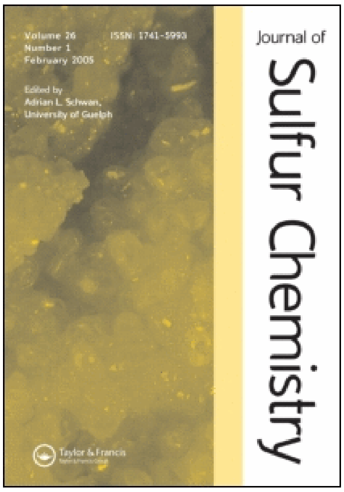

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THE CHEMISTRY OF 1,4-DITHIINS

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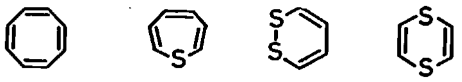
The advances of the chemistry of 1,4-dithiins after the 1960's are reviewed. The preferred structure of 1,4-dithiin has attracted considerable attention from both theoretical and experimental chemists. Although 1,4-dithiin is comprised of a cyclic 8π-electron system, it is neither antiaromatic in character, nor aromatic as suggested earlier on the basis of possible d-orbital participation. The ring favors a boat structure and the chemical properties are predominantly olefinic. The olefinic carbon atoms as well as the sulfur atoms can enter into the reactions. Thus 1,4-dithiin ring compounds provide versatile reactions not only with electrophiles but also with nucleophiles. In some thermal and photochemical reactions valence isomerizations, as encountered in the isoelectronic cyclooctatetraene, are involved as transient species. The synthetic routes to 1,4-dithiin compounds are also covered.

Key words: 1,4-Dithiins.

Replacement of an ethylenic moiety in cyclooctatetraene with a sulfur atom yields a seven-membered heterocycle, thiepin,[1] and further replacement of another ethylenic C=C bond with a sulfur atom results in the six-membered dithiin ring system. Dithiin is, therefore, isoelectronic with cyclooctatetraene. Two isomers may be considered for the dithiin ring system, one is 1,2-dithiin and the other is 1,4-dithiin. Examples of the former are rare, the mother compound being prepared in the mid-1960's.[2] On the other hand, the latter isomer was first reported by Levi in 1890, who described its preparation by reaction of dithioacetic acid with phosphorus trisulfide.[3] However, subsequent attempts to repeat this synthesis were not successful. It was not until 1953 that Parham and co-workers achieved a reliable synthesis of 1,4-dithiin,[4] although 2,5-diphenyl-1,4-dithiin had been prepared in 1936.[6] Afterwards the chemistry of 1,4-dithiin was extensively pursued by Parham and enjoyed its early vintage. In 1961, he summarized the work on 1,4-dithiin in a review article.[5] Here in this article we review the developments of the chemistry of 1,4-dithiin ring compounds after Parham, covering preparation, structure, and reactions.



Benzo-1,4-dithiin and thianthrene, which may be regarded as dibenzo-1,4-dithiins. are not included in this review unless particularly related to the 1,4-dithiin ring system.

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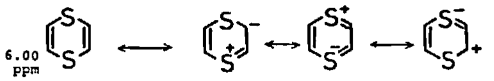
I. STRUCTURE

I.1. Ring Conformation

There has been some confusion concerning the nature of the cyclic conjugation in the 1,4-dithiin ring which bears a direct relationship with the molecular confirmation of this ring.

Earlier, this ring system was considered to be aromatic. If four π-electrons in two C=C bonds and two p-electrons of a sulfur atom can enter into cyclic conjugation through d-orbitals of the sulfur atom, the molecule would attain 6π-aromaticity. The occurrence of electrophilic substitution[5] such as nitration and bromination are also reminiscent of aromaticity of the 1,4-dithiin ring. An early calculation using the SCF-MO method predicted the resonance energy of the 1,4-dithiin ring in the boat structure to be 13 kcal mol^{-1}.[7] However, aromaticity is explicitly excluded because of the non-existence of a diamagnetic ring current.[8] In ^{1}H NMR 1,4-dithiin (**1**) exhibits a singlet signal at 6.00 ppm, which is almost equal to the value observed in dihydro-1,4-dithiin (**2**). Even in compound **3**, where d–π conjugation should operate more effectively, the proton chemical shifts are not different from those of the corresponding dihydro compound **4**.



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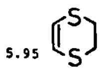

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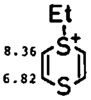

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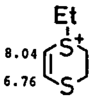

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The chemical shifts thus provide no indication of a ring current and are in reasonable agreement with the predicted value of 6.14 ppm for the –S–CH=CH–S– fragment, based on the shifts of methyl vinyl sulfide.

Antiaromaticity would be more reasonable to be assumed for a cyclic 8π-electron systems if it had a planar structure. Hess Jr. has performed calculations which show a negative resonance energy of -0.017β per π-electron in the 1,4-dithiin ring system.[9] Gupta has also reported a negative resonance energy of -0.053 eV.[10] A technique based on combinations of perturbation theory and the graph-theoretical definition of resonance energy again leads to the estimation of a negative resonance energy.[11] The thermal stability in spite of the presence of an 8π-antiaromatic system is explained by the requirement of orbital phase continuity.[12] The cyclic electron delocalization in the 1,4-dithiin ring is discontinuous, as the lone-pair electrons at the sulfur atoms as donors and the C=C bonds as acceptors are alternatively arranged to diminish the consequences of Hückel's rule.

All the above descriptions of antiaromaticity assume a planar molecular conformation. However, in order to avoid the destabilization present in the planar form, a non-planar conformation would be preferred. A variety of theoretical calculations have been carried out concerning the ring conformation, most of which demonstrate the boat

TABLE I

Calculations of 1,4-Dithiin in the Boat Conformation: Flap Angle[a] and Energy Relative to the Planar Conformation

Computation method	Flap angle θ°	$E_{boat} - E_{planar}$ kcal mol^{-1}	Ref.
HMO	132	−6.4	13
EHT	140	−2.16	14
STO-3G	131	−14.6	16
STO-3G/gradient	153.0	0.02	15
MNDO/FP[b]	162.7	0.38	15
3-21G	132.9	3.0	17
MM	150.3	0.2	17
3-21G*	137	2.3	18
6-21G		2.6	17
6-31G*	136.6	1.8	18

[a] The flap angle is defined as the angle between the two S–C=C–S planes.

[b] Fletcher–Powell energy minimization algorithm.

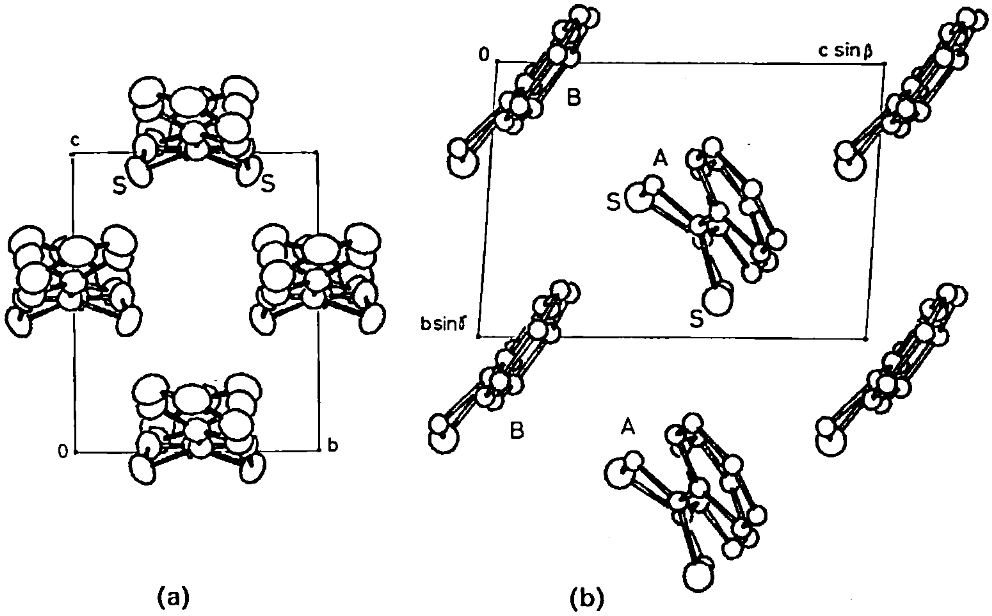
form to be more stable than the planar form, although some conflicting results have been reported, as shown in Table I.

