isolated in pure form because of the foregoing thermal instability of **113**. Meanwhile, treatment of **112a** with 2.2 molar amounts of DMD at 0 °C for 1 h provided the expected selenophene 1,1-dioxide **115a** in 97% yield as a yellow crystalline compound (Scheme 26). In similar ways, a series of selenophene 1,1-dioxides **115b**—**g** were satisfactorily synthesized (Table 2), though some selenophenes failed to give the correspond-

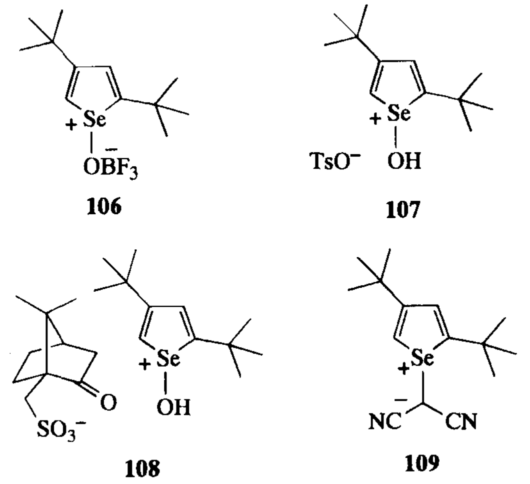


Chart 8.

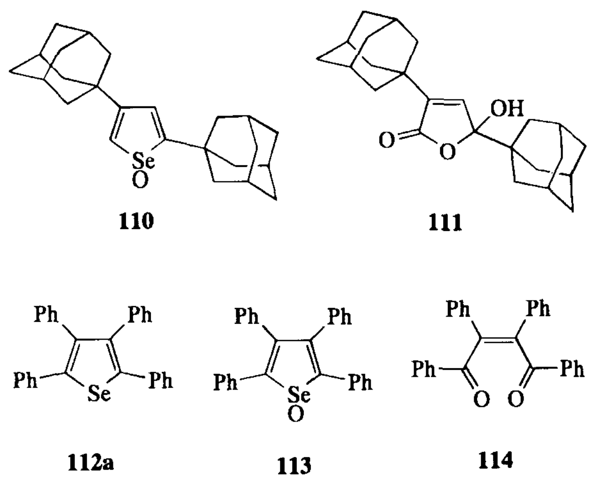
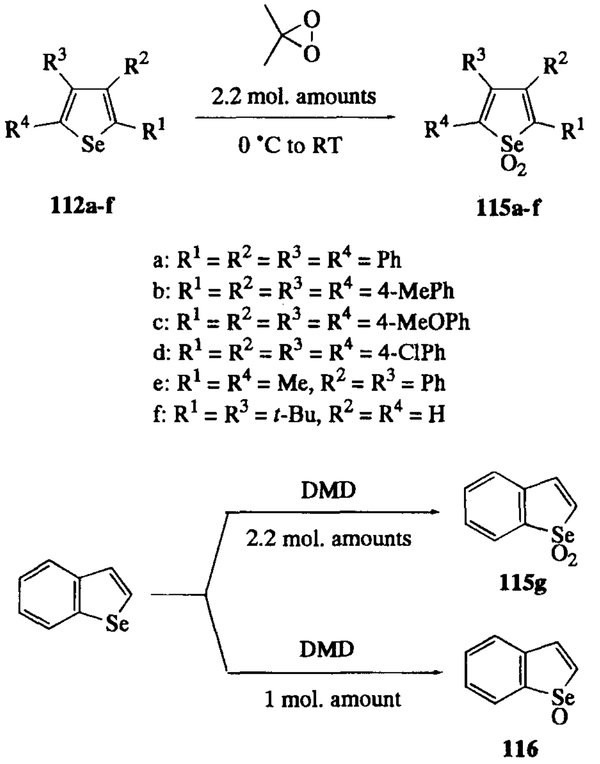


Chart 9.



112a-f **115a-f**

a: $R^1 = R^2 = R^3 = R^4 = Ph$
b: $R^1 = R^2 = R^3 = R^4 = 4\text{-}MePh$
c: $R^1 = R^2 = R^3 = R^4 = 4\text{-}MeOPh$
d: $R^1 = R^2 = R^3 = R^4 = 4\text{-}ClPh$
e: $R^1 = R^4 = Me, R^2 = R^3 = Ph$
f: $R^1 = R^3 = t\text{-}Bu, R^2 = R^4 = H$

115g **116**

Scheme 26.

