New Consecutive Photochemical Reactions of Naphtho[1,8-*de*]-1,3-dithiin Derivatives *via* Through-space Interaction between Two Sulfur Atoms

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A dissertation submitted to the Doctorial Program
in Chemistry, the University of Tsukuba
in partial fulfillment of the requirements for the
degree of Doctor of Philosophy (Science)

January, 1996

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Chapter 1

General Introduction

General Introduction

Organosulfur compounds

Organic chemistry has been developed with carbon compounds of which origin comes from the biological substances. On the other hand, recently, the chemistry of main group elements excluded carbon has provoked a great deal of controversy in chemical science. Especially, the chemistry of heteroatoms has been focused attention. Heteroatoms are defined as follows: 1) the elements except group 1 and 2 from the main group elements and those belonging from group 13 to group 17 and third to six row in the Periodic Table; 2) elements whose electronegativities are more than 2.0 (the value by Pauling) among those belonging from Group 13 to Group 17 except typical main group elements of first and second rows, while other elements bearing the electronegativity less than 2.0 are regarded as typical metals. This definition suggests that the heteroatoms should have binary characteristic properties of both typical and metallic elements, and hence heteroatom chemistry may provide a new field in organic chemistry, not only for playing important roles in the modern organic synthesis but also in the structural chemistry through investigation of their physical behaviors.

Among these heteroatoms, sulfur has been investigated most intensely because organosulfur compounds widely exist in nature and play important roles in modern organic syntheses.[1] Sulfur belongs to the third row of group 16 elements in the Periodic Table and its configuration of electrons is $1s^2 2s^2 2p^6 3s^2 3p^4$ in which the outer shell electrons, $3s^2 3p^4$ participate to make chemical bonding. Normally, dicoordinate compounds such as

thiols and sulfides are the most popular derivatives. However, many other compounds, having not only tri-, tetra-, but also penta- and hexa-coordinate sulfur compounds have generally been prepared. Especially, among these organosulfur compounds, thiols and disulfides have been widely studied because they play important roles as biologically active substances.

Table 1-1. The Electonegativity of the Elements Belonging to the Groups 13-17.

Group / Period	13	14	15	16	17
2	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
3	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
4	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
5	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
6	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2

Element
Electronegativity by Pauling

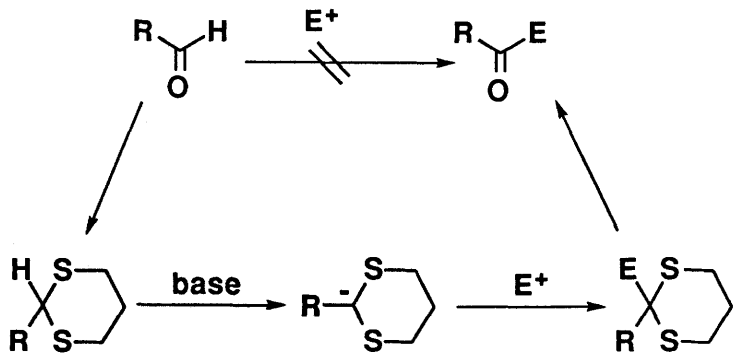
Characteristic properties of sulfur atom in the organic compounds are illustrated as follows: 1) the oxidation state of a sulfur atom is variable from +2 to +6; 2) the lone pair electrons attached to the divalent sulfur atoms are soft enough to exhibit significant nucleophilicity; 3) divalent sulfur groups can also facilitate formation of a cation on its adjacent α- and β-carbon atoms by 3p-2p π conjugation; and 4) sulfur

functionalities such as sulfinyl, sulfonyl, and even sulfenyl groups can stabilize an adjacent α-carbanion. Earlier, the effect for stabilization of α-thiocarbanion was considered to be due to the 3d-2p π resonance by using expansion of an 3d-orbital on the sulfur atom.[2] Recently, however, many MO calculation showed that the contribution of 3d-2p π-bonding may be insignificant but found that hyperconjugation between 2p(carbanion)-σ^*(C-S) is quite important in the stabilization of α-thiocarbanion, particularly in the case of divalent sulfur groups.[3]

Three most important concerns in organic syntheses are the formation of a C-C bond, the transformation of one functional group into another, and the protection of a functional group with an appropriate group which can be released readily. A sulfur atom in the organic compounds can provide effective clues to solve all of these problems.

For the formation of a C-C bond, nucleophilic substitution of a carbanion or electrophilic attack of a carbenium cation on a carbon atom is frequently utilized. When a compound having either the sulfenyl group, sulfinyl group, or sulfonyl group is treated with strong bases such as butyllithium, lithium diisopropylamide (LDA), or NaH, a carbanion can be readily generated at the carbon atom adjacent to these functional groups. In either nucleophilic substitution with alkyl halides or nucleophilic addition to carbonyl compounds or the electrophilic olefins, the carbanion thus formed reacts with suitable electrophiles to result in the formation of a C-C bond.

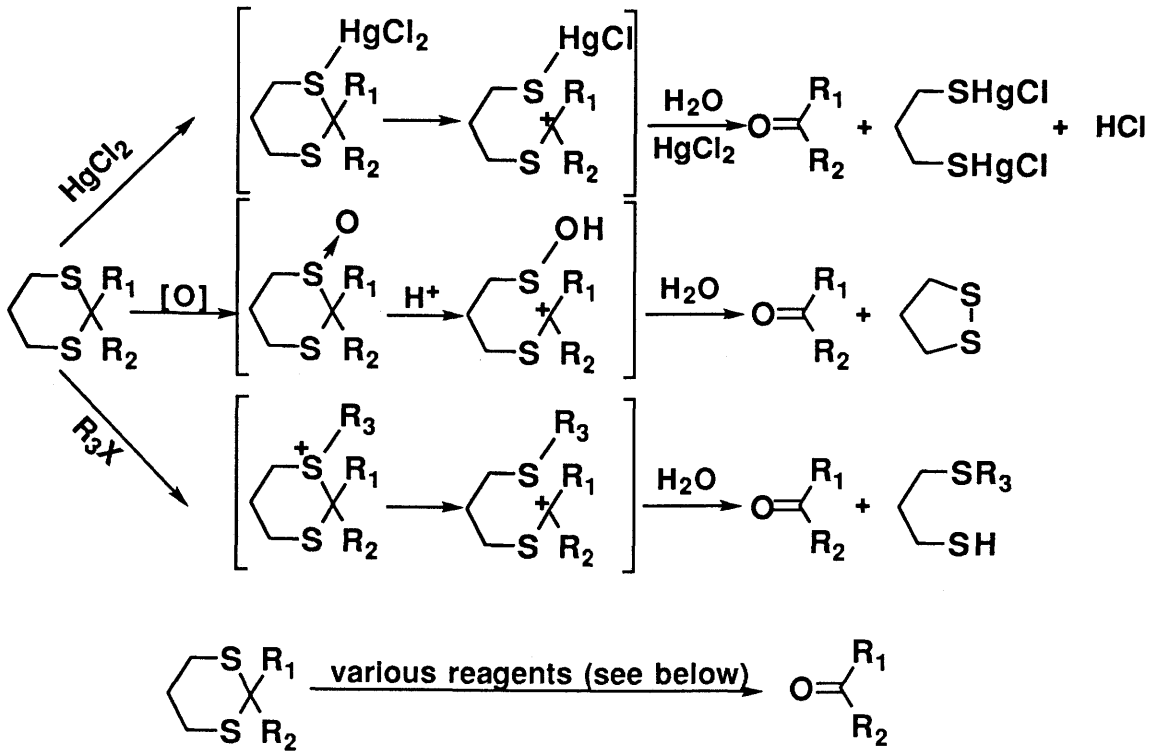
Another distinct feature of sulfur compounds is that many types of reactions are available for cleavage of a C-S bond.



Scheme 1-1

A variety of reactions have hitherto been developed for either the homolytic or the heterolytic dissociation of a C-S bond to produce a new functional group. For example, Raney nickel is a well-known desulfurization reagent for converting R-SR' to R-H,[4] while pyrolysis of RCH_2CH_2SOAr gives an olefin $RC{=}CH_2$ *via* an *Ei* process.[5] Therefore, a combination of these desulfurization reactions with the sulfur-assisted C-C bond formation described above realizes a wide range of methodology in organic syntheses using the sulfur compounds. In this result, for example, carbanions derived from 1,3-dithiane can be used for new homologation as depicted in the following process as shown in Scheme 1-1. 1,3-Dithianes are easily formed from the carbonyl compounds and 1,3-propanedithiol under the influence of Lewis acids and boron reagents. The reaction of dithianes with n-butyllithium in tetrahydrofuran (THF) at low temperature leads to the anion. After the reaction with an electrophilic compound, the hydrolysis can generally be carried out in polar solvents such as acetone, alcohols, and acetonitrile to release the corresponding carbonyl compounds. This method was first introduced and developed by Corey and

Seebach, and is termed "Umpolung of the reactivity".[6,7,8] These compounds are employed on general concepts based on the facile conversion of sulfur functional groups to the better leaving groups, following by hydrolysis (Scheme 1-2). In the model compounds shown in Scheme 1-2, the modification of 1,3-dithianes can be achieved by complexation with thiophilic heavy metal ions[9] such as Ag^+, Hg^+, and Cu^{2+}, by oxidation[10] of sulfur atoms with, *e.g.*, iodine, halosuccinimides, ammonium

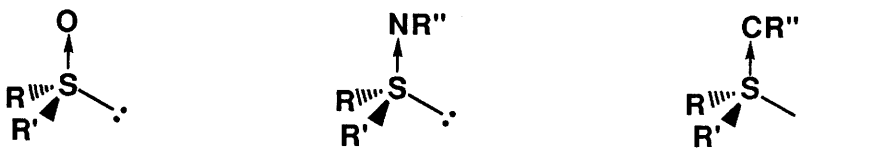


$Hg(II)/BF_3$, THF/H_2O, 50 °C, 86%
$AgNO_3$, EtOH/H_2O, 50 °C, 55%
$CuCl_2/CuO$, acetone, Δ, 85%
NBS, H_2O/MeCN or acetone, 70-100%
I_2, DMSO, 90 °C, 75-85%
Isopentyl nitrite, 65%
$Ce(NH_4)_2(NO_3)_6$, MeCN/H_2O, 70-87%
$O_2/h\nu$, 60-80%
MeI, MeOH/H_2O, Δ, 60-80%
$Et_3O^+BF_4^-$, 3%aq., $CuSO_4$, 81%
$h\nu$ (λ>360nm)/O_2, $TPPClO_4$/MeCN, 31-95%
Anodic oxidation, MeCN/H_2O 60-100%

Scheme 1-2

cerium nitrate, $NaIO_4$, chloramine-T, singlet oxygen, and also by conversion to sulfonium salts[11] through alkylation with methyl iodide or oxonium salts.

Many tricoordinate organosulfur compounds, such as sulfoxides, sulfilimines, and sulfonium ylides, have been synthesized and especially interested in studying their stereochemistry since these compounds are intrinsically chiral when the three different substituents are attached, and can be used as good models for studying the stereochemistry of *i.e.*, the nucleophilic substitution at tricoordinate sulfur atoms. All these tricoordinate compounds are represented to have tetrahedral pyramidal structures (Scheme 1-3). Many of these tricoodinate sulfur compounds are found in nature, while others are available as artificially eligible compounds that are utilized commonly as dyestuffs, medicinal-, agro-chemicals, detergents, vulcanizing agents, and others.



Sulfoxide **Sulfilimine** **Sulfonium ylide**

Scheme 1-3

Among the tricoordinate organosulfur compounds, sulfoxides have been investigated extensively, partly due to the versatile utility of dimethyl sulfoxide (DMSO) as a typical aprotic solvent and a source of α-sulfinyl carbanion, while sulfilimines and sulfonium ylides have been accepted as convenient starting materials for many useful organic synthesis.

Photochemistry or Sulfur-Containing Compounds

The electronic transition of sulfur-containing compounds are induced by radiation of appreciably longer wavelengths than those for the corresponding oxygen compounds. For example, the absorption (UV-vis/λ_{max}) of methyl mercaptan (CH_3SH), diethyl sulfide ($C_2H_5SC_2H_5$), diethyl disulfide and (C_2H_5S-SC_2H_5) are 230, 210, and 252 nm, respectively, and that of methanol (CH_3OH), diethyl ether ($C_2H_5OC_2H_5$), and diethyl peroxide (C_2H_5O-OC_2H_5) are 184, 185, and 220 nm, respectively. However, the primary photochemical processes for sulfur- and oxygen-containing compounds are generally of the same type (C-S or C-O cleavage). Since the C-S bond is weaker (bond energy *ca.* 270 kJ mol^{-1}) than the C-O bond (bond energy *ca.* 360 kJ mol^{-1}), and thiyl and alkoxy radicals display markedly different behaviors, the secondary processes and hence the products of the reactions may differ appreciably in the two series.

The photochemistry of sulfur-containing compounds such as thiols, sulfides, sulfoxides, sulfones have been widely studied because they play important roles in organic syntheses.[12-15]

$$RSH \xrightarrow{h\nu} RS\cdot + H\cdot$$

$$RSH + H\cdot \xrightarrow{h\nu} R\cdot + H_2S$$

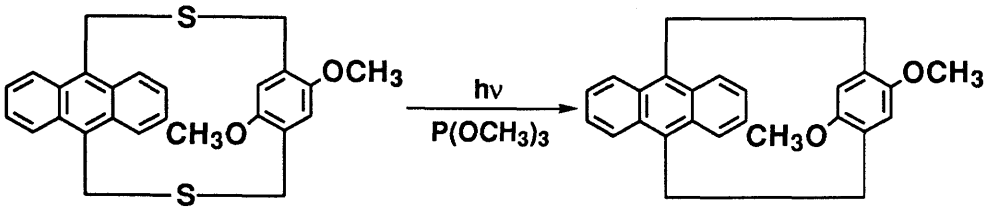
$$RSH + R'CH{=}CH_2 \longrightarrow R'\dot{C}HCH_2SR$$

$$R'\dot{C}HCH_2SR + RSH \longrightarrow R'CHCH_2SR + RS\cdot$$

Scheme 1-4

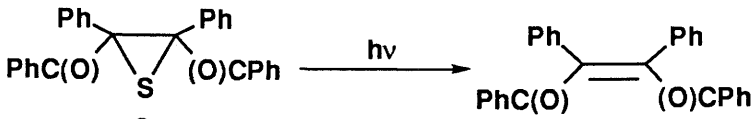
The dominant photoreaction of thiols is the homolytic cleavage of the S-H bond rather than the C-S bond. The thiyl

radical from the S-H bond homolysis combines either with one another or with alkyl radicals giving disulfides or sulfides, respectively. The RS· radicals produced photochemically and the HS· radicals similarly obtained from H_2S undergo efficient anti-Markovnikoff addition to alkenes by a chain reaction to give the corresponding sulfides (Scheme 1-4). This process occurs for a wide range of substrates including alkenes, cycloalkenes, styrenes, vinyl and allyl ethers as well as ethynes, and provides a convenient synthesis of a variety of sulfides of interest in the pharmaceutical, agrochemical, and petrochemical industries.[16)]



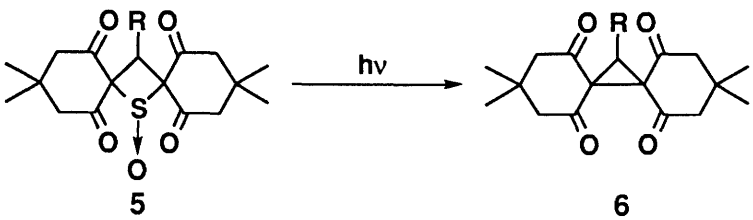
1 2

Scheme 1-5



3 4

Scheme 1-6



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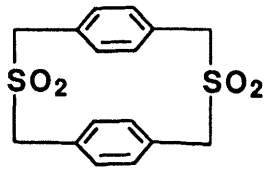
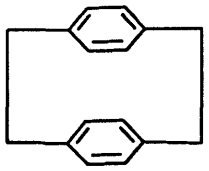
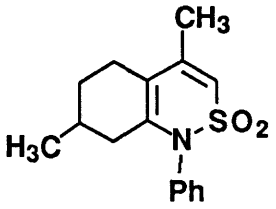
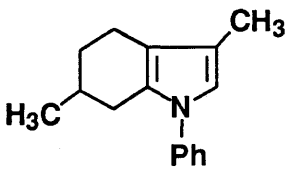
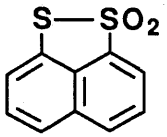
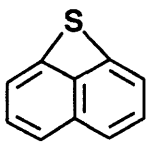
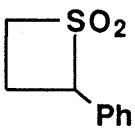
Scheme 1-7

The major interest in photochemistry of sulfides, sulfoxides, and sulfones is photodesulfurization in the synthesis of cyclophanes and a variety of small-ring

Table 1-2. Example of Photosulfurization of Sulfones.

Sulfone	Product	Yield
		100%
		61%
		97%
		95%

heterocycles and carbocycles. Irradiation of cyclic sulfides **1** induces C-S bond cleavage and in the presence of trialkyl phosphonate overall desulfurization occurs giving the carbocyclic compounds **2** (Scheme 1-5).[12, 13] This is a very useful procedure for the removal of a sulfur atom in a bridge and has been applied to the synthesis of a variety of strained cyclic systems, particularly cyclophanes. Thianes **3** undergo photodesulfurization in the absence of phosphonates in an essentially stereospecific elimination process producing quantitative yields of olefin **4** (Scheme 1-6).[13] Likewise, irradiation of a series of thietane oxides (**5**) in benzene gave the corresponding cyclopropane **6** although in some cases products

resulting from ring-expansion to cyclic sulfenates (see below) were observed (Scheme 1-7).[14] The photodesulfurization of cyclic sulfones undergoes more effectively than that of analogous sulfides and sulfoxides, as illustrated by the examples given in Table 1-2.[14, 15]. The attractive point of this method is not only that the reaction occurs under mild conditions but also that for many systems the chemical yields are excellent.

Photolysis of Sulfoxides

A common mechanistic process accepted for many photochemical reactions of sulfoxides is that the first step is the homolytic cleavage of a C-S bond, or α-cleavage.[14, 17] Gollnicks and Stracke concluded that the primary photochemical reaction of DMSO, both neat and in solvents such as water or acetonitrile results in the excitation to the singlet state (E_S = 105 kcal mol^{-1}), and the process depends on the nature of the electron excited, e.g. $n_S \rightarrow \pi^*$ or $n_O \rightarrow \pi^*$, though the detailed process remains ambiguous.[18] The major primary photochemical reactions resulting from this excitation are both fragmentation by the C-S bond fission and disproportionation as shown in Scheme 1-8.

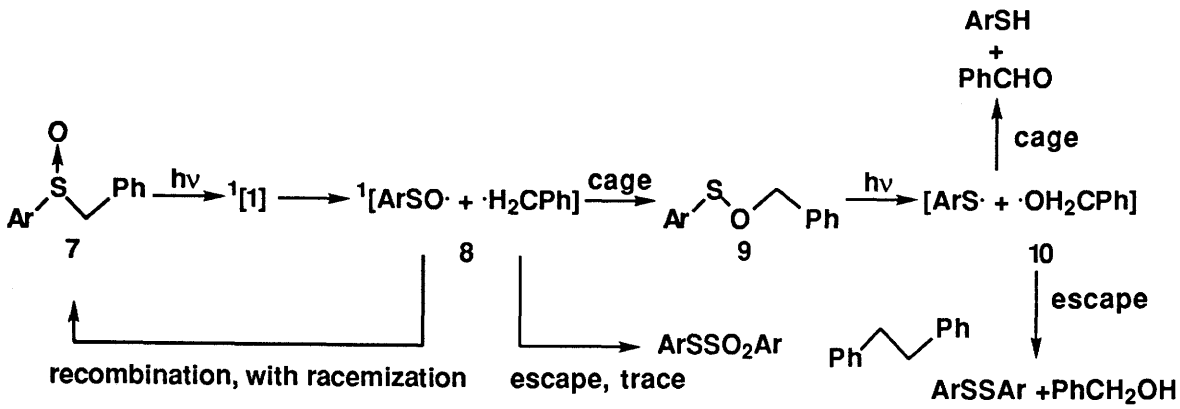
$$CH_3SOCH_3 \xrightarrow{h\nu} [CH_3SO]^{\cdot} + CH_3^{\cdot}$$

$$[CH_3SOCH_3]^* + CH_3SOCH_3 \longrightarrow CH_3SCH_3 + CH_3SO_2CH_3$$

Scheme 1-8

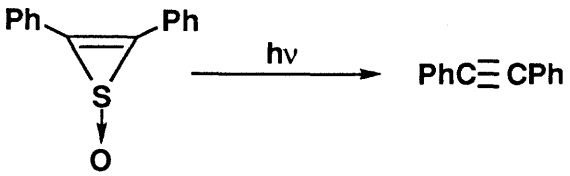
The formation of dimethyl sulfide, dimethyl sulfone, and methane (by H-abstraction) observed in these phtolyses was explained in terms of the hydrogen abstraction by the methylsulfinyl radical affording methanesulfenic acid as a very reactive molecule, which rapidly undergoes a series of secondary reactions to produce the methanesulfonic acid, methyl methanethiosulfonate, and dimethyl disulfide which were also observed during these photolyses.

Quite recently, Jenks and Guo payed considerable attention on the photolysis of aryl benzyl sulfoxides (**7**) (Scheme 1-9).[19] They concluded that the homolytic cleavage of sulfur-carbon bond on the photolysis of optically active benzyl *p*-tolyl sulfoxide was reversible with racemization by way of a cage recombination process. Racemization may result from the recombination of the geminated radical pair **8** which partitions between formation of sulfenic ester (**9**) and reversion to the starting material **7**. In this case, sulfenic ester (**9**) plays no part in racemization, as photolysis of **9** does not yield **7**. Photolysis of **9** proceeds through S-O bond cleavage to yield both the sulfenyl and alkoxyl radicals **10** which afford thiol and aldehyde by disproportionation.

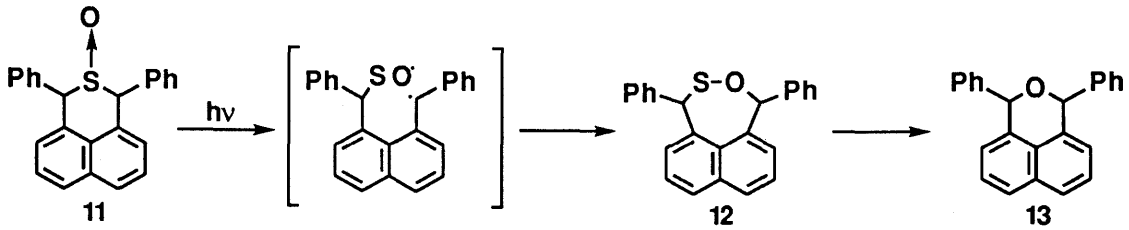


Scheme 1-9

One of the major areas of interest in the photochemistry of cyclic sulfoxides is photodesulfurization. The three- and four-membered cyclic sulfoxides, or strained bicyclic sulfoxides are particularly good candidates for photo-sulfur extrusion process. For example, the photolysis of 2,3-diphenylthiirene-1-oxide has been reported by Carpino and Chen to lead rapidly and almost quantitatively to the formation of diphenylacetylene (Scheme 1-10).[20]



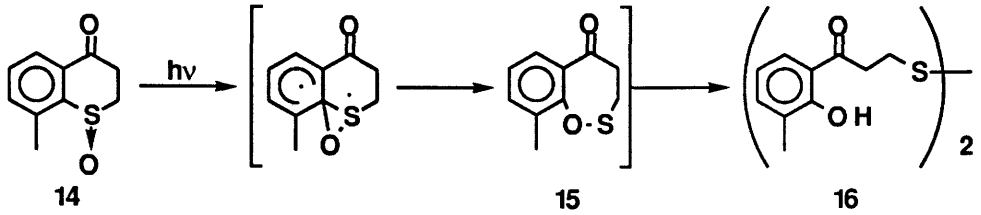
Scheme 1-10



Scheme 1-11

The course of the photolysis of a number of cyclic sulfoxides has been shown not to involve simple photo-sulfur extrusion processes. In fact, Schultz and Sclessinger have reported that the formation of pyran derivatives (**13**) on the direct irradiation of the cis- and trans-thiopyrane oxides (**11**) proceeded by way of initial conversion to a cyclic sulfenate (**12**), the formation of which was supported by spectroscopic evidence (Scheme 1-11).[21] Still and co-workers studied the photolysis of a series of 4-thiochromanone sulfoxides (**14**), and found that the initial α-cleavage of sulfoxide took place

preferentially on the aryl side leading *via* intermediates such as sulfenic ester (**15**) by the oxygen migration, to the eventual phenolic disulfide product (**16**) (Scheme 1-12).[22]



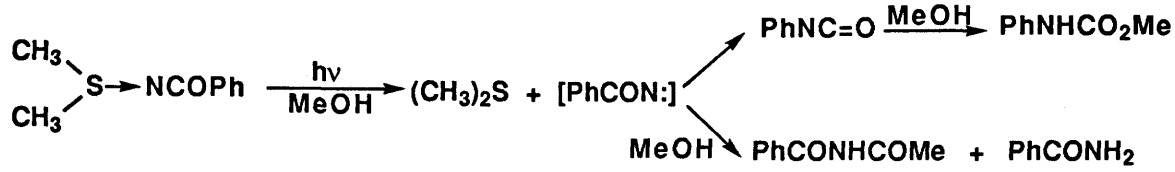
14 15 16

Scheme 1-12

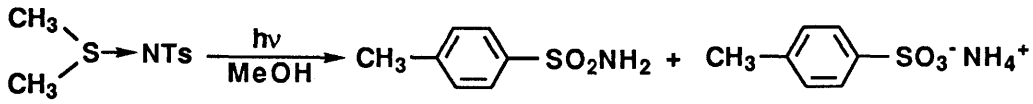
Photolysis of Sulfilimines

In general, photodecomposition of sulfilimines has been utilized as generation of nitrenes. Lerch and Mattingly have reported that the photolysis of *S,S*-dimethyl-*N*-benzoylsulfilimine in methanol afforded phenyl isocyanate as the photo-Curtius rearrangement product, and hydroxylamine as insertion product of nitrene into the O-H linkage of methanol (Scheme 1-13).[23] In addition, the photolysis of dimethyl-*N*-*p*-tosylsulfilimine has produced *p*-toluenesulfonamide and ammonium *p*-toluenesulfonate (Scheme 1-14).[24] Hayashi and Swern have studied on the photolysis of dimethyl-*N*-ethoxycarbonylsulfilimine (**17**) in the presence of cyclohexene and cyclohexane, and compared the results obtained in similar experiments with ethyl azidoformate (**18**) as the nitrene source (Scheme 1-15).[25] The amount of aziridine formed by the photolysis of sulfilimine (**17**) is only half of that formed in azide (**18**). The nitrene formed by photolysis of sulfilimine (**17**) mainly abstracts hydrogen from cyclohexane, whereas the main reaction of the nitrene from the azide (**18**) seems to be the C-H insertion into cyclohexane. The results of photolysis of

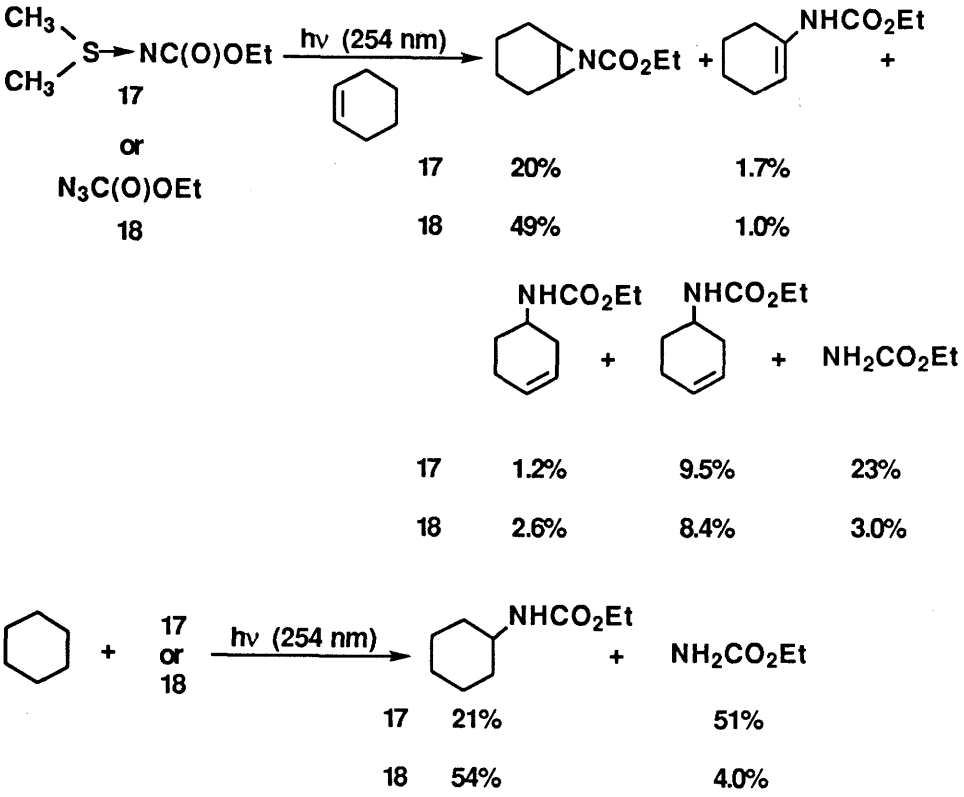
sulfilimine (**17**) in cyclohexene and cyclohexane suggested that the considerable triplet nitrene was present, while different from that of azide and was reported to give a 3 : 1 mixture of singlet and triplet state nitrenes.[26)]



Scheme 1-13



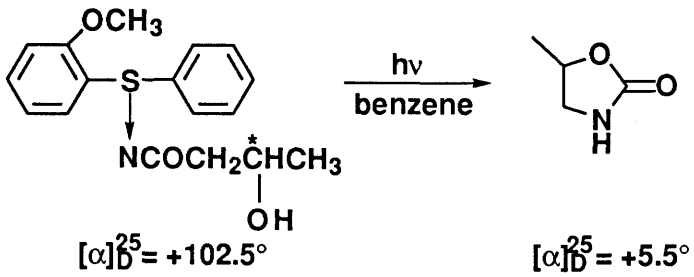
Scheme 1-14



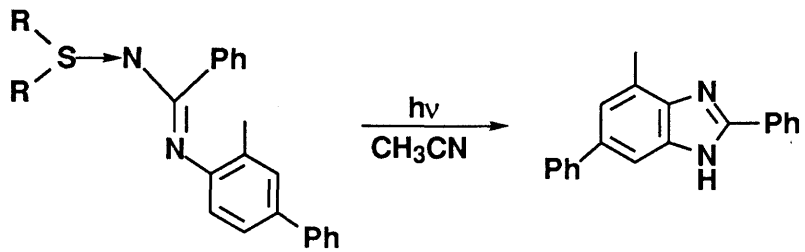
Scheme 1-15

The photolysis of an optically active sulfilimine to afford an optically active heterocycle was carried out as a synthetic application of this reaction (Scheme 1-16).[27]

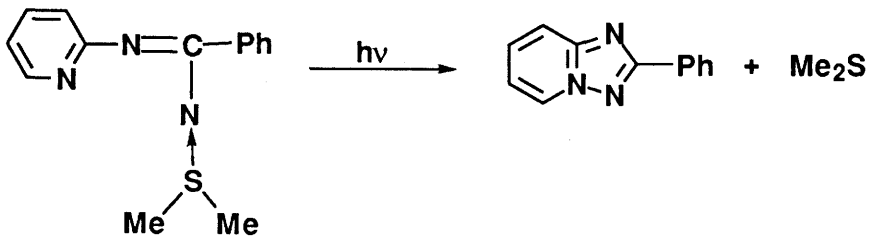
There have been a few attempts to prepare heterocyclic compounds by the photolysis of sulfilimines.[28] Photolysis of *N*-acylbenzimidoylsulfilimine was found to give benzimidazole, an intramolecular insertion product, in 30-95% yields (Scheme 1-17). Similarly, photolysis of *N*-pyridylbenzimidoylsulfilimine also afforded the internal cyclization product (Scheme 1-18).



Scheme 1-16



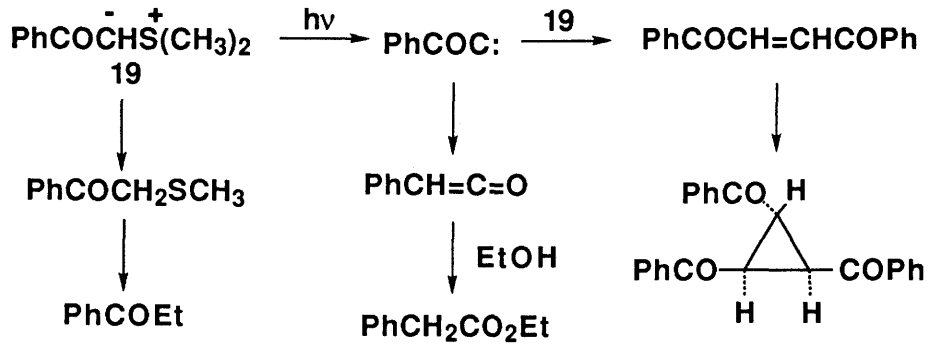
Scheme 1-17



Scheme 1-18

Photolysis of Sulfonium Ylides

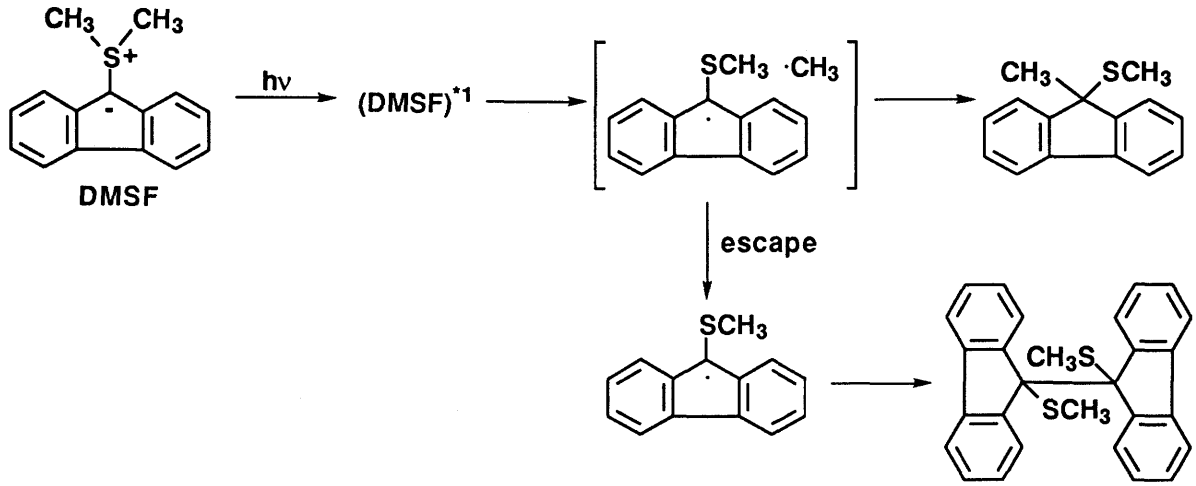
One way to prepare sulfonium ylides is the treatment of sulfides with carbene generated in situ by the decomposition of diazocompounds. The reverse reaction is the generation of carbenes by photodecomposition of sulfonium ylides. Trost has reported that irradiation of dimethylsulfoniumphenacylide (**19**) gave the *trans*-1,2,3-tribenzoylcyclopropane as a major product of the Michael addition product of **19** into olefinic linkage of dibenzoylethylene which was formed from the reaction of the carbene with **19**, ethyl phenylacetate, the Wolff rearrangement product, and a small amount of propiophenone obtained from presumably the secondary photolysis of the photo-Stevens rearrangement product (Scheme 1-19).[29] It was also found that photodecomposition of diphenylsulfonium allylide afforded both the carbene derived and Stevens-rearrangement products.[30]



Scheme 1-19

Caserio and co-workers studied the photochemistry of some cyclic, carbonyl-stabilized sulfonium ylides and reported the products characteristic of the Stevens rearrangement.[31] Maki and Hiramitsu observed that irradiation of some heterocyclic ylides gave the products derived from the Stevens

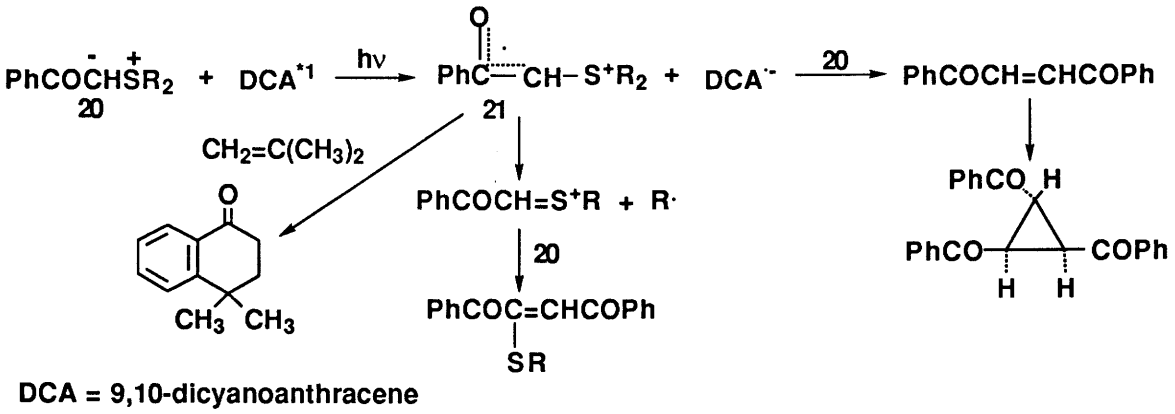
rearrangement.[32] Griller and co-workers have reported that irradiation of diazofluorene in the presence of sulfides gave the Stevens-rearrangement products presumably by the secondary photolysis of the initially formed ylide.[33] Since some ylides that do not rearrange thermally undergo the facile photo-Stevens reaction, this route could prove to be a useful, general, synthetic transformation.