HMO[13] and EHT[14] semiempirical calculations claim the boat structure to be more stable than the planar form by 6.4 and 2.2 kcal mol^{-1}, respectively. On the other hand, MNDO semi-empirical calculations indicate the planar form to be favored over the boat structure by 0.4 kcal mol^{-1}.[15] There is also disagreement among two ab initio calculations using the STO-3G basis set. Gassolo reported that a boat conformer ($\theta = 131°$) is favored over the planar form by 14.6 kcal mol^{-1},[16] whereas, according to calculations including Fletcher–Powell minimization, the boat and planar conformations have virtually identical energies, the former (with $\theta = 153°$) being only 0.4 kcal mol^{-1} higher in energy.[15]

Recently Kao *et al.* have carried out more extensive theoretical calculations using the larger 3-21G basis set yielding the energy difference between boat ($\theta = 133°$) and planar form as 3.0 kcal mol^{-1}.[17] Calculations using the 6-21G basis set with full structural optimization predict a slightly smaller value, 2.6 kcal mol^{-1}. The MM energy difference of 0.2 kcal mol^{-1} between boat ($\theta = 150°$) and planar conformations is considerably smaller than the 3-21G and 6-21G values.[17] Saebo has shown, by ab initio calculations using 6-31G*, that 1,4-dithiin exists preferably in a boat form ($\theta = 136.6°$) and the barrier to ring flapping is 1.9 kcal mol^{-1}.[18]

Then, what are the experimental results concerning the structure of the 1,4-dithiin ring system?

An X-ray diffraction study of the mother compound 1,4-dithiin (**1**) has revealed a boat structure,[19] in the solid state, with a butterfly-flapping angle (θ) of 137° or 141° between the two S–C=C–S planes. This work has been often cited. However, discrepancies exist in the analysis owing to non-equivalent interatomic distances which should, because of



(a) (b)

Figure 1 Projections of the Crystal Structures Along a-Axis. (a) Uncomplexed 2,5-Diphenyl-1,4-dithiin. (b) 1 : 1 Molecular Complex of 2,5-Diphenyl-1,4-dithiin (A) and 2,4-Diphenylthiophene (B).

symmetry, be equivalent. More recently the crystal and molecular structure has been determined for 2,5-diphenyl-1,4-dithiin (5) by X-ray analysis.[20a] The dithiin ring is arranged in a boat structure with a flapping angle of 132.7°.

A variety of 2,5-diaryl-1,4-dithiins have been shown to form stable 1 : 1 molecular complexes with 2,4-diarylthiophenes.[20b] An X-ray analysis has been reported for the complex of 2,5-diphenyl-1,4-dithiin and 2,4-diphenylthiophene.[20b] In the complex the 1,4-dithiin ring has a slightly twisted boat conformation, whereas uncomplexed 2,5-diphenyl-1,4-dithiin has a typical boat form in the crystal.[20a] This conformational difference is clearly indicated in Figure 1, which shows the crystal structures projected along the *a* axis. These observations would suggest that the 1,4-dithiin ring system is conformationally mobile enough to be subject to conformational change by the packing forces in the crystal. Another interesting point is the formation of 1 : 1 complexes regardless of the electron-donating or electron-accepting properties of the substituents on the phenyl rings. Distinct intermolecular charge-transfer interaction, hydrogen bonding or clathrate inclusion is not found in the complexes. Thus no distinct intermolecular interaction can be recognized.

The structures of tetracyano-1,4-dithiin (6),[21] sulfoxide 7,[22] and sulfone 8[23] have been determined by X-ray diffraction. The structural comparisons are summarized in Table II. The dithiin rings adopt boat structures and a trend is seen: the more highly oxidized a sulfur atom is, the larger is the flap angle, resulting in a flatter molecular geometry.

TABLE II

X-Ray Structural Comparison of 1,4-Dithiin Derivatives

	1	5	6	7	8
C–S (Å)	1.78	1.755 1.767	1.755	1.711	1.738 1.755
$C–S_{ox}$ (Å)				1.755	1.733 1.777
C–S–C (°)	101.2	101.8	97.3	103.3	103.53
$C–S_{ox}–C$ (°)				98.2	103.61
Flap angle (°)	137	132.7	124	142	145
Boat angle[a] (°)	152	147.5	154	146 165	150 155
Reference	19	20a	21	22	23

[a] The boat angle is the angle between the C–S–C planes and the plane of the olefinic C atoms.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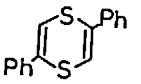
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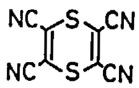
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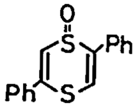
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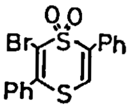
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It is interesting to note that the sulfinyl oxygen in sulfoxide 7 occupies an axial position in the solid state. The conformation in solution, however, has not been examined so far.

Thianthrene has been known to be folded along the S–S axis, so that the two benzene rings lie in two planes at an angle of 128°.[24] Yamaguchi has reported the molecular structure of 1,4-dithiintetracarboxylic acid *N,N'*-dimethyldiimide in its 1 : 1 complex with acridine, where the 1,4-dithiin molecule is planar.[25]

Dipole moments provide some information about the ring conformation in solution. Thus, boat conformations have been suggested for 2,5-diphenyl-1,4-dithiin (μ = 1.77 D),[26] and tetracyano-1,4-dithiin ($\mu = 4.0 \pm 0.5$ D).[27] Recent dipole moment measurements on 1,4-dithiin (μ = 1.14 D) suggest a flap angle of 136 ± 7°,[28] which is consistent with the X-ray results.

The calculated dipole moment using the MM method is 0.95 D for 1,4-dithiin,[17] which is in rather good agreement with the experimental value.

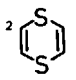
The NMR proton coupling constants in a nematic phase do not allow a choice between a boat or the planar structure.[29,30] The UV photoelectron spectra of 1,4-dithiins have been assigned with the help of ab initio and semiempirical calculations.[31] This also fails to distinguish between the boat and planar structure.

No studies using dynamic NMR technique have been reported so far. This could be due to the small energy difference between the boat and planar conformations; hence it would be difficult to freeze out one conformation, even at a low temperature.

I.2. Electronic Properties

The electronic structure of 1,4-dithiin has been investigated experimentally. The ionization energy of 1,4-dithiin has been measured by means of UV photoelectron spectroscopy and the molecular orbitals have been assigned by quantum mechanical calculations.[31] The IP values calculated by the X_α-SCF method using Koopman's theorem can be related to the experimental values by a simple linear relation such as IP(exp.) = $2.6 + \mathrm{IP}(X_\alpha\text{-SCF})$. The lowest ionization energy observed is 8.15 eV.[31] The calculations based on the X_α methodology provide the energies of the optical transitions in good agreement with the experimental spectra.[17] The small ionization energy of the HOMO of 1,4-dithiin compounds makes them readily susceptible to oxidation.

Cyclic voltammetry of 1,4-dithiin exhibits two one-electron oxidation waves with $E^1_{1/2} = 0.69$ and $E^2_{1/2} = 1.16$ V vs. SCE.[34] The fusion of benzene rings to the dithiin ring brings about an increase in the oxidation potential (Table III).



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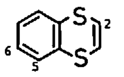

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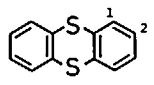

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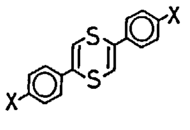
TABLE III

Half-Wave Oxidation Potentials as Measured by Cyclic Voltammetry in Acetonitrile[34]

Compd.	**1**	**9**	**10**
$E^1_{1/2}$ (V *vs.* SCE)	0.69	0.80	0.96
$E^2_{1/2}$ (V *vs.* SCE)	1.16	1.34	1.31

The increasing trend in going from **1** to **9** to **10** can be rationalized in terms of a decrease in electron density in the dithiin ring with the changes in bond order.