Table 2. Preparation of Selenophene 1,1-Dioxides **115a**—**g**

Selenophene 1,1-dioxdes	Yields (%)	Mp (°C) (decomp)	$\delta(^{77}Se)$[a] (ppm)	$\nu(SeO_2)$[b] (cm^{-1})
115a	97	> 148	1036	876, 937
115b	89	> 145	1035	875, 933
115c	99	> 140	1035	900, 933
115d	69	> 155	1032	909, 938
115e	97	> 155	1042	880, 928
115f	97	> 152	1054	877, 932
115g	71	> 135	1018	880, 927

a) Determined with D_2SeO_3 (δ = 1282) as the external standard for $CDCl_3$ solutions (76 MHz). b) Taken for KBr disks.

ing 1,1-dioxides.[51,52] In the case of benzo[*b*]selenophene, the oxidation with 2.2 molar amounts of DMD gave the 1,1-dioxide **115g**, whereas the oxidation with an equimolar amount of DMD furnished the 1-oxide **116** as a thermally labile crystalline compound which is soluble in water. A several-gram scale synthesis of **115a** is possible by using DMD, generated in situ by oxidation of Me_2CO with Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$). Slow addition of Oxone® (31.0 g) to a well-stirred mixture of **112a** (4.35 g), $NaHCO_3$ (14.5 g), Me_2CO (40 ml), CH_2Cl_2 (40 ml), and H_2O (40 ml) thus furnished 4.63 g (99%) of **115a**.[52]

All of the selenophene 1,1-dioxides decompose gradually on heating without showing distinct melting points (Table 2).[51,52] The ^{77}Se NMR of **115a** appeared at δ = 1036 with D_2SeO_3 as the external standard, which is much lower than that of **112a** (δ = 605). The other 1,1-dioxides showed the ^{77}Se signals in the range of δ = 1018—1054. This is slightly lower than those of common alkyl phenyl selenones and dialkyl selenones (δ = 980—1040). The IR spectra of **115a**—**g** showed strong SeO_2 asymmetric and symmetric stretching vibrations in the ranges 875—909 and 927—938 cm^{-1}, respectively (Table 2). The UV/vis spectrum of **115a**, λ_{max} (log ε) (MeCN) 330 (3.8), 375 nm (3.8), closely resembles that of tetraphenylthiophene 1,1-dioxide. In the MS spectrum, the most intense peak is observed at *m*/*z* 372, which corresponds to the tetraphenylfuran radical cation formed from the molecular ion peak by loss of SeO.

A molecular structure of **115a** is given in Fig. 7.[47,51,52] The five-membered ring retains a nearly planar structure regardless of the loss of aromaticity. However, bond alternation is evident from the bond length data: C1–C2, 1.354(5); C3–C4, 1.345(5); C2–C3, 1.516(5) Å. The O–Se–O bond angle is 114.9(2)° and is bisected by the plane of the five-membered ring.

The 1,1-dioxide **115a** is thermally labile and decomposes easily, whereas tetraphenylthiophene 1,1-dioxide is thermally highly stable. Thus, heating a 3 mM solution of **115a** in PhMe at reflux for 1.5 h afforded tetraphenylfuran (**117**)

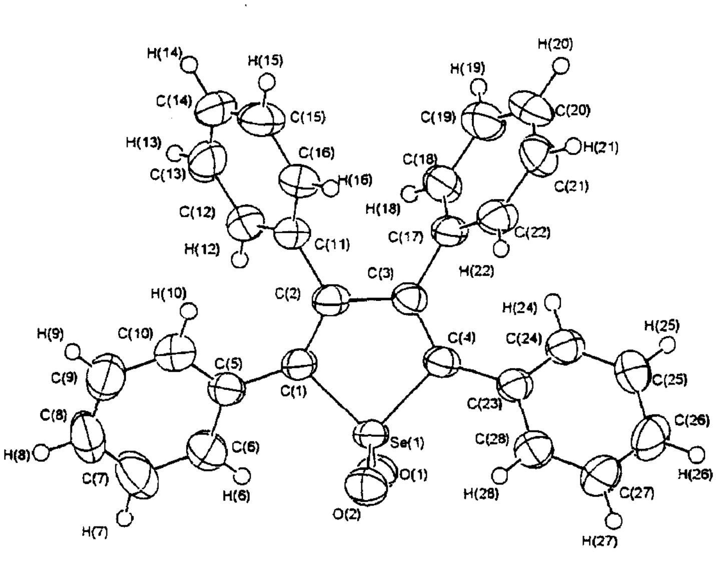
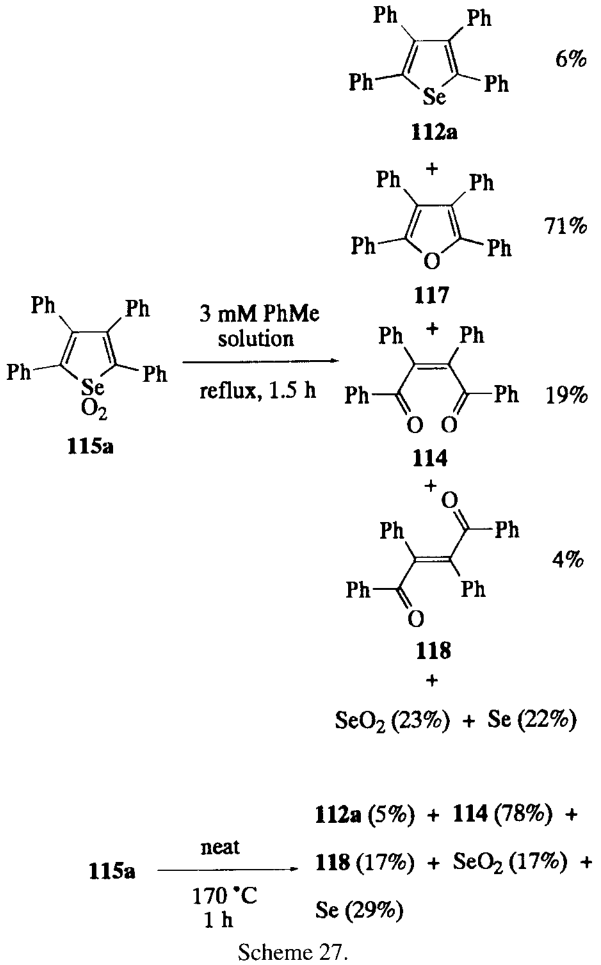