Scheme 1-20

The mechanism for the photo-Stevens rearrangement has been carefully investigated by Zhang and Schuster.[34] They concluded that the direct irradiation of 9-dimethylsulfonium fluorenylide in acetonitrile or THF leads to homolysis of a carbon-sulfur bond in the $n\sigma^*$ singlet state and initial formation of the 9-(methylthio)fluorenyl and methyl radicals (Scheme 1-20). This process was supported by the product analysis, isotope tracer experiments, solvent viscosity studies. On the other hand, Lepley has considered single-electron oxidation of the ylide as the key initial step in the Stevens rearrangement reaction.[35] This process yields a radical cation, which could rearrange to give the Stevens products.

Recently, this possibility was considered by Radom and co-workers who calculated theoretically the energy of the reaction paths for some ionized ylides which they call "ylidon".[36] Their findings suggest that the prototype sulfonium ylidon ($H_2SCH_2^{\cdot +}$) exists in a potential minimum and will not spontaneously rearrange. However, Zhang and Schuster have reported that photochemical one-electron oxidation of phenacylsulfonium ylides (**20**) gave the ylidons (**21**), which in some instances undergoes C-S bond cleavage to give free radical. In other process these are attacked by nucleophiles, and in some cases react with alkenes to give addition products (Scheme 1-21).[37]



DCA = 9,10-dicyanoanthracene

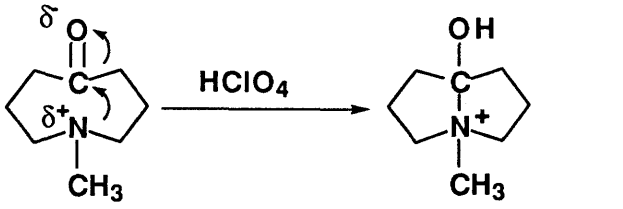
Scheme 1-21

Transannular Interactions

σ-Bond Formation by Transannular Interactions

It is well known that the transannular interaction has been observed in seven or eight membered ring compounds bearing two functional groups. Earlier, Leonard et al. found that the transannular interaction between the amino nitrogen and the carbonyl group in 1-methyl-1-azacyclooctan-5-one (**22**) was

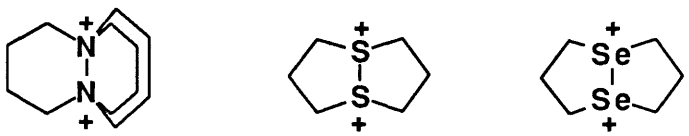
detected by examining the IR and UV spectra, dipole moment, optical rotatory dispersion,[38] ^{17}O-NMR,[39] and ^{13}C-NMR[40] spectra (Scheme 1-22). On treatment of the compound **22** with $HClO_4$, a σ-bond formation has been observed between the nitrogen and carbonyl carbon atoms *via* transannular interaction producing the conjugated acid **23** of **22** which is readily detected by IR and NMR spectra and by the disappearance of UV absorption originally observable in the starting amino ketone.



22 **23**

Transannular interaction **Transannular reaction**

Scheme 1-22

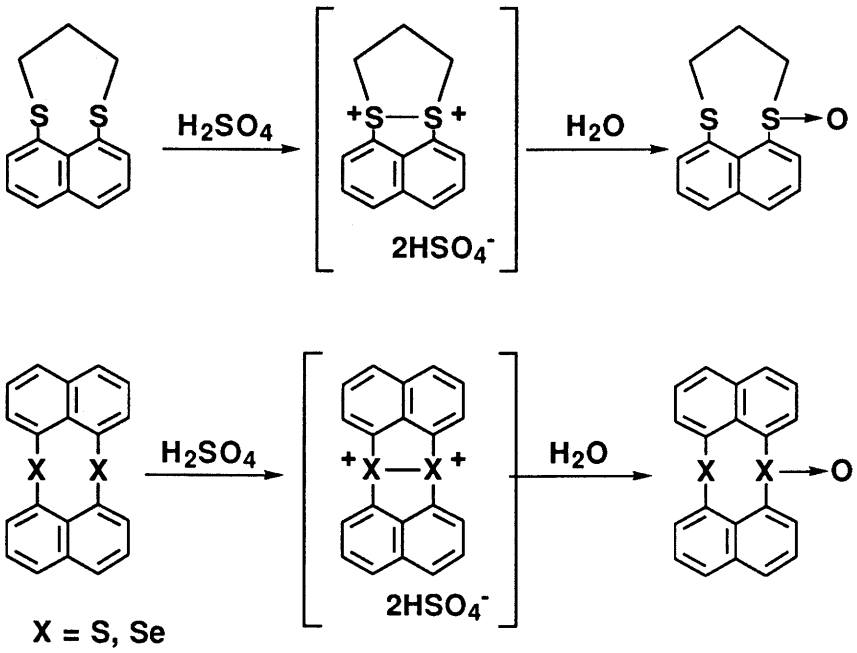


$2CF_3SO_3^-$ $2CF_3SO_3^-$ $2BF_4^-$

Scheme 1-23

Recently, there have been considerable interests in the transannular interaction or σ-bond formation between heteroatoms in medium-sized heterocyclic compounds containing nitrogen, sulfur, and selenium atoms.[41] Transannular σ-bond formation between the two heteroatoms such as a combination of N-N, S-S, and Se-Se atoms in the oxidation of diazabicyclo[3.3.3]-nonane,[42] 1,5-dithiacyclooctane,[43] and 1,5-diselenacyclooctane[44] have been observed and, their diaza, dithia, and diselena dication salts have been actually isolated,

and their structures have been determined by X-ray crystallographic analysis (Scheme 1-23). On the other hand, sterically congested two or more heteroatoms substituted at the suitable positions in the aromatic ring have been found to show exceptionally strong transannular interaction between them. As typical examples, formation of dithiadication *via* a through-space interaction between the two sulfur or selenium atoms in 1,8-bis(alkylthio or arylthio)- or 1,8-bis(arylseleno)-naphthalenes has been reported by Furukawa[45] and by Glass[46] (Scheme 1-24).

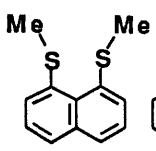
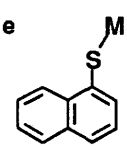
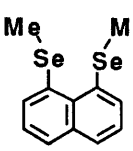
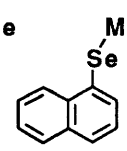
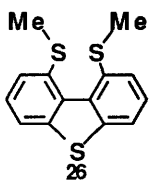
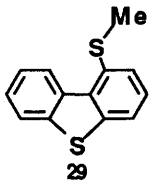


Scheme 1-24

Reactions *via* Transannular Interactions

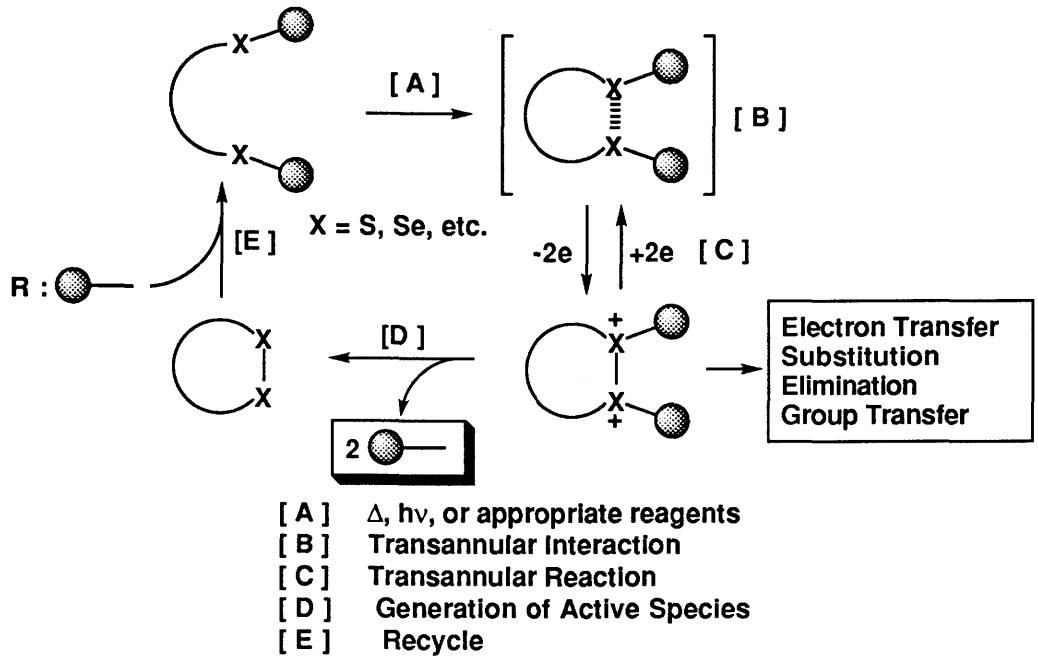
As described above, transannular interaction or through-space interaction has been observed between two or more heteroatoms that are arranged appropriately in one molecule. For example, 1,8-bis(methylthio)naphthalene (**24**),[47] 1,8-bis(methylseleno)naphthalene (**25**),[47] and 1,9-bis(methylthio)-

Table 1-3. Oxidation Potentials of Compounds 24-29.

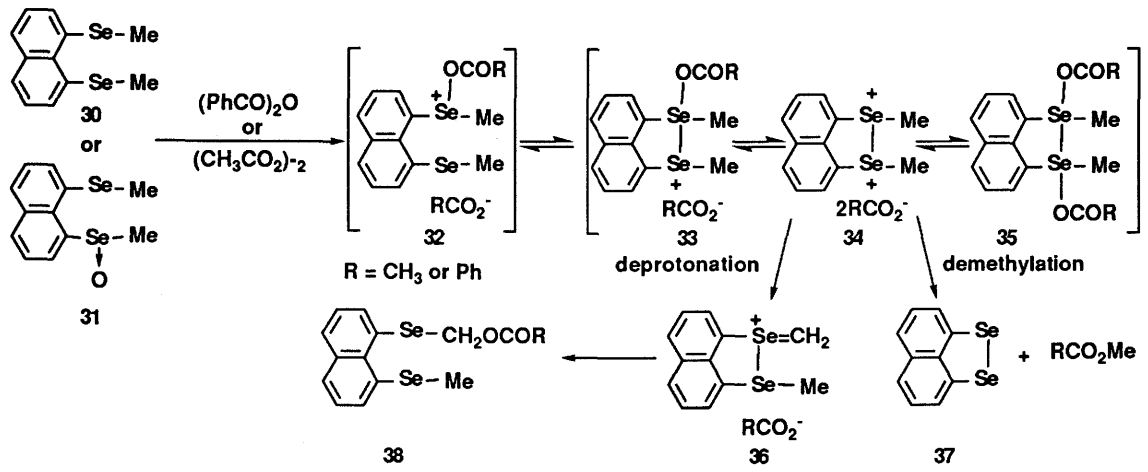
Compound	 24	 27	 25	 28	 26	 29
Ep (V)	0.70	0.97	0.48	0.82	0.76	1.02
Reversibility	(I)	(I)	(R)	(I)	(I)	(I)

dibenzothiophene (**26**)[48] have unusually low oxidation potentials as compared with that of mono-substituted derivatives **27-29** by cyclic voltammetry using Ag/$AgNO_3$ as a working electrode (Table 1-3). When these sulfur or selenium compounds and their monooxides were treated with strong acids or acid anhydrides such as concentrated sulfuric acid or trifluoromethanesulfonic anhydride [$(CF_3SO_2)_2O$], they gave the corresponding dithia dications *via* the initial formation of cation radicals which were identified by measurement of the ^1H- and ^{13}C-NMR spectrum, and the dithia or diselena dications were treated with water to give the corresponding sulfoxides or selenoxides in high yields.[47-49] It is rational to assume that the formation of dications activates the molecules to convert compounds (**24-26**) the labile species from which the substituents on the sulfur or selenium atoms are released to give both reactive species and the corresponding thermodynamically stable disulfides or diselenides.[50] Therefore, this concept may create a new methodology for generating reactive organic species or provides new reactions as illustrated in Scheme 1-25. The disulfides or diselenides recovered are converted again to the starting materials after treating with appropriate reagents. In fact, Furukawa and co-

workers have found that the *Se*-demethylation in either the seleno-Pummerer reaction of 1,8-bis(methylseleno)naphthalene with benzoyl peroxide or of *Se*-oxide with carboxylic acid anhydrides, although the reaction of methyl phenyl selenoxide with acetic anhydride gives selenurane without demethylation (Scheme 1-26).[50d]

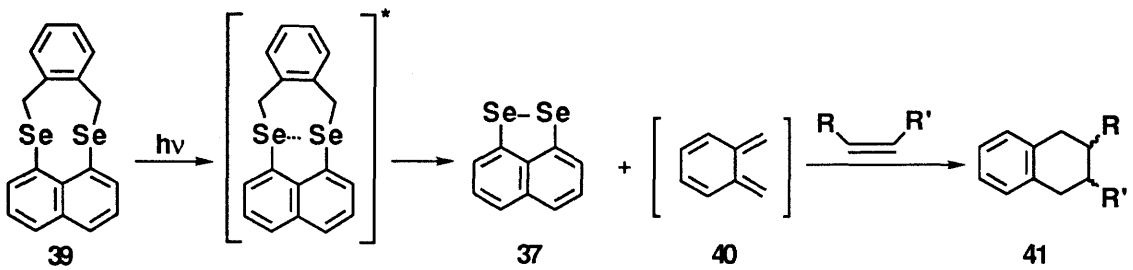


Scheme 1-25. Transannular Interaction and Activation of Molecules.



Scheme 1-26

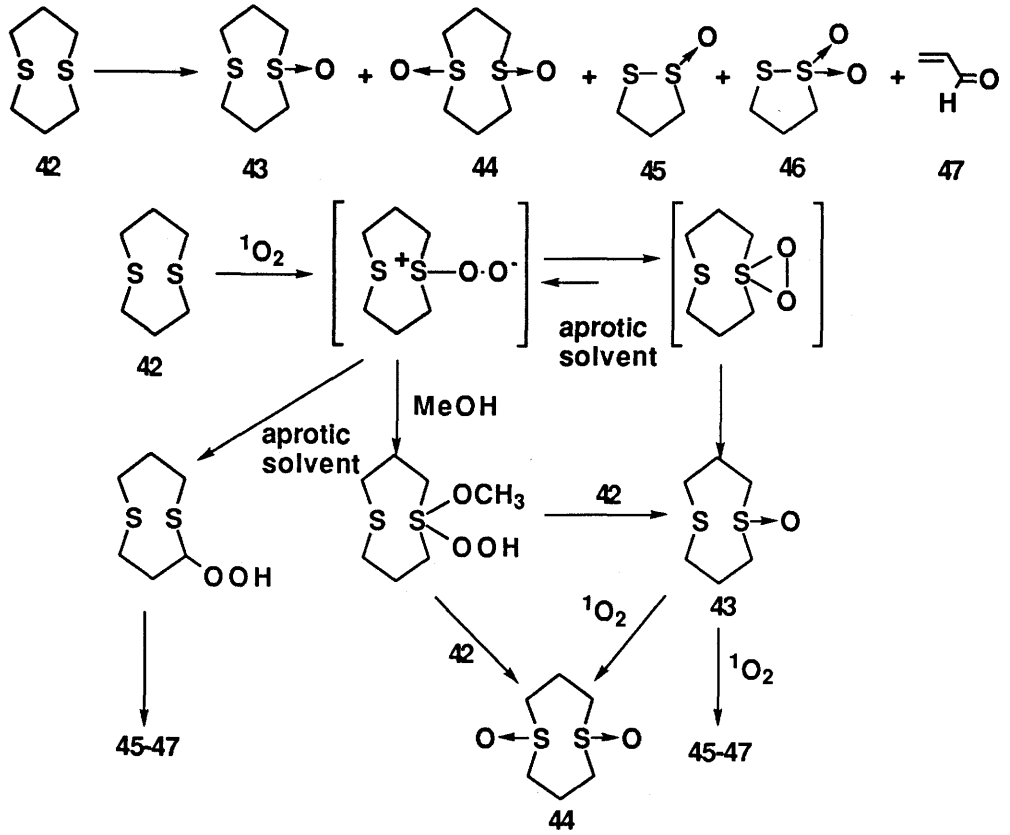
These seleno-Pummerer reactions proceed *via* an initial formation of the selenonium cation (**32**) which is stabilized by the remote selenium participation by either the reaction of **30** with BPO or the reaction of **31** with an acid anhydride affording the corresponding selenonio selenurane (**33**), diselena dication (**34**), or bis-selenurane (**35**) as an intermediate. The Pummerer-rearrangement may proceed *via* addition of a carboxylate anion ($CH_3CO_2^-$ of $PhCO_2^-$) to the alkylidene selenonium ion (**36**) generated from the α-proton abstraction of **33**, **34**, or **35** by a carboxylate anion. Finally, demethylation may undergo either by the nucleophilic substitution of the carbon atom of the methyl group of **33** or **34** with a carboxylate anion, or ligand coupling reaction in **35**. Furthermore, 8,13-dihydrobenzo[*g*]naphtho[1,8-*bc*][1,5]diselenonin (**39**) underwent photo-induced cleavage of the C-Se bond to generate the *o*-quinodimethane quantitatively together with naphtho[1,8-*cd*]-1,2-



Scheme 1-27

diselenole (**37**) (Scheme 1-27).[50c] The mechanism for photolysis of **39** can be explained that the formation of *o*-quinodimethane (**40**) proceeds *via* an initial photoexcitation of **39** following by the transannular interaction between the two selenium atoms to give unstable diselena dication, which undergoes C-Se bond cleavage to exclude *o*-quinodimethane (**40**)

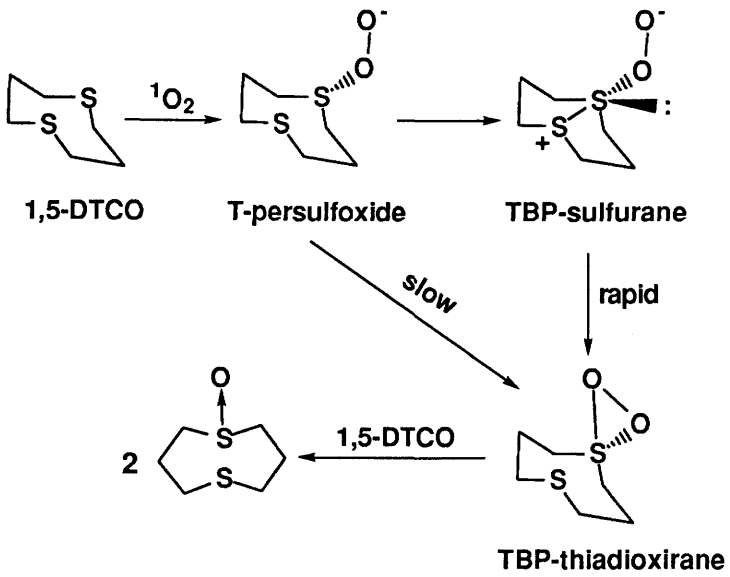
which can be trapped quantitatively by olefins to give the Diels-Alder [4+2] cycloadducts (**41**).



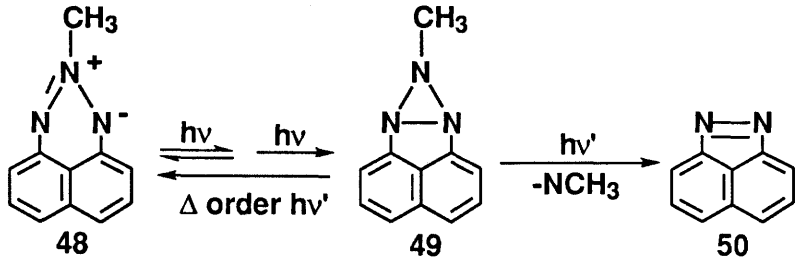
Scheme 1-28

Recently, Foote and co-workers have reported that photooxidation of 1,5-dithiacyclooctane (1,5-DTCO) (**42**) in the presence of a sensitizer afforded 1,2-dithiolane-1-oxide (**45**), and 1,2-dithiolane-1,1-dioxide (**46**), acrolein (**47**), C-S bond cleavage products (Scheme 1-28).[51] They have considered that this unique C-S bond cleavage of 1,5-DTCO caused by a transannular interaction between the two mesocyclic sulfur atoms in the intermediate because of 1,5-DTCO has no acidic hydrogens and photooxidation of 1,4-dithiane or 1,3-dithiane does not give any cleavage product. Clennan and co-workers have also studied that the photooxidation of 1,5-DTCO with oxygen in the presence

of a sensitizer, and compared the results obtained in similar experiments with 1,4-dithiane and pentamethylene sulfide.[52] The photooxidation of 1,5-DTCO shows different behavior from other normal sulfides in several aspects: the ratio of chemical quenching to total quenching of singlet oxygen during photooxidation of 1,5-DTCO was 70%, in comparison to 5% for 1,4-dithiane and 2.9% for pentamethylene sulfide and a sulfone was produced in all of the photooxidations except that of 1,5-DTCO. A strong sulfur-sulfur interaction during photooxidation of 1,5-dithiacyclooctane is utilized in order to explain these results (Scheme 1-29).

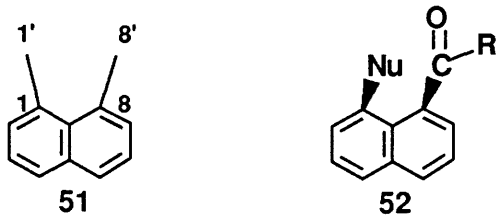


Kaupp and Dohle have found that laser photolysis of azimine (**48**) proceeds *via* an initial formation of triaziridine (**49**) to produce nitromethane and compound **50** (Scheme 1-30).[53] They concluded that compound **48** is excited by two photon excitation within 14 ns into an excited state in which it has a real 1,3-dipolar character, and from which it cyclizes to **49**.



Scheme 1-30

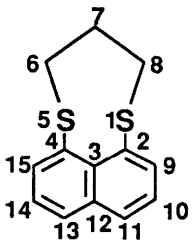
***peri* Interaction in Naphthalene Derivatives**



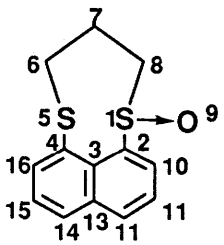
Nu = $N(CH_3)_2$, OCH_3, OH
R = CH_3, $N(CH_3)_2$, OCH_3, OH

In the naphthalene molecule, the 1,8-positions are said to be *peri* to each other. In view of the relative geometry of the two substituents in naphthalene, the substituents located at the 1,8-positions (*peri*) are in much closer proximity than the similar substituents located the *ortho* or the 1,2-positions to each other. This closer proximity effect of two substituents becomes to be responsible for the appearance of several unique properties of *peri*-substituted naphthalene. The X-ray crystallographic analysis of 1,8-disubstituted naphthalenes shows distorted configurations being consistent due to repulsive forces between the two substituents. The exocyclic bonds are splayed outwards as shown in **51** and the substituents are displaced to opposite sides in the naphthalene plane to make the none bonded C(1')···C(8') distance at longer than the idealized

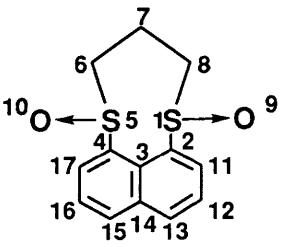
naphthalene skeleton with 120° bond angle (*ca.* 2.45 Å). For example, the distance between the *t*-butyl carbon atoms bonded to the *peri* positions in 1,3,6,8-tetra(*t*-butyl)naphthalene is 3.86 Å.[54] On the other hand, the two exocyclic bonds of nucleophilic and electrophilic centers at the 1,8-positions of naphthalene show a characteristic distortional pattern as shown in **52**; namely, the bond to the electrophilic carbon substituent is splayed outward, in which the bond to the nucleophile is inward.[55] This distortion is indicated that an approach between these groups tends to occur with a Nu···C=O angle of 94-108° and it is accompanied by pyramidalization of the carbonyl atom.



53



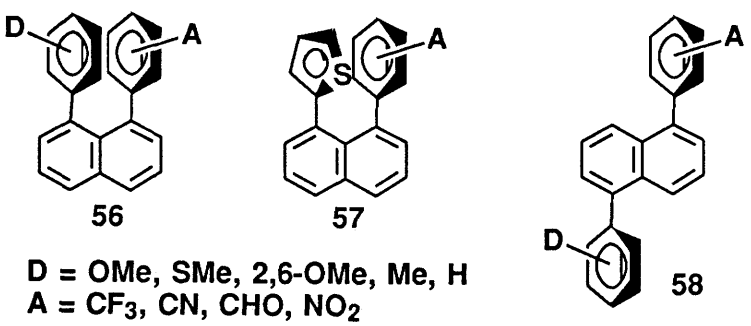
54



55

Recently, Glass and co-workers have been reported that the nonbonded interaction between two sulfur atoms in naphtho[1,8-*b,c*]-1,5-dithiocin (**53**) and its 1-oxide (**54**) and 1,1-dioxide (**55**) using X-ray crystallographic method.[56] The S···S intramolecular distances of 3.00 and 3.05 Å for compounds **54** and **55**, respectively, are about 0.2 Å closer than the S···S distance in dithioether **53** (3.23 Å) and markedly smaller than the van der Waals radii (3.7 Å) of the two sulfur atoms. The C(2)-S(1)-O(9) and C(8)-S(1)-O(9) bond angles in compound **54** are 104.2 and 102.3°, these angles for compound **55** are 106.6 and 104.6°, respectively, which is small compared to the average value of

106.8° for the same bond angles in other six-, seven-, and eight-membered-ring sulfoxides.[57] Furthermore, the S(5)···S(1)-O(9) angle is nearly a linear configuration of 174.2 and 170.3° for compounds **54** and **55**, respectively. Thus the angle distortions about the sulfoxide sulfur atoms in **54** and **55** and the short S···S intramolecular contact for **54** and **55** suggest a distorted trigonal-bipyramidal structure at S(1) with S(5) and O(9) occupying the apical positions. On the basis of the X-ray data of compounds **54** and **55** should have a stabilizing nonbonded interaction due to the short S···S distances and angle distortions at the S(1) atom.



1,8-Di(hetero)arylnaphthalenes **56** and **57** are the candidates for a novel blue-transparent frequency-doubling devices.[58] The X-ray structure analysis of **56** (A = NO_2, D = OMe) shows that both aryl rings attached at the 1,8-positions subtend an angle of 62.6° with the plane of the naphthalene. Similarly high torsional angles are observed in other 1,8-diarylnaphthalenes[59] and lead to the face-to-face arrangement of the π-electron systems. The distance of the two phenyl rings in 1,8-naphthalene is 2.98 Å which is markedly shorter than the van der Waals distance for two face-to-face aromatic group arrangement in space (3.40 Å). Therefore, a transannular π-π interaction

of the two 1,8-aryl rings may cause the observed nonlinear optics (NLO) activity. Compounds **56** and **57** show a stronger NLO-activity than 1,5-disubstituted naphthalene (**58**).

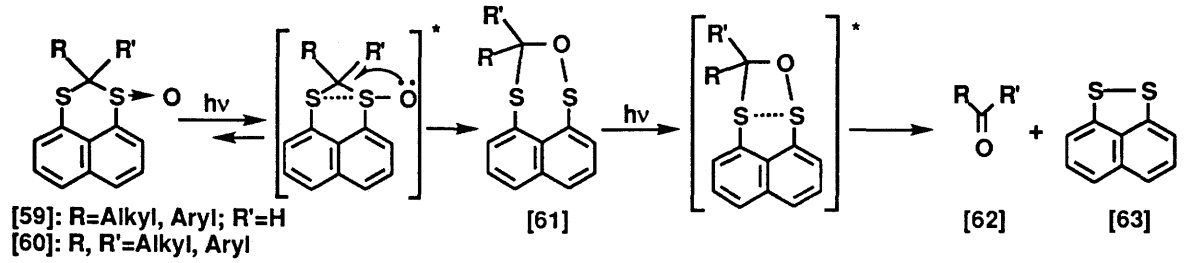
Introduction to the Thesis

The organosulfur compounds play important roles not only in the organic syntheses but also in biochemistry and material sciences. On the other hand, through-space interaction or transannular interaction has been often observed in organic compounds bearing more than two heteroatoms in close proximity. These compounds are expected to have new chemical and physical properties, and show the unusual reactivities. Sterically congested two heteroatoms substituted at the suitable positions in the aromatic ring (*i. e.*, 1,8-disubstituted naphthalene) have also been found to provide exceptionally strong transannular interaction between them. However, application of these interactions to organic syntheses and reactions have been little studied yet. Therefore, the author forcused attention on the above results and tried to expand the investigation about through-space interaction between heteroatoms with special attention in the case of compounds containing sulfur atom.

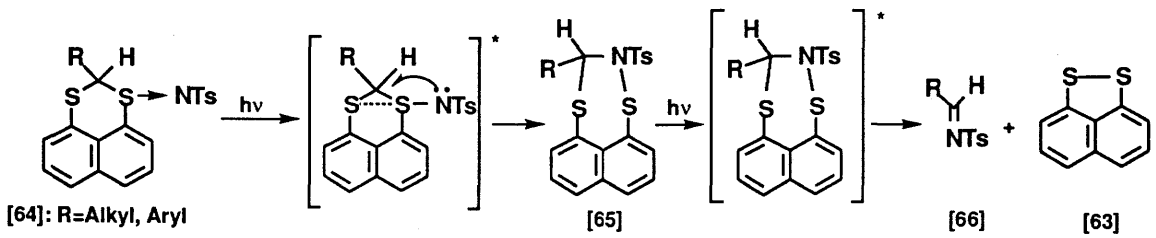
This thesis presents the following novel results on through-space interaction between the two sulfur atoms on the reaction of congested aromatic compounds bearing sulfur atoms.

Chapter 2: Naphthalene-1,8-dithiol reacted with aldehydes to give dithioacetals which were oxidized to 2-substituted naphtho[1,8-*de*]-1,3-dithiin-1-oxides (**59**). 2, 2-Disubstituted naphtho[1,8-*de*]-1,3-dithiin-1-oxides (**60**) were obtained on treatment of **59** with sodium hydride/ electrophiles. Photolysis

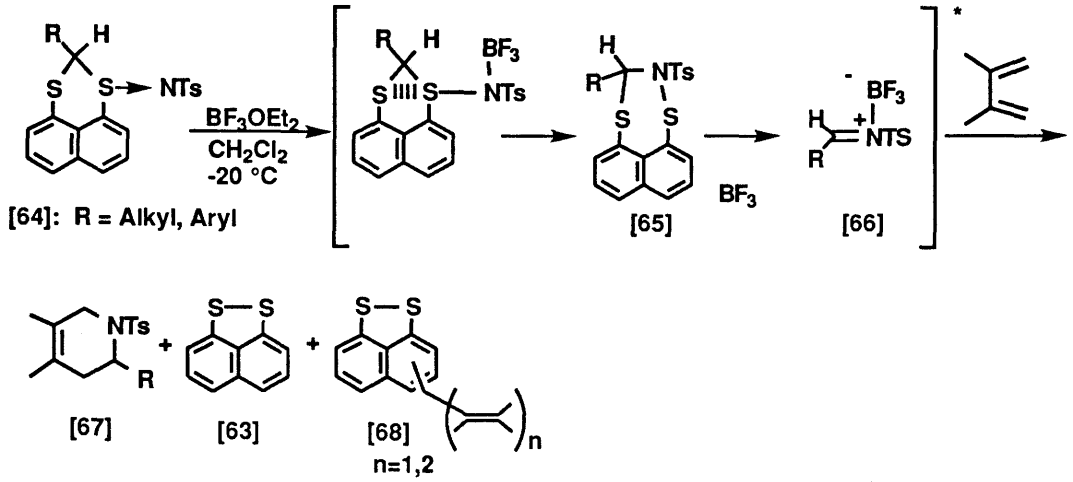
of **59** and **60** undergoes intramolecular oxygen rearrangement to generate aldehydes and ketones quantitatively together with naphtho[1,8-*cd*]-1,2-dithiole (**63**) *via* the through-space interaction between the two sulfur atoms at the 1,8-positions of naphthalene. The mechanism for the photoreaction has been determined by ^{18}O tracer, cross-over experiment, and light intensity studies.