The peak potentials during cyclic voltammetry for the oxidation of a series of *p*-substituted diaryl-1,4-dithiins are found to vary in the order *p*-NO_2 > Br ~ Cl > H > MeO and the life times of the resulting radical cations are unexpectedly found to fall into the same order.[35]



Dissolving 1,4-dithiin in concentrated H_2SO_4[36] or treating 1,4-dithiin with $AlCl_3$[37] produces a radical cation due to one-electron oxidation. The ESR spectrum of this radical cation shows a hyperfine splitting ascribable to ^{33}S, indicating that the large spin density is located at the sulfur atoms.[38]

TABLE IV

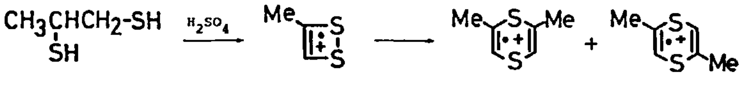
ESR Parameters of the Radial Cations from 1, 9, and 10

Compd.	1	9	10
^{33}S hyperfine splitting (G)[38]	9.84	9.35	9.15
^{1}H hyperfine splitting (G)[36]	$a_2 = 2.80$	$a_2 = 3.20$ $a_5 < 0.5$ $a_6 = 1.05$	$a_2 = 1.30$ $a_1 < 0.5$

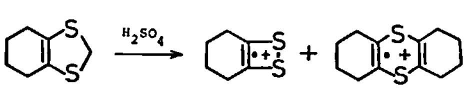
Condensation with the 1,4-dithiin nucleus causes a slight decrease in the spin density on sulfur as shown in the series 1, 9, and 10 (Table IV). This lowering is clearly associated with increased delocalization of the unpaired electron.[38]

A correlation of the proton hyperfine splittings with theoretical spin density distributions has been shown for the 1,4-dithiin radical cation. Two models have been tested: one involving only p-orbitals and the other involving expansion of the sulfur valence shell to include 3d-orbitals. Both models are in fairly good agreement with the experiments; the 3d-model gives somewhat better results.[36] The data concerning the hyperfine splittings are summarized in Table IV.

Radical cations of 1,4-dithiin compounds are observed when α-hydroxyketones or diketones are treated with a hydrogen sulfide source in sulfuric acid.[40] Treatment of 1,2-propanedithiol (**11**) with conc. H_2SO_4 gives first the 3-methyl-1,2-dithiete radical cation (**12**), which slowly gives rise to a mixture of two 1,4-dithiin radical cations, *i.e.* **13** and **14**.[41] Treatment of **15** with conc. H_2SO_4 gives the dithiete radical cation **16** and the 1,4-dithiin radical cation **17** by extrusion of the methylene moiety.[41]



11 12 13 14



15 16 17

Electron affinity is characteristic of 1,4-dithiin rings bearing electron-withdrawing substituents. Thus, treatment of tetracyano-1,4-dithiin (**6**) with potassium metal in THF produces the corresponding radical anion. The G value (2.0024) in the ESR spectra and consideration of the HMO suggest direct π–π overlap of the ethylenic moieties.[39]

The ^{13}C-NMR spectra of a series of 2,5-diaryl-1,4-dithiins have been investigated.[32] A Hammett correlation has been found between the ^{13}C chemical shifts of the dithiin ring carbons C-3 and C-6 and the σ_p^+ parameter attributable to the *p*-substituents.

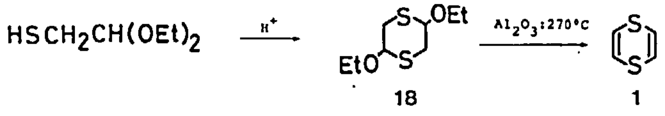
The ^{13}C–H satellite patterns for 1,4-dithiin have been observed and analyzed,[33] giving 6.97 Hz for the ethylenic H–H coupling constant.

II. PREPARATION

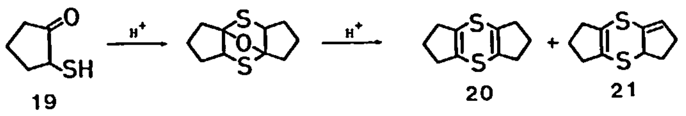
Since Parham and co-workers established a reliable synthetic route to 1,4-dithiin,[4] a variety of synthetic strategies have been developed to construct such 1,4-dithiin ring systems. Of the several methods developed over the past decades, methods involving condensation, cleavage of heterocyclic rings, or cycloaddition are of greater synthetic importance.

II.1. Via α-Mercaptoketones or Bunte Salts

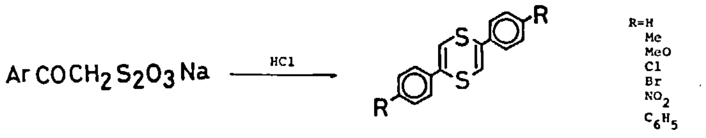
The parent dithiin is obtained, starting from α-mercaptoacetoaldehyde, by vapor-phase dealkoxylation of 2,5-dialkoxy-1,4-dithianes (**18**) over alumina at 270 °C.[5] The yield is 50%. Dimethyl substituted 1,4-dithiin has been prepared in 14–38% yield according to a similar method in the 1950's.[5]



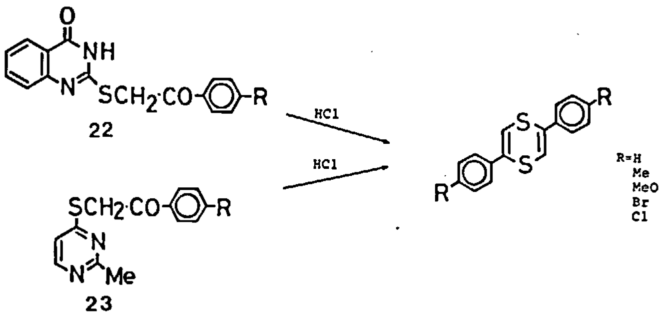
Acid-catalysed reaction of α-mercaptocycloalkanones gives rise to head-to-tail condensation and subsequent dehydration to afford polymethylene-bridged 1,4-dithiins. Thus, octahydrodibenzo-1,4-dithiin can be prepared in good yield.[42] In the case of mercaptocyclopentanone **19**, however, the isomer **21** having an exocyclic double bond is also formed, which makes the isolation of the 1,4-dithiin **20** difficult.[43]



The synthesis of 2,4-diphenyl-1,4-dithiin involves the formation of the Bunte salt from phenacyl halides with sodium thiosulfate followed by cyclization under acidic condition.[5] This procedure is widely applicable to the preparation of 2,5-diaryl-1,4-dithiins (50–75%).[44]



Modifications of this method have been reported; the treatment of the phenacylthio derivatives **22** or **23** with conc. HCl or $HClO_4$ affords 2,5-diaryl-1,4-dithiins (45–65%).[45]



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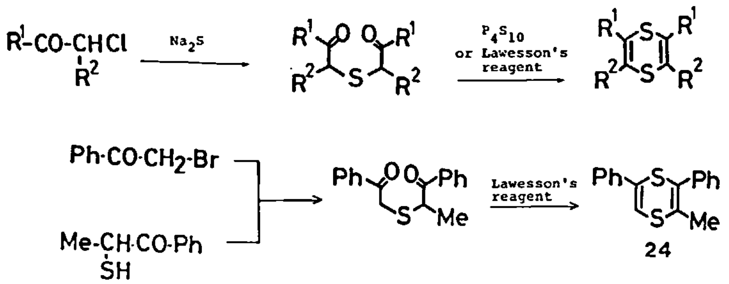
The construction of the 1,4-dithiin ring system *via* Bunte salt formation is severely limited in its flexibility concerning the substitution pattern, allowing substituents only at the 2- and 5-positions due to head-to-tail condensation. This difficulty is, however, overcome by using diketo sulfides and phosphorus pentasulfide or Lawesson's reagent.[46] According to this method it is possible to introduce substituents into arbitrary positions (especially the 2- and 6-positions) of the 1,4-dithiin nucleus. Even unsymmetrically substituted 1,4-dithiins such as 24 are obtained in 50% yield.