Fig. 7. Molecular structure of tetraphenylselenophene 1,1-dioxide (**115a**).

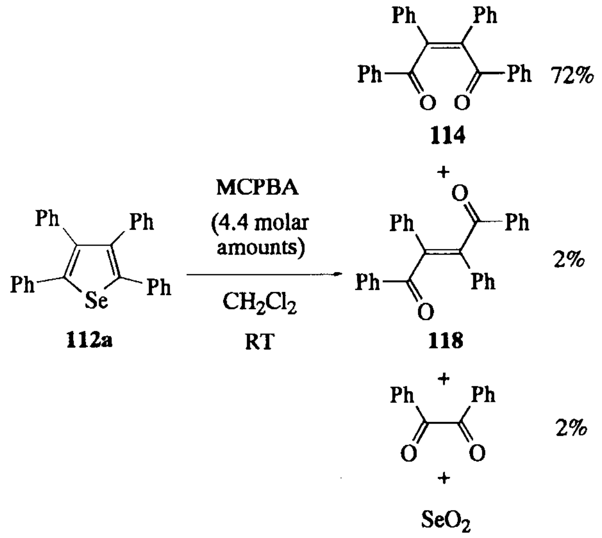
in 71% yield along with small amounts of the selenophene **112a** and butenediones **114** and **118** (Scheme 27).[56] The formation of the furan **117** is also observed with thermolysis of tetraphenylthiophene 1,1-dioxide, and is consistent with the appearance of the tetraphenylfuran radical cation as the most intense peak in the mass spectrum. Meanwhile, thermolysis of **115a** without solvent afforded the dione **114** as the major product (78%). Although the decomposition mechanisms of **115a** and some other 1,1-dioxides were investigated in some detail, the whole story still remains unclear.[56]

Oxidation of tetraarylselenophenes with MCPBA and some other oxidants was investigated in some detail.[52,57] For example, the oxidation of **112a** with 4.4 molar amounts of MCPBA produced **114** (72%) in addition to small amounts of **118** and benzil with recovery of **112a** in 14% yield (Scheme 28). Neither 1-oxide **113** nor 1,1-dioxide **115a** was obtained in this oxidation. The formation of **114** might be explained by decomposition of the 1-oxide intermediate **103**, though other explanations seem equally possible.

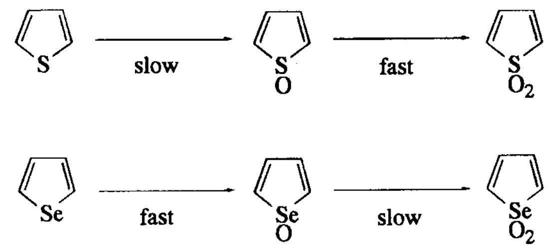
It is thus safe to say that the chemistry of selenophene 1-oxdies and 1,1-dioxides has been just born by their successful synthesis, subsequently to set the next stage for the development of their chemistry.



Scheme 27.



Scheme 28.



Scheme 29.

Differences in the Oxidation Rate between Thiophenes and Selenophenes

Finally, differences in oxidation rate between thiophenes and selenophenes should be stressed. Oxidation of thiophenes, including the parent thiophene, is difficult to stop at the 1-oxide stage because of much faster oxidation of 1-oxides to 1,1-dioxides relative to the oxidation of thiophenes to thiophene of 1-oxides (Scheme 29). This would be explained by the fact that thiophenes, whose aromaticity is the greatest in the five-membered, one chalcogen atom-containing heteroaromatics, resist the oxidation that results in the loss of the aromaticity, but, once they are oxidized, the oxidation of 1-oxides to 1,1-dioxides takes place much more easily. By contrast, the oxidation of selenophenes is easily quenched at the 1-oxide stage because of much slower oxidation of 1-oxides to 1,1-dioxides relative to the oxidation of selenophenes to selenophene 1-oxides. This might be explained partly by smaller aromaticity of selenophenes relative to thiophenes and partly by decreased electron density on the selenium atom of selenophene 1-oxides because of the highly polarized Se–O bond, which makes electrophilic oxidation slower.

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