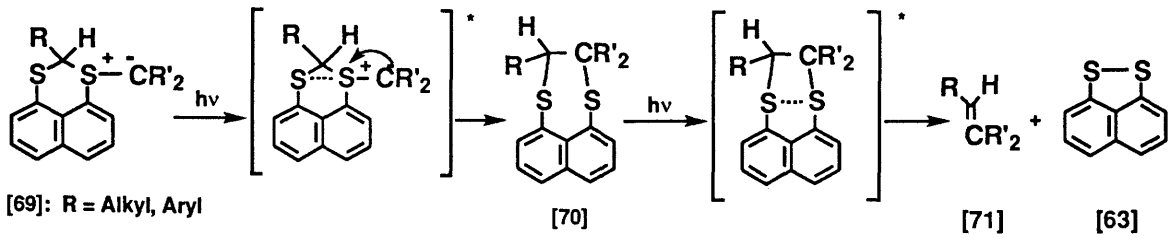
Chapter 3: Naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimines (**64**) were prepared by the reaction of naphtho[1,8-*de*]-1,3-dithiins with chloramine-T. The sulfilimines (**64**) underwent intramolecular photo-imino rearrangement giving *N*-tosylaldimines (**66**) quantitatively together with naphtho[1,8-*cd*]-1,2-dithiole (**63**) *via* the through-space interaction between the two sulfur atoms at the 1,8-positions of naphthalene. The mechanism of this reaction was determined by cross-over experiment and isolation of the reaction intermediate (**65**).



Chapter 4: Naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimines (**64**) were treated with boron trifluoride etherate to give the imino[4+2]cyclo-adducts (**67**), naphtho[1,8-*cd*]-1,2-dithiole (**63**), and ring-expanded product (**65**), the allylnaphtho[1,8-*cd*]-1,2-dithiole (**68**).



Chapter 5: Naphtho[1,8-*de*]-1,3-dithiin-1-bis(ethoxycarbonyl)methylides (**69**) were prepared by the reaction of naphtho[1,8-*de*]-1,3-dithiins with diethyl diazomalonate in the presence of copper acetylacetonate. The direct irradiation of sulfonium ylides **69** gave the corresponding olefins **71** quantitatively together with naphtho[1,8-*cd*]-1,2-dithiole (**63**) *via* the through-space interaction between the two sulfur atoms at the 1,8-positions of naphthalene. The mechanism of this reaction was determined by product analyses, cross-over experiment, and light intensity studies.



Chapter 6: Treatment of naphtho[1,8-*de*]-1,3-dithiins with diethyl diazomalonate in the presence of cupric sulfate in benzene under reflux conditions gave the corresponding naphtho[1,8-*ef*][1,4]dithiepins (**70**), which may be formed from the sulfonium ylides by the Stevens type rearrangement. Irradiation of naphtho[1,8-*ef*][1,4]dithiepins at 313 nm gave the corresponding olefins (**71**) and naphtho[1,8-*cd*]-1,2-dithiole (**63**) quantitatively. Experimental results and MO calculation suggest that this photodecomposition proceeds *via* the S_1 state, and that a through-space interaction between the two sulfur atoms induced upon photo-excitation plays an important role.

References

1) a) Block, E. "Reactions of Organosulfur Compounds" Academic Press, New York 1978; b) Oae, S., Ed. "Organic Chemistry of Sulfur" Plenum Press, New York, 1977; c) Oae, S., Ed. "Chemistry of Organosulfur Compounds" Yuki-iou-kagaku, in Japanese, Kagaku-Doujin, Kyoto, 1982.

2) a) Price, C.C.; Oae, S. "Sulfur Bonding" The Ronald Press, New York, 1962, pp.61; b) Yano, Y,; Oae, S. "3d Orbital Resonance in the Bivalent Sulfur Atom, Mechanisms of Reactions of Sulfur Compounds" Vol. 4, Intra-Science, 1969, p, 167.

3) a) Streitwieser, Jr. A.; William, Jr. J. E. *J. Am. Chem. Soc.* **1975**, 97, 191; b) Epiotis, N. D.; Yates, R. L.; Bernardi, F.; Wolfe, S. *ibid.* **1976**, 98, 5435; c) Lehn, J. M.; Wipff, G. *ibid.* **1976**, 98, 7498.

4) a) Pettit, G. R. Org. React.(N.Y.), **1966**, 12, 356; b) Hauptmann, H.; Walter, W. F. Chem. Rev. **1962**, 62, 347; c) Boeckelheide, V.; Anderson, P. H.; Hylton, T. A. *J. Am. Chem. Soc.* **1974**, 96, 1558; d) Jones, J. B.; Graysham, R. *J, Chem, Soc. D* **1970**, 141; e) Trost, B. M., Chem. Rev. **1978**, 78, 363.

5) a) Kingsbury, C. A.; Cram, D. J. *J. Am. Chem. Soc.* **1960**, 82, 1810.

6) Grobel, B.-T.; Seebach, D. *Synthesis* **1977**, 357.

7) Seebach, D.; Corey, E. J. *J, Org, Chem.* **1975**, 40, 231, and references therin.

8) Hase, T. A.; Koskimes, J. K., *Aldrichimica Acta* **1981**, 14, 73; **1982**, 15, 35.

9) a) Corey, E. J.; Erickson, B. W. *J. Org. Chem.* **1971**, 36, 3553; b) Seebach, D.; Neumann, H., *Chem. Ber.* **1974**, 107, 847; Ballini, R.; Petrini, M. *Synthesis* **1990**, 336; c) Taguchi, T.; Okamura, H.; Takei, H. *Chem. Lett.* **1975**, 853.

10) a) Chattopadhyahya, J. B.; Rama Rao, A. V. *Tetrahedron Lett.* **1973**, 3735; b) Huurdeman, W. F. J.; Wynberg, H.; Emerson, D. W. *ibid.* **1971**, 3449; c) Hojo, M.; Masuda, R. *Synthesis* **1976**, 678; d) Nishida, K.; Yokota, K.; Nakayama, D.; Sumiya, T.; Node, M.; Fuji, K. *Tetrahedron Lett.* **1993**, 34, 345.

11) a) Fetizon, M.; Jurion, M. *J. Chem. Soc., Chem. Commun.* **1972**, 382; b) Wang-Chang, H. L., *Tetrahedron Lett.* **1972**, 1989; Oishi, T.; Takechi, H.; Kamemoto, K.; Ban, Y. *ibid.* **1972**, 1085; c) Stahl, I.; Hetscchko, M.; Gosselck, J., *ibid.* **1971**, 4077; d) Ho, T. L.; Wong, C. M. *Synthesis* **1972**, 561.

12) Still, I, W. J. *Studies Organic Chem.* **1985**, 19, 596.

13) Coyle, J. D. *Chem. Soc. Rev.* **1974**, 4, No.4, 523.

14) Still, I. W. J. "Photochemistry of Sulphoxides and Sulphones", Patai, S.; Rappaport, Z,; Stirling, C. J. M. Eds.; John Wiley & Sons Ltd.; New York, **1988**, 873.

15) Givens, R. S. "Organic Photochemistry", Padwa, A. Ed.; Marcel Dekker, New York, **1981**, 228.

16) Cox, A. "Light Chemical Change and Life", Coyle, J. D.; Hill, R. R.; Roberts, D. R. Eds.; Open University Press, Buckingham, **1982**, 252.

17) Still, I. W. J. "Organic Sulfur Chemistry", Bernardi, F.; Csizmadia, I. G.; Mangini, A., Eds.; Elsevier, Lausanne, **1985**, 606.

18) Gollnick, K.; Stracke, H.-U. *Pure Appl. Chem.* **1973**, 22, 217.

19) Guo, Y.; Jenks, W. S. *J. Org. Chem.* **1995**, 60, 5480.

20) Carpino, L. A.; Chen, H.-W. *J. Am. Chem. Soc.* **1979**, 101, 2366.

21) Schults, A. G.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, 3605.

22) Still, I. W. J.; Arora, P. C.; Chauhan, M. S.; Kwan, M.-H.; Tomas, M. T. *Can. J. Chem.* **1976**, 54, 455.

23) Lerch, U.; Moffatt, J. G. *J. Org. Chem.* **1971**, 36, 3391.

24) Lerch, U.; Moffatt, J. G. *J. Org. Chem.* **1971**, 36, 3686.

25) Hayashi, Y.; Swern, D. *Tetrahedron Lett.* **1972**, 1921.

26) a) Lwowski, W.; Mattingly, I. W. *J. Am. Chem. Soc.* **1965**, 87, 1947; b) Felt, C. R.; Linke, S.; Lwowski, W. *Tetrahedron Lett.* **1972**, 2037.

27) a) Furukawa, N.; Fukumura, M.; Nishio, T.; Oae, S. *Phosphorus Sulfur* **1978**, 5, 231; b) Furukawa, N.; Nishio, T.; Fukumura, M.; Oae, S. *Chem. Lett.* **1978**, 209; c) Abramovitch, R. A.; Chelleathyrai, T.; Holcomb, W. D.; McMaster, I. I.; Vanderpool, D. P. *J. Org. Chem.* **1977**, 42, 2920.

28) Gilchrist, T. L.; Moody, C. J.; Rees, C. W., *J. Chem, Soc., Perkin Trans 1* **1975**, 1964.

29) Trost, B. M. *J. Am. Chem. Soc.* **1966**, 88, 1587; **1967**, 89, 138.

30) Trost, B. M.; LaRochelle, R. W. *J. Am. Chem. Soc.* **1970**, 92, 5804.

31) Fish, R. H.; Chow, L. C.; Caserio, M. C. *Tetrahedron Lett.* **1969**, 1259.

32) Maki, Y.; Hiramitsu, T. *Chem. Pharm. Bull.* **1977**, 25, 292.

33) Alberti, A.; Griller, D.; Nazran, A. S.; Pedulli, G. F. *J. Am. Chem. Soc.* **1986**, 108, 3024.

34) Zhang, J.-J.; Schuster, G. B. *J. Org. Chem.* **1988**, 53, 716.

35) Lepley, A. R. *J. Am. Chem. Soc.* **1969**, 22, 663.

36) a) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, 106, 5805; b) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1987**, 109, 2251.

37) Zhang, J.-J.; Schuster, G. B. *J. Am. Chem. Soc.* **1989**, 111, 7149.

38) Leonard, N. J. *Acc. Chem. Res.* **1979**, 12,423.; Leonard, N. J.; Adamcik, J. A.; Djerassi, C.; Halpern, O. *J. Am. Chem. Soc.* **1958**, 80, 4858.

39) Dahn, H.; Schlunke, H.-P.; Temler, J. *Helv. Chim. Acta* **1972**, 55, 907.

40) Nakashima, T. T.; Maciel, G. E. *Org. Magn. Resonance* **1972**, 4, 321.

41) a) Alder, R. W. *Tetrahedron* **1990**, 46, 683; b) Asmus, K.-D. *Acc. Chem. Res.* **1979**, 12, 436; c) Musker, W. K. *Acc. Chem. Res.* **1980**, 13, 200; d) Akiba, K.; Takee, K.; Shimizu, Y.; Ohkata, K. *J. Am. Chem. Soc.* **1986**, 108, 6320; e) Fujihara, H.; Akaishi, R.; Furukawa, N. *Tetrahedron* **1993**, 49, 1605.

42) Alder, R. W.; Orpen, A. G.; White, J. M. *J. Chem. soc. Chem. Commun*, **1985**, 949.

43) a) Fujihara, H.; Akaishi, R.; Furukawa, N. *J. Chem. Soc., Chem. Commun.* **1987**, 930; b) Iwasaki, F.; Toyoda, N.; Akaishi, R.; Furukawa, N. *Bull. Chem. Soc. Jpn.* **1988**, 61, 2563.

44) a) Fujihara, H.; Akaishi, R.; Erata, T.; Furukawa, N. *J. Chem. Soc., Chem. Commun.* **1989**, 1789; b) Iwasaki, F.; Morimoto, M.; Yasui, M.; Akaishi, R.; Fujihara, H.; Furukawa, N. *Acta Cryst.* **1991**, *C47*, 1463.

45) Fujihara, H.; Chiu, J.-J.; Furukawa, N. *Chem. Lett.* **1990**, 2217.

46) Glass, R. S.; Broeker, J. L.; Firouzabadi, H. *J. Org. Chem.* **1990**, 55, 5739.

47) Fujihara, H.; Yabe, M.; Chiu, J.-J.; Furukawa, N. *Tetrahedron Lett.* **1991**, *32*, 4345-4348.

48) Kimura, T.; Horie, Y.; Ogawa, S.; Fujihara, H.; Iwasaki, F.; Furukawa, N. *Heterocycles* **1992**, *33*, 101-104.

49) a) Glass, R. S.; Andreuski, S. W.; Broeker, J. L.; Firouzabadi, H.; Steffen, L. K.; Wilson, G. S. *J. Am. Chem. Soc.* **1989**, 111, 4036; b) Kimura, T.; Horie, Y.; Ogawa, S.; Furukawa, N. *Heteroatom Chem.* **1993**, 4, 243; c) Furukawa, N.; Kimura, T.; Fujihara, H.; Ogawa, S. *Tetrahedron Lett.* **1992**, 33, 1489.

50) a) Kimura, T.; Ishikawa, Y.; Ueki, K.; Horie, Y.; Furukawa, N. *J. Org. Chem.* **1994**, 59, 7117; b) Furukawa, N.; Shima, H.; Kimura, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1762; c) Fujihara, H.; Yabe, M.; Furukawa, N. *J. Org. Chem.* **1993**, 58, 5291; d) Fujihara, H.; Saito, R.; Yabe, M.; Furukawa, N. *Chem. Lett.* **1992**, 1437

51) Sheu, C.; Foote, C. S.; Gu, C.-L. *J. Am. Chem. Soc.* **1992**, 114, 3015.

52) Clennan, E. L.; Wang, D.-X.; Yang, K.; Hodgson, D. J.; Oki, A. R. *J. Am. Chem. Soc.* **1992**, 114, 3021.

53) Kaupp, G.; Dohle, J. A. *Angew. Chem. Int. Ed. Engl.* **1986**, 25, 828.

54) Handal, J.; White, J. G.; Franck, R. W.; Yuh, T. H.; Allinger, N. L. *J. Am. Chem. Soc.* **1977**, 99, 3345.

55) Schweizer, W. B.; Procter, G.; Kaftory, M.; Dunitz, J. D. *Helv. Chim. Acta.* **1978**, 61, 264.

56) Glass, R. S.; Adamowicz, L.; Broeker, J. L. *J. Am. Chem. Soc.* **1991**, 113, 1065.

57) Glass, R. S.; Adamowich, L.; Broeker, J. I. *J. Mol. Struct.* **1989**, 186, 273.

58) Bahl, A.; Grahn, W.; Stadler, S.; Feiner, F.; Bourhill, G.; Brauchle, C.; Reisner, A.; Jones, P. G. *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 1485.

59) Clough, R. L.; Kung, W. J.; Marsh, R. E.; Roberts, J. D. *J. Org. Chem.* **1976**, 41, 3603.

Chapter 2

Mechanism for Photodecomposition of Naphtho[1,8-*de*]-1,3-dithiin-1-oxides: A Convenient Method for Preparation of Aldehydes and Ketones

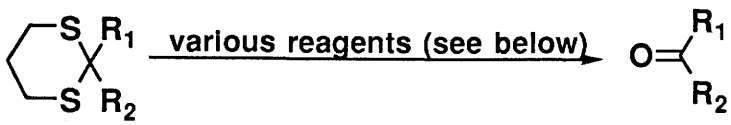
Abstract

1,8-Naphthalenedithiol reacted with aldehydes to give dithioacetals which were oxidized to 2-substituted naphtho[1,8-*de*]-1,3-dithiin-1-oxides (**7**). 2, 2-Disubstituted naphtho[1,8-*de*]-1,3-dithiin-1-oxides (**8**) were obtained on treatment of **7** with NaH/ electrophiles. Photolysis of **7** and **8** undergoes intramolecular oxygen rearrangement to generate aldehydes and ketones quantitatively together with naphtho[1,8-*cd*]-1,2-dithiole.

Introduction

Earlier, synthesis of aldehydes from formaldehyde mercaptals was achieved by Froling and Arens.[1] This method was developed and introduced by Corey and Seebach to the generally applicable aldehydes and ketones syntheses by using 1,3-dithiane, and is termed "Umpolung of the reactivity".[2,3,4]

The concept is based on the conversion of the sulfenyl sulfur to the better leaving group, following by hydrolysis. The modification of the sulfides can be achieved by desulfurization with many efficient methods such as metal-induced,[5] oxidative,[6] alkylative,[7] photo-induced,[8] and electrolytic[9] decompositions. Formaldehyde dimethyl dithioacetale S-oxide (FAMSO) and methylthiomethyl sulfone have also been utilized as carbonyl syntones.[10] However, the transformation of these compounds to the corresponding aldehydes and ketones requires rather complicated process.



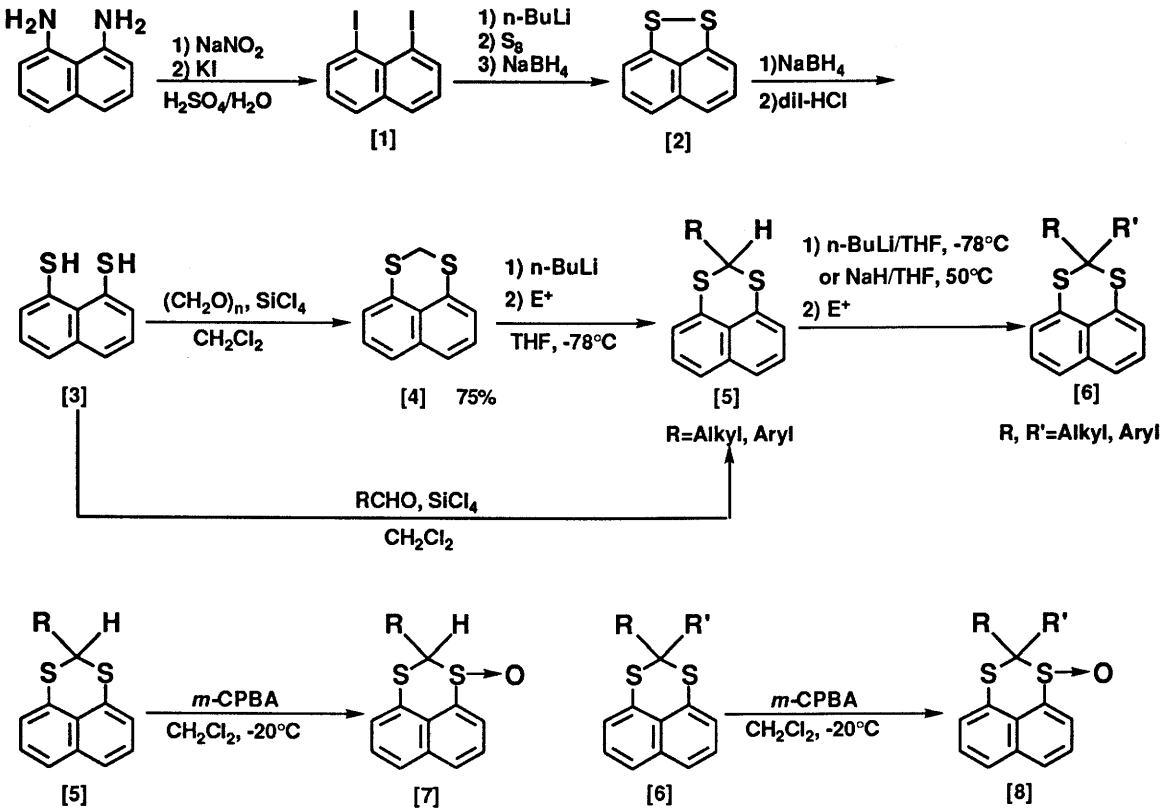
$Hg(II)/BF_3$, THF/H_2O, 50 °C, 86%
$AgNO_3$, EtOH/H_2O, 50 °C, 55%
$CuCl_2/CuO$, acetone, Δ, 85%
NBS, H_2O/MeCN or acetone, 70-100%
I_2, DMSO, 90 °C, 75-85%
Isopentyl nitrite, 65%
$Ce(NH_4)_2(NO_3)_6$, MeCN/H_2O, 70-87%
$O_2/h\nu$, 60-80%
MeI, MeOH/H_2O, Δ, 60-80%
$Et_3O^+BF_4^-$, 3%aq., $CuSO_4$, 81%
$h\nu$ (λ>360nm)/O_2, $TPPClO_4$/MeCN, 31-95%
Anodic oxidation, MeCN/H_2O 60-100%

1,8-Bis(alkylthio)- or 1,8-bis(alkylseleno)-naphthalene derivatives are presumably the candidates for generating various active species or creating new reactions initiated by the through-space interaction between two sulfur or two

selenium atoms.[11] In fact, 1,8-dithia or -diselena naphtho[1,8-*bc*]dithiocins undergo unusual Pummerer and thio-Claisen rearrangement reactions *via* the formation of the dications.[12] Furthermore, quinodimethane is generated from photolysis of 8,13-dihydrobenzo[*g*]naphtho[1,8-*bc*][1,5] diselenonin.[13] As a further extension of these studies, the author prepared naphtho[1,8-*de*]dithiins and found that photolysis of the corresponding monooxides became a convenient procedure to yield the carbonyl compounds. This chapter reports the results on the intramolecular photo-oxygen rearrangement reaction of naphtho[1,8-*de*]dithiin-1-oxides to the aldehydes and ketones.

Results and Discussion

Synthesis of Naphtho[1,8-*de*]-1,3-dithiin-1-oxides



Scheme 2-1

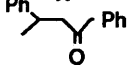
2-Substituted naphtho[1,8-*de*]-1,3-dithiin-1-oxides (**7**) and 2,2-disubstituted naphtho[1,8-*de*]-1,3-dithiin-1-oxides (**8**) were prepared according to the following procedures shown in Scheme 2-1. 1,8-Diiodonaphthalene (**1**) and naphtho[1,8-*cd*]-1,2-dithiole (**2**) were prepared according to the method reported in the literature[14, 15]. Reduction of **2** with sodium borohydride in tetrahydrofuran (THF)-ethanol at room temperature gave almost quantitatively 1,8-naphthalene dithiol (**3**). Compound **3** was treated with paraformaldehyde in the presence of tetrachlorosilane ($SiCl_4$) in dichloromethane affording the

corresponding naphtho[1,8-*de*]-1,3-dithiin (**4**) in 71% yields. 2-Substituted naphtho[1,8-*de*]-1,3-dithiins (**5**) were prepared by

Table 2-1. Preparation of **5** and **6**.

		Yield of **5** (%)				Yield of **6** (%)
R_1	R_2	**3→5**	**4→5**	R_1	R_2	**5→6**
Ph	H	98	-	Ph	CH_3	97
p-Tol	H	97	-	Ph	Et	98
$CH_3(CH_2)_5$	H	98	89	Ph	PhCH(OH)	96
PhCH=CH	H	88	73			
	H	87	86			

Table 2-2. Preparation of **7** and **8**.

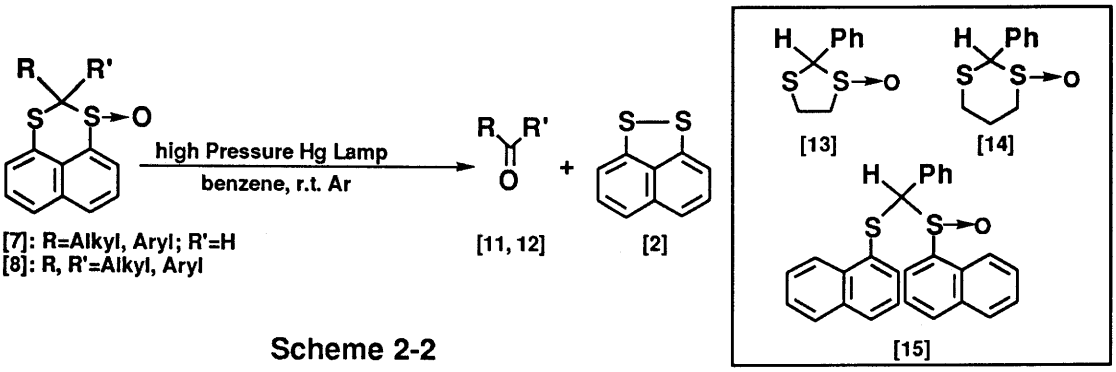
		Yield of **7** (%)			Yield of **8** (%)	
R_1	R_2	**5→7** (7:7')[a]	R_1	R_2	**6→8** (8:8')[a]	**7→8** (8:8')[a]
Ph	H	98 (5:1)	Ph	CH_3	97 (9:2)	76 (3:2)
p-Tol	H	91 (3:1)	Ph	Et	95 (6:1)	72 (2:1)
$CH_3(CH_2)_5$	H	85 (7:1)	Ph	PhCH(OH)	93 (2:1)	-
PhCH=CH	H	88 (5:3)	Ph	PhCH(OMe)	94 (4:1)	-
	H	96 (10:3)	Ph		-	80 (2:1)
			Ph		-	83 (14:1)

a) Diastereomeric ratios were determined by ^{1}H-NMR spectroscopy.

the reaction of 2-lithiated **4** with several electrophiles. Compounds **5** were also obtained by the reaction of **3** and aldehydes in the presence of $SiCl_4$ in dichloromethane in high yields (Table 2-1). However, 2,2-disubstituted naphtho[1,8-*de*]-1,3-dithiins (**6**) were obtained in poor yields on analogous treatment with ketones and **3** and hence dithioketals **3** were prepared from the reaction of 2-lithiated **2** with several electrophiles. 2-Substituted naphtho[1,8-*de*]-1,3-dithiin-1-oxides (**7**) and 2,2-disubstituted naphtho[1,8-*de*]-1,3-dithiin-1-oxides (**8**) were obtained in high yields with high diastereoselectivities by oxidation using *m*-chloroperbenzoic acid

(*m*CPBA) in dichloromethane at -20 °C (Table 2-2). Furthermore, compounds **8** were also converted to dithioketal monooxides **7** by the reaction with sodium hydride in THF at 50 °C and then with several electrophiles in moderate yields.

Photolysis of Naphtho[1,8-*de*]-1,3-dithiin-1-oxides

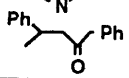


Scheme 2-2

Although compounds **5** and **6** were thermally and photochemically stable molecules, monooxides **7** and **8** were found to decompose to the corresponding aldehydes and ketones quantitatively with complete recovery of naphtho[1,8-*cd*]-1,2-dithiole (**2**) on exposure to high pressure mercury lamp (400 W) in benzene for 20 h (Scheme 2-2). After evaporation of benzene and work-up, the residue was chromatographed to give **11** or **12** and **2** quite readily. Protic and aprotic solvents including ethanol, acetonitrile, THF, dichloromethane, chloroform, and benzene were examined on the photoreaction of **7a**. The photodecomposition reactions gave **11a** and **2** quantitatively. As shown in Table 2-3, the results reveal that the reactions are clean and aldehydes or ketones were obtained quantitatively with recovered naphtho[1,8-*cd*]-1,2-dithiole (**2**). Other five- and six-membered 1,3-dithia

derivatives **13** and **14** were unreactive under the present photolysis conditions. Although 1-naphthyldithioacetal monooxide (**15**) underwent photodecomposition under identical conditions, the products obtained were a mixture of intractable compounds which were unable to separate by a simple procedure.

Table 2-3. Photolysis of Dithioacetal Monooxides **7** and Dithioketal Monooxides **8** in Benzene[a].

	R	R'	Yield of **11** and **12**/%[b]	Yield of **2**/%[b]
7a	Ph	H	>99	>99
7b	*p*-Tol	H	>99	>99
7e	$CH_3(CH_2)_5$	H	>99	>99
7f	PhCH=CH	H	>99 (97)[c]	>99 (98)[c]
7g		H	>99	>99
8a	Ph	D	>99	>99
8b	Ph	CH_3	>99 (93)[c]	>99 (100)[c]
8c	Ph	CH_3CH_2	>99 (95)[c]	>99 (99)[c]
8d	Ph	PhCH(OH)-	- (82)[c]	- (91)[c]
8e	Ph	$PhCH(OCH_3)$-	>99 (97)[c]	>99 (98)[c]
8f	Ph		>99 (96)[c]	>99 (98)[c]
8g	Ph		>99 (98)[c]	>99 (100)[c]

a) 400 W high pressure Hg lamp, λ> 300 nm, Substrates (0.1 mmol), Benzene (5 ml). b) Yields weredetermined by gas chromatography and ^{1}H-NMR spectroscopy. c) Isolated yields.

In order to understand the mechanism for decomposition of **7** and **8**, formation of the product evolution and disappearance of the starting material during photoreaction of compound **7a** (major product) were followed by time interval ^{1}H-NMR spectroscopy. The reaction profiles for photoreaction of **7a** under irradiation with a high pressure mercury lamp (500 W, 313 nm) (Figure 2-1). When the ^{1}H-NMR signals of the starting material **7a** gradually reduced, new peaks started to appear at 5.53 (s), 6.73 (s), 7.14 (d, J = 7.6 Hz) and 10.03 ppm (s) corresponding to those of the intermediate **10a** together with

other peaks from **11a**, **2**, and isomerization of **7a** to **7a'**, the structures of which were determined by comparing with the spectral data of the authentic compounds. The ^{1}H-NMR signals of the intermediate **10a** increased gradually but disappeared soon and the spectra were converted to those of the products **11a** and **2**. The intermediate **10a** could be obtained in 95% purity by liquid chromatography of the reaction mixture by stopping the photolysis of **7a** at the optimum point of conversion of **7a** to **10a**. The intermediate **10a** is an unstable, acid-sensitive and oily material and its ^{1}H-, ^{13}C-NMR, and mass spectral data support the structure (see Scheme 2-5). The results demonstrate that the mechanism for the present reaction proceeds *via* an initial formation of the intermediate **10** affording the corresponding aldehyde **11** or ketone **12** and naphtho[1,8-*cd*]-1,2-dithiole (**2**).

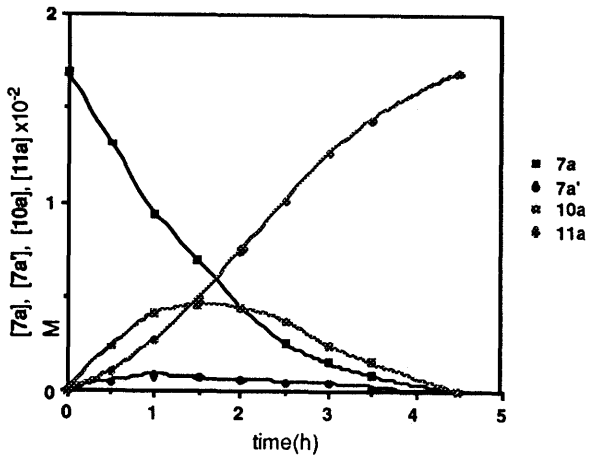


Figure 2-1. Time course of photolysis of **7a** (1.69 x10^{-2} M **7a** in $CDCl_3$).

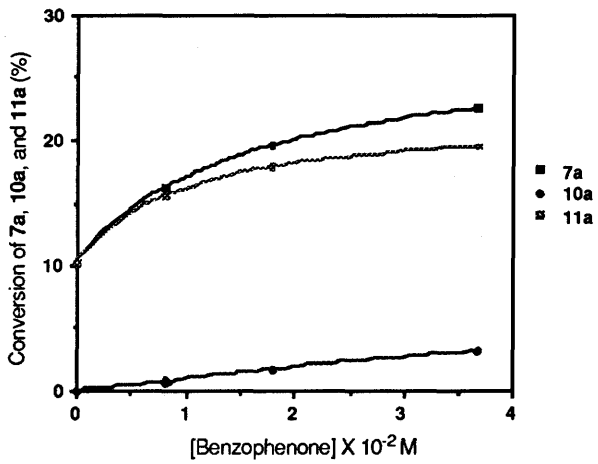


Figure 2-2. Benzophenone dependence on irradiation of **7a** with high presure Hg lamp (500 W, 366nm) (2.28x10^{-2} M **7a** in CH_2Cl_2).

The consumption of **7a** and formation of products **11a** and **2** were sensitized by the addition of benzophenone as a triplet

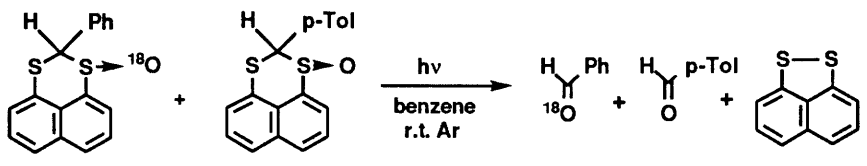
sensitizer, indicating that both reactions can proceed through the triplet state (Figure 2-2). However, the use of triplet quencher, isoprene, as found to be the same reaction mode as compared with that in direct irradiation experiment (Table 2-4). These results show the existence of two pathways on this photodecomposition.

Table 2-4. Irradiation of **7a** in the Presence of Isoprene.[a)]

Entry	Solvent	Consumption of **7a**(%)	Formation of **10a** and **2**
1	CH_2Cl_2	10.9	7.7
2	5%-Isoprene-CH_2Cl_2	10.1	8.3
3	10%-Isoprene-CH_2Cl_2	10.6	8.2
4	10%-Isoprene-CH_2Cl_2[c)]	10.2	8.1

a) 500W high pressure Hg lamp (λ = 366 nm), Substrates (4.65 x 10^{-3} M in CH_2Cl_2), Reaction time (60 min) b) Yields were determined by HPLC. c) In the presence of O_2.

A cross-over experiment was carried out in order to decide whether the intermediate **9** was obtained by an inter- or intramolecular process. Irradiation of a 1 : 1 mixture of ^{18}O labeled compound **7a**-^{18}O (^{18}O content=97 %) and **7b** under photolysis conditions as described above gave the aldehydes **11a** (^{18}O content=94 %) and **11b** along with **2** as shown in Scheme 2-3. The results demonstrate that formation of the intermediate **10** clearly proceeds by an intramolecular reaction.



[7a]-^{18}O [7b] [11a]-^{18}O [11b] [2]

^{18}O : 97% ^{18}O : 94%

Scheme 2-3

The effect of light intensity on photolysis of sulfoxide **7a** was studied in order to understand whether the reaction proceeds by a one-, two- or multi-photon process. The loss of **7a** was proportional to the first power of the intensity of 313 nm light, whereas the formation of **11a** was proportional to the square of the intensity as shown in Figure 2-3 These results imply that the consumption of **7a** proceeds by a one-photon process to give an intermediate **10a** in the primary photochemical step. Thereafter, the intermediate **10a** should be converted to the corresponding **11a** and **2** *via* the S···S through-space interaction in the secondary photochemical step.