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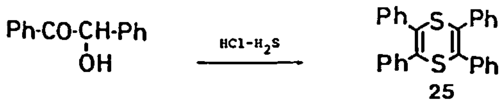
Tetraphenyl-1,4-dithiin (25) is obtained by the action of HCl and H_2S on benzoin.[47]



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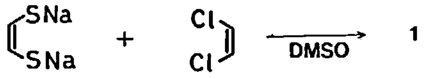
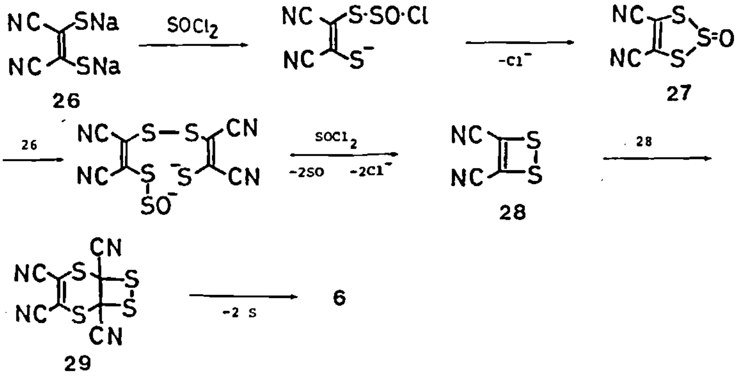
II.2. *Via Thiolates or Thiols*

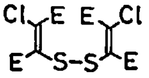
Another strategy in the synthesis of the 1,4-dithiin ring system is to make use of the dianions of dimercapto species. An example is seen in the reaction of *cis*-1,2-dichloroethylene with disodium *cis*-ethylenedithiolate in DMSO to give 1,4-dithiin.[30] The yield of this reaction is very low and this nucleophilic reaction is more suited for the preparation of 1,4-dithiin compounds with electron-withdrawing substituents.



Disodium dimercaptomaleonitrile (**26**) reacts with thionyl chloride to give tetracyano-1,4-dithiin (**6**) in almost quantitative yield.[48] The mechanism of this fascinating reaction is assumed to involve **27** and **28** as intermediates, which could actually be isolated.[49]



Treatment of the disulfide **30** with sodium benzenethiolate was previously reported to produce the 1,2-dithiin derivative **31**.[50] However, the structural assignment has been revealed to be in error and was later corrected to the 1,4-dithiin derivative **32**.[51] The mechanism is considered to involve cleavage of the sulfur–sulfur bond by nucleophilic attack of the thiolate anion.



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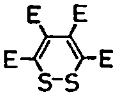

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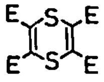
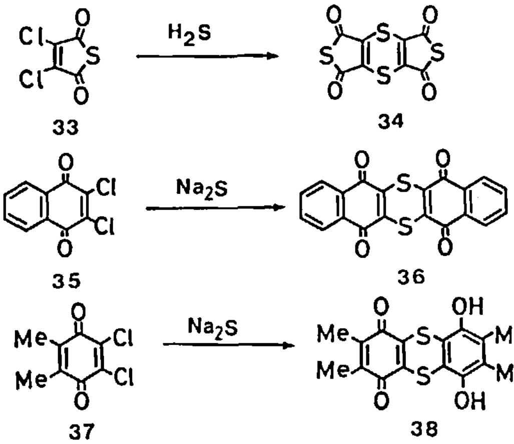


32

E=COOMe

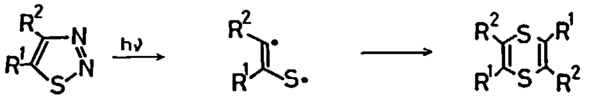
Condensed 1,4-dithiins have been prepared quite often by nucleophilic substitution.[102] Dichloromaleic acid thioanhydride (**33**) reacts with H_2S to give the 1,4-dithiin-tetracarboxylic acid derivative **34**.[52] Likewise, **36** is obtained from **35** and sodium sulfide. When this type of reaction is applied to the benzoquinone **37**, compound **38** is obtained in 92% yield.[52]



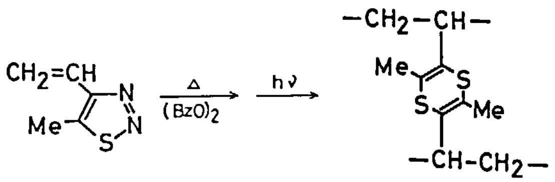
II.3. Via Cleavage of Heterocyclic Rings

The third major route to the 1,4-dithiin ring system is cleavage of heterocyclic rings. Such cleavages are brought about either photochemically or by thermal reactions.

1,2,3-Thiadiazoles when photolyzed eliminate a molecule of nitrogen and a diradical intermediate is formed. The diradical dimerizes to afford a 1,4-dithiin. The yields are generally not high since 1,3-dithiole, thiophene, and other by-products are also formed.[53,54]

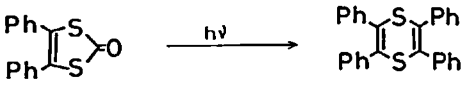


The similar photolysis of polymethylene-bridged 1,2,3-thiadiazoles is reported to yield 1,4-dithiins.[55] The yield of the reaction is shown to depend on the ring size (R^1, R^2 = $-(CH_2)_n-$). This type of photoreaction is nicely applied to photo-cross linkage; poly(5-methyl-4-vinyl-1,2,3-thiadiazole), which is prepared by spontaneous polymerization of **39** in the presence of benzoyl peroxide, is irradiated to give polymers cross-linked by 1,4-dithiin rings.[56]



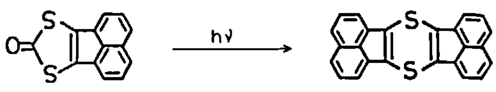
39 40

Photodecarbonylation occurs when 4,5-diphenyl-1,3-dithiole-2-one (**41**) is irradiated and tetraphenyl-1,4-dithiin (**25**) is formed in 82% yield.[57]



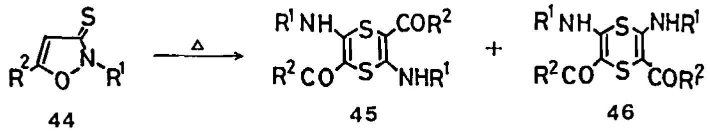
41 25

p-Substitution with dimethylamino groups on the phenyl groups of **41** brings about the formation of the corresponding dithiobenzil upon photolysis.[58] Thus, photolysis of **41** is suggested to occur *via* a dithiobenzil intermediate. A similar type of photochemical conversion has recently been reported for the acenaphthene derivative **42**.[103]

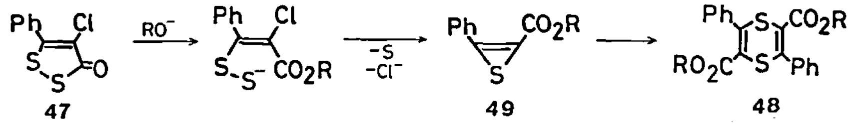


42 43

Heterocyclic thiones give rise to 1,4-dithiin derivatives upon pyrolysis. A series of 4-isoxazolin-3-thiones (**44**) have been pyrolyzed in boiling toluene and the regioisomeric 1,4-dithiins **45** and **46** were isolated.[59] The isomeric dithiins are separated by several recrystallizations from acetone. The formation of both head-to-tail and head-to-head connections suggests that the photolysis proceeds *via* a thiirene intermediate.



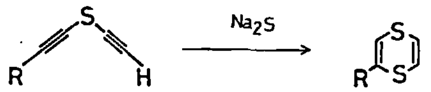
In addition to thermal and photochemical transformations of heterocyclic ring systems, nucleophilic ring opening of the 4-chloro-1,2-dithiole-3-one (**47**) is observed to give the 1,4-dithiin derivative **48** in 77% yield.[60]



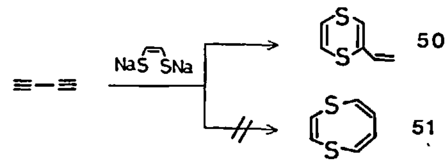
Ring opening and subsequent loss of sulfur followed by recyclization to give the thiirene intermediate **49** may be considered to constitute the reaction mechanism.