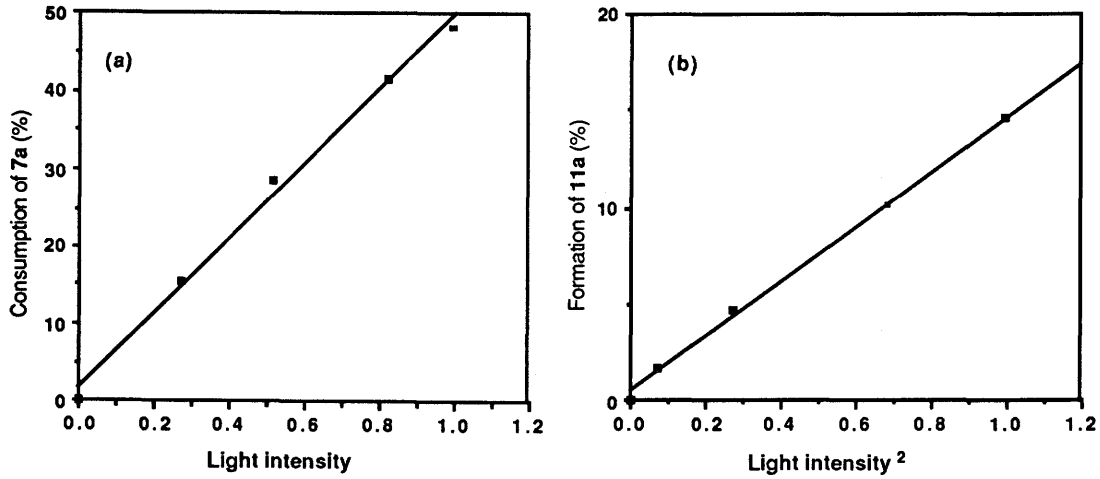
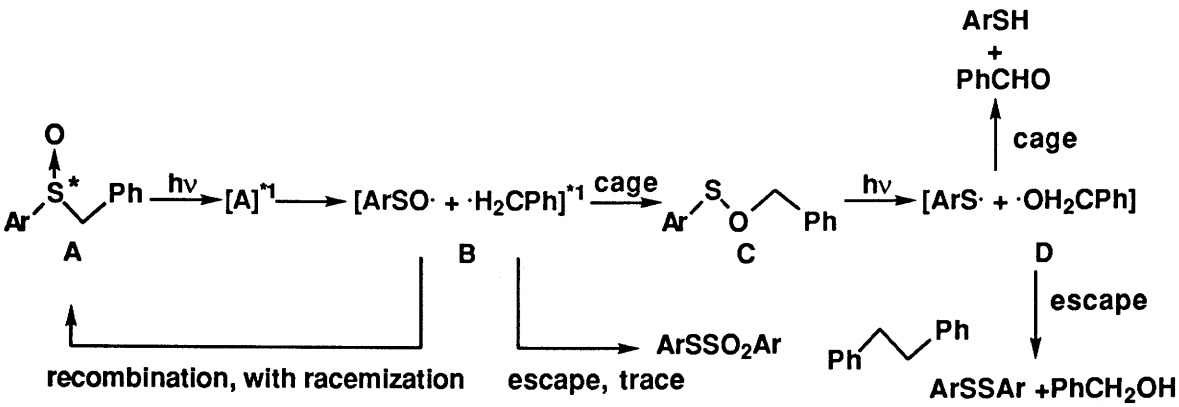


Figure 2-3. Light intensity dependence on the consumption of **7a** (a) and the formation of **11a** (b). (4.87×10^{-3} M **7a** in CH_2Cl_2).

The quantum yields for the consumption of compound **7a** ($\Phi_{consumed}$) and the formation of **11a** and **2** (Φ_{formed}), and isomerization of **7a** to **7a'** ($\Phi_{inv.}$) using a high pressure mercury lamp (500 W, 313 nm) at room temperature in deoxygenated dichloromethane was measured by comparison with fulgide actinometry to be 0.29 and 0.07, 0.07, and 0.02, respectively, whereas these yields of the consumption of

compound **7a'** ($\Phi_{consumed}$) and the formation of **11a** and **2** (Φ_{formed}), and isomerized compound **7a** ($\Phi_{inv.}$) to be 0.69 and 0.10, 0.10, and 0.07, respectively, being also indicative of the existence of intermediate on photolysis of **7a** to **11a** and **2**. The observed value of $\Phi_{consumed}$ of **7a** is lower than that of **7a'**. These observations may be attributed to the lack of through-space interaction between the 1,8-dithia substituents of **7a** than that of **7a'**. The absorptions due to the S=O group present at 1054 cm^{-1} for **7a** and 1036 cm^{-1} for **7a'** in the infrared spectrum. The decrease of the absorption of frequency in **7a'** is suggestive of a strong interaction between the positively polarized sulfinyl sulfur and transannular sulfur, which results in decrease of the electron density on the sulfur to be oxidized. This consideration also explains the longer absorption band of wavelength light of **7a'** (λmax = 331 nm, ε = 1.10 X 10^4) than **7a** (λmax = 313 nm, ε = 1.12 X 10^4) in UV-vis spectra.



Scheme 2-4

A common mechanistic assumption for many photochemical reactions of sulfoxides is that the first step is homolytic

cleavage of a C-S bond, or α-cleavage.[16] Recently, Jenks and Guo have received considerable attention on photolysis of aryl benzyl sulfoxides (**A**) (Scheme 2-4).[17] They concluded that the homolytic cleavage of sulfur-carbon bond on the photolysis of optically active benzyl *p*-tolyl sulfoxide was reversible with racemization by way of a cage recombination process. Racemization may result from the recombination of the geminated radical pair **B** which partitions between formation of sulfenic ester (**C**) and reversion to starting material **A**. In this case,

Table 2-5. Quantumn Yield for Consumption of **7a** and **7a'**.[a]

	Φ_{loss}[b]	$\Phi_{inv.}$[b]	$\Phi_{rot.}$	$\Phi_{loss}/\Phi_{cleave}$
7a	0.27	0.02	0.31	0.87
7a'	0.62	0.07	0.76	0.82
A[c]	0.21	0.10	0.42	0.50

a) Light was provided by a 500 W high pressure-Hg lamp filtered through a Toshiba UVD33s and a monochromator set at 313 nm. b) Fulugid was the actinometer. c) Irradiation of (*S*)-benzyl-*p*-tolyl sulfoxide in propanol with a 150 W Xe lamp (267 nm). Azoxybenzene was the actinometer. ref. 17.

$$\Phi_{loss} = \Phi_{consumed} - \Phi_{inv.}$$

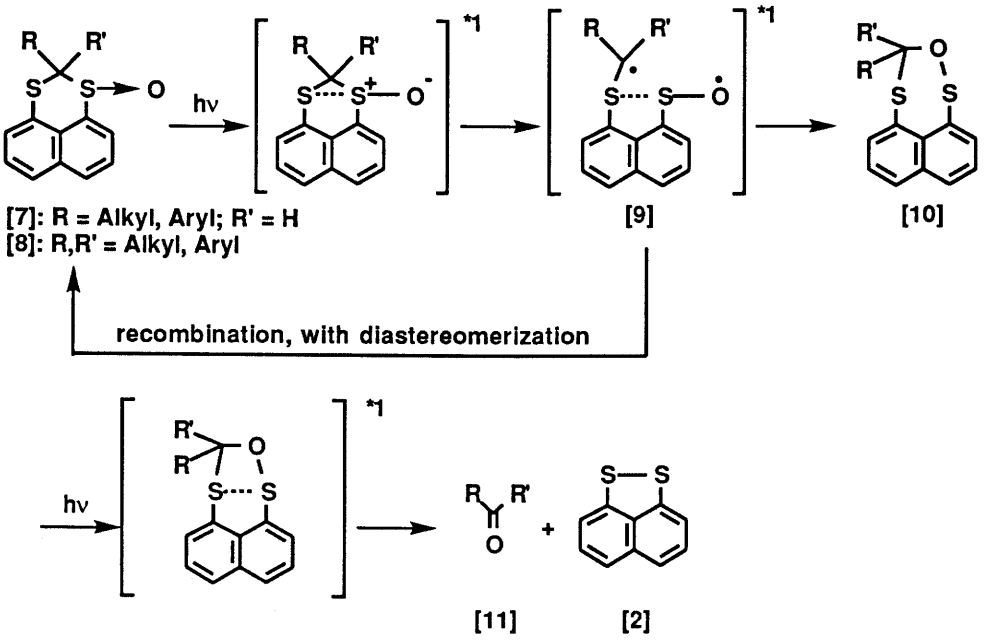
$$\Phi_{inv.} = (\Phi_{rot} - \Phi_{loss})/2.$$

$$\Phi_{cleave} = \Phi_{loss} + 2\Phi_{inv.} = \Phi_{rot.}$$

$$\Phi_{cleave} \geq \Phi_{lot.} > \Phi_{loss}$$

sulfenic ester (**C**) plays no part in racemization, as photolysis of **C** does not yield **A**. Photolysis of **C** proceeds through S-O bond cleavage to yield sulfinyl and alkoxyl radicals **D** which afford thiol and aldehyde by disproportionation. Therefore, They used the observed values of the quantum yield for the loss

of **A** (Φ_{loss}) and loss of optical activity ($\Phi_{rot.}$) to estimate the quantum yield of α-cleavage (Table 2-5). The difference between $\Phi_{rot.}$ and Φ_{loss} for (*S*)-**A** is attributed to the formation of the sulfinyl-benzyl radical pairs **B** which revert to **A**. If the initial cleavage produces a radical pair which has an equal probability of forming (*S*)- or (*R*)-sulfoxide on recombination, then $\Phi_{rot.}$ is identical to the quantum yield for cleavage, Φ_{cleave}. Because the reversion of **B** is a geminate process of a singlet radical pair, there may actually be a preference for returning to the original enantiomer. Therefore, the actual Φ_{cleave} may be somewhat higher than $\Phi_{rot.}$



Scheme 2-5

If the excited states of **7** and **8** were reversible with racemization by recombination of the geminate radical pair **9** or had a very low barrier for inversion, the through-space interaction between the two sulfur atoms at the 1,8-positions

of naphthalene plays an important role particularly for the formation of sulfenic ester **10** on photolysis of **7** and **8**. As shown in Table 2-5, on the basis of disappearance of **7a** and **7a'** and their partial racemization, quantum yields of the cleavage (Φ_{cleave}) of **7a** and **7a'** and their conversion (Φ_{loss}) to **9** are estimated at ≥0.31 and ≥0.76, and 0.27 and 0.62, respectively. The estimated values of $\Phi_{loss}/\Phi_{cleave}$ of **7a** and **7a'** are 0.87 and 0.82, respectively, which are closer to 1 than that of **A** (0.50). The results demonstrate that photoreaction of **7** and **8** proceeds through the mechanism outlined in Scheme 2-5. An excited singlet state initiated cleavage of the carbon-sulfur bond in **7** and **8** gives the diradical **9** to form the reactive intermediates **10** *via* the S-S through-space interaction. Finally, the intermediate sulfenic esters **10** should be converted to the corresponding aldehydes or ketones and naphtho[1,8-*bc*]-1,2-dithiole (**2**).

Experimental Section

General All melting points were uncorrected and were taken on a Yanaco micro melting point apparatus and LABORATORY DEVICES, USA, Model MRX-TEMP II. IR spectra were recorded on a JASCO FT/IR-5000 spectrometer. All NMR spectra were obtained with a JEOL LMN-EX-270 and a BRUKER MSL-400 FT-NMR spectrometer. Mass spectra were taken with a Shimadzu QP-2000 and a JEOL JMX SX102 mass spectrometer. Ultraviolet-visible spectra were recorded on a Hitachi U-3000. Preparative liquid chromatography was performed on a Japan Analytical Industry Co., Ltd., Model LC-09 and LC-908. Gas-chromatographic (GC) data were obtained with a Hitachi 263 gas chromatography equipped with an FID detector and a 5m OV-17 column. High performance liquid chromatography (HPLC) data were collected with a Shimadzu LC-10A system, using a TSK gel ODS-ST column (length, 250 mm; internal diameter, 4.6 mm) and methanol-water as an eluent with monitoring at 254 nm. Photolyses were carried out in a Pyrex round-bottomed flask using a 400 W high pressure mercury lamp. Quantum yield, the sensitization, a cross over, and intensity effect experiments were performed by irradiation with a 500 W ultrahigh pressure mercury lamp equipped with a glass filter and monochromator. All photo-reactions were monitored and quantified by GC, HPLC, or ^{1}H-NMR. Analytical thin-layer chromatography (TLC) was carried out on Merck precoated TLC plate (Kieselgel 60 F_{254}). Silica-gel used for column chromatography was Wako-gel C-200 and Merck kieselgel 60. Elemental analyses were carried out by Chemical Analysis Center at this University.

Materials All reagents were obtained from Wako Pure Chemical Industries, Ltd., Tokyo Kasei Kogyo, Co., Ltd., Kanto Chemicals Co., Inc., or Aldrich Chemical Co. The reagents used as reaction solvents were further purified by general methods.

Synthesis of 1,8-Diiodonaphthalene (1)

In a 3L flask was placed 83.3 g (0.53 mol) of 1,8-diaminonaphthalene in 975 ml of aqueous 6.9 M sulfuric acid cooled to -20 °C and then a solution of 108 g (1.59 mol) of sodium nitrite in ca. 400 ml of water was added, dropwise and with stirring, while the temperature of the mixture was kept at -15 °C to -20 °C. As soon as the addition was complete a solution of 538 g (3.24 mol) of potassium iodide in ca. 450 ml of water was added, dropwise and with stirring. During this addition the reaction mixture was kept at -15 °C to -20 °C and additional portions of concentrated sulfuric acid were added as needed to keep the reaction mixture from freezing. The resulting mixture was warmed to 80 °C, rapidly and with stirring, and then cooled to room temperature. The mixture was filtrated and the black solid residues were collected, pulverized and extracted with several portions of boiling ether (total volume 5 l). The ethereal solution was washed with a saturated aqueous sodium thiosulfate and then dried and concentrated. The residue was separated by silica-gel column chromatography (eluent, hexane) and then recrystallization from hexane gave yellow crystals of diiodine **1** (111 g) in 55%.

1,8-Diiodonaphthalene (1)

mp. 109-110 °C ((lit.[14]) 109 °C); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.05 (t, *J*= 7.8 Hz, 2H, ArH), 7.82 (dd, J = 7.8 Hz, 1.8 Hz, 2H, Ar-H), 8.40 (dd, J_1 = 7.8 Hz, J_2 =1.8 Hz, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 95.99, 126.90, 131.00, 132.06, 135.74, 143.99; MS (m/z) 380 (M^+).

Synthesis of Naphtho[1,8-*cd*]-1,2-dithiole (2)

n-Butyllithium (96 ml of 1.67 N solution in hexane, 160 mmol) was added dropwise at -78 °C to a solution of 1,8-diiodonaphthalene (**1**) (15.2 g, 40 mmol) in tetrahydrofuran (400 ml). After 2 h, elemental sulfur was added at -20 °C, as soon as sulfur had dissolved, with stirring for 6h. To the reaction mixture was added slowly a suspension of sodium borohydride (15.2 g) in 300 ml of ethanol at room temperature. An exothermic reaction occurred and the mixture was kept stirring at room temperature overnight. Aqueous 200 ml of 2 N hydrochloric acid solution was added to decompose excess hydride and then iodine was added until the mixture changed to brown color. The mixture was extracted with ether. The organic layer was dried over anhydrous magnesium sulfate and then evaporated. The residue was separated by silica-gel column chromatography (eluent, hexane) and then recrystallization from hexane to give the red crystals of disulfide **2** (4.3 g) in 56%.

Naphtho[1,8-*cd*]-1,2-dithiole (2)

mp. 115-116 °C ((lit.[15]) 116 °C); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.14 (d, J = 7.6 Hz, 2H, ArH), 7.26 (t, J= 7.6 Hz,, 2H, ArH), 7.35 (d, j = 7.6 Hz, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ

115.90, 121.60, 127.89, 134.74, 135.71, 144.04; MS (m/z) 190 (M^+).

Synthesis of 1,8-Naphthalenedithiol (3)

A solution of naphtho[1,8-*cd*]-1,2-dithiole (**2**) (950 mg, 5.0 mmol) in dry tetrahydrofuran (20 ml) was added into an ice-cooled suspension of sodium borohydride (50 mg, 1.3 mmol) in ethanol (6 ml) under an argon atmosphere. The mixture was stirred for 30 min, quenched with 10% hydrochloric acid, and extracted with ether. The extract was washed with water, dried (magnesium sulfate), and concentrated in vacuum to give dithiol **3** (941 mg, 98%). Recrystallization from tetrahydrifuran-hexane in argon atmosphere afforded colorless leaflets.

1,8-Naphthalenedithiol (3)

mp. 119-120 °C (lit.[18] 115 °C); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 4.14 (s, 2H, SH), 7.21 (t, J = 7.6 Hz, 2H, ArH), 7.51 (d, J = 7.6 Hz,, 2H, ArH), 7.63 (d, J = 7.6 Hz, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 125.68, 128.13, 128.98, 131.62, 132.02, 136.41; MS (m/z) 190 (M^+ -2).

General Procedure for Dithioacetalization

To a well stirred solution of 5 mmol of carbonyl compound and 5 mmol of 1,8-naphthalenedithiol (**3**) in 20 ml of dichloromethane at -20 °C was added dropwise 5 mmol of tetrachlorosilane. The solution was warmed up to room temperature and monitored by TLC. When the reaction was complete (within 2 h.), the solution was quenched with a 10 ml of 5% sodium bicarbonate solution and extracted with

dichloromethane (3 X 100 ml). After drying with magnesium sulfate and removal of the solvent, the residue was separated by silica-gel column chromatography (eluent, tetrachloromethane) and then recrystallization from ethyl acetate-hexane gave the pure product.

Naphtho[1,8-*de*]-1,3-dithiin (4)

Yield 71%; mp. 121-122 °C (lit.[19] 124-125.5 °C); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 4.13 (s, 2H, CH_2), 7.36 (t, J = 8.1 Hz, 2H, ArH), 7.42 (d, J = 8.1 Hz, 2H, ArH), 7.64 (d, J = 8.1 Hz, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 27.92, 125.30, 125.89, 126.24, 127.58, 129.34, 135.09; MS (m/z) 204 (M^+).

2-Phenyl-naphtho[1,8-*de*]-1,3-dithiin (5a)

Yield 98%; mp. 124-125 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 5.42 (s, 1H, CH), 7.36-7.49 (m, 7H, ArH), 7.55-7.58 (m, 2H, ArH), 7.70-7.73 (m, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 46.83, 125.27, 125.48, 125.91, 127.71, 128.84, 129.02, 129.06, 132.04, 135.06, 136.51; MS (m/z) 280 (M^+); Anal. Calcd for $C_{17}H_{12}S_2$: C, 72.82, H, 4.31. Found: C, 72.71, H, 4.21.

2-*p*-Tolyl-naphtho[1,8-*de*]-1,3-dithiin (5b)

Yield 97%; mp. 135-136 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.37 (s, 3H, CH_3). 5.37 (s, 1H. CH), 7.21 (d, J = 7.8 Hz, 2H, ArH), 7.36 (d, J = 7.8 Hz, 2H, ArH), 7.42-7.46 (m, 4H, ArH), 7.68 (d, J = 7.8 Hz, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 21.26, 46.58, 125.25, 125.45, 125.84, 127.60, 128.12, 129.69, 132.22, 133.42, 135.02, 138.99; MS (m/z) 294 (M^+); Anal. Calcd for $C_{18}H_{14}S_2$: C, 73.43, H, 4.79. Found: C, 73.48, H, 4.70.

2-Hexyl-naphtho[1,8-*de*]-1,3-dithiin (5e)

Yield 98%; Oil; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.90 (t, J = 7.3 Hz, 3H, CH_3), 1.28-1.38 (m, 6H, CH_2), 1.57-1.66 (m, 2H, CH_2), 2.02 (q, J = 7.3 Hz, 2H, CH_2), 4.31 (t, J = 7.3 Hz, 1H, CH), 7.35 (t, J = 7.6 Hz, 2H, ArH), 7.43 (dd, J_1 = 7.6 Hz, J_2 = 1.1 Hz, 2H, ArH), 7.63 (dd, J_1 = 7.6 Hz, J_2 = 1.1 Hz, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 14.04, 22.52, 27.01, 28.70, 31.54, 34.67, 42.98, 125.48, 126.04, 126.29, 127.33, 130.21, 134.95; MS (m/z) 288 (M^+).

2-(3-phenyl-2-propene)-naphtho[1,8-*de*]-1,3-dithiin (5f)

Yield 88%; mp. 148-149 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 5.07 (dd, J_1 = 8.4 Hz, J_2 = 1.1 Hz, 1H, CH), 6.39 (dd, J_1 = 15.4 Hz, J_2 = 8.4 Hz, 1H, C=CH), 6.85 (dd, J_1 = 15.4 Hz, J_2 = 1.1 Hz, 1H, C=CH), 7.26-7.41 (m, 9H, ArH), 7.47 (dd, J_1 = 8.1 Hz, J_2 = 1.4 Hz, 2H, ArH), 7.69 (dd, J_1 = 8.1 Hz, J_2 = 1.4 Hz, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 43.76, 124.21, 125.61, 126.36, 126.41, 126.76, 127.66, 128.36, 128.61, 129.81, 134.38, 134.91, 135.71; MS (m/z) 306 (M^+); Anal. Calcd for $C_{19}H_{14}S_2$: C, 74.47, H, 4.60. Found: C, 74.25, H, 4.57.

2-(2-Furyl)-naphtho[1,8-*de*]-1,3-dithiin (5g)

Yield 87%; mp. 67-68 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 5.33 (s, 1H. CH), 6.31 (dd, J_1 = 3.2 Hz, J_2 = 1.9 Hz, 1H, 2-furylH), 6.35 (d, J = 3.2 Hz, 1H, 2-furylH), 7.36-7.40 (m, 2H, ArH), 7.47 (dd, J_1 = 8.1 Hz, J_2 = 1.1 Hz, 2H, ArH), 7.70 (dd, J_1 = 8.1 Hz, J_2 = 1.1 Hz, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 38.60, 109.04, 110.82, 125.46, 125.61, 126.34, 127.84, 129.76, 134.91,

142.73, 150,08; MS (m/z) 270 (M^+); Anal. Calcd for $C_{15}H_{10}O_1S_2$: C, 66.64, H, 3.73. Found: C, 66.50, H, 3.67.

Benzalaldehyde bis(1-naphthyl) dithioacetal (15)

Yield 82%; Oil; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 5.34 (s, 1H, CH), 7.18-7.24 (m, 3H, ArH), 7.25-7.34 (m, 6H, ArH), 7.39 (t, J = 8.4 Hz, 2H, ArH), 7.57 (d, J = 8.4 Hz, 2H, ArH), 7.77 (d, J = 8.4 Hz, 2H, ArH), 7.80 (d, J = 8.4 Hz, 2H, ArH), 8.13 (d, J = 8.4 Hz, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 61.10, 125.36, 125.41, 126.10, 126.70, 127.72, 127.97, 128.36, 128.49, 129.49, 131.27, 133.91, 133.97, 134.05, 140.03; MS (m/z) 408 (M^+).

General Procedure for 2-Substituted Naphtho[1,8-*de*]-1,3-dithiin

n-Butyllithium (1.3 ml of 1.67 N solution in hexane, 2.2 mmol) was added dropwise at -78 °C to a solution of naphtho[1,8-*de*]-1,3-dithiin (**4**) (408 mg, 2.0 mmol) in tetrahydrofuran (20 ml) and stirred for 1 h. To this solution was added electrophiles (2.2 mmol) for 1 h at -78 °C with stirring then warmed up to room temperature and monitored by TLC. When the reaction was complete, the solution was quenched with a 5 ml of water and extracted with dichrolomethane. After drying with magnesium sulfate and removal of the solvent, the residue was separated by silica-gel column chromatography (eluent, tetrachloromethane) and then recrystallization from ethyl acetate-hexane to give the pure product.

General Procedure for 2,2-Disubstituted Naphtho[1,8-*de*]-1,3-dithiin

n-Butyllithium (1.3 ml of 1.67 N solution in hexane, 2.2 mmol) was added dropwise at -78 °C to a solution of 2-phenyl-naphtho[1,8-*de*]-1,3-dithiin (**5a**) (408 mg, 2.0 mmol) in tetrahydrifuran (20 ml) and stirred for 1 h. To this solution was added electrophiles (2.2 mmol) for 1 h at -78 °C with stirring then warmed up to room temperature and monitored by TLC. After the reaction and usual work-up process, the products were separated by silica-gel column chromatography using carbon tetrachloride as an eluent and then recrystallization from ethylacetate-hexane to give the pure product.

2-Methyl-2-phenyl-naphtho[1,8-*de*]-1,3-dithiin (6b)

Yield 97%; mp. 116-117 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.09 (s, 3H, CH_3), 7.25-7,30 (m, 1H, ArH), 7.33-7.39 (m, 4H, ArH), 7.47 (dd, J_1 = 8.0 Hz, J_2 = 1.1 Hz, 2H, ArH), 7.67 (dd, J_1 = 8.0 Hz, J_2 = 1.1 Hz, 2H, ArH), 7.82-7.84 (m, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 30.39, 51.86, 125.23, 125.71, 126.13, 127.48, 127.60, 128.12, 128.50, 131.36, 134.75, 141.90; MS (m/z) 294 (M^+); Anal. Calcd for $C_{18}H_{14}S_2$: C, 73.43, H, 4.79. Found: C, 73.42, H, 4.75.

2-Ethyl-2-phenyl-naphtho[1,8-*de*]-1,3-dithiin (6c)

Yield 98%; mp. 66-67 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.91 (t, J = 7.56, 3H, CH_3), 2.34 (q, J = 7.56, 2H, CH_2), 7.19-7,36 (m, 5H, ArH), 7.47 (dd, J_1 = 8.0 Hz, J_2 = 1.4 Hz, 2H, ArH), 7.61 (dd, J_1 = 8.0 Hz, J_2 = 1.4 Hz, 2H, ArH), 7.76-7.79 (m, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 9.49, 35.38, 57.41, 125.71, 126.09, 126.36, 127.49, 127.60, 127.89, 128.28, 130.55, 134.66, 140.56;

MS (m/z) 308 (M^+); Anal. Calcd for $C_{19}H_{16}S_2$: C, 73.98, H, 5.23. Found: C, 73.83, H, 5.27.

2-(1-Phenyl-1-hydroxy-benzyl)-naphtho[1,8-*de*]-1,3-dithiin (6d) Yield 96%; mp. 142-143 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.02 (d, J = 3.0 Hz, 1H, OH), 5.11 (d, J = 3.0, 1H, CH), 6.83-6.87 (m,2H, ArH), 7.09-7.15 (m, 2H, ArH), 7.18-7.24 (m, 3H, ArH), 7.33-7.41 (m, 3H, ArH), 7.51-7.57 (m, 4H, ArH), 7.65 (dd, J_1 = 8.1 Hz, J_2 = 1.1 Hz, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 49.33, 57.32, 125.73, 126.42, 126.52, 126.97, 127.46, 127.55, 127.98, 128.05, 128.46, 130.05, 130.80, 134.61, 134.86, 140.54; MS (m/z) 386 (M^+); IR(KBr) 3558 cm^{-1} (O-H); Anal. Calcd for $C_{24}H_{18}O_1S_2$: C, 74.58, H, 4.69. Found: C, 74.71, H, 4.66.

Conversion of 6d to the Corresponding Ether 6e

To a 20 ml of tetrahydrofuran solution containing sodium hydride (32 mg, 1.34 mmol) was added **6d** (356 mg, 0.89 mmol) dissolved in 10 ml of tetrahydrifuran with stirring at 0 °C for 30 min and was added subsequently methyl iodide (82 μl, 1.34 mmol) for 1 h. After the reaction and usual work-up, the product was purified by silica-gel column chromatography using ethylacetate-hexane = 1 : 9 as an eluent and then recrystallization from ethylacetate-hexane to give the product **6e** (238 mg, 67%)

2-(1-Phenyl-1-methoxy-benzyl)-naphtho[1,8-*de*]-1,3-dithiin (6e) mp. 117-118 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.28 (s, 3H, CH_3), 4.77 (s, 1H, CH), 6.88-6.90 (m,2H, ArH), 7.05-7.08 (m, 3H, ArH), 7.16-7.21 (m, 2H, ArH), 7.24-7.30 (m, 3H, ArH), 7.41-7.43

(m, 1H, ArH), 7.47-7.55 (m, 3H, ArH), 7.60-7.64 (m, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 57.99, 62.48, 88.66, 125.70, 126.47, 126.52, 127.22, 127.30, 127.53, 128.45, 128.91, 129.63, 130.17, 130.26, 134.45, 135.44, 137.86; MS (m/z) 400 (M^+); IR(KBr) 1207, 1075 cm^{-1} (C-O-C); Anal. Calcd for $C_{24}H_{18}O_1S_2$: C, 74.96, H, 5.03. Found: C, 75.07, H, 4.93.

General Procedure for Naphtho[1,8-*de*]-1,3-dithiin-1-oxides

To a solution of sulfide (1.5 mmol) in 50 ml dichloromethane, *m*-chloroperbenzoic acid (259 mg, 1.5 mmol) dissolved in 50 ml dichloromethane was added at -20 °C. The solution was stirred for 12 h and then allowed to warm to room temperature. Ammonia gas was bubbled into the reaction mixture for a few minutes at room temperature, and white precipitates, ammonium *m*-chlorobenzoate, was formed. A white solid was filtered off and the solvent was evaporated. The reaction mixture was purified by silica-gel column chromatograpy (eluent, ethylacetate-hexane) to give the products as the diasteroisomers.

2-Phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-oxide

7a; Yield 98%; mp. 150-151 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 4.92 (s, 1H, CH), 7.45-7.59 (m, 6H, ArH), 7.62 (dd, J_1 = 7.6 Hz, J_2 = 1.4 Hz, 1H, ArH), 7.72 (t, J = 7.6 Hz, 1H, ArH), 7.84 (dd, J_1 = 7.6 Hz, J_2 = 1.4 Hz, 1H, ArH), 8.30 (dd, J_1 = 7.6 Hz, J_2 = 1.4 Hz, 1H, ArH), 8.28 (dd, J_1 = 7.6 Hz, J_2 = 1.4 Hz, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 63.45, 125.93, 126.16, 126.22, 126.33, 126.78, 127.48, 128.91, 129.13, 129.31, 129.65, 131.70,

131.73, 134.34, 141.60; IR (KBr) 1054 cm^{-1} (SO); MS (m/z) 296 (M^+); Anal. Calcd for $C_{17}H_{12}O_1S_2$: C, 68.89, H, 4.08. Found: C, 68.74, H, 3.97.

7a'; Yield 16%; mp. 137-138 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 5.35 (s, 1H, CH), 7.45-7.59 (m, 5H, ArH), 7.71 (t, J = 7.6 Hz, 1H, ArH),7.76 (t, J = 7.6 Hz, 1H, ArH), 7.89 (dd, J_1 = 7.6 Hz, J_2 = 1.4 Hz, 1H, ArH), 7.98 (dd, J_1 = 7.6 Hz, J_2 = 1.4 Hz, 1H, ArH), 8.12 (dd, J_1 = 7.6 Hz, J_2 = 1.4 Hz, 1H, ArH), 8.20 (dd, J_1 = 7.6 Hz, J_2 = 1.4 Hz, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) Broad peaks; IR (KBr) 1036 cm^{-1} (SO); MS (m/z) 296 (M^+); Anal. Calcd for $C_{17}H_{12}O_1S_2$: C, 68.89, H, 4.08. Found: C, 68.83, H, 4.10.

2-*p*-Tolyl-naphtho[1,8-*de*]-1,3-dithiin-1-oxide

7b; Yield 68%; mp. 230-231 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.40 (s, 3H, CH_3). 4.90 (s, 1H. CH), 7.28 (d, J = 8.2 Hz, 2H, ArH), 7.41 (d, J = 8.2 Hz, 2H, ArH), 7.49 (t, J = 7.8 Hz, 1H, ArH), 7.62 (d, J = 7.8 Hz, 1H, ArH), 7.72 (t, J = 7.8 Hz, 1H, ArH), 7.84 (d, J = 7.8 Hz, 1H, ArH), 8.03 (d, J = 7.8 Hz, 1H, ArH), 8.28(d, J = 7.8 Hz, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 21.33, 63.42, 126.00, 126.424, 126.36, 126.39, 126.77, 127.48, 128.68, 128.81, 129.42, 130.12, 131.68, 134.41, 139.84, 141.83; IR (KBr) 1050 cm^{-1} (SO); MS (m/z) 310 (M^+); Anal. Calcd for $C_{18}H_{14}O_1S_2$: C, 69.64, H, 4.53. Found: C, 69.62, H, 4.52.

7b'; Yield 23%; mp. 200-201 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.27 (s, 3H, CH_3). 5.31 (s, 1H. CH), 7.04-7.07 (br m, 2H, ArH), 7.21-7.24 (br m, 2H, ArH), 7.46-7.54 (m, 1H, ArH), 7.68-7.80 (m, 3H, ArH), 7.91-8.00 m, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$)

Broad peaks; IR (KBr) 1048 cm^{-1} (SO); MS (m/z) 310 (M^+); Anal. Calcd for $C_{18}H_{14}O_1S_2$: C, 69.64, H, 4.53. Found: C, 69.58, H, 4.50.

2-Hexyl-naphtho[1,8-*de*]-1,3-dithiin-1-oxide (7e)

7e; Yield 74%; Oil; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.87-0.91 (m, 3H, CH_3), 1.29-1.34 (m, 6H, CH_2), 1.39-1.41 (m, 1H, CH_2), 1.42-1.45 (m, 1H, CH_2), 1.78-1.81 (m, 1H, CH_2), 1.91-1.94 (m, 1H, CH_2), 2.47-2.50 (m, 1H, CH_2), 3.98 (dd, J_1 = 9.6 Hz, J_2 = 3.8 Hz, 1H, CH), 7.44 (t, J = 7.7 Hz, 1H, ArH), 7.59 (d, J = 7.7 Hz, 1H, ArH), 7.67 (t, J = 7.7 Hz, 1H, ArH), 7.78 (d, J = 7.7 Hz, 1H, ArH), 7.98 (d, J = 7.7 Hz, 1H, ArH), 8.18 (d, J = 7.7 Hz, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 13.97, 22.43, 25.91, 28.24, 28.83, 31.37, 60.17, 125.93, 126.03, 126.12, 126.30, 126.96, 127.27, 127.99, 130.91, 131.68, 134.28; IR (KBr) 1079 cm^{-1} (SO); MS (m/z) 304 (M^+).

7e'; Yield 10%; Oil; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.79-0.83 (m, 3H, CH_3), 1.18-1.23 (m, 7H, CH_2), 1.26-1.33 (m, 1H, CH_2), 1.63-1.65 (m, 1H, CH_2), 2.10-2.14 (m, 1H, CH_2), 4.15 (dd, J_1 = 10.6 Hz, J_2 = 3.3 Hz, 1H, CH), 7.47 (t, J = 7.7 Hz, 1H, ArH), 7.58 (d, J = 7.7 Hz, 1H, ArH), 7.69 (t, J = 7.7 Hz, 1H, ArH), 7.79 (d, J = 7.7 Hz, 1H, ArH), 7.98 (d, J = 7.7 Hz, 1H, ArH), 8.13 (d, J = 7.7 Hz, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) Broad peaks; IR (KBr) 1060 cm^{-1} (SO); MS (m/z) 304 (M^+).

2-(3-phenyl-2-propene)-naphtho[1,8-*de*]-1,3-dithiin-1-oxide

7f; Yield 55%; mp. 184-185 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 4.73 (d, J = 8.9 Hz, 1H, CH), 6.30 (dd, J_1 = 15.9 Hz, J_2 = 8.9 Hz,

1H, C=CH), 6.96 (d, J = 15.9 Hz, 1H, C=CH), 7.29-7.37 (m, 3H, ArH), 7.41-7.44 (m, 2H, ArH), 7.49 (t, J = 7.7 Hz, 1H, ArH), 7.63 (d, J = 7.7 Hz, 1H, ArH), 7.70 (t, J = 7.7 Hz, 1H, ArH), 7.83 (d, J = 7.7 Hz, 1H, ArH), 8.03 (d, J = 7.7 Hz, 1H, ArH), 8.21 (d, J = 7.7 Hz, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 62.25, 118.22, 125.93, 126.00, 126.11, 126.15, 127.01, 127.15, 127.55, 127.69, 128.34, 128.66, 128.88, 132.27, 134.38, 135.27, 139.10; IR (KBr) 1065 cm^{-1} (SO); MS (m/z) 306 (M^+); Anal. Calcd for $C_{19}H_{14}O_1S_2$: C, 70.77, H, 4.38. Found: C, 70.84, H, 4.37.

7f'; Yield 33%; mp. 135-136 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 4.95 (d, J = 8.4 Hz, 1H, CH), 5.79 (dd, J_1 = 15.8 Hz, J_2 = 8.4 Hz, 1H, C=CH), 6.84 (d, J = 15.8 Hz, 1H, C=CH), 7.08-7.17 (m, 5H, ArH), 7.50 (t, J = 7.8 Hz, 1H, ArH), 7.63 ((d, J = 7.8 Hz, 1H, ArH), 7.70 (d, J = 7.8 Hz, 1H, ArH), 7.82 (d, J = 7.8 Hz, 1H, ArH), 8.00 (d, J = 7.8 Hz, 1H, ArH), 8.14 (d, J = 7.7 Hz, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) Broad peaks; IR (KBr) 1052 cm^{-1} (SO); MS (m/z) 306 (M^+); Anal. Calcd for $C_{19}H_{14}O_1S_2$: C, 70.77, H, 4.38. Found: C, 70.74, H, 4.40.

2-(2-Furyl)-naphtho[1,8-*de*]-1,3-dithiin-1-oxide

7g; Yield 74%; mp. 118-119 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 5.12 (s, 1H. CH), 6.46 (dd, J_1 = 3.0 Hz, J_2 = 1.9 Hz, 2H, 2-furylH), 6.58 (d, J = 3.0 Hz, 1H, 2-furylH), 7.50 (t, J = 7.7 Hz, 1H, ArH), 7.54 (dd, J_1 = 3.0 Hz, J_2 = 1.9 Hz, 1H, 2-furylH), 7.63 (dd, J_1 = 7.7 Hz, J_2 = 1.4 Hz, 1H, ArH), 7.71 (t, J = 7.7 Hz, 1H, ArH), 7.85 (dd, J_1 = 7.7 Hz, J_2 = 1.4 Hz, 2H, ArH), 8.04 (dd, J_1 = 7.7 Hz, J_2 = 1.4 Hz, 2H, ArH), 8.24 (dd, J_1 = 7.7 Hz, J_2 = 1.4 Hz, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 57.39,

111.40, 112.31, 125.86, 126.08, 126.18, 127.06, 127.16, 127.70, 128.33, 132.22, 134.43, 140.71, 144.55, 144.65; IR (KBr) 1056 cm^{-1} (SO); MS (m/z) 286 (M^+); Anal. Calcd for $C_{15}H_{10}O_2S_2$: C, 62.91, H, 3.52. Found: C, 62.77, H, 3.50.

7g'; Yield 22%;mp. 164-165 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 5.50 (s, 1H. CH), 5.78-5.83 (br s, 1H, 2-furylH), 6.12-6.18 (br s, 1H, 2-furylH), 7.23-7.25 (br s, 1H, 2-furylH), 7.51 (t, J = 7.7 Hz, 1H, ArH), 7.63 (dd, J_1 = 7.7 Hz, J_2 = 0.8 Hz, 1H, ArH), 7.67 (t, J = 7.7 Hz, 1H, ArH), 7.83 (dd, J_1 = 7.7 Hz, J_2 = 0.8 Hz, 1H, ArH), 8.03 (dd, J_1 = 7.7 Hz, J_2 = 0.8 Hz, 1H, ArH), 8.08 (dd, J_1 = 7.7 Hz, J_2 = 0.8 Hz, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) Broad peaks; IR (KBr) 1015 cm^{-1} (SO); MS (m/z) 286 (M^+); Anal. Calcd for $C_{15}H_{10}O_2S_2$: C, 62.91, H, 3.52. Found: C, 62.98, H, 3.61.

2-(1-Phenyl-1-hydroxy-benzyl)-naphtho[1,8-*de*]-1,3-dithiin-1-oxide

8d; Yield 62%; mp. 205-206 °C (decomp.); 5.30 (s, 1H, OH), 5.48-5.54 (br s, 1H, CH), 6.79-6.83 (br s, 1H, ArH), 7.04-7.23 (m, 4H, ArH), 7.43-7.64 (m, 4H, ArH), 7.65-7.83 (m, 3H, ArH), 7.98 (d, J = 7.8 Hz, 1H, ArH), 8.14 (d, J = 7.8 Hz, 1H, ArH), 8.22 (d, J = 7.8 Hz, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) Broad peaks; IR (KBr) 3214 cm^{-1} (OH), 1027 cm^{-1} (SO); MS (m/z) 402 (M^+); Anal. Calcd for $C_{24}H_{18}O_2S_2$: C, 71.61, H, 4.50. Found: C, 71.84, H, 4.48.

8d';Yield 31%; mp. 195-196 °C (decomp.); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 5.21 (d, J = 3.0 Hz, 1H, OH), 5.96 (d, J = 3.0 Hz, 1H,

CH), 6.94-7.05 (m, 5H, ArH), 7.09-7.23 (m, 5H, ArH), 7.37-7.49 (m, 2H, ArH), 7.65 (dd, J_1 = 8.0 Hz, J_2 = 1.4 Hz, 1H, ArH), 7.81-7.85 (m, 2H, ArH), 7.91 (dd, J_1 = 8.0 Hz, J_2 = 1.4 Hz, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 60.36, 81.22, 123.40, 125.21, 126.67, 126.95, 127.35, 127.51, 127.71, 127.94, 128.14, 128.34, 128.55, 129.00, 132.29, 133.10, 133.50, 134.11, 135.56, 137.20; IR (KBr) 3194 cm^{-1} (OH), 1027 cm^{-1} (SO); MS (m/z) 402 (M^+); Anal. Calcd for $C_{24}H_{18}O_2S_2$: C, 71.61, H, 4.50. Found: C, 71.77, H, 4.52.

2-(1-Phenyl-1-methoxy-benzyl)-naphtho[1,8-*de*]-1,3-dithiin-1-oxide

8e; Yield 74%; mp. 250-251 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.41 (s, 3H, CH_3), 5.04 (s, 1H, CH), 6.84-7.11 (m, 5H, ArH), 7.16-7.22 (m, 2H, ArH), 7.27-7.34 (m, 2H, ArH), 7.36-7.48 (m, 3H, ArH), 7.60-7.66 (m, 2H, ArH), 7.82-7.93 (m, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) Broad peaks; IR(KBr) 1094 cm^{-1} (C-O-C), 1065 cm^{-1} (SO); MS (m/z) 416 (M^+); Anal. Calcd for $C_{24}H_{18}O_1S_2$: C, 72.09, H, 4.84. Found: C, 72.00, H, 4.77.

8e'; Yield 19%; mp. 199-200 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.34 (s, 3H, CH_3), 5.19 (s, 1H, CH), 6.84-6.98 (m, 3H, ArH), 7.11-7.19 (m, 2H, ArH), 7.26-7.42 (m, 5H, ArH), 7.36-7.48 (m, 3H, ArH), 7.61-7.63 (m, 1H, ArH), 7.71-7.77 (m, 1H, ArH), 7.82-7.89 (m, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) Broad peaks; IR(KBr) 1094 cm^{-1} (C-O-C), 1060 cm^{-1} (SO); MS (m/z) 416 (M^+); Anal. Calcd for $C_{24}H_{18}O_1S_2$: C, 72.09, H, 4.84. Found: C, 72.12, H, 4.89.

Benzalaldehyde bis(1-naphthyl)-dithioacetal-S-oxide (15)

Yield 89%; mp. 112-113 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.73 (s, 1H, CH), 7.29-7.35 (m, 5H, ArH), 7.36-7.42 (m, 2H, ArH), 7.63-7.68 (m, 2H, ArH), 7.79-7.82 (m, 2H, ArH); IR(KBr) 1060 cm^{-1} (SO); MS (m/z) 424 (M^+); Anal. Calcd for $C_{27}H_{20}O_1S_2$: C, 76.38, H, 4.74. Found: C, 76.04, H, 4.30.

General Procedure for 2,2-Disubstituted Naphtho[1,8-*de*]-1,3-dithiin-1-oxides

2,2-Disubstituted naphtho[1,8-*de*]-1,3-dithiin-1-oxides were prepared from 2-phenyl-naphtho[1,8-*de*]-1,3-dithiin (**7a**) with several electrophiles in the presence of base by the general methods (A) and (B)

(A): a Lithium diisipropylamide solution was prepared from diisopropylamide (0.21 ml, 1.5 mmol) in 10 ml of a tetrahydrofuran solution and 1.0 ml of a 1.67 M n-butyllithium (in hexane solution) at -20 °C. To this solution was added 2-phenyl-naphtho[1,8-*de*]-1,3-dithiin (420 mg, 1.5 mmol) in 10 ml of tetrahydrofuran at -78 °C and stirred for 1 h. To this solution was added electrophiles (2.2 mmol) for 1h at -78 °C with stirring then warmed up to room temperature and monitored by TLC. After the reaction and usual work-up process, the products were separated by silica-gel column chromatography using tetrachloromethane as an eluent to give the products as the diasteroisomers.

(B): To a 20 ml of tetrahydrofuran solution containing sodium hydride (36 mg, 1.5 mmol) was added 2-phenyl-naphtho[1,8-*de*]-1,3-dithiin (420 mg, 1.5 mmol) dissolved in 10 ml of tetrahydrofuran with stirring at 50 °C for 30 min and was

added subsequently electorophiles (1.5 mmol) for 2 h. After the reaction and usual work-up, the product was purified by silica-gel column chromatography using ethylacetate-hexane as an eluent to give the products as the diasteroisomers.

2-Methyl-2-phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-oxide

8b; Yield 46%; mp. 161-162 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.73 (s, 3H, CH_3), 7.41-7.51 (m, 3H, ArH), 7.54 (t, J = 7.8 Hz, 1H, ArH), 7.67 (dd, J_1 = 7.8 Hz, J_2 = 1.4 Hz, 2H, ArH), 7.71-7.76 (m, 3H, ArH), 7.84 (dd, J_1 = 7.8 Hz, J_2 = 1.4 Hz, 2H, ArH), 8.02 (dd, J_1 = 7.8 Hz, J_2 = 1.4 Hz, 2H, ArH), 8.22 (dd, J_1 = 7.8 Hz, J_2 = 1.4 Hz, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ Broad peaks; IR (KBr) 1048 cm^{-1} (SO); MS (m/z) 310 (M^+); Anal. Calcd for $C_{18}H_{14}O_1S_2$: C, 69.64, H, 4.53. Found: C, 69.62, H, 4.52.

8b'; Yield 30%; mp. 137-138 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.18 (s, 3H, CH_3), 6.95-7.08 (br s, 3H, ArH), 7.41-7.54 (m, 2H, ArH), 7.55-7.58 (m, 2H, ArH), 7.63-7.69 (m, 2H, ArH), 7.78 (d, J = 7.6 Hz, 1H, ArH), 8.01 (d, J = 7.6 Hz, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) Broad peaks; IR (KBr) 1025 cm^{-1} (SO); MS (m/z) 310 (M^+); Anal. Calcd for $C_{18}H_{14}O_1S_2$: C, 69.64, H, 4.53. Found: C, 69.55, H, 4.52.

2-Ethyl-2-phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-oxide

8c; Yield 48%; mp. 141-142 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.86 (t, J = 7.3 Hz, 3H, CH_3), 2.47 (q, J = 7.3, 2H, CH_2), 7.30-7,82 (m, 11H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) Broad peaks; IR (KBr)

1064 cm^{-1} (SO); MS (m/z) 324 (M^+); Anal. Calcd for $C_{19}H_{16}O_1S_2$: C, 70.33, H, 4.97. Found: C, 70.10, H, 4.91.

8c'; Yield 24%; mp. 118-120 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.04 (t, J = 7.3 Hz, 3H, CH_3), 2.44 (q, J = 7.3, 1H, CH_2), 2.87 (q, J = 7.3, 1H, CH_2), 6.97-7.01 (m, 3H, ArH), 7.41-7.55 (m, 4H, ArH), 7.65-7.78 (m, 2H, ArH), 7.76 (d, J = 8.1 Hz, 1H, ArH), 7.99 (d, J = 8.1 Hz, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) Broad peaks; IR (KBr) 1058 cm^{-1} (SO); MS (m/z) 324 (M^+); Anal. Calcd for $C_{19}H_{16}O_1S_2$: C, 70.33, H, 4.97. Found: C, 70.22, H, 4.50.

2-Phenyl-2-(2-pyridyl)-naphtho[1,8-*de*]-1,3-dithiin-1-oxide

8f; Yield 53%; p. 214-215 °C (decomp.); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 6.84-7.12 (br s, 3H, ArH), 7.30-7.59 (m, 5H, ArH), 7.51-7.89 (m, 4H, ArH), 8.06-8.22 (br s, 2H, ArH), 8.61-8.76 (br s, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) Broad peaks; IR (KBr) 1060 cm^{-1} (SO); MS (m/z) 373 (M^+); Anal. Calcd for $C_{22}H_{15}N_1O_1S_2$: C, 70.75, H, 4.05, N, 3.75. Found: C, 70.67, H, 4.03, N, 3.75.

8f'; Yield 27%; mp. 198-199 °C (decomp.); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 6.91-7.13 (br s, 4H, ArH), 7.14-7.43 (m, 3H, ArH), 7.49-7.71 (m, 5H, ArH), 7.76-7.84 (m, 1H, ArH), 8.12-8.26 (br s, 1H, ArH), 8.72-8.85 (br s, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) Broad peaks; IR (KBr) 1064 cm^{-1} (SO); MS (m/z) 373 (M^+); Anal. Calcd for $C_{22}H_{15}N_1O_1S_2$: C, 70.75, H, 4.05, N, 3.75. Found: C, 70.60, H, 4.10, N, 3.64.

2-(1,3-Diphenyl-1-oxopropyl)-2-phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-oxide (8g)

Yield 77%; mp. 190-191 °C (decomp.); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.90 (dd, J_1 = 17.6 Hz, J_2 = 3.0 Hz, 1H, CH_2), 4.34 (dd, J_1 = 17.6 Hz, J_2 = 3.0 Hz, 1H, CH_2), 4.71 (dd, J_1 = 3.0 Hz, J_2 = 1.1 Hz, 1H, CH), 6.82-6.89 (m, 3H, ArH), 7.18-7.34 (m, 5H, ArH), 7.38-7.43 (m, 2H, ArH), 7.50-7.58 (m, 5H, ArH), 7.66-7.73 (m, 3H, ArH), 7.88-7.91 (m, 2H, ArH), 8.19 (d, J = 7.8 Hz, 1H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 40.00, 50.26, 73.08, 126.04, 126.15, 127.26, 127.30, 127.46, 127.67, 127.75, 127.78, 127.89, 128.01, 128.09, 128.50, 128.88, 129.45, 129.94, 130.60, 133.08, 133.42, 133.69, 136.60, 137.20, 139.16, 196.73; IR(KBr) 1692 cm^{-1} (CO), 1042 cm^{-1} (SO); MS (m/z) 504 (M^+); Anal. Calcd for $C_{32}H_{20}O_2S_2$: C, 76.16, H, 4.79. Found: C, 76.02, H, 4.77.

Synthesis of ^{18}O-Labeled 2-Phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-oxide

To a solution of 2-phenyl-naphtho[1,8-*de*]-1,3-dithiin **7a** (280 mg, 1.0 mmol) in dichloromethane (3 ml) was added at room temperature a solution of ^{18}O-labeled water (^{18}O content>99%) (0.15 ml, 8.3 mmol) in pyridine (0.6 ml) followed by dropwise addition of a solution of bromine (1.1 mmol) in dichloromethane (3 ml) at -78 °C. The solution was stirred for 1 h, and sodium thiosulfate (0.3 g) was added. After usual work up and purification by silica-gel column chromatograpy (eluent, ethylacetate-hexane = 1 : 1), ^{18}O-labeled 2-phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-oxide was obtained in 30% yield (^{18}O content>97%).

General Photolysis Procedure

A solution of sulfoxides (0.1 mmol) in a solvent (5 ml) was placed in a Pyrex round-bottomed flask equipped with a stirred bar and rubber septum. The solution was bubbled with Ar for 30 min to remove O_2. Irradiation of samples were carried out using a 400 W high pressure mercury lamp while being stirred. The reaction progress was monitored by GC, HPLC, or ^{1}H NMR spectroscopy. After irradiation, the solvent was evaporated and purified by preparative HPLC, and the products were characterized by NMR and GC-MS spectroscopies.

Product Identification

Identification of the products such as **11a-e** and **12a-c** was carried out based on comparison of the authentic samples in GC, GC-mass, HPLC, or ^{1}H-NMR data.

1-Phenyl-1-hydroxy-acetophenone (12d)

^{1}H-NMR (270 MHz, $CDCl_3$) δ 4.55 (d, J = 6.0 Hz, 1H, OH), 5.96 (d, J = 6.0 Hz, 1H, C=CH), 7.26-7.34 (m, 5H, ArH), 7.37-7.42 (m, 2H, ArH), 7.50-7.55 (m, 1H, ArH),7.90-7.93 (m, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 76.21, 127.76, 128.57, 128.68, 129.10, 129.13, 133.46, 133.91, 138.98, 198.94; MS (m/z) 212 (M^+).

1-Phenyl-1-methoxy-acetophenone (12e)

^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.46 (s, 1H. CH_3), 5.51 (s, 1H, CH), 7.29-7.54 (m, 8H, ArH), 7.97-8.01 (m, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 57.47, 86.18, 127.62, 128.46, 128.55, 128.86, 129.02, 133.23, 134.97, 136.03, 179.92; MS (m/z) 226 (M^+).

2-Benzoylpyridine (12f)

^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.46-7.52 (m, 3H, ArH), 7.57-7.63 (m, 1H, ArH), 7.88-7.94 (m, 1H, ArH), 8.03-8.08 (m, 3H, ArH), 8.72-8.74 (m, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 124.60, 126.15, 128.14, 130.94, 132.90, 136.21, 137.04, 148.55, 155.04, 193.89; MS (m/z) 183 (M^+).

1,2,3-Triphenyl-1,4-butanedione (12g)

^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.30 (dd, J_1 = 18.0 Hz, J_2 = 3.7 Hz, 1H, CH_2), 4.22 (dd, J_1 = 18.0 Hz, J_2 = 10.0 Hz, 1H, CH_2), 5.33 (dd, J_1 = 10.0 Hz, J_2 = 3.7 Hz, 1H, CH_2), 7.25-7.55 (m, 11H, ArH), 7.96-8.00 (m, 2H, ArH), 8.02-8.05 (m, 2H, ArH); MS (m/z) 314 (M^+).

Sulfenic ester **10a** was unable to isolate by silica-gel chromatography which results in decomposition of **10a** and hence the compound **10a** was obtained by liquid chromatography of the reaction mixture by stopping the photolysis of **7a** at the optimum point of conversion of **7a** to **10a**. Compound **10a** was approximately 95% pure as determined by ^{1}H-NMR spectroscopy. The major impurity was naphtho[1,8-*cd*]-1,2-dithiole and benzaldehyde.

3-Hydro-3-phenyl-naphtho[1,8-*ef*][1,4]dithia[2]oxepine (10a)

Oil ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.73 (s, 1H, CH), 7.29-7.35 (m, 5H, ArH), 7.36-7.42 (m, 2H, ArH), 7.63-7.68 (m, 2H, ArH), 7.79-7.82 (m, 2H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 97.17, 125.73, 126.14, 126.25, 128.49, 128.82, 128.90, 130.92, 131.24, 131.38,

134.35, 134.62, 136.48, 138.44, 139.08; UV-vis (CH_2Cl_2) λ_{max} = 352 nm ($\varepsilon = 3.58 \times 10^4$); MS (m/z) 296 ($M^+$).

Irradiation of 2-Phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-oxide at 313 nm

A solution of 2-phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-oxide (10 mg, 0.03 mmol) in a solvent (5 ml) was placed in a cylindrical quartz tube equipped with a stirred bar and silicon septum. The solution was bubbled with Ar for 30 min to remove O_2. Irradiation of samples was carried out using the output of a 500 W high pressure mercury lamp filtered through a Toshiba UVD33S filter and a monochromator set at 313 nm under conditions of complete light absorption. The reaction progress was monitored by HPLC or ^1H NMR spectroscopy. After irradiation, the solvent was evaporated and purified by the preparative HPLC, and the products were characterized by NMR and GC-MS spectroscopies.

Benzophenone Dependence on the Photolysis of 2-Phenyl naphtho[1,8-*de*]-1,3-dithiin-1-oxide

A solution of 2-phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-oxide (5 mg, 1.68×10^{-2} mmol) and benzophenone (0.04, 0.09, and 0.17 mmol, respectively) in dichloromethane was placed in a cylindrical quartz tube equipped with a stirrer bar and silicon septum. The solution was bubbled with Ar for 30 min to remove O_2. Irradiation of samples was carried out using the output of a 500 W high pressure mercury lamp filtered through a Toshiba UVD33S filter and a monochromator set at 366 nm. Quantification was done with HPLC. Maleic anhydride was used

as an external standard for HPLC. Yields were determined from solutions and irradiation times were kept under 1 h. The measurement of yields was several times by HPLC detection.

Cross over of ^{18}O-Labeled 2-Phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-oxide and 2-*p*-Tolyl-naphtho[1,8-*de*]-1,3-dithiin-1-oxide

2-Phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-oxide (29.6 mg, 0.1 mmol) and 2-*p*-tolyl-naphtho[1,8-*de*]-1,3-dithiin-1-oxide (31.0 mg, 0.1 mmol) were dissolved in 10 ml of deoxygenated benzene. The solution was irradiated with a high pressure mercury lamp (400 W) until sulfoxides completely disappeared. The products and the ^{18}O content were determined with GC-MS spectrometry.

Quantum Yields

The measurement of the quantum yields was carried out using the output of a 500 W high pressure mercury lamp filtered through a Toshiba UVD33S filter and a monochromator set at 313 nm under conditions of complete light absorption. The fulgide, (E)-α-(2,5-dimethyl-3-furyl-ethylidene)(isopropylidene) succinic anhydride, which has a quantum yield of 0.20 for its photocolouration at 313 nm in toluene was used as an actinometer. Quantification was done with HPLC. Maleic anhydride was used as an external standard for HPLC. Sample and actinometer cells were sequentially irradiated. The actinometer cells were used to determine the photo-flux which was then used to convert the rate of loss of the material into a quantum yield. All quantum yields were determined from solutions that began at concentration of 3-6 mM, and

conversions were kept under 5%. The measurement of quantum yields was several times by HPLC detection.

Effect of Light Intensity

The measurement of the light intensity effect was carried out using the output of a 500 W high pressure mercury lamp filtered through a Toshiba UVD33S filter and a monochromator set at 313 nm under conditions of complete light absorption. The light intensity was attenuated by using a quartz filter (313 nm; 27%, 52%, and 83%). Quantification was done with HPLC. Maleic anhydride was used as an external standard for HPLC. Yields were determined from solutions that began at concentration of 6 mM, and irradiation times were kept under 1 h. The measurement of yields was several times by HPLC detection.

References

1) a) Arens, J. F.; Froling, A. *Rec. Trav. Chim. Pays-Bas* **1959**, 78, 663. b) Froling, A. Arens, J. F. *Rec. Trav. Chim. Pays-Bas* **1962**, 81, 1009.

2) Grobel, B.-T.; Seebach, D. *Synthesis* **1977**, 357.

3) Seebach, D.; Corey, E. J. *J, Org, Chem.* **1975**, 40, 231, and references therin.

4) Hase, T. A.; Koskimes, J. K., *Aldrichimica Acta* **1981**, 14, 73; **1982**, 15, 35.

5) a) Corey, E. J.; Erickson, B. W. *J. Org. Chem.* **1971**, 31, 3553; b) Seebach, D.; Neumann, H. *Chem. Ber.* **1974**, 107, 847; c) Ballini, R.; Petrini,M. *Synthesis* **1990**, 336; d) Taguchi, T.; Okamura, H.; Takei, H. *Chem. Lett.* **1975**, 853.

6) a) Chattopadhyahya, J. B.; Rama Rao, A. V. *Tetrahedron Lett.* **1973**, 3735; b) Huurdeman, W. F. J.; Wynberg, H.; Emerson, D. W. *ibid.* **1971**, 3449; c) Hojo, M.; Masuda, R. *Synthesis* **1976**, 678; d) Nishida, K.; Yokota, K.; Nakayama, D.; Sumiya, T.; Node, M.; Fuji, K. *Tetrahedron Lett.* **34**, 345 (1993).

7) a) Fetizon, M.; Jurion, M. *J. Chem. Soc., Chem. Commun.* **1972**, 382; b) Wang-Chang, H. L. *Tetrahedron Lett.* **1972**, 1989; c) Oishi, T.; Takechi, H.; Kamemoto, K.; Ban, Y. *ibid.* **1972**, 1085; d) Stahl, I.; Hetscchko, M.; Gosselck, J. *ibid.* **1971**, 4077; e) Ho, T. L.; Wong, C. M. *Synthesis* **1972**, 561.

8) a) Takahashi, T. T.; Nakamura, C. Y.; Satoh, J. Y. *J. Chem. Soc., Chem. Commun.* **1977**, 680; b) Hoshino, O.; Sawai, S. ; Umezawa, B. *Chem. Pharm. Bull.* **1979**, 27, 538; c) Kamata,

M.; Kato, Y.; Hasegawa, E. *Tetrahedron Lett.* **1991**, 32, 4349.

9) a) Martre, A. M.; Mousset, B.; Rhlid, R. B.; Veschambre, H. *Tetrahedron Lett.* **1990**, 31, 2599; b) Glass, R. S.; Petsom, A.; Wilson, G. S. *J. Org. Chem.* **1986**, 51, 4337; c) Gourcy, J.; Martigny, P.; Simonet, J.; Jeminet, G. *Tetrahedron* **1981**, 37, 1495; d) Porter, Q. N.; Utley, J. H. P. *J. Chem. Soc., Chem. Commun.* **1978**, 255; e) Planten, M.; Steckhan, E. *Chem. Ber.* **1984**, 117, 1679.

10) a) Ogura, K.; Tsuchihashi, G. *Tetrahedron Lett.* **1971**, 2599; b) Ogura, K.; Yamashita, M.; Suzuki, M.; Tsuchihashi, G.*Tetrahedron Lett.* **1974**, 3653; c) Ogura, K.; Yamashita, M.; Furakawa, S.; Suzuki, M.; Tsuchihashi, G. *Tetrahedron Lett.* **1975**, 2767; d) Ogura, K.; Yamashita, M.; Suzuki, M.; Furukawa, S.; Tsuchihashi, G. *Bull. Chem. Soc. Jpn.* **1984**, 57, 1637; e) Newkome, G. R.; Robinson, J. M.; Sauer, J. D. *J. Chem. Soc., Chem. Commun.* **1974**, 255; f) Schill, G.; Jones, P. R.; *Synthesis* **1974**, 117; .

11) a) Glass, R. S.; Andreuski, W.; Broeker, J. L.; Firouzabadi, H.; Steffen, L. K.; Wilson, G. S. *J. Am. Chem. Soc.* **1989**, 111, 4036; b) Glass, R. S.; Adamowicz, L.; Broeker, J. L. *ibid.* **1991**, 113, 1065; c) Fujihara, H.; Chiu, J. -J.; Furukawa, N. *Chem. Lett.* **1990**, 2217; d) Fujihara, H.; Yabe, M.; Chiu, J. -J.; Furukawa, N. *Tetrahedron Lett.* **1991**, 32, 4345.

12) a) Fujihara, H.; Saito, R.; Yabe, M.; Furukawa, N. *Chem. Lett.* **1992**, 1437; b) Furukawa, N.; Shima,H.; Kimura, T. *J. Chem. Soc. Chem. Commun.*, **1993**, 1762.

13) Fujihara, H.; Yabe, M.; Furukawa, N. *J. Org. Chem.* **1993**, 58, 5291.

14) House, H. O.; Koepsell, D. G.; Campbell, W. J. *J. Org. Chem.* **1972**, 37, 1003.

15) Meinwald, J.; Dauplaise, D.; Wudl, F.; Hauser, J. J. *J. Am. Chem. Soc.* **1977**, 99, 255.

16) a) Still, I. W. J. "The chemistry of sulphones and sulphoxides," ed by Patai, S.; Rappoport, Z.; Stirling, C. J. M. John Wiley & Sons, Chichester (1988), p. 873; b) Ditlmer, D. C.; Kuhlman, G. C. *J. Org. Chem.* **1970**, 35, 3676 ; c) Schultz, A. G.; Schlessinger, R. H. *J. Chem. Soc., Chem. Commun.* **1970**, 1294; d) Schultz, A. G.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, 3605; Kobayashi, K.; Mutai, K. *ibid.* **1981**, 22, 5201; e) Still, I. W. J.; Arora, P. C.; Chauhan, M. S.; Kwan, M. H.; Thomas, M. T. *Can. J. Chem.* **1976**, 54, 455.

17) Guo, Y.; Jenks, W.S. *J. Org. Chem.* **1995**, 60, 5480.

18) Nakayama, J.; Dan. S.; Hoshino, M. *J. Chem. Soc., Perkin Trans. 1* **1981**, 413.

19) Yui, K.; Aso, Y.; Otubo, T.; Ogura, F. *Chem. Lett.* **1986**, 551.

Chapter 3

Mechanism for Photodecomposition of Naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimines: A Convenient Method for Preparation of *N*-Tosylaldimines

Abstract

Naphtho[1,8-*de*]dithiin-1-*N*-tosylsulfilimines (**16**) were prepared by the reaction of naphtho[1,8-*de*]-1,3-dithiins with chloramine-T. Photolysis of **16** undergoes intramolecular imino group rearrangement to give *N*-tosylaldimines quantitatively together with naphtho[1,8-*cd*]-1,2-dithiole.

Introduction

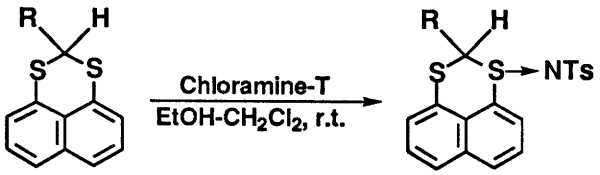
N-Sulfonylaldimines have been considered as an important reagent in organic chemistry because they are one of the few electron-deficient imines that are stable enough to be isolated but highly reactive to undergo addition reactions.[1-4] Lichtenburger and Kreatar first prepared aldimines by a Lewis acid catalyzed direct condensation, a method that appears to be limited to aromatic aldehydes.[5-7] Rearrangements of sulfinate esters of oximes have also served as a convenient approach for preparation. Kreze carried out pioneering work on the imino-transfer reactions with aromatic aldehydes utilizing sulfinylsulfinamides;[6a, 7] namely this procedure was adopted recently for aliphatic aldehydes.[2b] Diaryl- and dialkyl-tellurium analogues have also been useful but less convenient.[6c, 7c]

1,8-Bis(alkylthio)- or 1,8-bis(alkylseleno)-naphthalene derivatives are presumably the candidates for generation of various active species initiated by the through-space interaction between the two sulfur or two selenium atoms.[8] In fact, naphtho[1,8-*de*]dithiin monooxides undergo photo-oxygen rearrangement to release carbonyl compounds quantitatively together with naphtho[1,8-*cd*]-1,2-dithiole as described in Chapter 2. In further extension of these studies, the author prepared *N*-tosylsulfilimines of naphtho[1,8-*de*]dithiin (**5**) and found that their photolysis provides a convenient procedure to yield the corresponding *N*-sulfonylaldimines. In Chapter 3, the author describes the intramolecular photo-migration of the

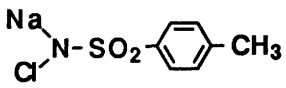
imino group to *N*-tosylaldimines (**7**) using *N*-tosylsulfilimines (**5**).

Results and Discussion

Synthesis of Naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimines



Chloramine-T=



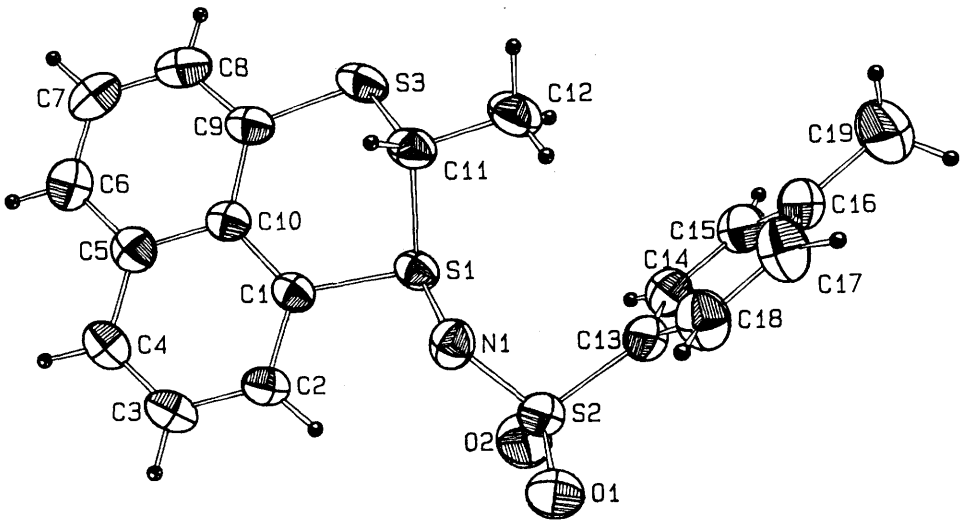
[5a]: R = Ph	[16a]: 70%[a)]
[5b]: R = *p*-tol	[16b]: 75%
[5c]: R = CH_3	[16c]: 73%
[5d]: R = Et	[16d]: 73%
[5e]: R = $CH_3(CH_2)_5$	[16e]: 70%
[5f]: R = PhCH=CH	[16f]: 68%
[5g]: R = 2-furyl	[16g]: 42%

a) Isolated yield

Scheme 3-1

Reduction of naphtho[1,8-*cd*]-1,2-dithiole (**2**) with sodium borohydride in tetrahydrofuran-ethanol at room temperature gave almost quantitatively 1,8-naphthalene dithiol (**3**). Compound **3** was treated with parafolmaldehyde in the presence of tetrachlorosilane in dichloromethane affording the corresponding naphtho[1,8-*de*]-1,3-dithiin (**4**) in 71% yields. 2-Substituted naphtho[1,8-*de*]-1,3-dithiins(**5**) were prepared by the reaction of 2-lithiated **4** with several electrophiles. Compound **5** was also obtained by the reaction of **3** and aldehydes in the presence of tetrachlorosilane in dichloromethane in high yields. 2,2-Disubstituted naphtho[1,8-*de*]-1,3-dithiins (**6**) were prepared from the reaction of 2-lithiated **5** with several electrophiles. 2-Substituted naphtho[1,8-*de*]-1,3-dithiin-*N*-tosylsulfilimines (**16**) were prepared in moderate yields as a single diasteroisomer (R_S, S_C or S_S, R_C) by the reaction of **5**

with chloramine-T in ethanol-dichloromethane at room temperature (Scheme 3-1). The structure of **16c** was determined to be a trans isomer by X-ray crystallographic analysis (Figure 3-1). The S(1)···S(2) distance of **16c** is 2.9 Å which is markedly shorter than the sum of the van der Waals radii (3.7 Å) of the two sulfur atoms. However, 2,2'-disubstituted naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimines were not obtained on similar treatment of 2,2'-disubstituted naphtho[1,8-*de*]-1,3-dithiins (**6**) with chloramine-T.