II.4. Via [5+1]- and [4+2]-Cyclization

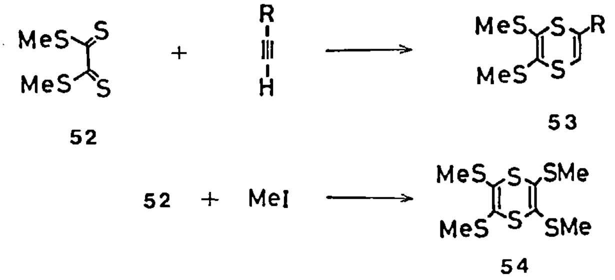
1,4-Dithiins can also be generated by cyclization of a five-atom fragment and a one-atom unit. 1-Alkynyl ethynyl sulfides react with sodium sulfide in methanol to afford monosubstituted 1,4-dithiins (55–75%), an example of a [5+1]-cyclization.[61] The reaction is also applicable to the preparation of 1,4-thiaselenins and 1,4-thiatellurins. In contrast to the reactions involving dimerization or head-to-tail condensation, this route is suitable for the preparation of unsymmetrically substituted 1,4-dithiins. Likewise, di(1-alkynyl) sulfides interact with sodium sulfide in a mixture of liquid ammonia and methanol to give 2,6-dialkyl-1,4-dithiins (65–80%).[62]



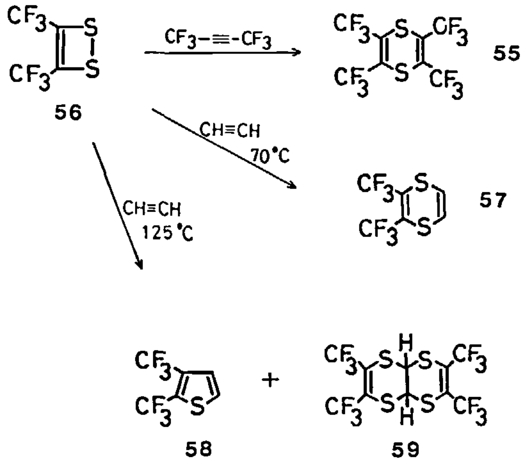
Cyclization of a four-atom and two-atom fragment is another general synthesis of the 1,4-dithiin ring system. *cis*-1,2-Ethylenedithiolate reacts with 1,3-butadiyne to give 2-vinyl-1,4-dithiin (**50**) in 20% yield rather than 1,4-dithiocin (**51**).[63]



Dimethyl tetrathiooxalate (**52**) undergoes a [4+2]-cycloaddition with acetylenic compounds to give the 1,4-dithiin ring compounds **53** (50–80%).[64] Methylation of **52** with methyl iodide also gives rise to tetrakis(methylthio)-1,4-dithiin (**54**) along with other products.[65]



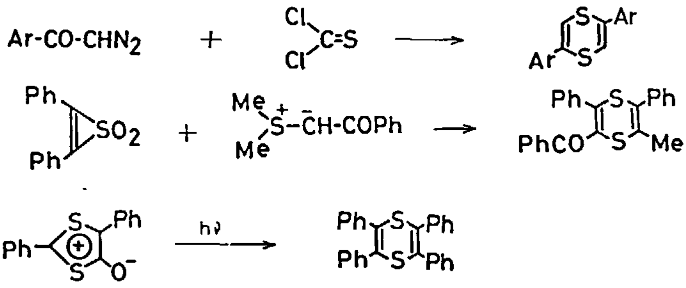
Tetrakis(trifluoromethyl)-1,4-dithiin (55) is obtained in 33% yield by the reaction of hexafluoro-2-butyne and sulfur in the presence of iodine at 100 °C and under pressure.[65] The 1,2-dithiete **56**, which corresponds to a valence isomer of a dithiobiacetyl, is involved in this preparation. Acetylene also can be added to **56** at a somewhat lower temperature (70 °C), resulting in the formation of 2,3-bis(trifluoromethyl)-1,4-dithiin (**57**). At higher temperature (125 °C), however, thiophene **58** and the bicyclic compound **59** are formed.[66]



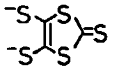
II.5 *Miscellaneous*

Unexpected formation of 1,4-dithiin compounds has been found in several reactions.

Diphenylthiirene dioxide is reported to react with a sulfur ylide to form a multisubstituted dithiin in 12% yield along with other products.[67] The reaction of benzoyldiazomethane with thiophosgene has been reported to give 2,5-diphenyl-1,4-dithiin.[68] Photolysis of a mesoionic compound also affords a 1,4-dithiin ring.[69]



Also electrochemical methods have been used to obtain condensed 1,4-dithiin systems.[70] Electrochemical reduction of carbon disulfide to the dianion **60**, followed by alkylation with 1,2-dibromoethane, gives the trithiocarbonate **61**. Hydrolysis of **61**, alkylation, and then dehydrogenation leads to the formation of the condensed 1,4-dithiin **62** in 47% yield.[70] Compound **62**, unlike the isomeric tetrathiafulvalene (**63**), is not readily oxidized to a radical cation.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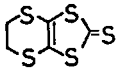
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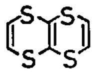
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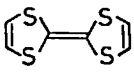

63

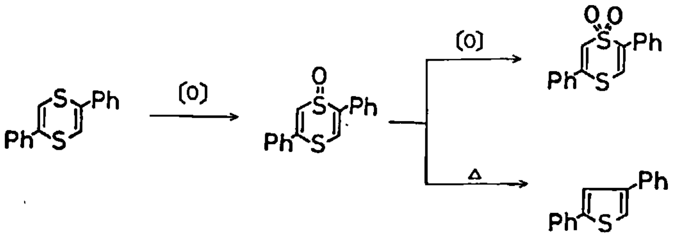
III. REACTIONS

1,4-Dithiins are capable of a variety of reactions. Both electrophilic and nucleophilic attack can occur at carbon as well as at sulfur. This is ascribable to the soft sulfur atom and the electron-rich π-bond. The dithiins are also susceptible to thermal and photochemical excitation, where cycloaddition and valence isomerization are involved in analogy with the isoelectronic cyclooctatetraene.

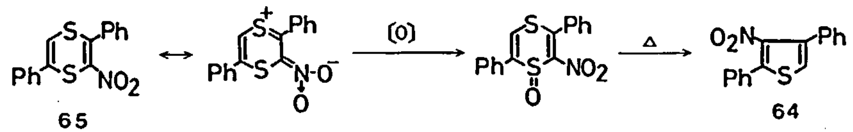
III.1. Oxidation

The oxidation of the sulfur atoms of 1,4-dithiin is a fascinating reaction. Depending upon the quantity of the oxidizing agents used either one or both sulfur atoms are oxidized to different oxidation states. Usually the monosulfoxide is unstable in comparison with the mono- or disulfone.

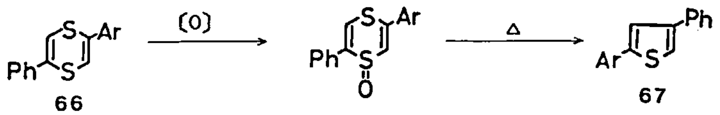
According to the early observations of Parham,[5] oxidation of 1,4-dithiins always led to the formation of thiophenes. The results have been interpreted as the extrusion of SO_2 from the sulfone intermediate. Contrary to the original suggestion by Parham the successful preparation of the monosulfoxide has demonstrated conclusively that desulfoxylation or dethionylation is responsible for the formation of thiophene.[71] Thus the sulfoxides can be either decomposed thermally or further oxidized to the corresponding sulfones under carefully controlled oxidation conditions.



The presence of electron-withdrawing substituents such as a nitro group in 2,5-diphenyl-1,4-dithiin affects the electron density of the sulfur atoms considerably, facilitating the preferential oxidation of the sulfur atom close to the nitro group.[5] Thus 3-nitro-2,4-diphenylthiophene (**64**) is isolated in 46% yield in the oxidation of **65** followed by extrusion of SO.[5] An unsymmetrical 2,5-diaryl-1,4-dithiin, namely 2-*p*-methoxyphenyl-5-phenyl-1,4-dithiin (66) has been oxidized with peracetic acid and the product ratios have been determined, 2-*p*-methoxyphenyl-4-phenylthiophene (67) being isolated as the major product (49%).[72]

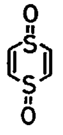


65 64



66 67

Several attempts have been made to prepare the disulfoxide of 1,4-dithiin (68). In almost all cases only monosulfones are obtained. In the case of condensed 1,4-dithiins, however, such disulfoxides have been isolated with iodobenzene dichloride as the oxidizing agent.[73] An oxidation state with both monosulfoxide and monosulfone functionalities such as 69 has never been reported.



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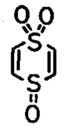

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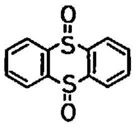
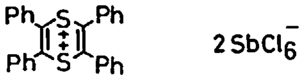


cis trans

Oxidation of 1,4-dithiins by chloramine-T to give the corresponding sulfilimine derivative has also been reported.[79,100]

Because of low oxidation potential as noted earlier, the 1,4-dithiin ring readily undergoes one-electron oxidation to give a radical cation. Also the dication can be generated by two-electron oxidation; tetraphenyl-1,4-dithiin reacts with antimony pentachloride in benzene giving the dication salt (70) as stable dark violet crystals.[8b]

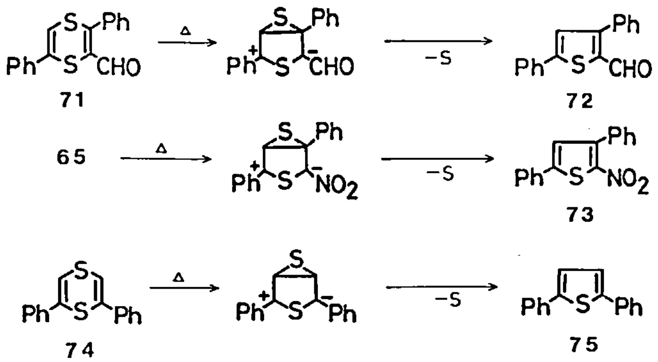


70

III.2. *Thermolysis*

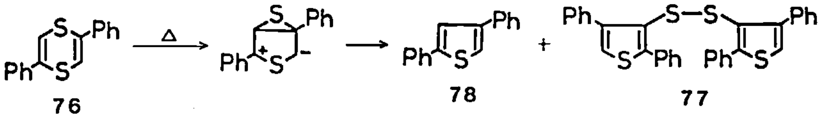
The parent unsubstituted 1,4-dithiin is thermally stable and can be distilled at 190 °C without decomposition.[5] The presence of two methyl groups in the 2- and 5-positions is sufficient to permit some degree of extrusion of sulfur at 204 °C, yielding 2,4-dimethylthiophene.[5] A variety of substituted 1,4-dithiins undergo ring contraction when subjected to the action of heat. If aryl groups are present in the 2- and 5-positions, extrusion of sulfur occurs efficiently. The major products formed from unsymmetrically substituted 1,4-dithiins by thermal extrusion of sulfur correspond to preponderant formation of one thiophene isomer of the possible two. Thus, 2-formyl-3,6-diphenyl-1,4-dithiin (71) gives 2-formyl-3,5-diphenylthiophene (72) and 65 gives 2-nitro-3,5-diphenylthiophene (73) as the major product.

Thermolysis of 2,6-diphenyl-1,4-dithiin (74) is also found to give 2,5-diphenylthiophene (75) predominantly over 3,4-diphenylthiophene in various solvents.[74] All these observations provide evidence that the thermal extrusion of sulfur occurs by way of a zwitterionic thiirane intermediate; the major products are rationalized as arising from that thiirane compound which is more stabilized by charge delocalization due to the substituent than the other thiirane isomer is.

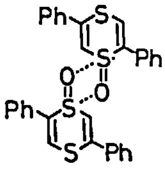


This mechanism has been recently discussed by Grigg on the basis of a [4*n*+2]-disrotatory electrocyclic process leading to a *cis*-fused thiirane intermediate.[75]

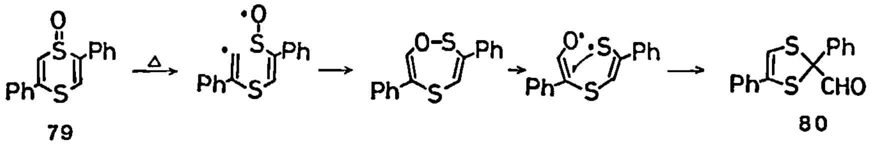
Stronger evidence for a mechanism involving valence isomerization to a bicyclic thiirane is provided by the isolation of bis(2,4-diphenyl-3-thienyl) disulphide (77) during the thermal decomposition of 2,5-diphenyl-1,4-dithiin (76).[76] The disulfide must obviously arise from the rearrangement to the thiophenethiol, *via* valence isomerization, followed by oxidation. The rate of the thermal decomposition of 76 follows first-order kinetics despite the formation of two products, 78 and 77.[76] Thus, these products are generated *via* a common intermediate, which must be formed in the rate-determining step. The activation parameters are $\Delta H^{\ddagger} = 21.6\,\mathrm{kcal\,mol^{-1}}$ and $\Delta S^{\ddagger} = -27.6\,\mathrm{e.u.}$ in *o*-dichlorobenzene.[76] The highly negative entropy of activation suggests a highly ordered transition state, consistent with the thiirane intermediate mechanism.



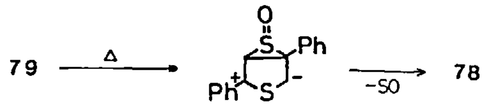
The products and their distribution in the thermolysis of 1,4-dithiin sulfoxides show concentration as well as solvent dependence. In solvents capable of association with the sulfoxide moiety clean extrusion of sulfur oxide is observed.[79,80] Higher concentration of the sulfoxide inevitably leads to the formation of a self-associated complex which usually undergoes bimolecular disproportionation to thiophene and dithiin.[77]



Thermal decomposition of 2,5-diphenyl-1,4-dithiin 1-oxide (**79**) in dilute acetonitrile solution has been found to involve a novel rearrangement to 2-formyl-2,4-diphenyl-1,3-dithiole (**80**) rather than the extrusion of sulfur oxide.[78] In carbon tetrachloride exclusive formation of **80** is observed. This rearrangement is believed to occur *via* the radical mechanism as shown below.

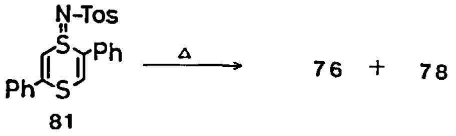


Addition of triethylamine to an acetonitrile solution of **79** suppresses the formation of **80**, leading to the exclusive formation of **78**. Under these conditions a kinetic study has been carried out.[79] Based on the activation parameters ($\Delta H^{\ddagger} = 22.2\,\mathrm{kcal\,mol^{-1}}$, $\Delta S^{\ddagger} = -9.8\,\mathrm{e.u.}$) the formation of the thiophene **78** is again suggested to involve valence isomerization to a bicyclic thiirane oxide intermediate.

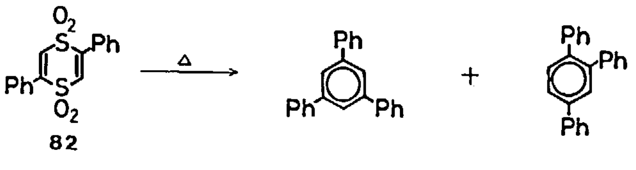


The importance of solvation has been shown in thermolyses carried out in DMSO. The exclusive formation of the thiophene has been interpreted in terms of the solvation of the extruded transient SO as well as of the ground state of the substrate.[80] The kinetics of SO extrusion of **79** in polar solvents like DMSO, sulfolane, and chloroform has been studied.[81] The activation parameters tend to suggest an increased solvation in the transition state as compared to the ground state.

The thermolysis of the sulfilimine **81** affords the mother compound 1,4-dithiin **76** and the thiophene **78**.[79] The latter product is the result of the extrusion of a Tos-N=S moiety.

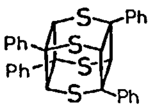


Massive decomposition of 2,5-diphenyl-1,4-dithiin tetroxide (**82**) at its melting point leads to vigorous evolution of SO_2 and formation of a mixture of 1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene, possibly formed by cycloaddition of primary products formed by desulfonylation.[82] Pyrolysis of **82** in the presence of selenium results in the formation of 2,5-diphenylselenophene and 2,4-diphenylsenenophene.[82]



III.3. Photolysis

Almost all 1,4-dithiin compounds are colored materials and hence photochemically sensitive. An ethereal solution of **76** upon irradiation gives the *cis,syn* half-closed dimer **84** and the *anti* cage dimer **83**.[83] The yields, however, are only 2.5% and 13%, respectively. Photolysis of the parent 1,4-dithiin **1** leads to [2+2]-cyclodimerization (in the absence of oxygen).[84] In this case only the half-cage dimer **85** is formed to the extent of 80%.