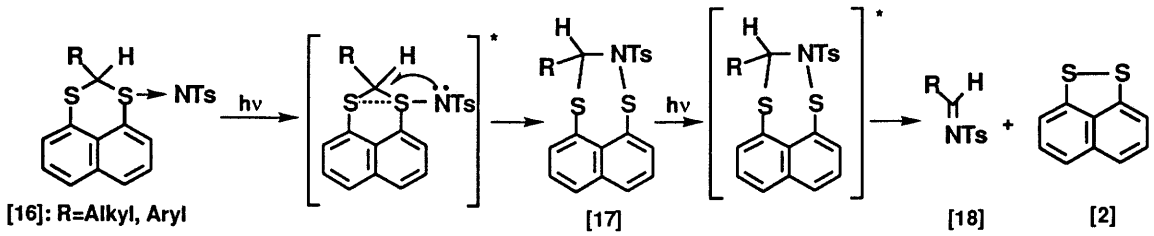
Trans isomer
Config. *Rs,Sc* or *Ss,Rc*

Figure 3-1. ORTEP Drawing of the Structure of **16c**

Photolysis of Naphtho[1,8-*de*]-1,3-dithiin-*N*-tosylsulfilimines

Compounds **16** were thermally stable but decomposed to the corresponding *N*-tosylaldimines quantitatively with a complete recovery of naphtho[1,8-*cd*]-1,2-dithiole (**2**) on exposure to a

high pressure mercury lamp (400 W) in benzene for 18 h (Scheme 3-2). After evaporation of benzene and usual work-up, the residue was chromatographed to give **18** and **2** quite readily as shown in Table 3-1. Polar and nonpolar solvents including ethanol, acetonitrile, tetrahydrofuran, dichloromethane, chloroform, and benzene were examined on a photoreaction of **16a**. Photodecomposition reactions gave **18a** and **2** quantitatively. Interestingly, this procedure can be applied to the synthesis of aliphatic imines **18d** and **18e** derived from enolizable aldehydes.



Scheme 3-2

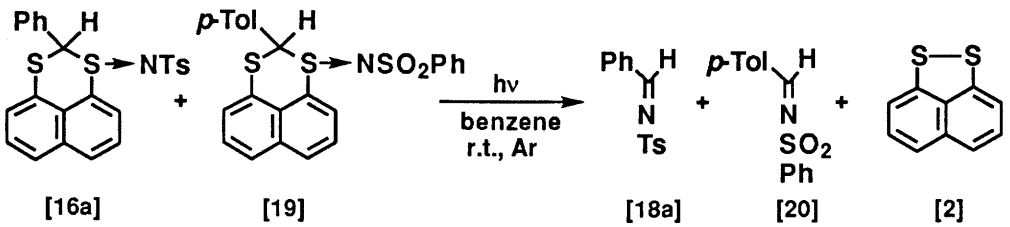
Table 3-1. Photolysis of 1,3-Dithiin-1-*N*-tosylsulfilimines [**16**].[a)]

[16]	R	Solvent	Yield of **18** (%)[b)]	Yield of **2** (%)[b)]
a	Ph	C_6H_6	>99 (98)[c)]	>99 (100)[c)]
a	Ph	$CHCl_3$	>99 (98)[c)]	>99 (99)[c)]
a	Ph	CH_2Cl_2	>99 (96)[c)]	>99 (98)[c)]
a	Ph	THF	>99 (91)[c)]	>99 (97)[c)]
a	Ph	CH_3CN	>99 (90)[c)]	>99 (98)[c)]
b	*p*-Tol	C_6H_6	>99 (91)[c)]	>99 (98)[c)]
c	CH_3	C_6H_6	-	- (95)[c)]
d	Et	C_6H_6	>99	>99
e	$CH_3(CH_2)_5$	C_6H_6	>99 (93)[c)]	>99 (100)[c)]
f	PhCH=CH	C_6H_6	>99 (90)[c)]	>99 (98)[c)]
g	2-furyl	C_6H_6	>99 (90)[c)]	>99 (100)[c)]

a) 400 W high pressure Hg lamp, λ> 300 nm, Substrates (0.1 mmol), Solvent (5 ml) b) Yields were determined by gas chromatography and ^{1}H-NMR spectroscopy. c) Isolated yields.

The consumption of **16** and the formation of products **18** and **2** were unaffected by the addition of benzophenone as a triplet sensitizer, indicating that both reactions probably proceeds through the singlet state. The quantum yields of the consumption of compound **16** and the formation of **18** and **2** using a high pressure mercury lamp (500 W, 313 nm) at room temperature in deoxygenated dichloromethane was measured by comparison with fulgide actinometry[9] to be 0.74 and 0.06 respectively, being indicative of the existence of a stable intermediate on photolysis of **16** to **18** and **2**.

The photolysis of **16** presumably proceeds by the initial photo-excitation of the sulfilimine to form the reactive intermediate **17** by the intramolecular migration of the *N*-tosyl group to the 2-carbon atom *via* the S···S through-space interaction. Finally, the intermediate **17** should be converted to the corresponding *N*-tosylaldimines (**18**) and naphtho[1,8-*cd*]-1,2-dithiole (**2**).



Scheme 3-3

In order to determine whether the nitrogen migration is intra- or intermolecular, a cross-over experiment using a 1 : 1 mixture of **16a** and naphtho[1,8-*de*]-1,3-dithiin-1-*N*-benzenesulfonylsulfilimine (**19**) was carried out under a similar photolysis condition as shown in Scheme 3-3. The reaction proceeded cleanly to give the aldimines **18a** and **20**, and

compound **2** quantitatively. After separation of the aldimines and **2**, the ^{1}H- and ^{13}C-NMR spectra of the aldimines were found to be identical with those of a 1 : 1 mixture of **18a** and **20**, and hence no cross-over products were detected at all indicating clearly that their photo-migration proceeds intramolecularly.

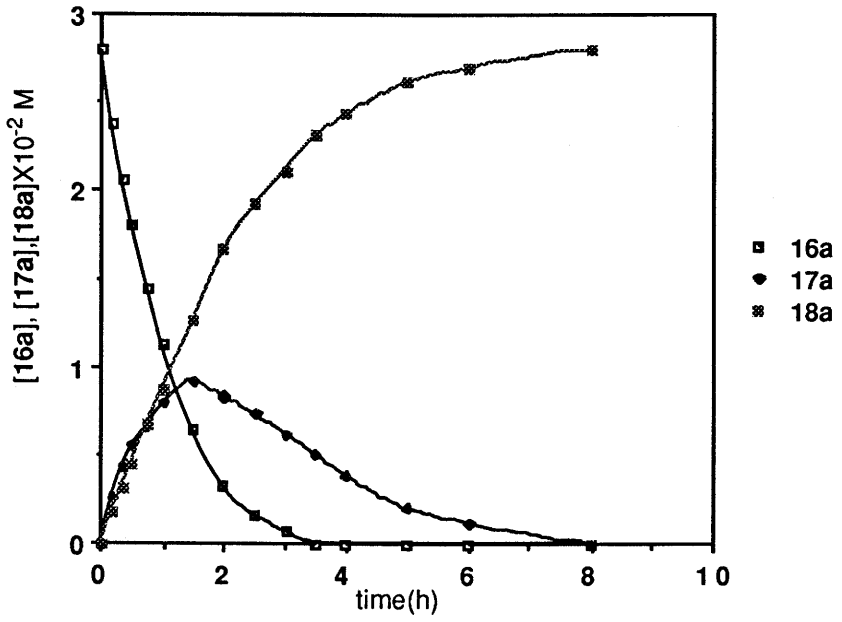


Figure 3-2. Time course of photolysis of 1-phenyl-naphtho[1,8-*de*] -1,3-dithiin-1-*N*-tosylsulfilimine **16a** ($2.8X10^{-2}$ M **16a** in $CDCl_3$).

In order to understand the mechanism for decomposition of **16**, the ^{1}H-NMR spectra of the reaction of **16a** under irradiation with a high pressure Hg lamp in $CDCl_3$ was monitored at various time intervals (Figure 3-2). When the ^{1}H-NMR signals of the starting material **16a** gradually reduced, new peaks started to appear at 2.17 ppm (s), 6.62 ppm (d, J = 8.4 Hz), 6.90 ppm (s), 7.14 (d, J = 7.6 Hz), and 9.03 (S) corresponding to that of intermediate **17a** together with other peaks from compounds **18a** and **2** by comparing with their spectral data of the

authentically prepared compounds. The ^{1}H-NMR signals of the intermediate **17a** increased gradually but disappeared soon and the spectra were converted to that of the products **18a** and **2**. Actually, this intermediate **16a** could be isolated by liquid chromatography of the reaction mixtures by stopping the photolysis of **16a** at the highest conversion of **16a** to **17a**. The intermediate **17a** is a solid material of which ^{1}H-, ^{13}C-NMR, IR, mass spectra and elemental analysis data support the structure (see Scheme 3-2). Furthermore the structure of **17a** was determined by X-ray crystallographic analysis as shown in Figure 3-3. Consequently, the results demonstrate clearly that the mechanism for the present reaction proceeds *via* an initial formation of intermediate **17** affording the corresponding *N*-tosylaldimines (**18**) and naphtho[1,8-*cd*]-1,2-dithiole (**2**).

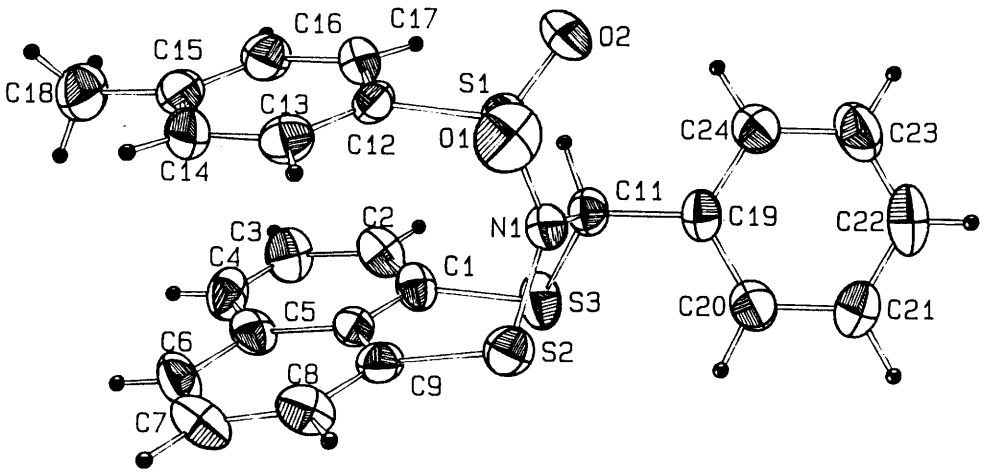


Figure 3-3. ORTEP Drawing of the Structure of **17a**

The effect of light intensity on photolysis of the sulfilimine **16a** was studied in order to understand whether the reaction proceeds by a one-, two- or multi-photon process. The loss of **16a** was proportional to the first power of the 313 nm light, whereas the formation of **2** was proportional to the square of the intensity as shown in Figure 3-4. These results imply that the consumption of sulfilimines **16** proceeds by a one-photon process to give an intermediate **17**, which seems to be formed by a radical or a concerted rearrangement in the primary photochemical step. Thereafter, the intermediate **17** should be converted to the corresponding *N*-tosylaldimines **18** and naphtho[1,8-*cd*]-1,2-dithiole (**2**) *via* the S···S through-space interaction in the secondary photochemical step.

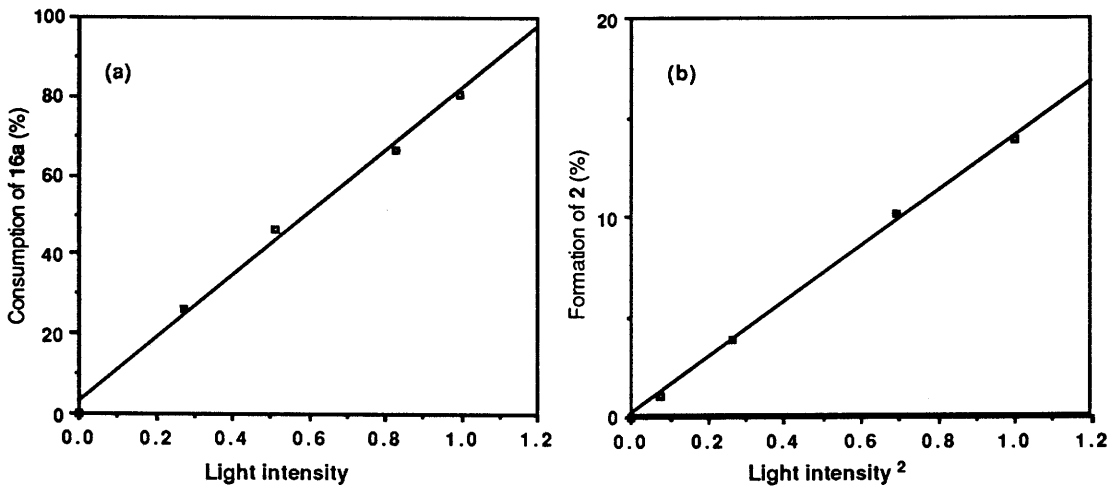


Figure 3-4. Light intensity dependence on the consumption of **16a** (a) and the formation of **2** (b). (4.87×10^{-3} M **16a** in CH_2Cl_2).

X-ray Crystallographic Analysis of Naphtho[1,8-*de*]-1,3-dithiin (4) and 2-Methyl-naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimine (16c)

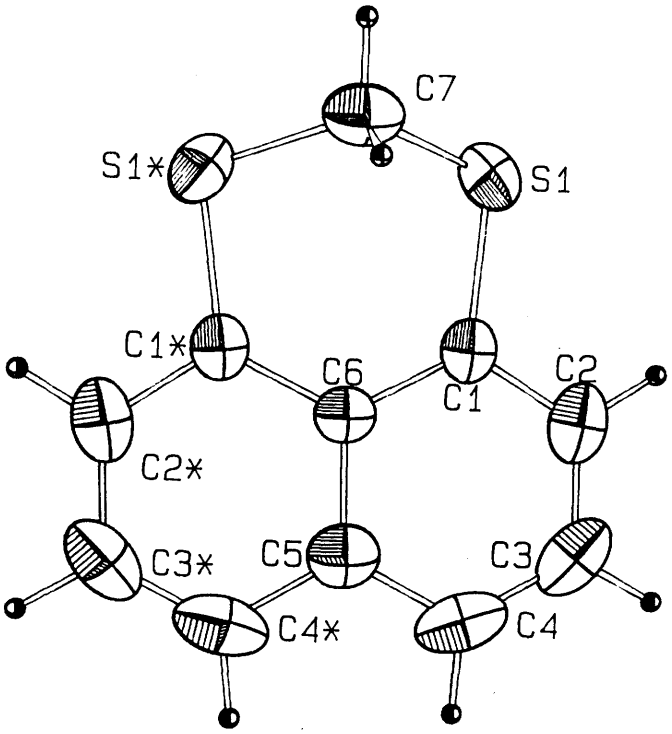


Figure 3-5. ORTEP Drawing of the Structure of **4**

The detailed structural analyses of **4** and **16c** were performed by X-ray crystallographic analysis. The bond angles and bond distances of **4** and **16c** are collected in Table 3-2 and 3-3. The ORTEP drawings of **4** and **16c** are depicted in Figure 3-1 and 3-5, respectively. The molecular structure of **16c** is transisomer with phenyl and *N*-tosyl group occupying the equatorial positions. The S(1)···S(3) distance of **16c** is 2.856 Å, which is about 0.1 Å closer than the S(1)···S(1)* distance of **4**, significantly shorter than the sum of the van der Waals radii of the two sulfur atoms (3.70 Å). The S(1)-C(11)-S(3) bond angle in compound **16c** (104.4°) is smaller than the S(1)-C(7)-S(1)* bond angle of **4** (111°). The C(9)-S(3)-C(11) bond angle of **16c** is 101.6°, which is large compared to the C(1)-S(1)-C(7) bond of **4** (99.4°). These observations are reasonably attributed to a stabilizing transannular interaction

between the S(1) and S(3) atoms at compound **16c**. The sulfur of sulfilimino group S(1) is positively polarized and attractive interaction with S(3) acts to compress the C(11) valence angle and hence short S···S intramolecular distance in compound **16c**.

Table 3-2. Selected Distances (Å) and Angles (deg) for 2-Methyl-naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimine (**16c**).[a)]

Distance			
S1-N1	1.620 (3)	S1-C1	1.792 (3)
S2-N1	1.632 (3)	S1-C11	1.821 (4)
S2-O1	1.432 (3)	S3-C9	1.760 (3)
S2-O2	1.444 (4)	S3-C11	1.793 (3)
S1···S3	2.856		
Angles			
N1-S1-C1	130.0 (1)	S1-C1-C2	115.5 (2)
N1-C1-C11	105.6 (2)	S1-C1-C10	123.1 (2)
C1-S1-C11	99.1 (2)	S3-C9-C8	117.8 (2)
C9-S3-C11	101.6 (1)	S3-C9-C10	120.0 (3)
S3···S1-N1	142.7		

a)Estimated standard deviations in paratheses. The atom-labeling scheme is shown in Figure 3-1.

Table 3-3. Selected Distances (Å) and Angles (deg) for Naphtho[1,8-*de*]-1,3-dithiin (**4**).[a)]

Distance			
S1-C1	1.764 (4)	S1-C7	1.793 (4)
S1···S1*	2.595		
Angles			
C1-S1-C7	99.4 (2)	S1-C1-C6	123.5 (3)
S1-C1-C2	115.7 (3)	S1-C7-S1*	111.0 (0)

a)Estimated standard deviations in paratheses. The atom-labeling scheme is shown in Figure 3-5.

X-ray Crystallographic Analysis of 3-Hydro-3-phenyl-naphtho[1,8-*ef*][1,4]dithia[2]azepin (17a)

Table 3-4. Selected Bond Distances (Å) for 3-Hydro-3-phenyl-naphtho[1,8-*ef*][1,4]dithia[2]azepin (**17a**)[a].

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
S1	O1	1.428(4)	S2	C9	1.781(4)
S1	O2	1.430(4)	S3	C1	1.779(4)
S1	N1	1.664(4)	S3	C11	1.812(4)
S1	C12	1.759(4)	N1	C11	1.492(6)
S2	N1	1.696(4)			

a) Numbers in parentheses are estimated standard deviations in the least significant digits. The atoms-labeling scheme is shown in Figure 3-3.

Table 3-5. Selected Bond Angles (deg) for 3-Hydro-3-phenyl-naphtho[1,8-*ef*][1,4]dithia[2]azepin (**17a**).[a]

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1	S1	O2	119.8(2)	C3	C4	C5	122.0(4)
O1	S1	N1	108.1(2)	C4	C5	C6	120.8(4)
O1	S1	C12	108.6(2)	C4	C5	C10	119.9(4)
O2	S1	N1	105.1(2)	C6	C5	C10	119.3(4)
O2	S1	C12	108.4(2)	C6	C5	C10	119.3(4)
N1	S1	C12	105.9(2)	C6	C7	C8	119.1(5)
N1	S2	C9	105.4(2)	C7	C8	C9	121.7(4)
C1	S3	C11	104.0(2)	S2	C9	C8	114.4(3)
S1	N1	S2	119.6(2)	S2	C9	C10	124.8(3)
S1	N1	C11	118.2(3)	C8	C9	C10	120.8(4)
S2	N1	C11	120.4(3)	C1	C10	C5	116.4(4)
S3	C1	C2	115.1(3)	C1	C10	C9	126.7(4)
S3	C1	C10	123.3(3)	C5	C10	C9	116.9(4)
C2	C1	C10	120.8(4)	S3	C11	N1	111.1(3)
C1	C2	C3	121.1(5)	S3	C11	C19	108.5(3)
C2	C3	C4	119.5(5)	S3	C11	H7	111.(2)

a) Numbers in parentheses are estimated standard deviations in the least significant digits. The atoms-labeling scheme is shown in Figure 3-3.

The detailed structural analysis of **17a** was performed by X-ray crystallographic analysis. Selected bond angles, bond distances and torsion angles of **17a** are collected in Table 3-5, 3-6, and 3-7. The ORTEP drawing of **17a** is depicted in Figure 3-3. The naphthalene ring in compound **17a** is slightly twisted about the C(5)-C(10) axis. The naphthalene ring and phenyl

Table 3-6. Selected Torsional Angles (deg) for 3-Hydro-3-phenyl-naphtho[1,8-*ef*][1,4]dithia[2]azepin (**17a**)[a].

Atom 1	Atom 2	Atom 3	Atom 4	Angle	
N1	S2	C9	C8	-134.84	(0.35)
N1	S2	C9	C10	42.93	(0.43)
C11	S3	C1	C2	113.52	(0.38)
C11	S3	C1	C10	-76.76	(0.41)
S3	C1	C2	C3	167.51	(0.39)
S3	C1	C10	C5	-163.61	(0.34)
S3	C1	C10	C9	17.70	(0.65)
C2	C1	C10	C5	5.56	(0.64)
C2	C1	C10	C9	-173.13	(0.45)
C1	C2	C3	C4	-2.00	(0.76)
C9	C8	C7	C1	-174.50	(0.17)
C9	C8	C7	C12	3.85	(0.27)
C10	C9	C8	S1	-178.12	(0.15)
C10	C9	C8	C7	-2.88	(0.28)
C6	C5	C10	C1	175.39	(0.43)
C6	C5	C10	C9	-5.78	(0.64)
C6	C7	C8	C9	-5.20	(0.76)
C7	C8	C9	S2	179.03	(0.39)
S2	C9	C10	C1	5.33	(0.67)
S2	C9	C10	C5	-173.36	(0.34)
C8	C9	C10	C1	-177.04	(0.45)
C8	C9	C10	C5	4.27	0.64)

a) Numbers in parentheses are estimated standard deviations in the least significant digits. The atoms-labeling scheme is shown in Figure 3-3.

ring of tosyl group are nearly parallel and the through space distance of these rings is about 3.3 Å, which is slightly smaller than the van der Waals distance for the two aromatic systems (about 3.4 Å). The exocyclic bonds of S(2)-C(9) and S(3)-C(1) are splayed outwards and the sulfur atoms in the 1,8-positions of naphthalene are displaced above and below the average plane of the naphthalene ring. More substantial twisting of the naphthalene ring has been observed in 1,8-disubstituted derivatives with bulky sudstituents.[10] The S(2)···S(3) distance of **17a** is 3.108 Å, which is significantly shorter than the sum of the van der Waals radii of the two sulfur atoms (3.70 Å), but about 0.3 Å. longer than the S(1)···S(3) distance of **16c**. These distortion pattern and increasing S···S intramolecular distance in compound **17a** support by a dipolar repulsion between the two sulfur atoms in the 1,8-positions of naphthalene.

Experimental Section

General All melting points were uncorrected and were taken on a Yanaco micro melting point apparatus and LABORATORY DEVICES, USA, Model MRX-TEMP II. IR spectra were recorded on a JASCO FT/IR-5000 spectrometer. All NMR spectra were obtained with a JEOL LMN-EX-270 and a BRUKER MSL-400 FT-NMR spectrometer. Mass spectra were taken with a Shimadzu QP-2000 and a JEOL JMX SX102 mass spectrometer. Ultraviolet-visible spectra were recorded on a Hitachi U-3000. X-Ray crystallographic analysis was performed on an Enraf-Nonius CAD4 automatic diffractometer. Preparative liquid chromatography was performed on a Japan Analytical Industry Co., Ltd., Model LC-09 and LC-908. Gas-chromatography (GC) data were obtained with a Hitachi 263 gas chromatography equipped with an FID detector and a 5m OV-17 column. High performance liquid chromatography (HPLC) data were collected with a Shimadzu LC-10A system, using a TSK gel ODS-ST column (length, 250 mm; internal diameter, 4.6 mm) and methanol-water as an eluent with monitoring at 254 nm. Photolyses were carried out in a Pyrex round-bottomed flask using a 400 W high pressure mercury lamp. Quantum yield, the sensitizatiion, a cross over, and intensity effect experiments were performed by irradiation with 500 W ultrahigh pressure mercury lamp equipped with a glass filter and monochromator. All photo-reactions were monitored and quantified by GC, HPLC, or ^{1}H-NMR. Analytical thin-layer chromatograph (TLC) was carried out on Merck precoated TLC plate (Kieselgel 60 F_{254}). Silica-gel used for column chromatography was Wako-gel C-200 and Merck kieselgel 60.

Elemental analyses were carried out by Chemical Analysis Center at this University.

Materials All reagents were obtained from Wako Pure Chemical Industries, Ltd., Tokyo Kasei Kogyo, Co., Ltd., Kanto Chemicals Co., Inc., or Aldrich Chemical Co. The reagents used as reaction solvents were further purified by general methods.

General Procedure for 2-Substituted Naphtho[1,8-*de*]-1,3-dithiin

n-Butyllithium (1.3 ml of 1.67 N solution in hexane, 2.2 mmol) was added dropwise at -78 °C to solution of naphtho[1,8-*de*]-1,3-dithiin (**4**) (408 mg, 2.0 mmol) in tetrahydrofurane (20 ml) and stirred for 1h. To this solution was added electrophiles (2.2 mmol) for 1h at -78 °C with stirring then warmed up to room temperature and monitored by TLC. When the reaction was complete, the solution was quenched with 5 ml of water and extracted with dichloromethane. The solution was dried with magnesium sulfate and then the solvent was removed under vaccum. The residue was separated by silica-gel column chromatography (eluent, tetrachloromethane) and then recrystallization from ethyl acetate-hexane to give the pure product.

2-Methyl-naphtho[1,8-*de*]-1,3-dithiin (5c)

Yield 99%; mp. 57-58 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.72 (d, J = 7.0 Hz, 3H, CH_3), 4.38 (q, J = 7.0 Hz, 1H. CH), 7.29 (t, J = 8.2 Hz, 2H, ArH), 7.38 (dd, J_1 = 8.2 Hz, J_2 = 1.3 Hz, 2H, ArH), 7.59 (dd, J_1 = 8.2 Hz, J_2 = 1.3 Hz, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 20.45, 37.68, 125.39, 125.55, 126.06, 127.31,

130.35, 134.86; MS (m/z) 218 (M^+); Anal. Calcd for $C_{12}H_{10}S_2$: C, 66.02, H, 4.62. Found: C, 65,78, H, 4.52.

2-Ethyl-naphtho[1,8-*de*]-1,3-dithiin (5d)

Yield 94%; mp. 66-67 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.16 (t, J = 7.3 Hz, 3H, CH_3), 2.02 (q, J = 7.3 Hz, 2H, CH_2), 4.19 (t, J = 7.3 Hz, 1H. CH), 7.31 (t, J = 8.0 Hz, 2H, ArH), 7.40 (dd, J_1 = 8.0 Hz, J_2 = 1.3 Hz, 2H, ArH), 7.60 (dd, J_1 = 8.0 Hz, J_2 = 1.3 Hz, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ11.96, 28.23, 44.56, 125.43, 126.22, 126.49, 127.34, 130.11, 150.14; MS (m/z) 218 (M^+); Anal. Calcd for $C_{19}H_{16}S_2$: C, 73.98, H, 5.23. Found: C, 73.83, H, 5.27.

General Procedure for 2-Substituted Naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimines

2-Substituted naphtho[1,8-*de*]-1,3-dithiins (**5**) (1 mmol) and chloramine-T (281 mg, 1 mmol) were dissolved in 20 ml of ethanol-dichloromethane and stirred for 12 h under an Ar atmosphere. To this solution was added a 1M sodium hydride solution. The precipitates were filtered, washed with water and recrystallized from dichloromethane-ethanol to give the pure products **16**.

2-Phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimine (16a)

Yield 70%; mp. 192-193 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.35 (s, 3H, CH_3), 5.09 (s, 1H, CH), 6.97 (d, J = 8.2 Hz, 2H, ArH), 6.96-7.25 (m, 3H, ArH), 7.26-7.37 (m, 4H, ArH), 7.52 (t, J = 7.8 Hz, 1H, ArH), 7.63 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 1H, ArH), 7.76 (t, J = 7.8 Hz, 1H, ArH), 7.90 (dd, J_1 = 7.8 Hz, J_2 = 1.1

Hz, 1H, ArH), 8.80 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 1H, ArH), 8.47 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 21.37, 61.04, 126.04, 126.20, 126.61, 127.40, 127.71, 128.37, 128.68, 129.02, 129.13, 129.27, 129.34, 129.87, 130.10, 132.85, 133.68, 134.59, 140.58, 141.15; IR (KBr) 980 cm^{-1} (SN), 1137, 1280 cm^{-1} (SO_2); MS (m/z) 449 (M^+); Anal. Calcd for $C_{24}H_{19}N_1O_2S_3$: C, 64.11, H, 4.26, N, 3.12. Found: C, 64.00, H, 4.16, N, 3.06.

2-*p*-Tolyl-naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimine (16b)

Yield 75%; mp. 200-201 °C (decomp.); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.37 (s, 3H, CH_3). 2.38 (s, 3H, CH_3), 5.04 (s, 1H. CH), 6.96-7.03 (m, 4H, ArH), 7.16-7.23 (m, 2H, ArH), 7.35-7.38 (m, 2H, ArH), 7.52 (t, J = 7.8 Hz, 1H, ArH), 7.61 (d, J = 7.8 Hz, 1H, ArH), 7.76 (t, J = 7.8 Hz, 1H, ArH), 7.89 (d, J = 7.8 Hz, 1H, ArH), 8.08 (d, J = 7.8 Hz, 1H, ArH), 8.48 (d, J = 7.8 Hz, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ21.40, 21.44, 60.85, 126.11, 126.18, 126.61, 126.69, 127.58, 127.66, 128.30, 128.77, 129.15, 129.24, 129.67, 129.85, 132.79, 133.76, 134.57, 140.45, 149.75, 140.95; IR (KBr) 1002 cm^{-1} (SN), 1149, 1282 cm^{-1} (SO_2); MS (m/z) 463 (M^+); Anal. Calcd for $C_{25}H_{21}N_1O_2S_3$: C, 65.66, H, 4.45, N, 2.94. Found: C, 65.49, H, 4.59, N, 3.07.

2-Methyl-naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimine (16c)

Yield 73%; mp. 164-165 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.69 (d, J = 7.2 Hz, 3H, CH_3), 2.43 (s, 3H, CH_3), 4.13 (q, J = 7.2 Hz, 1H. CH), 7.30 (d, J = 7.9 Hz, 2H, ArH), 7.49 (t, J = 7.2 Hz, 1H, ArH), 7.57 (d, J = 7.9 Hz, 2H, ArH), 7.61 (t, J = 7.2 Hz, 1H,

ArH), 7.83 (d, J = 7.2 Hz, 1H, ArH), 7.92 (d, J = 7.9 Hz, 2H, ArH), 8.01 (d, J = 7.2 Hz, 1H, ArH), 8.06 (d, J = 7.2 Hz, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ14.70, 21.46, 52.83, 126.02, 126.27, 126.38, 126.81, 127.69, 128.18, 128.41, 129.43, 19.50, 130.91, 132.81, 134.56, 141.20, 142.12; IR (KBr) 938 cm^{-1} (SN), 1147, 1313 cm^{-1} (SO_2); MS (m/z) 387 (M^+); Anal. Calcd for $C_{19}H_{17}N_1O_2S_3$: C, 58.89, H, 4.42, N, 3.61. Found: C, 58.99, H, 4.41, N, 3.60.

2-Ethyl-naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimine (16d)
Yield 73%; mp. 158-159 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.10 (t, J = 7.6 Hz, 3H, CH_3), 1.83-1.95 (m, 1H, CH_2), 2.35-2.41 (m, 1H, CH_2), 2.45 (s, 3H, CH_3), 4.09 (dd, J_1 = 8.8 Hz, J_2 = 3.5 Hz, 1H. CH), 7.30 (d, J = 8.1 Hz, 2H, ArH), 7.49 (t, J = 7.7 Hz, 1H, ArH), 7.57-7.63 (m, 2H, ArH), 7.83 (d, J = 7.7 Hz, 1H, ArH), 7.92 (d, J = 8.1 Hz, 2H, ArH), 7.99-8.05 (m, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ9.90, 21.46, 21.71, 59.71, 126.04, 126.29, 126.42, 126.85, 128.07, 128.18, 128.57, 129.43, 129.46, 131.27, 132.78, 134.59, 141.19, 142.12; IR (KBr) 975 cm^{-1} (SN), 1145, 1299 cm^{-1} (SO_2); MS (m/z) 401 (M^+); Anal. Calcd for $C_{20}H_{19}N_1O_2S_3$: C, 59.82, H, 4.77, N, 3.49. Found: C, 59.92, H, 4.66, N, 3.47.

2-Hexyl-naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimine (16e)
Yield 70%; mp. 167-168 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3H, CH_3), 1.21-1.37 (m, 6H, CH_2), 1.59-1.71 (m, 3H, CH_2), 2.15-2.21 (m, 1H, CH_2), 2.43 (s, 3H, CH_3), 4.10 (dd, J_1 = 9.6 Hz, J_2 = 3.5 Hz, 1H, CH), 7.30 (d, J = 8.4 Hz, 2H, ArH), 7.49 (t, J = 7.8 Hz, 1H, ArH), 7.59 (dd, J_1 = 7.8 Hz, J_2 = 1.1

Hz, 1H, ArH), 7.64 (t, J = 7.8 Hz, 1H, ArH), 7.84 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 1H, ArH), 7.92 (d, J = 8.4 Hz, 2H, ArH), 8.02 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 1H, ArH), 8.14 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 13.98, 21.46, 22.48, 25.43, 28.09, 28.68, 31.29, 58.26, 126.13, 126.27, 126.38, 126.43, 126.88, 128.01, 128.19, 128.68, 129.43, 131.50, 132.78, 134.59, 141.35, 142.08; IR (KBr) 975 cm^{-1} (SN), 1141, 1296 cm^{-1} (SO_2); MS (m/z) 457 (M^+); Anal. Calcd for $C_{24}H_{27}N_1O_2S_3$: C, 62.99, H, 5.94, N, 3.06. Found: C, 63.06, H, 5.86, N, 2.96.

2-(3-Phenyl-2-propene)-naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimine (7f)

Yield 68%; mp. 193-194 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.19 (s, 3H, CH_3), 4.85 (d, J = 8.9 Hz, 1H, CH), 5.92 (dd, J_1 = 15.7 Hz, J_2 = 8.9 Hz, 1H, C=CH), 6.85 (d, J = 15.7 Hz, 1H, C=CH), 6.91 (d, J = 7.8 Hz, 2H, ArH), 7.22-7.25 (m, 2H, ArH), 7.34-7.35 (m, 3H, ArH), 7.53 (t, J = 7.7 Hz, 1H, ArH), 7.64 (d, J = 7.7 Hz, 1H, ArH), 7.72-7.77 (m, 3H, ArH), 7.89 (d, J = 7.7 Hz, 1H, ArH), 8.07 (d, J = 7.7 Hz, 1H, ArH), 8.39 (d, J = 7.7 Hz, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ21.42, 60.13, 115.86, 126.12, 126.33, 126.63, 126.70, 127.30, 128.01, 128.39, 128.60, 129.16, 129.36, 133,01, 133.45, 134.61, 134.66, 137.05, 140.97, 141.67, 141.89, 143.82; IR (KBr) 909 cm^{-1} (SN), 1164, 1354 cm^{-1} (SO_2); MS (m/z) 475 (M^+); Anal. Calcd for $C_{26}H_{21}N_1O_2S_3$: C, 65.66, H, 4.45, N, 2.94. Found: C, 65.49, H, 4.59, N, 3.07.

2-(2-Furyl)-naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimine (16g)

Yield 42%; mp. 170-171 °C (decomp); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.19 (s, 3H. CH_3), 6.40 (dd, J_1 = 3.2 Hz, J_2 = 1.8 Hz, 1H, 2-furylH), 6.56 (d, J = 3.2 Hz, 1H, 2-furylH), 6.66 (d, J = 8.2 Hz, 2H, ArH), 6.98 (s, 1H, CH), 7.15 (d, J = 8.2 Hz, 2H, ArH), 7.20 (t, J = 7.7 Hz, 1H, ArH), 7.31 (t, J = 7.7 Hz, 1H, ArH), 7.44 (d, J = 1.8 Hz, 1H 2-furylH), 7.49 (dd, J_1 = 7.7 Hz, J_2 = 1.1 Hz, 1H, ArH), 7.59 (dd, J_1 = 7.7 Hz, J_2 = 1.1 Hz, 1H, ArH), 7.69 (dd, J_1 = 7.7 Hz, J_2 = 1.1 Hz, 1H, ArH), 7.82 (dd, J_1 = 7.7 Hz, J_2 = 1.1 Hz, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 21.33, 68.03, 108.86, 110.76, 125.28, 126.15, 126.84, 128.43, 128.79, 129.37, 129.65, 131.83, 132.72, 135.14, 135.70, 136.21, 136.37, 137.73, 143.16, 150.16; MS (m/z) 439 (M^+); Anal. Calcd for $C_{22}H_{17}N_1O_3S_3$: C, 60.11, H, 3.90, N. 3.19. Found: C, 64.11, H, 4.26, N, 3.12.

Synthesis of 2-*p*-Tolyl-naphtho[1,8-*de*]-1,3-dithiin-1-*N*-benzenesulfonylsulfilimine (19)

2-tolyl-naphtho[1,8-*de*]-1,3-dithiin (**5b**) (294 mg, 1 mmol) and chloramine-B (267 mg, 1 mmol) was dissolved in 20 ml of ethanol-dichloromethane and stirred for 12 h under an Ar atmosphere. To this solution was added a 1M sodium hydride solution. The precipitates were filtered, washed with water and recrystallized from dichloromethane-ethanol to give the *N*-benzenesulfonylsulfilimine (**19**) in 69% yield.

2-*p*-Tolyl-naphtho[1,8-*de*]-1,3-dithiin-1-*N*-benzenesulfonyl-sulfilimine (19)

mp. 198-199 °C ; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.35 (s, 3H, CH_3), 5.05 (s, 1H. CH), 7.01 (d, J = 8.2 Hz, 2H, ArH), 7.15-7.20 (m,

4H, ArH), 7.36 (t, J = 7.6 Hz, 1H, ArH)), 7.49 (d, J = 8.2 Hz, 2H, ArH), 7.54 (d, J = 7.8 Hz, 1H, ArH), 7.63 (d, J = 7.6 Hz, 1H, ArH), 7.77 (t, J = 7.6 Hz, 1H, ArH), 7.90 (d, J = 7.6 Hz, 1H, ArH), 8.09 (d, J = 7.6 Hz, 1H, ArH), 8.47 (d, J = 7.6 Hz, 1H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ21.42, 60.90, 126.11, 126.22, 126.58. 126.63, 127.58, 127.73, 128.21, 128.34, 129.13, 129.22, 130.06, 130.48, 130.58, 132.87. 133.71, 134.61, 140.49, 143.61; IR (KBr) 996 cm^{-1} (SN), 1145, 1284 cm^{-1} (SO_2); MS (m/z) 449 (M^+); Anal. Calcd for $C_{24}H_{19}N_1O_2S_3$: C, 64.11, H, 4.25, N, 3.12. Found: C, 64.02, H, 4.24, N, 3.07.

General Photolysis Procedure

A solution of sulfilimines (0.1 mmol) in solvent (5 ml) was placed in a Pyrex round-bottomed flask equipped with a stirrer bar and a rubber septum. The solution was bubbled with Ar for 30 min to remove O_2. Irradiation of the samples was carried out using a 400 W high pressure mercury lamp while being stirred. The reaction progress was monitored by GC, HPLC, or ^{1}H NMR spectroscopy. After irradiation, the solvent was evaporated and the residue was purified by the preparative HPLC, and the products were characterized by NMR and GC-MS spectroscopies.

***N*-Benzylidene-4-methylbenzenesulfonamide (18a)**

mp. 112-113 °C (lit.[6a] 107 °C); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.44 (s, 3H, CH_3), 7.35 (d, J = 8.1 Hz, 2H, ArH), 7.52 (t, J = 7.6 Hz, 2H, ArH), 7.62 (t, J = 7.6 Hz, 1H, ArH), 7.89 (d, J = 8.1 Hz, 2H, ArH), 7.93 (t, J = 7.6 Hz, 1H, ArH) 9.03 (s, 1H, CH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 21.66, 128.10, 129.15, 129.79,

131.30, 132.38, 134.93, 135.13, 144.60, 170.13; MS (m/z) 259 (M^+).

4-Methyl-*N*-(4-methylbenzylidene)benzenesulfonamide (18b)

mp. 118-119 °C (lit.[6a] 116.5-117 °C); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.42 (s, 3H, CH_3). 2.44 (s, 3H, CH_3), 7.29 (d, J = 8.5 Hz, 2H, ArH), 7.34 (d, J = 8.5 Hz, 2H, ArH), 7.81 (d, J = 8.5 Hz, 2H, ArH), 7.88 (d, J = 8.5 Hz, 2H, ArH), 8.99 (s, 1H, CH); MS (m/z) 273 (M^+).

4-Methyl-*N*-(propylidene)benzenesulfonamide (18d)

Melting point was unmeasurable; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.17 (t, J = 4.1 Hz, 3H, CH_3), 2.55 (oct, J = 4.1 Hz, 2H, CH_2), 7.35 (d, J = 8.1 Hz, 2H. ArH), 7.35 (d, J = 8.1 Hz, 2H. ArH), 8.63 (t, J = 4.1 Hz, 1H, CH); MS (m/z) 211 (M^+).

***N*-Heptylidene-4-methylbenzenesulfonamide (18e)**

Melting point was unmeasurable; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.83-0.89(m, 3H, CH_3), 1.26-1.29 (m, 6H, CH_2), 1.58-1.64 (m, 2H, CH_2), 2.44 (s, 3H, CH_3), 2.47-2.54 (m, 2H, CH_2), 7.34 (d, J = 8.1 Hz, 2H, ArH), 7.81 (d, J = 8.1 Hz, 2H, ArH), 8.60 (t, J = 4.6 Hz, 1H); MS (m/z) 267 (M^+).

(*E*)-1-[[(4-Methylphenyl)sulfonyl]imino]-3-phenyl-2-propene (18f)

mp. 113-114 °C (lit.[7d] 109-110 °C); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.44 (s, 3H, CH_3), 6.99 (dd, J_1 = 15.7 Hz, J_2 = 9.5 Hz, 1H, C=CH), 7.31 (d, J = 8.1 Hz, 2H, ArH), 7.36-7.46 (m, 3H, C=CH,

ArH), 7.52-7.57 (m, 3H, ArH), 7.86 (d, J = 8.1 Hz, 2H, ArH), 8.78 (d, J = 9.5 Hz, 1H, C=CH); MS (m/z) 285 (M^+).

4-Methyl-*N*-(2-furylmethylidene)benzenesulfonamide (18g)
mp. 102-103 °C (lit.[6a] 100-102 °C); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 5.33 (s, 1H. CH), 6.31 (dd, J_1 = 3.2 Hz, J_2 = 1.9 Hz, 1H, 2-furylH), 6.35 (d, J = 3.2 Hz, 1H, 2-furylH), 7.36-7.40 (m, 2H, ArH), 7.47 (dd, J_1 = 8.1 Hz, J_2 = 1.1 Hz, 2H, ArH), 7.70 (dd, J_1 = 8.1 Hz, J_2 = 1.1 Hz, 2H, ArH); MS (m/z) 270 (M^+).

Reaction intermediate **17a** was isolated by silica-gel chromatography and liquid chromatography of the reaction mixture by stopping the photolysis of **16a** at the optimum point of conversion of **16a** to **17a**. Compound **17a** was stable, solid material.

3-Hydro-3-phenyl-naphtho[1,8-*ef*][1,4]dithia[2]azepin (17a)
m.p. 153-154 °C; IR (KBr): 1352, 1162 cm^{-1} (SO_2); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.17 (s, 3H), 6.62 (d, *J* = 8.4 Hz, 2H), 6.90 (s, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.16-7.22 (m, 1H), 7.27-7.32 (m, 1H), 7.35-7.42 (m, 3H), 7.49-7.51 (m, 1H), 7.57-7.60 (m, 3H), 7.67-7.70 (m, 1H), 7.81-7.84 (m, 1H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 21.3, 75.2, 125.3, 126.1, 126.8, 126.9, 128.4, 128.8, 129.0, 129.5, 129.8, 130.2, 131.6, 132.8, 135.2, 135.9, 136.1, 136.2, 138.0, 143.0; MS (m/z): 449 (M^+); Anal. Calcd for $C_{24}H_{19}NO_2S_3$: C, 64.11; H, 4.26; N, 3.12; Found: C, 64.10; H, 4.18; N, 3.07.

Irradiation of 2-Phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimine (16a)

A solution of 2-phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimine (**16a**) (10 mg, 0.02 mmol) in solvent (5 ml) was placed in a cylindrical quartz tube equipped with a stirrer bar and a silicon septum. The solution was bubbled with Ar for 30 min to remove O_2. Irradiation of samples was carried out using the output of a 500 W high pressure mercury lamp filtered through a Toshiba UVD33S filter and a monochromator set at 313 nm under conditions of complete light absorption. The reaction progress was monitored by HPLC or ^1H NMR spectroscopy. After irradiation, the solvent was evaporated and the residue was purified by preparative HPLC, and the product were characterized by NMR and GC-MS spectroscopies.

Benzophenone Dependence on the Photolysis of 2-Phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimine (16a)

A solution of 2-phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimine (**16a**) (7 mg, 0.02 mmol) and benzophenone (0.1 mmol) in dichloromethane was placed in a cylindrical quartz tube equipped with a stirrer bar and a silicon septum. The solution was bubbled with Ar for 30 min to remove O_2. Irradiation of samples was carried out using the output of a 500 W high pressure mercury lamp filtered through a Toshiba UVD33S filter and a monochromator set at 366 nm. Quantification was done with HPLC. Maleic anhydride was used as an external standard for HPLC. Yields were determined from solutions and irradiation times were kept under 1 h. The measurement of yields was several times by HPLC detection.

Cross-over of 2-Phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimine (16a) and 2-*p*-Tolyl-naphtho[1,8-*de*]-1,3-dithiin-1-*N*-benzenesulfonylsulfilimine (19)

2-Phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimine (**16a**) (22.5 mg, 0.05 mmol) and 2-*p*-tolyl-naphtho[1,8-*de*]-1,3-dithiin-1-*N*-benzenesulfonylsulfilimine (**19**) (23.1 mg, 0.1 mmol) were dissolved in 10 ml of deoxygenated benzene. The solution was irradiated with a high pressure mercury lamp (400 W) until the sulfoxides disappeared completely. The products were determined with ^{1}H-NMR and GC-MS spectroscopies.

***N*-(4-Methylbenzylidene)benzenesulfonamide (20)**

mp. 109-110 °C (lit.[6a] 107 °C); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.43 (s, 3H, CH_3), 7.30 (d, J = 8.3 Hz, 2H, ArH), 7.51-7.63 (m, 3H, ArH), 7.83 (d, J = 8.3 Hz, 2H, ArH), 7.99-8.03 (m, 2H, ArH), 9.02 (s, 1H, CH); MS (m/z) 259 (M^+).

Quantum Yields

The measurement of the quantum yield was carried out using the output of a 500 W high pressure mercury lamp filtered through a Toshiba UVD33S filter and a monochromator set at 313 nm under conditions of complete light absorption. The fulgide, (E)-α-(2,5-dimethyl-3-furyl-ethylidene)(isopropylidene)succinic an-hydride, which has a quantum yield of 0.20 for its photocolouration at 313 nm in toluene was used as an actinometer. Quantification was done with HPLC. Maleic anhydride was used as an external standard for HPLC. Sample and actinometer cells were sequentially irradiated. The actinometer cell were used to determined the photo flux, which

was then used to convert the rate of loss of the material into a quantum yield. All quantum yields were determined from the solutions that began at concentration of 3-6 mM, and conversions were kept under 5%. The measurement of quantum yields was several times by HPLC detection.

Effect of Light Intensity

The measurement of the light intensity effect was carried out using the output of a 500 W high pressure mercury lamp filtered through a Toshiba UVD33S filter and a monochromator set at 313 nm under conditions of complete light absorption. The light intensity was attenuated by using a quartz filter (313 nm; 27%, 52%, and 83%). Quantification was done with HPLC. Maleic anhydride was used as an external standard for HPLC. Yields were determined from the solutions that began at concentration 3 mM, and irradiation times were kept under 1 h. The measurement of yields was several times by HPLC detection.

Detailed Information of the X-ray Crystal Analysis of Naphtho[1,8-*de*]-1,3-dithiin (4)

Crystal Data

$C_{11}H_8S_2$

F.W. 204.31 F(000)=424

crystal dimensions: 0.10x0.10x0.30 mm

peak width at half-height=0.00

Mo Kα radiation (λ=0.71073 Å)

temperature=23±1 °C

orthorhombic space group Pnma

a=7.511(0) Å b=14.539(1) Å c=8.761(1) Å

V=951.7 $Å^3$

Z=4 ρ=1.43 g/cm^3

μ=4.8 cm^{-1}

Intensity Measurements

Instrument:	Enraf-Nonius CAD4 diffractometer
Monochromator:	Graphite crystal, incident beam
Attenuator:	Zr foil, factor 13.4
Take-off angle:	2.8°
Detector aperture:	1.4 to 1.6 mm horizontal
	4.0 mm vertical

Crystal-detector dist.:21 cm

Scan type:	ω–2θ
Scan rate:	1-20 °/min (in omega)
Scan width, deg:	0.5+0.640tan θ
Maximum 2θ:	50.0°

No. of refl. measured: 1006 total, 998 unique

Corrections:	Lorentz-polarization
	Linear decay (from 1.000 to 1.004 on I)
	Emprical absorption (from 0.98 to 1.00 on I)

Structure Solution and Refinement

Solution:	Direct methods
Hydrogen atoms:	Included as fixed contribution to the structure factor
Refinement:	Full-matrix least-squares
Minimization function:	$\Sigma w(\|Fo\|-\|Fc\|)^2$
Least-squares weights:	$4Fo^2/\sigma^2(Fo^2)$
Anomalous dispersion:	All non-hydrogen atoms
Reflection included:	512 with $Fo^2>3.0\sigma(Fo^2)$
Parameter refined:	64
Unweighted agreement factor:	0.037
Weighted agreement factor:	0.038
Esd of obs. of unit weight:	0.93
Convergence, large shifts:	0.04σ
High peak in final diff. map:	0.20 (5) e/Å^3
Low peak in final diff. map:	-0.25 (0) e/Å^3
Computer hardware:	VAX
Computer software:	MolEn (Enraf-Nonius)

Table of Positional Parameters and Their Estimated Standard Deviations.

Atom	x	y	z	B(A2)
S1	0.5377(2)	0.35177(7)	0.6512(1)	4.33(2)
C1	0.3487(5)	0.3379(2)	0.5334(4)	2.92(7)
C2	0.2682(6)	0.4178(3)	0.4854(5)	4.03(9)
C3	0.1156(6)	0.4165(3)	0.3964(5)	4.6(1)
C4	0.0428(6)	0.3353(3)	0.3536(5)	4.9(1)
C5	0.1194(8)	0.250	0.3992(6)	3.6(1)
C6	0.2775(7)	0.250	0.4915(6)	2.7(1)
C7	0.6580(8)	0.250	0.5989(8)	4.2(1)
H2	0.3249	0.475	0.5154	4.0*
H3	0.0609	0.475	0.3675	4.0*
H4	-0.0584	0.329	0.2912	4.0*
H7	0.7690	0.250	0.6439	4.0*
H7'	0.6764	0.250	0.4765	4.0*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Table of General Displacement Parameter Expressions - B's.

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	Beqv
S1	4.54(4)	3.38(3)	5.07(5)	-0.95(4)	-0.93(5)	-0.33(5)	4.33(2)
C1	3.2(2)	2.7(1)	2.8(1)	0.1(1)	0.4(1)	0.0(1)	2.92(7)
C2	5.1(2)	2.9(1)	4.0(2)	0.4(2)	0.9(2)	0.3(2)	4.03(9)
C3	5.3(2)	4.7(2)	4.0(2)	1.9(2)	0.4(2)	1.1(2)	4.6(1)
C4	3.8(1)	7.6(2)	3.3(2)	1.3(2)	-0.4(2)	0.6(2)	4.9(1)
C5	3.4(3)	4.6(3)	2.6(2)	0	0.3(2)	0	3.6(1)
C6	2.5(2)	3.3(2)	2.2(2)	0	0.2(2)	0	2.7(1)
C7	2.8(3)	5.1(3)	4.7(3)	0	-0.3(3)	0	4.2(1)

The form of the anisotropic displacement parameter is: exp[-0.25{h2a2B(1,1) + k2b2B(2,2) + l2c2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3)}]where a, b, and c are reciprocal lattice constants.

Table of Refined Displacement Parameter Expressions - Beta's.

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
S1	0.0201(2)	0.00400(4)	0.0167(2)	-0.0044(2)	-0.0071(4)	-0.0013(2)
C1	0.0143(7)	0.0032(2)	0.0092(5)	0.0003(7)	0.003(1)	0.0001(6)
C2	0.023(1)	0.0035(2)	0.0133(6)	0.0018(8)	0.007(1)	0.0012(6)
C3	0.0236(9)	0.0055(2)	0.0130(7)	0.0087(8)	0.003(1)	0.0043(7)
C4	0.0168(7)	0.0090(3)	0.0108(5)	0.006(1)	-0.003(1)	0.0023(9)
C5	0.015(1)	0.0054(2)	0.0087(8)	0)	0.002(2)	0
C6	0.011(1)	0.0039(2)	0.0073(7)	0	0.002(1)	0
C7	0.012(1)	0.0060(3)	0.016(1)	0	-0.002(2)	0

The form of the anisotropic displacement parameter is: exp[-(B(1,1)*h2 + B(2,2)*k2 + B(3,3)*l2 + B(1,2)*hk + B(1,3)*hl + B(2,3)*kl)].

Table of General Displacement Parameter Expressions - U's.

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
S1	0.0574(5)	0.0428(4)	0.0642(6)	-0.0120(5)	-0.0118(6)	-0.0041(6)
C1	0.041(2)	0.035(2)	0.035(2)	0.001(2)	0.005(2)	0.000(2)
C2	0.065(3)	0.037(2)	0.051(2)	0.005(2)	0.012(2)	0.004(2)
C3	0.067(3)	0.059(2)	0.050(3)	0.024(1)	0.005(2)	0.014(2)
C4	0.048(2)	0.096(3)	0.041(2)	0.017(3)	-0.005(2)	0.007(3)
C5	0.044(3)	0.058(3)	0.033(3)	0	0.004(3)	0
C6	0.032(3)	0.042(3)	0.028(3)	0	0.002(2)	0
C7	0.036(3)	0.064(4)	0.060(4)	0	-0.004(3)	0

The form of the anisotropic displacement parameter is: exp[-2pI2{h2a2U(1,1) + k2b2U(2,2) + l2c2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)}] where a, b, and c are reciprocal lattice constants.

Table of Root-Mean-Square Amplitudes of Anisotropic Displacement in Angstroms.

Atom	Min.	Int'med.	Max.
S1	0.182	0.240	0.271
C1	0.181	0.186	0.209
C2	0.190	0.211	0.270
C3	0.186	0.215	0.251
C4	0.186	0.222	0.319
C5	0.179	0.212	0.240
C6	0.164	0.182	0.204
C7	0.187	0.247	0.254

Table of Bond Distances in Angstroms.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
S1	C1	1.764(4)	C3	C4	1.354(6)
S1	C7	1.793(4)	C3	H3	0.979(4)
S1	C11	1.821(4)	C4	C5	1.423(5)
C1	C2	1.375(5)	C4	H4	0.939(4)
C1	C6	1.432(4)	C5	C6	1.434(8)
C2	C3	1.384(6)	C7	H7	0.922(6)
C2	H2	0.966(4)	C7	H7	1.075(7)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Bond Angles in Degrees.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C1	S1	C7	99.4(2)	C3	C4	C5	121.3(4)
S1	C1	C2	115.7(3)	C3	C4	H4	124.9(5)
S1	C1	C6	123.5(3)	C5	C4	H4	113.8(5)
C2	C1	C6	120.8(4)	C4	C5	C4*	121.1(5)
C1	C2	C3	121.5(4)	C4	C5	C6	119.4(3)
C1	C2	H2	116.5(4)	C1	C6	C1*	126.2(4)
C3	C2	H2	121.9(4)	C1	C6	C5	116.9(2)
C2	C3	C4	120.1(4)	S1	C7	S1*	111.3(3)
C2	C3	H3	118.7(4)	S1	C7	H7	110.4(3)
C4	C3	H3	121.3(4)	S1	C7	H7'	108.5(3)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Torsional Angles in Degrees.

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C7	S1	C1	C2	-150.16 (0.34)
C7	S1	C1	C6	31.40 (0.41)
S1	C1	C2	C3	-177.97 (0.34)
C6	C1	C2	C3	0.51 (0.65)
S1	C1	C6	C5	177.94 (0.37)
C2	C1	C6	C5	-0.42(0.67
C1	C2	C3	C4	-0.54 (0.67)
C2	C3	C4	C5	0.49 (0.68)
C3	C4	C5	C6	178.43 (0.45)
C4	C5	C6	C1	0.37 (0.73)

Detailed Information of the X-ray Crystal Analysis of 2-Methyl-naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimine (16c)

Crystal Data

$C_{19}H_{17}NO_2S_3$

F.W. 387.54 F(000)=404

crystal dimensions: 0.50x0.40x0.20 mm

peak width at half-height=0.00

Mo Kα radiation (λ=0.71073 Å)

temperature=23±1 °C

orthorhombic space group P1

a=10.158(0) Å b=12.257(1) Å c=8.390(1) Å

α=104.96(28) Å β=109.05(30) Å γ67.81(28) Å

V=903.3 $Å^3$

Z=2 ρ=1.42 g/cm^3

μ=4.1 cm^{-1}

Intensity Measurements

Instrument:	Enraf-Nonius CAD4 diffractometer
Monochromator:	Graphite crystal, incident beam
Attenuator:	Zr foil, factor 13.4
Take-off angle:	2.8°
Detector aperture:	1.4 to 1.6 mm horizontal
	4.0 mm vertical
Crystal-detector dist.:	21 cm
Scan type:	ω–2θ
Scan rate:	1-20 °/min (in omega)
Scan width, deg:	0.5+0.470tan θ
Maximum 2θ:	50.0°

No. of refl. measured: 3390 total, 3156 unique

Corrections: Lorentz-polarization

Linear decay (from 1.000 to 1.029 on I)

Emprical absorption (from 0.67 to 1.00 on I)

Structure Solution and Refinement

Solution: Direct methods

Hydrogen atoms: Included as fixed contribution to the structure factor

Refinement: Full-matrix least-squares

Minimization function: $\Sigma w(|Fo|-|Fc|)^2$

Least-squares weights: $4Fo^2/\sigma^2(Fo^2)$

Anomalous dispersion: All non-hydrogen atoms

Reflection included: 2483 with $Fo^2>3.0\sigma(Fo^2)$

Parameter refined: 226

Unweighted agreement factor: 0.043

Weighted agreement factor: 0.046

Esd of obs. of unit weight: 0.82

Convergence, large shifts: 0.02σ

High peak in final diff. map: 0.45(6) e/Å^3

Low peak in final diff. map: -0.319 (0) e/Å^3

Computer hardware: VAX

Computer software: MolEn (Enraf-Nonius)

Table of Positional Parameters and Their Estimated Standard Deviations.

Atom	x	y	z	B(A2)
S1	0.39958(9)	0.34096(7)	0.4968(1)	2.75(2)
S2	0.6590(1)	0.19471(8)	0.6591(1)	3.51(2)
S3	0.1824(1)	0.43719(9)	0.2079(1)	3.89(2)
O1	0.7916(3)	0.2052(3)	0.7821(4)	5.21(8)
O2	0.5677(3)	0.1474(2)	0.7039(3)	4.94(7)
N1	0.5672(3)	0.3277(2)	0.6078(4)	3.24(7)
C1	0.2933(3)	0.4675(3)	0.6159(4)	2.68(7)
C2	0.3438(4)	0.4758(3)	0.7904(4)	3.19(8)
C3	0.2670(4)	0.5685(3)	0.8946(4)	3.62(9)
C4	0.1408(4)	0.6504(3)	0.8271(4)	3.58(9)
C5	0.0831(4)	0.6442(3)	0.6475(4)	3.16(8)
C6	-0.0522(4)	0.7272(3)	0.5771(5)	3.88(9)
C7	-0.1081(4)	0.7205(3)	0.4049(5)	4.3(1)
C8	-0.0302(4)	0.6329(3)	0.2968(5)	4.1(1)
C9	0.0998(4)	0.5497(3)	0.3573(4)	3.15(8)
C10	0.1607(3)	0.5513(3)	0.5378(4)	2.77(7)
C11	0.3739(4)	0.4079(3)	0.3143(4)	3.14(8)
C12	0.4675(4)	0.3206(3)	0.2000(4)	4.3(1)
C13	0.7060(4)	0.1054(3)	0.4720(4)	3.27(8)
C14	0.6198(4)	0.0382(3)	0.3617(5)	3.57(9)
C15	0.6494(4)	-0.0211(3)	0.2071(5)	4.0(1)
C16	0.7654(5)	-0.0169(3)	0.1609(5)	4.3(1)
C17	0.8532(4)	0.0497(4)	0.2732(5)	4.9(1)
C18	0.8242(4)	0.1093(4)	0.4288(5)	4.3(1)
C19	0.7984(6)	-0.0806(5)	-0.0068(6)	6.5(2)
H2	0.437(3)	0.417(3)	0.829(4)	4.0*
H3	0.298(3)	0.570(3)	1.007(4)	4.0*
H4	0.083(3)	0.711(3)	0.895(4)	4.0*
H6	-0.108(3)	0.784(3)	0.645(4)	4.0*
H7	-0.199(3)	0.774(3)	0.363(4)	4.0*
H8	-0.061(3)	0.627(3)	0.192(4)	4.0*

Table of Positional Parameters and Their Estimated Standard Deviations (continue).

Atom	x	y	z	B(A2)
H11	0.397(3)	0.479(3)	0.348(4)	4.0*
H12	0.4543	0.3556	0.1053	4.0*
H12'	0.5681	0.3007	0.2627	4.0*
H12"	0.4399	0.2506	0.1619	4.0*
H14	0.541(3)	0.046(3)	0.385(4)	4.0*
H15	0.588(3)	-0.071(3)	0.117(4)	4.0*
H17	0.953(3)	0.048(3)	0.251(4)	4.0*
H18	0.887(3)	0.168(3)	0.506(4)	4.0*
H19	0.7350	-0.1218	-0.0745	4.0*
H19'	0.7950	-0.0222	-0.0726	4.0*
H19"	0.8995	-0.1344	0.0098	4.0*

Starred atoms were refined isotropically.Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Table of General Displacement Parameter Expressions - B's.

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	Beqv
S1	3.57(3)	2.74(3)	2.28(3)	-1.51(2)	0.75(2)	0.21(2)	2.75(2)
S2	4.02(3)	3.30(3)	2.85(3)	-0.94(3)	0.71(3)	0.46(3)	3.51(2)
S3	4.78(4)	4.75(4)	1.99(3)	-2.04(3)	0.34(3)	0.19(3)	3.89(2)
O1	4.6(1)	5.6(1)	3.3(1)	-1.0(1)	-0.3(1)	0.0(1)	5.21(8)
O2	6.6(1)	4.6(1)	4.9(1)	-1.77(8)	2.48(8)	1.48(8)	4.94(7)
N1	3.2(1)	2.7(1)	3.6(1)	-1.11(8)	0.69(9)	0.10(9)	3.24(7)
C1	3.1(1)	2.9(1)	2.3(1)	-1.41(8)	0.71(8)	0.17(9)	2.68(7)
C2	3.3(1)	3.9(1)	2.4(1)	-1.21(9)	0.58(9)	0.7(1)	3.19(8)
C3	3.9(1)	4.8(1)	2.3(1)	-1.9(1)	0.7(1)	0.1(1)	3.62(9)
C4	3.8(1)	4.0(1)	3.0(1)	-1.5(1)	1.3(1)	-0.3(1)	3.58(9)
C5	3.4(1)	3.1(1)	3.3(1)	-1.45(8)	0.86(9)	0.3(1)	3.16(8)
C6	3.6(1)	3.5(1)	4.6(2)	-1.1(1)	1.2(1)	0.5(1)	3.88(9)
C7	3.6(1)	4.0(1)	5.1(2)	-0.7(1)	0.4(1)	2.0(1)	4.3(1)
C8	4.3(1)	4.8(1)	3.4(1)	-1.8(1)	-0.1(1)	1.7(1)	4.1(1)
C9	3.8(1)	3.6(1)	2.5(1)	-1.86(9)	0.34(9)	0.61(9)	3.15(8)
C10	3.1(1)	3.0(1)	2.6(1)	-1.50(8)	0.63(8)	0.53(9)	2.77(7)
C11	4.3(1)	3.1(1)	2.5(1)	-1.69(9)	0.94(9)	0.46(9)	3.14(8)
C12	6.1(2)	4.2(1)	3.1(1)	-1.7(1)	1.9(1)	0.7(1)	4.3(1)
C13	3.6(1)	2.8(1)	3.1(1)	-0.8(1)	0.8(1)	0.5(1)	3.27(8)
C14	3.9(1)	2.9(1)	4.0(1)	-1.16(9)	1.0(1)	0.7(1)	3.57(9)
C15	5.0(2)	2.7(1)	3.7(2)	-1.3(2)	0.7(2)	0.1(1)	4.0(1)
C16	5.1(2)	3.1(1)	3.8(2)	-0.3(1)	1.3(1)	0.2(1)	4.3(1)
C17	4.6(1)	5.1(2)	5.3(2)	-1.4(2)	2.4(1)	0.0(1)	4.9(1)
C18	4.0(1)	4.3(2)	4.5(2)	-1.8(1)	1.2(1)	-0.3(1)	4.3(1)
C19	8.0(2)	5.5(2)	5.0(2)	-1.3(2)	2.7(2)	-0.7(2)	6.5(1)

The form of the anisotropic displacement parameter is: exp[-0.25{h2a2B(1,1) + k2b2B(2,2) + l2c2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3)}]where a, b, and c are reciprocal lattice constants.

Table of Refined Displacement Parameter Expressions - Beta's.

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
S1	0.01081(8)	0.00544(5)	0.0093(1)	-0.00738(9)	-0.0053(2)	0.0012(1)
S2	0.0122(1)	0.00656(6)	0.0116(1)	-0.0046(1)	0.0050(2)	0.0026(1)
S3	0.0144(1)	0.00944(7)	0.0081(1)	-0.0100(1)	0.0024(2)	0.0011(2)
O1	0.0141(4)	0.0112(3)	0.0133(5)	-0.0048(5)	-0.0021(7)	0.0001(6)
O2	0.0199(3)	0.0091(2)	0.0198(4)	-0.0087(4)	0.0174(5)	0.0084(4)
N1	0.0097(3)	0.0054(2)	0.0145(5)	-0.0054(4)	0.0048(6)	0.0006(5)
C1	0.0095(3)	0.0057(2)	0.0094(4)	-0.0069(4)	0.0050(6)	0.0010(5)
C2	0.0101(4)	0.0077(3)	0.0097(5)	-0.0059(5)	0.0041(6)	0.0038(6)
C3	0.0118(4)	0.0095(3)	0.0093(5)	-0.0091(5)	0.0050(7)	0.0008(6)
C4	0.0116(4)	0.0079(3)	0.0124(5)	-0.0076(5)	0.0093(7)	-0.0015(6)
C5	0.0102(3)	0.0061(2)	0.0135(5)	-0.0071(4)	0.0060(7)	0.0017(6)
C6	0.0110(4)	0.0069(3)	0.0186(6)	-0.0054(5)	0.0085(8)	0.0031(7)
C7	0.0108(4)	0.0079(3)	0.0209(7)	-0.0032(6)	0.0028(9)	0.0112(7)
C8	0.0131(4)	0.0095(3)	0.0136(6)	-0.0088(5)	-0.0006(8)	0.0094(6)
C9	0.0113(4)	0.0071(2)	0.0102(5)	-0.0091(4)	0.0024(7)	0.0035(5)
C10	0.0094(3)	0.0060(2)	0.0108(5)	-0.0074(4)	0.0045(6)	0.0030(5)
C11	0.0131(4)	0.0061(2)	0.0103(5)	-0.0083(4)	0.0066(7)	0.0026(5)
C12	0.0185(5)	0.0084(3)	0.0125(5)	-0.0081(6)	0.0136(7)	0.0038(6)
C13	0.0109(4)	0.0055(2)	0.0128(5)	-0.0038(5)	0.0054(7)	0.0026(6)
C14	0.0119(4)	0.0058(2)	0.0163(6)	-0.0057(5)	0.0070(8)	0.0039(6)
C15	0.0151(5)	0.0055(3)	0.0151(6)	-0.0065(5)	0.0047(9)	0.0005(6)
C16	0.0153(5)	0.0061(3)	0.0155(6)	-0.0015(6)	0.0093(9)	0.0011(7)
C17	0.0139(5)	0.0100(4)	0.0215(7)	-0.0066(6)	0.0167(8)	0.0000(8)
C18	0.0122(4)	0.0086(3)	0.0182(7)	-0.0088(5)	0.0081(9)	-0.0019(8)
C19	0.0243(7)	0.0110(5)	0.0205(8)	-0.0064(9)	0.019(1)	-0.004(1)

The form of the anisotropic displacement parameter is: exp[-(B(1,1)*h2 + B(2,2)*k2 + B(3,3)*l2 + B(1,2)*hk + B(1,3)*hl + B(2,3)*kl)].

Table of General Displacement Parameter Expressions - U's.