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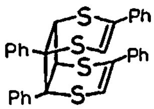

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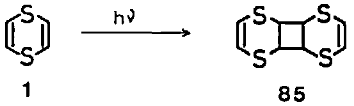
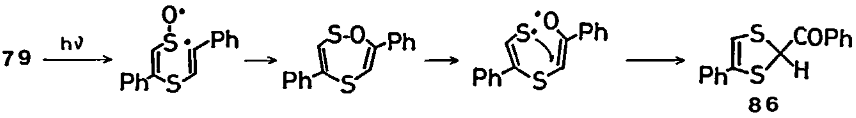
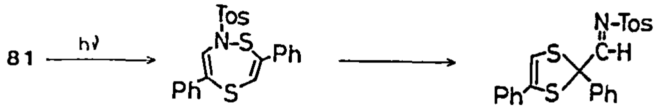


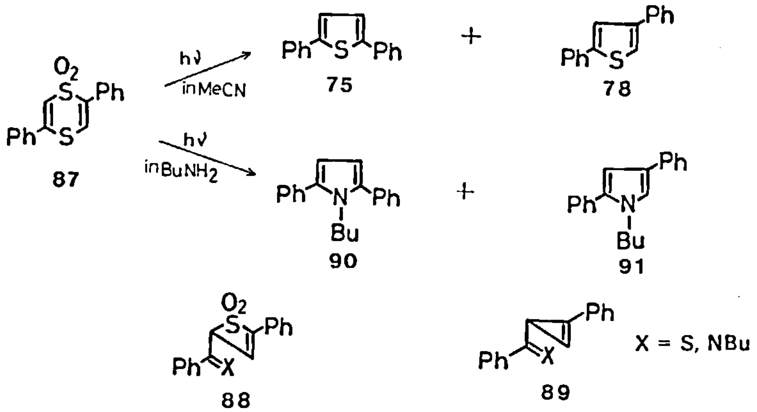
In the photolysis of the sulfoxide **79** no photodimer is obtained; however, the rearranged products, 2-formyl-2,4-diphenyl-1,3-dithiole (**80**) and 2-benzoyl-4-phenyl-1,3-dithiole (**86**) are formed.[78,79] The former isomer is the same as the thermolysis product. Thus, in the photolysis either of the two possible ring expansions might be considered to occur initially, probably *via* a radical path, to give rise to isomeric cyclic sulfenates, each of which then affords different 1,3-ditholes, **80** and **86**.



Photolysis of the sulfilimine **81** also gives a rearranged 1,3-dithiole compound.[79]

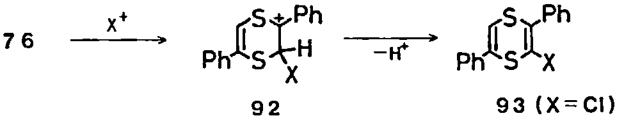


The sulfone **87** undergoes a novel photorearrangement with extrusion of SO_2 to give 2,5-diphenylthiophene (**75**) along with 2,4-diphenylthiophene (**78**), though in small quantities.[85] The formation of the isomeric thiophenes probably involves a valence isomerization to thioketone **88** which in turn extrudes SO_2 to give the cyclopropenylthioketone **89**. The isolation of the pyrrole derivatives **90** and **91** during the photolysis of **87** in *n*-butylamine has been cited as supporting evidence for such a mechanism.



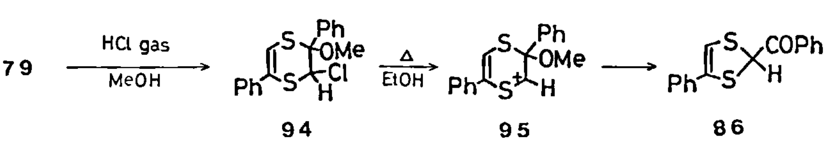
III.4. Reactions with Electrophiles

An important reaction shown by 1,4-dithiins is electrophilic attack on the carbon atoms of the ring system. A variety of electrophilic substitution reactions of 2,5-diphenyl-1,4-dithiin have been reported including formylation, nitration, bromination, acetylation, and chloromercuration as well as sulfenylation.[5,86] These reactions are rationalized in terms of addition-elimination processes. The carbocation intermediate **92** derived from a Markovnikoff-type electrophilic addition affords the observed substitution products after elimination of the β-hydrogen.



The parent 1,4-dithiin gives no substitution products; instead it undergoes polymerization in the presence of Lewis acid.[5]

Treatment of the sulfoxide **79** with hydrochloric acid in dioxane causes a skeletal rearrangement to give 2-benzoyl-4-phenyl-1,3-dithiole (**86**) (32%), together with the deoxygenated **76** (45%) and the chlorodithiin **93** (3%).[87] The reaction with gaseous hydrogen chloride in methanol affords the adduct **94** (due to an additive Pummerer reaction) which is also converted to **86** by heating in 95% ethanol.[87] In these skeletal rearrangements the carbocation **95** is assumed to play a role.

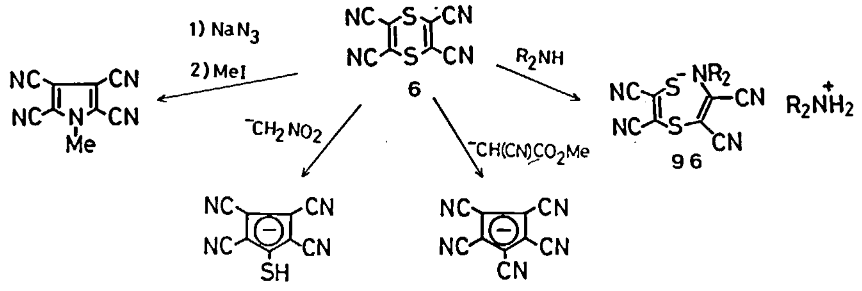


III.5. Reactions with Nucleophiles

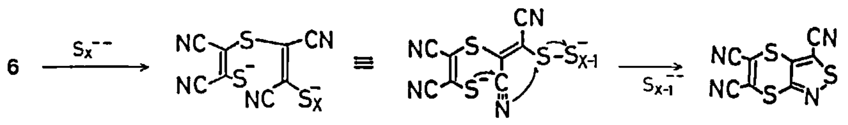
The presence of electron-withdrawing substituents on the 1,4-dithiin ring facilitates nucleophilic attack at carbon. A typical case of such attack is the reaction of tetracyano-1,4-dithiin (**6**). Even secondary amines react with this dithiin to lead to ring-opened salts

96.[88] Likewise potassium acetate, potassium xanthogenate, and phenoxide afford similar ring-opened products.[89]

Dupont's group has explored the reaction of 6 with various nucleophiles resulting in the formation of a variety of five-membered rings, as shown below.[89]



When heated with sulfur in the presence of base 6 gives the isothiazole derivative 97 in about 60% yield.[90] The mechanism is supposed to involve sulfur insertion-rearrangement (on the basis of ^{13}C label experiments). The reaction of 6 with a large excess of sulfur in the presence of sodium iodide affords bis(isothiazolo)-1,4-dithiin 98 corresponding to double sulfur insertion-rearrangement.[91]



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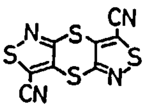
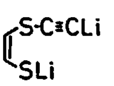
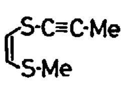


98

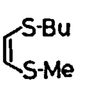
The parent 1,4-dithiin, when allowed to react with 2 equiv. of *n*-butyllithium in THF, forms the 2-lithio derivative at −110 °C.[92] The ring opens up to give the dilithium salt 99 on warming to −60 °C and subsequent methylation gives 100. When 3 equiv. of *n*-butyllithium are used, butylthio(methylthio)ethylene 101 is obtained. The 2-lithio compound can be quenched with the thiolsulfonate $CH_3SSO_2CH_3$ to yield methylthio-1,4-dithiin (102). Thus, 1,4-dithiin is suitable as starting material for the preparation of *cis*-1,2-ethylenedithiol derivatives.



99



100



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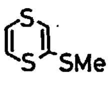
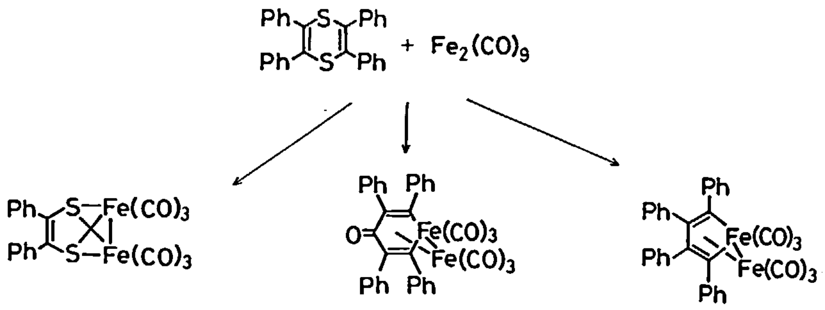


102

The reaction between $Fe_2(CO)_9$ and tetraphenyl-1,4-dithiin yields the (dithiolato)-diiron hexacarbonyl complex 103 as well as the ferracyclic complexes 104 and 105.[93]

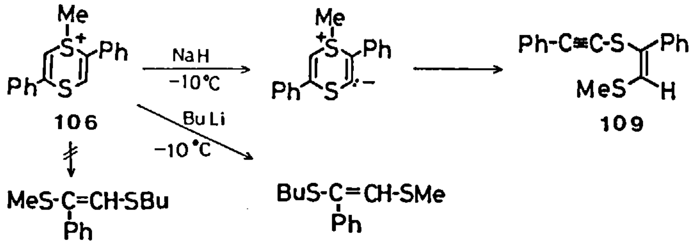


103 **104** **105**

Alkylation of **76** by alkyl iodides in the presence of silver 2,4,6-trinitrobenzenesulfonate, mercuric iodide, or silver perchlorate has been reported to give high yields of 1-alkyl-1,4-dithiinium salt such as **106**.[94] These salts can also enter into reactions with nucleophiles.

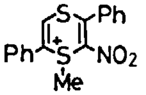
When *n*-butyllithium attacks **106**, ring scission occurs to give 1-butylthio-2-methylthio-1-phenylethylene (**107**) and phenylacetylene, whereas no products are formed due to ring scission with another regiochemistry, such as compound **108**.[94]

The reaction of sodium hydride with the dithiinium compound **106** is all the more interesting because abstraction of a hydrogen from the 3-position gives a quantitative yield of 1-phenylethynylthio-2-methylthio-1-phenylethylene (**109**).

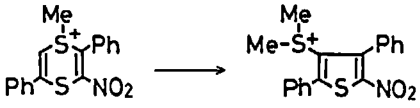


106 **109** **108** **107**

3-Nitro-2,5-diphenyl-1,4-dithiin on methylation with MeI-AgBF$_4$ is reported to yield 1-methyl-6-nitro-2,5-diphenyl-1,4-dithiinium tetrafluoroborate as the major product.[95] This compound **110** undergoes ring cleavage on an alumina column in pH 6.8 phosphate buffer or triethylamine to yield 1-phenylethynylthio-2-methylthio-2-nitro-1-phenylethylene. By the action of iodomethane on the nitro-1,4-dithiin another sulfur atom is also methylated to give **111**; however, this minor salt is unstable and rearranges easily to the thiophene **112**.[95]



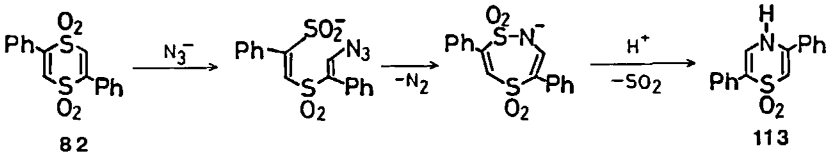
110

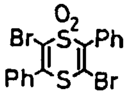


111 **112**

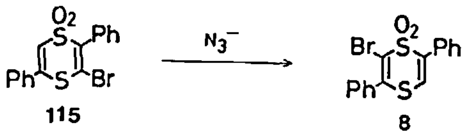
Methyl transfer from the dithiinium salt to thioanisole as well as to aniline has been observed.[96] A kinetic study carried out in acetonitrile established a pseudo-first order reaction. It has been shown that the dithiinium salt **106** methylates aniline almost ten times faster than iodomethane.

The disulfone **82** is attacked by azide ion to give the thiazine **113** *via* a seven-membered ring intermediate.[97] The dibromo analog of the sulfone, **114**, however, reacts with azide ion to give (E)- and (Z)-dicyanostilbene. An unusual rearrangement of 3-bromo-2,5-diphenyl-1,4-dithiin 1,1-dioxide (**115**) to the 2-bromo isomer **8** has also been observed in this context.



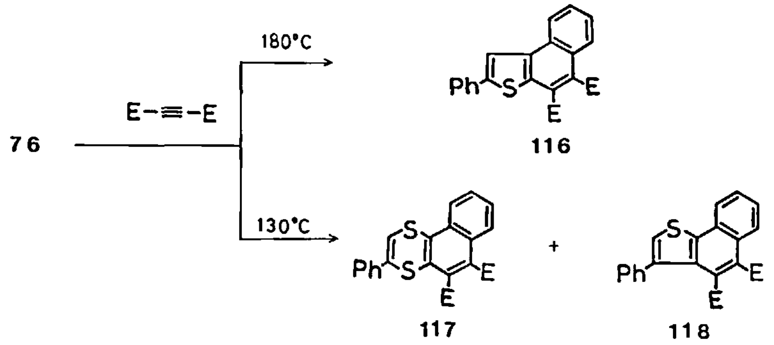


114



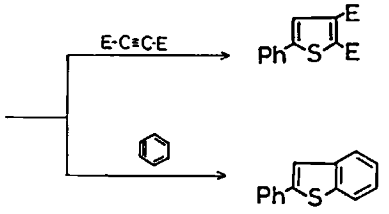
III.6. Cycloaddition

When **76** is heated with dimethyl acetylenedicarboxylate in *o*-dichlorobenzene at 130 °C, dimethyl 3-phenylnaphthol[1,2-b]-thiophene-4,5-dicarboxylate (**118**) and the naphthodithiin **117** are formed in 8 and 9% yield, respectively.[98] Under more vigorous conditions (refluxing at 180 °C) an isomeric naphthothiophene **116** is obtained in 35% yield, resulting from the Diels–Alder reaction of the primary thermal product, 2,4-diphenylthiophene, with acetylenedicarboxylate.

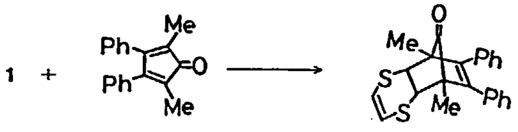


Cycloaddition-elimination reactions of the sulfone **87** with dimethyl acetylenedicarboxylate as well as benzyne have been reported.[99] These reactions are regarded as unusual examples of 1,3-cycloadditions of a vinyl sulfide moiety with acetylenic compounds.

87

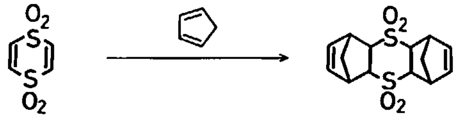


Photochemical cyclodimerizations have already been noted. Unsubstituted 1,4-dithiin reacts as dienophile only with reactive dienes like 2,5-dimethyl-3,4-diphenylcyclopentadienone to give the [2+4]-cycloaddition product **119** in 95% yield.[84]

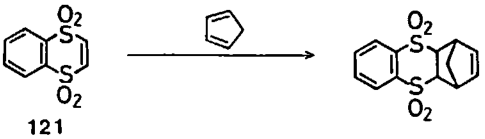


119

1,4-Dithiin tetroxide gives the adduct **120** by Diels–Alder reaction with cyclopentadiene.[100] Similarly, benzo-1,4-dithiin tetroxide **121** behaves as a dienophile and undergoes facile Diels–Alder reactions with a large number of dienes under mild conditions.[101]

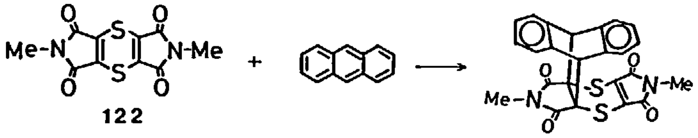


120



121

The maleimide derivative of 1,4-dithiin, **122**, is reported to form a charge-transfer complex with anthracene in THF which is unstable and converts to the Diels–Alder adduct when left at room temperature for 2 months.[102]



122

Recently, cycloaddition reactions of **122** with various anthracene derivatives have been extensively investigated.[15] The 1,4-dithiin **122** reacts smoothly with electron-rich anthracenes *via* charge-transfer complexes to give Diels–Alder adducts in high yields. In contrast, **122** reacts slowly with the electron-deficient 9-anthraldehyde to afford an adduct without passing through a charge-transfer complex.

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