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
S1	0.0453(3)	0.0346(3)	0.0289(3)	-0.0191(2)	0.0095(3)	0.0026(3)
S2	0.0509(4)	0.0418(4)	0.0361(4)	-0.0119(3)	0.0090(3)	0.0058(3)
S3	0.0605(5)	0.0602(5)	0.0252(4)	-0.0259(4)	0.0043(3)	0.0024(3)
O1	0.059(2)	0.072(2)	0.041(1)	-0.012(1)	-0.004(1)	0.000(1)
O2	0.083(1)	0.058(1)	0.062(1)	-0.022(1)	0.031(1)	0.019(1)
N1	0.0041(1)	0.035(1)	0.045(1)	-0.014(1)	0.009(1)	0.001(1)
C1	0.040(1)	0.036(1)	0.029(1)	-0.018(1)	0.009(1)	0.002(1)
C2	0.042(1)	0.049(2)	0.030(1)	-0.015(1)	0.007(1)	0.008(1)
C3	0.049(2)	0.061(2)	0.029(2)	-0.024(1)	0.009(1)	0.002(1)
C4	0.049(2)	0.051(2)	0.039(2)	-0.020(1)	0.017(1)	-0.003(1)
C5	0.043(1)	0.039(1)	0.042(2)	-0.018(1)	0.011(1)	0.004(1)
C6	0.046(2)	0.044(2)	0.058(2)	-0.014(1)	0.015(1)	0.007(1)
C7	0.045(2)	0.050(2)	0.065(2)	-0.008(1)	0.005(2)	0.025(1)
C8	0.055(2)	0.061(2)	0.042(2)	-0.023(1)	-0.001(1)	0.021(1)
C9	0.048(2)	0.045(1)	0.032(1)	-0.024(1)	0.004(1)	0.008(1)
C10	0.039(1)	0.038(1)	0.033(1)	-0.019(1)	0.008(1)	0.007(1)
C11	0.055(2)	0.039(1)	0.032(1)	-0.021(1)	0.012(1)	0.006(1)
C12	0.078(2)	0.054(2)	0.039(2)	-0.021(1)	0.025(1)	0.009(1)
C13	0.046(2)	0.035(2)	0.040(2)	-0.010(1)	0.010(1)	0.006(1)
C14	0.050(2)	0.037(1)	0.051(2)	-0.015(1)	0.013(1)	0.009(1)
C15	0.063(2)	0.035(2)	0.047(2)	-0.017(1)	0.009(2)	0.001(1)
C16	0.064(2)	0.039(2)	0.048(2)	-0.004(2)	0.017(2)	0.002(2)
C17	0.058(2)	0.064(2)	0.067(2)	-0.017(2)	0.030(2)	0.000(2)
C18	0.051(2)	0.055(2)	0.057(2)	-0.023(1)	0.015(2)	-0.004(2)
C19	0.102(3)	0.070(3)	0.064(3)	-0.016(2)	0.034(2)	-0.008(2)

The form of the anisotropic displacement parameter is: exp[-2pI2{h2a2U(1,1) + k2b2U(2,2) + l2c2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)}] where a, b, and c are reciprocal lattice constants.

Table of Root-Mean-Square Amplitudes of Anisotropic Displacement in Angstroms.

Atom	Min.	Int'med.	Max.
S1	0.168	0.172	0.216
S2	0.190	0.204	0.236
S3	0.158	0.239	0.256
O1	0.185	0.246	0.321
O2	0.186	0.254	0.297
N1	0.179	0.202	0.224
C1	0.168	0.176	0.206
C2	0.171	0.206	0.222
C3	0.169	0.215	0.251
C4	0.182	0.211	0.242
C5	0.181	0.205	0.213
C6	0.209	0.213	0.241
C7	0.186	0.236	0.272
C8	0.181	0.228	0.269
C9	0.176	0.184	0.234
C10	0.166	0.183	0.210
C11	0.169	0.187	0.236
C12	0.172	0.231	0.280
C13	0.187	0.199	0.223
C14	0.186	0.225	0.225
C15	0.180	0.221	0.264
C16	0.187	0.225	0.280
C17	0.206	0.256	0.279
C18	0.205	0.226	0.267
C19	0.214	0.298	0.335

Table of Bond Distances in Angstroms.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
S1	N1	1.620(3)	C13	C18	1.382(7)
S1	C1	1.792(3)	C14	C15	1.380(5)
S1	C11	1.821(4)	C14	H14	0.86(4)
S2	O1	1.432(3)	C15	C16	1.367(7)
S2	O2	1.444(4)	C15	H15	1.04(3)
S2	N1	1.632(3)	C16	C17	1.398(6)
S2	C13	1.760(3)	C16	C19	1.499(6)
S3	C9	1.760(3)	C17	C18	1.386(6)
S3	C11	1.793(3)	C17	H17	1.08(4)
C1	C2	1.375(4)	C18	H18	1.09(4))
C1	C10	1.423(4)	C19	H19	0.922(6)
C2	C3	1.388(5)	C19	H19'	0.995(7)
C2	H2	0.96(3)	C19	H19"	0.976(5)
C3	C4	1.350(4)			
C3	H3	0.89(3)			
C4	C5	1.421(5)			
C4	H4	0.95(3)			
C5	C6	1.413(4)			
C5	C10	1.421(4)			
C6	C7	1.363(5)			
C6	H6	0.91(3)			
C7	C8	1.387(5)			
C7	H7	0.93(3)			
C8	C9	1.363(4)			
C8	H8	0.82(3)			
C9	C10	1.434(4)			
C11	C12	1.505(5)			
C11	H11	0.94(4)			
C12	H12	0.947(4)			
C12	H12'	0.953(4)			
C12	H12"	0.947(4)			
C13	C14	1.387(5)			

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Bond Angles in Degrees.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N1	S1	C1	130.0(1)	C7	C8	C9	122.0(3)
N1	S1	C11	105.6(2)	C7	C8	H8	122.(2)
C1	S1	C11	99.1(2)	C7	C8	C9	122.0(3)
O1	S2	O2	118.6(2)	C9	C8	H8	116.(2)
O1	S2	N1	105.5(2)	S3	C9	C8	117.8(2)
O1	S2	C13	108.0(2)	S3	C9	C10	122.0(2)
O2	S2	N1	111.1(2)	C8	C9	C10	120.0(3)
O2	S2	C13	107.9(2)	C1	C10	C5	117.3(3)
N1	S2	C13	105.0(2)	C1	C10	C9	117.5(2)
C9	S3	C11	101.6(1)	C5	C10	C9	117.5(2)
S1	N1	S2	113.1(2)	S1	C11	S3	104.4(2)
S1	C1	C2	115.5(2)	S1	C11	C12	109.5(2)
S1	C1	C10	123.1(2)	S1	C11	H11	112.(2)
C2	C1	C10	121.4(3)	S3	C11	C 12	110.7(2)
C1	C2	C3	120.2(3)	S3	C11	H11	110.(2))
C1	C2	H2	114.(2)	C12	C11	H11	110.(2)
C3	C2	H2	125.(2)	C11	C12	H12	109.5(3)
C2	C3	C4	120.9(3)	C11	C12	H12'	109.1(3)
C2	C3	H3	119.(2)	C11	C12	H12"	109.4(4)
C4	C3	H3	120.(2)	S2	C13	C14	120.8(3)
C3	C4	C5	120.9(3)	S2	C13	C18	119.3(3)
C3	C4	H4	123.(2)	C14	C13	C18	119.7(3)
C5	C4	H4	116.(4)	C13	C14	C15	119.9(4)
C4	C5	C6	120.7(3)	C13	C14	H14	117.(2)
C4	C5	C10	119.4(3)	C15	C14	H14	122.(2)
C6	C5	C10	119.8(3)	C14	C15	C16	121.2(4)
C5	C6	C7	120.7(3)	C14	C15	H15	124.(2)
C5	C6	H6	122.(2)	C16	C15	H15	115.(2)
C7	C6	H6	118.(2)	C15	C16	C17	118.9(4)
C6	C7	C8	119.8(3)	C15	C16	C19	121.7(4)
C6	C7	H7	119.(2)	C17	C16	C19	119.5(5)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Bond Angles in Degrees (continue).

Atom 1	Atom 2	Atom 3	Angle
C16	C17	C18	120.2(5)
C16	C17	H17	122.(2)
C18	C17	H17	117.(2)
C13	C18	C17	120.1(4)
C13	C18	H18	122.(2)
C17	C18	H18	118.(2)
C16	C19	H19	114.5(6)
C16	C19	H19'	109.6(4)
C16	C19	H19"	110.9(4)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Torsional Angles in Degrees.

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C1	S1	N1	S2	126.00 (0.18)
C11	S1	N1	S2	-130.53 (0.18)
N1	S1	C1	C2	-38.22 (0.32)
N1	S1	C1	C10	145.08 (0.30)
C11	S1	C1	C2	-146.63 (0.30)
C11	S1	C1	C10	36.67 (0.33)
N1	S1	C11	S3	-173.56 (0.15)
N1	S1	C11	C12	67.91 (0.29)
C1	S1	C11	S3	-67.19 (0.18)
C1	S1	C11	C12	174.28 (0.27)
O1	S2	N1	S1	-169.05 (0.19)
O2	S2	N1	S1	-39.40 (0.23)
C13	S2	N1	S1	77.02 (0.23)
O1	S2	C13	C14	152.28 (0.29)
O1	S2	C13	C18	-32.46 (0.35)
O2	S2	C13	C14	23.01 (0.34)
O2	S2	C13	C18	-161.72 (0.29)
N1	S2	C13	C14	-95.57 (0.31)
N1	S2	C13	C18	79.70 (0.33)
C11	S3	C9	C8	148.59 (0.32)
C11	S3	C9	C10	-35.12 (0.34)
C9	S3	C11	S1	67.58 (0.19)
C9	S3	C11	C12	-174.67 (0.25)
S1	C1	C2	C3	-178.03 (0.30)
C10	C1	C2	C3	-1.27 (0.57)
S1	C1	C10	C5	176.75 (0.27)
S1	C1	C10	C9	-3.48 (0.52)
C2	C1	C10	C5	0.23 (0.53)
C2	C1	C10	C9	-180.00 (0.66)
C1	C2	C3	C4	1.16 (0.61)
C2	C3	C4	C5	-0.02 (0.72)
C3	C4	C5	C6	177.35 (0.39)

Table of Torsional Angles in Degrees (continue).

Atom 1	Atom 2	Atom 3	Atom 4	Angle	
C3	C4	C5	C10	-1.01	(0.58)
C4	C5	C6	C7	-179.48	(0.78)
C10	C5	C6	C7	-1.12	(0.59)
C4	C5	C10	C1	0.89	(0.52)
C4	C5	C10	C9	-178.90	(0.34)
C6	C5	C10	C1	-177.49	(0.34)
C6	C5	C10	C9	2.72	(0.53)
C5	C6	C7	C8	-1.32	(0.64)
C6	C7	C8	C9	2.14	(0.66)
C7	C8	C9	S3	175.92	(0.34)
C7	C8	C9	C10	-0.44	(0.62)
S3	C9	C10	C1	2.06	(0.53)
S3	C9	C10	C5	-178.17	(0.28)
C8	C9	C10	C1	178.26	(0.37)
C8	C9	C10	C5	-1.97	(0.54)
S2	C13	C14	C15	173.12	(0.27)
C18	C13	C14	C15	-2.12	(0.53)
S2	C13	C18	C17	-173.09	(0.32)
C14	C13	C18	C17	2.22	(0.57)
C13	C14	C15	C16	1.24	(0.55)
C14	C15	C16	C17	-0.44	(0.57)
C14	C15	C16	C19	-179.79	(0.38)
C15	C16	C17	C18	0.54	(0.61)
C19	C16	C17	C18	179.91	(0.42)
C16	C17	C18	C13	-1.44	(0.62)

Detailed information of the X-ray Crystal Analysis of 3-Hydro-3-phenyl-2-tosyl-naphtho[1,8-*e,f*][1,4]dithia[2]azepine (17a)

Crystal Data

$C_{24}H_{19}NO_2S_3$

F.W. 449.62 F(000)=1872

crystal dimensions: 0.50x0.30x0.20 mm

peak width at half-height=0.00

Mo Kα radiation (λ=0.71073 Å)

temperature=23±1 °C

orthorhombic space group Pbca

a=18.672(2) Å b=11.699(1) Å c=19.171(1) Å

V=4187.7 $Å^3$

Z=8 ρ=1.43 g/cm^3

$\mu=3.6\ cm^{-1}$

Intensity Measurements

Instrument:	Enraf-Nonius CAD4 diffractometer
Monochromator:	Graphite crystal, incident beam
Attenuator:	Zr foil, factor 13.4
Take-off angle:	2.8°
Detector aperture:	1.3 to 2.6 mm horizontal
	4.0 mm vertical

Crystal-detector dist.:21 cm

Scan type:	ω–2θ
Scan rate:	1-20 °/min (in omega)
Scan width, deg:	0.4+1.290tan θ
Maximum 2θ:	50.0°

No. of refl. measured: 4115 total, 4104 unique

Corrections:	Lorentz-polarization
	Linear decay (from 1.001 to 1.082 on I)
	Emprical absorption (from 0.97 to 1.00 on I)

Structure Solution and Refinement

Solution:	Direct methods
Hydrogen atoms:	Included as fixed contribution to the structure factor
Refinement:	Full-matrix least-squares
Minimization function:	$\Sigma w(\|Fo\|-\|Fc\|)^2$
Least-squares weights:	$4Fo^2/\sigma^2(Fo^2)$
Anomalous dispersion:	All non-hydrogen atoms
Reflection included:	1911 with $Fo^2>3.0\sigma(Fo^2)$
Parameter refined:	271
Unweighted agreement factor:	0.041
Weighted agreement factor:	0.043
Esd of obs. of unit weight:	2.13
Convergence, large shifts:	0.06σ
High peak in final diff. map:	0.30(5) e/Å^3
Low peak in final diff. map:	-.13 (0) e/Å^3
Computer hardware:	VAX
Computer software:	MolEn (Enraf-Nonius)

Table of Positional Parameters and Their Estimated Standard Deviations.

Atom	x	y	z	B(A2)
S1	0.10441(7)	0.2029(1)	0.63381(6)	3.24(2)
S2	0.17005(7)	0.4092(1)	0.68855(6)	3.36(2)
S3	0.29755(7)	0.2566(1)	0.73530(6)	3.86(3)
O1	0.0543(2)	0.2803(3)	0.6032(2)	4.50(8)
O2	0.1293(2)	0.1066(3)	0.5948(2)	4.28(8)
N1	0.1778(2)	0.2761(3)	0.6543(2)	2.79(8)
C1	0.2380(2)	0.2315(4)	0.8061(2)	3.1(1)
C2	0.2589(3)	0.1465(5)	0.8516(2)	3.7(1)
C3	0.2250(3)	0.1325(5)	0.9164(2)	4.1(1)
C4	0.1728(3)	0.2048(5)	0.9353(2)	3.9(1)
C5	0.1482(3)	0.2920(4)	0.8906(2)	3.2(1)
C6	0.0931(3)	0.3678(5)	0.9122(2)	4.1(1)
C7	0.0673(3)	0.4500(4)	0.8697(3)	4.2(1)
C8	0.0926(3)	0.4568(4)	0.8013(3)	3.6(1)
C9	0.1470(2)	0.3881(4)	0.7778(2)	2.83(9)
C10	0.1790(2)	0.3051(4)	0.8225(2)	2.62(9)
C11	0.2470(3)	0.2127(4)	0.6592(2)	2.98(9)
C12	0.0690(2)	0.1534(4)	0.7133(2)	2.69(9)
C13	0.0156(2)	0.2145(4)	0.7463(3)	3.2(1)
C14	-0.0064(3)	0.1794(4)	0.8121(3)	3.7(1)
C15	0.0226(3)	0.0843(4)	0.8439(2)	3.6(1)
C16	0.0742(3)	0.0234(4)	0.8087(3)	3.6(1)
C17	0.0983(3)	0.0569(4)	0.7437(2)	3.3(1)
C18	-0.0010(3)	0.0516(5)	0.9161(3)	5.2(1)
C19	0.2936(3)	0.2293(4)	0.5951(2)	3.1(1)
C20	0.3307(3)	0.3297(4)	0.5842(2)	3.7(1)
C21	0.3748(3)	0.3427(5)	0.5264(3)	4.3(1)
C22	0.3803(3)	0.2541(6)	0.4798(3)	4.9(1)
C23	0.3433(3)	0.1553(5)	0.4889(3)	4.7(1)
C24	0.2998(3)	0.1420(4)	0.5465(3)	4.0(1)
H1	0.295(2)	0.096(4)	0.839(2)	4.0*

Table of Positional Parameters and Their Estimated Standard Deviations (continue).

Atom	x	y	z	B(A2)
H2	0.240(2)	0.074(4)	0.943(2)	4.0*
H3	0.151(2)	0.196(4)	0.971(2)	4.0*
H4	0.072(2)	0.362(4)	0.951(2)	4.0*
H5	0.028(2)	0.503(4)	0.884(2)	4.0*
H6	0.075(2)	0.514(4)	0.769(2)	4.0*
H7	0.232(2)	0.127(4)	0.663(2)	4.0*
H8	-0.005(2)	0.282(3)	0.725(2)	4.0*
H9	-0.045(2)	0.217(4)	0.829(2)	4.0*
H10	0.098(2)	-0.040(4)	0.827(2)	4.0*
H11	0.138(2)	0.019(4)	0.722(2)	4.0*
H12	0.0245	-0.0179	0.9293	4.0*
H13	0.0091	0.1087	0.9479	4.0*
H14	-0.0507	0.0335	0.9157	4.0*
H15	0.328(2)	0.395(4)	0.614(2)	4.0*
H16	0.403(2)	0.414(4)	0.520(2)	4.0*
H17	0.409(2)	0.261(4)	0.445(2)	4.0*
H18	0.347(2)	0.096(4)	0.456(2)	4.0*
H19	0.274(2)	0.069(4)	0.556(2)	4.0*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Table of General Displacement Parameter Expressions - B's.

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	Beqv
S1	3.79(5)	3.82(5)	2.11(4)	-0.57(6)	-0.28(5)	0.13(5)	3.42(2)
S2	4.45(5)	2.81(4)	2.82(4)	-0.12(5)	-0.07(5)	0.40(5)	3.36(2)
S3	3.05(4)	5.89(7)	2.63(4)	0.04(6)	0.04(4)	-0.06(6)	3.86(3)
O1	4.4(2)	5.5(2)	3.6(1)	-0.1(2)	-1.5(1)	1.3(1)	4.50(8)
O2	6.0(2)	4.3(2)	2.5(1)	-0.8(2)	0.4(1)	-1.1(1)	4.28(8)
N1	3.3(2)	2.8(2)	2.2(1)	-0.1(1)	0.3(1)	-0.0(1)	2.79(8)
C1	2.9(2)	4.1(2)	2.2(2)	0.1(2)	-0.3(8)	-0.2(2)	3.1(1)
C2	3.8(2)	4.3(2)	3.0(2)	1.0(2)	-0.6(2)	-0.2(2)	3.7(1)
C3	4.8(3)	4.9(3)	2.6(2)	0.5(2)	-0.5(2)	1.0(2)	4.1(1)
C4	4.1(2)	5.6(3)	2.1(2)	-1.1(2)	0.1(2)	0.3(2)	3.9(1)
C5	3.4(2)	3.9(2)	2.2(2)	-0.1(2)	-0.6(2)	-0.6(2)	3.2(1)
C6	4.4(2)	5.2(3)	2.6(2)	-0.2(2)	0.8(2)	-1.3(2)	4.1(1)
C7	4.8(3)	3.9(2)	4.1(2)	1.1(2)	-0.1(2)	-1.4(2)	4.2(1)
C8	4.5(2)	3.0(2)	3.3(2)	0.5(2)	-0.6(2)	-0.3(2)	3.6(1)
C9	3.4(2)	2.5(2)	2.5(2)	-0.6(2)	-0.2(2)	-0.1(2)	2.83(9)
C10	2.9(2)	3.2(2)	1.8(2)	-0.7(2)	-0.4(1)	-0.4(2)	2.62(9)
C11	3.2(2)	3.5(2)	2.3(2)	-0.1(2)	0.2(2)	0.2(2)	2.98(9)
C12	2.7(2)	3.0(2)	2.4(2)	-0.9(2)	0.1(2)	0.1(2)	2.69(9)
C13	2.8(2)	3.2(2)	3.6(2)	-0.2(2)	-0.4(2)	-0.0(2)	3.2(1)
C14	2.8(2)	4.5(2)	3.9(2)	-0.5(2)	0.9(2)	-1.0(2)	3.7(1)
C15	4.1(2)	4.1(2)	2.5(2)	-1.4(2)	0.2(2)	-0.2(2)	3.6(1)
C16	4.3(2)	3.2(2)	3.3(2)	-0.3(2)	0.1(2)	0.3(2)	3.6(1)
C17	3.9(2)	3.5(2)	2.7(2)	-0.3(2)	0.6(2)	-0.3(2)	3.3(1)
C18	5.8(3)	6.7(3)	3.2(2)	-1.7(3)	0.7(2)	-0.3(2)	5.2(1)
C19	3.5(2)	3.6(2)	2.3(2)	0.3(2)	0.4(2)	0.5(2)	3.1(1)
C20	4.4(2)	3.6(2)	3.0(2)	0.1(2)	0.4(2)	-0.2(2)	3.7(1)
C21	4.2(2)	4.7(3)	3.9(2)	-0.8(2)	1.1(2)	0.3(2)	4.3(1)
C22	4.7(2)	6.8(3)	3.3(2)	0.9(3)	1.6(2)	0.8(2)	4.9(1)
C23	5.7(3)	4.8(3)	3.5(2)	1.0(3)	1.4(2)	-0.7(2)	4.7(1)
C24	5.2(2)	3.2(2)	3.4(2)	-0.1(2)	0.7(2)	-0.1(2)	4.0(1)

The form of the anisotropic displacement parameter is: exp[-0.25{h2a2B(1,1) + k2b2B(2,2) + l2c2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3)}]where a, b, and c are reciprocal lattice constants.

Table of Refined Displacement Parameter Expressions - Beta's.

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
S1	0.00272(4)	0.00697(9)	0.00143(3)	-0.0013(1)	-0.00039(6)	0.0003(1)
S2	0.00319(4)	0.00513(8)	0.00192(3)	-0.0003(1)	-0.00009(7)	0.0009(1)
S3	0.00218(3)	0.0108(1)	0.00179(3)	0.0001(1)	0.00006(6)	-0.0001(1)
O1	0.0031(1)	0.0101(3)	0.0025(1)	-0.0002(4)	-0.0021(2)	0.0029(3)
O2	0.0043(1)	0.0078(3)	0.00173(9)	-0.0018(4)	0.0006(2)	-0.0025(3)
N1	0.0024(1)	0.0052(3)	0.0015(1)	-0.0003(3)	0.0004(2)	-0.0000(3)
C1	0.0021(1)	0.0076(4)	0.0015(1)	0.0002(4)	-0.0004(2)	-0.0004(4)
C2	0.0027(2)	0.0078(4)	0.0021(1)	0.0023(5)	-0.0008(3)	-0.0006(4)
C3	0.0035(2)	0.0089(5)	0.0018(1)	0.0012(5)	-0.0007(3)	0.0021(5)
C4	0.0029(2)	0.0102(5)	0.0014(1)	-0.0025(5)	0.0001(3)	0.0007(4)
C5	0.0025(1)	0.0070(4)	0.0015(1)	-0.0003(4)	-0.0008(2)	-0.0014(4)
C6	0.0032(2)	0.0094(5)	0.0017(1)	-0.0004(5)	0.0011(3)	-0.0029(5)
C7	0.0034(2)	0.0070(4)	0.0028(2)	0.0024(5)	-0.0002(3)	-0.0032(5)
C8	0.0032(2)	0.0054(4)	0.0023(1)	0.0011(5)	-0.0008(3)	-0.0007(4)
C9	0.0025(1)	0.0046(3)	0.0017(1)	-0.0014(4)	-0.0003(2)	-0.0003(4)
C10	0.0021(1)	0.0058(3)	0.0012(1)	-0.0017(4)	-0.0005(2)	-0.0009(4)
C11	0.0023(1)	0.0064(4)	0.0016(1)	-0.0003(4)	0.0003(2)	0.0003(4)
C12	0.0020(1)	0.0054(4)	0.0016(1)	-0.0020(4)	0.0001(2)	0.0003(4)
C13	0.0020(1)	0.0058(4)	0.0024(1)	-0.0004(4)	-0.0006(2)	-0.0001(4)
C14	0.0020(1)	0.0083(4)	0.0026(2)	-0.0011(4)	0.0012(3)	-0.0023(5)
C15	0.0029(2)	0.0075(4)	0.0017(1)	-0.0032(5)	0.0002(3)	-0.0005(4)
C16	0.0031(2)	0.0059(4)	0.0022(1)	-0.0007(5)	0.0001(3)	0.0006(4)
C17	0.0028(2)	0.0064(4)	0.0018(1)	-0.0006(5)	0.0008(3)	-0.0007(4)
C18	0.0041(2)	0.0122(6)	0.0022(2)	-0.0040(6)	0.0009(3)	-0.0006(6)
C19	0.0025(1)	0.0066(4)	0.0016(1)	0.0006(4)	0.0005(2)	0.0011(4)
C20	0.0032(2)	0.0066(4)	0.0021(1)	0.0003(5)	0.0006(3)	-0.0004(4)
C21	0.0030(2)	0.0086(5)	0.0027(2)	-0.0019(5)	0.0015(3)	0.0008(5)
C22	0.0034(2)	0.0124(6)	0.0022(1)	0.0020(6)	0.0022(3)	0.0018(6)
C23	0.0041(2)	0.0087(5)	0.0024(2)	0.0023(6)	0.0019(3)	-0.0015(5)
C24	0.0037(2)	0.0059(4)	0.0023(1)	-0.0002(5)	0.0010(3)	-0.0002(5)

The form of the anisotropic displacement parameter is: exp[-(B(1,1)*h2 + B(2,2)*k2 + B(3,3)*l2 + B(1,2)*hk + B(1,3)*hl + B(2,3)*kl)].

Table of General Displacement Parameter Expressions - U's.

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
S1	0.0480(6)	0.0483(6)	0.0267(5)	-0.0072(6)	-0.0035(6)	0.0016(6)
S2	0.0564(7)	0.0356(6)	0.0357(6)	-0.0015(8)	-0.0008(6)	0.0051(6)
S3	0.0386(5)	0.0746(8)	0.0333(6)	0.0005(8)	0.0006(6)	-0.0007(7)
O1	0.055(2)	0.070(2)	0.046(2)	-0.001(2)	-0.019(1)	0.017(2)
O2	0.076(2)	0.054(2)	0.032(2)	-0.010(2)	0.005(2)	-0.014(2)
N1	0.042(2)	0.036(2)	0.028(2)	-0.002(2)	0.003(2)	-0.000(2)
C1	0.036(2)	0.052(3)	0.027(2)	0.001(2)	-0.004(2)	-0.002(2)
C2	0.049(3)	0.054(3)	0.038(3)	0.013(3)	-0.007(2)	-0.003(3)
C3	0.061(3)	0.062(3)	0.033(2)	0.006(3)	-0.006(2)	0.012(3)
C4	0.052(3)	0.071(3)	0.026(1)	-0.0014(3)	0.001(2)	0.004(2)
C5	0.044(3)	0.049(3)	0.027(2)	-0.001(2)	-0.007(2)	-0.008(2)
C6	0.056(3)	0.065(3)	0.033(2)	-0.002(3)	0.010(2)	-0.016(3)
C7	0.061(3)	0.049(3)	0.051(3)	0.013(3)	-0.001(3)	-0.018(3)
C8	0.057(3)	0.038(3)	0.042(3)	0.006(2)	-0.007(3)	-0.004(2)
C9	0.043(2)	0.032(2)	0.032(2)	-0.008(2)	-0.003(2)	-0.002(2)
C10	0.037(2)	0.040(2)	0.023(2)	-0.009(2)	-0.005(2)	-0.005(2)
C11	0.040(2)	0.044(3)	0.029(2)	-0.002(2)	0.002(2)	0.002(2)
C12	0.035(2)	0.038(2)	0.030(2)	-0.011(2)	0.001(2)	0.001(2)
C13	0.036(2)	0.040(3)	0.045(3)	-0.002(2)	-0.005(2)	-0.000(2)
C14	0.035(2)	0.058(3)	0.049(3)	-0.006(2)	0.011(2)	-0.013(3)
C15	0.052(3)	0.052(3)	0.032(2)	-0.018(3)	0.002(2)	-0.003(2)
C16	0.054(3)	0.041(3)	0.041(3)	-0.004(2)	0.001(3)	0.004(2)
C17	0.049(3)	0.045(3)	0.034(2)	-0.004(2)	0.008(2)	-0.004(2)
C18	0.073(4)	0.085(4)	0.041(3)	-0.022(3)	0.008(3)	-0.004(3)
C19	0.044(2)	0.046(3)	0.029(2)	0.003(2)	0.005(2)	0.006(2)
C20	0.056(3)	0.046(3)	0.038(2)	0.002(3)	0.006(3)	-0.002(2)
C21	0.054(3)	0.060(3)	0.050(3)	-0.011(3)	0.014(3)	0.004(3)
C22	0.059(3)	0.086(4)	0.042(3)	0.011(4)	0.020(2)	0.010(3)
C23	0.072(4)	0.060(3)	0.045(3)	0.013(3)	0.017(3)	-0.009(3)
C24	0.066(3)	0.041(3)	0.043(3)	-0.001(3)	0.009(3)	-0.001(3)

The form of the anisotropic displacement parameter is: exp[-2pI2{h2a2U(1,1) + k2b2U(2,2) + l2c2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)}] where a, b, and c are reciprocal lattice constants.

Table of Root-Mean-Square Amplitudes of Anisotropic Displacement in Angstroms.

Atom	Min.	Int'med.	Max.
S1	0.162	0.203	0.236
S2	0.175	0.201	0.238
S3	0.182	0.197	0.273
O1	0.163	0.248	0.288
O2	0.159	0.235	0.287
N1	0.165	0.189	0.207
C1	0.161	0.193	0.230
C2	0.184	0.203	0.258
C3	0.164	0.246	0.262
C4	0.161	0.212	0.280
C5	0.149	0.215	0.227
C6	0.153	0.238	0.272
C7	0.171	0.236	0.275
C8	0.187	0.198	0.249
C9	0.162	0.182	0.219
C10	0.135	0.182	0.219
C11	0.168	0.200	0.212
C12	0.156	0.175	0.217
C13	0.181	0.202	0.218
C14	0.171	0.205	0.266
C15	0.177	0.185	0.264
C16	0.191	0.211	0.235
C17	0.173	0.206	0.233
C18	0.196	0.239	0.320
C19	0.163	0.204	0.226
C20	0.190	0.215	0.240
C21	0.183	0.245	0.264
C22	0.168	0.251	0.309
C23	0.174	0.252	0.289
C24	0.200	0.204	0.263

Table of Bond Distances in Angstroms.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
S1	O1	1.428(4)	C13	H8	0.97(4)
S1	O2	1.430(4)	C13	C15	1.380(7)
S1	N1	1.664(4)	C14	H9	0.90(4)
S1	C12	1.759(4)	C15	C16	1.375(7)
S2	N1	1.696(4)	C16	C17	1.381(7)
S2	C9	1.781(4)	C16	H10	0.93(4)
S3	C1	1.779(4)	C17	H11	0.96(4)
S3	C11	1.812(4)	C18	H12	0.977(6)
N1	C11	1.492(6)	C18	H13	0.924(6)
C1	C2	1.379(7)	C18	H14	0.954(6)
C1	C10	1.433(6)	C19	C20	1.380(7)
C2	C3	1.404(7)	C19	C24	1.388(7)
C2	H1	0.93(4)	C20	C21	1.388(7)
C3	C4	1.340(7)	C20	H15	0.95(4)
C3	H2	0.91(4)	C21	C22	1.374(8)
C4	C5	1.410(7)	C21	H16	1.00(4)
C4	H3	0.80(4)	C22	C23	1.363(8)
C5	C6	1.419(7)	C22	H17	0.85(4)
C5	C10	1.434(6)	C23	C24	1.380(7)
C6	C7	1.348(7)	C23	H18	0.94(4)
C6	H4	0.85(4)	C24	H19	1.00(4)
C7	C8	1.397(7)			
C7	H5	0.99(4)			
C8	C9	1.372(7)			
C8	H6	0.97(4)			
C9	C10	1.427(6)			
C11	C19	1.518(6)			
C11	H7	1.05(4)			
C12	C13	1.381(6)			
C12	C17	1.384(6)			
C13	C14	1.388(7)			

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Bond Angles in Degrees.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1	S1	O2	119.8(2)	C6	C7	C8	119.1(5)
O1	S1	N1	108.1(2)	C6	C7	H5	123.(2)
O1	S1	C12	108.6(2)	C8	C7	H5	118.(2)
O2	S1	N1	105.1(2)	C7	C8	C9	121.7(4)
O2	S1	C12	108.4(2)	C7	C8	H6	121.(2)
N1	S1	C12	105.9(2)	C9	C8	H6	117.(2)
N1	S2	C9	105.4(2)	S2	C9	C8	114.4(3)
C1	S3	C11	104.0(2)	S2	C9	C10	124.8(3)
S1	N1	S2	119.6(2)	C8	C9	C10	120.8(4)
S1	N1	C11	118.2(3)	C1	C10	C5	116.4(4)
S2	N1	C11	120.4(3)	C1	C10	C9	126.7(4)
S3	C1	C2	115.1(3)	C5	C10	C9	116.9(4)
S3	C1	C10	123.3(3)	S3	C11	N1	111.1(3)
C2	C1	C10	120.8(4)	S3	C11	C19	108.5(3)
C1	C2	C3	121.1(5)	S3	C11	H7	111.(2)
C1	C2	H1	120.(3)	N1	C11	C19	112.5(3)
C1	C2	H2	145.(1)	N1	C11	H7	104.(2)
C3	C2	H1	119.(3)	C19	C11	H7	110.(2)
C2	C3	C4	119.5(5)	S1	C12	C13	119.9(3)
C2	C3	H2	117.(3)	S1	C12	C17	119.0(3)
C2	C3	H3	141.(1)	C13	C12	C17	121.0(4)
C4	C3	H2	124.(3)	C12	C13	C14	118.5(4)
C3	C4	C5	122.0(4)	C12	C13	H8	121.(2)
C3	C4	H3	121.(3)	C14	C13	H8	120.(2)
C5	C4	H3	117.(3)	C13	C14	C15	121.6(4)
C4	C5	C6	120.8(4)	C13	C14	H9	115.(3)
C4	C5	C10	119.9(4)	C15	C14	H9	123.(3)
C6	C5	C10	119.3(4)	C14	C15	C16	118.4(4)
C5	C6	C7	121.9(4)	C14	C15	C18	119.8(5)
C5	C6	H4	122.(3)	C16	C15	C18	121.8(5)
C7	C6	H4	115.(3)	C15	C16	C17	121.6(4)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Bond Angles in Degrees (continue).

Atom 1	Atom 2	Atom 3	Angle
C15	C16	H10	124.(3)
C17	C16	H10	114.(3)
C12	C17	C16	118.9(4)
C12	C17	H11	120.(2)
C16	C17	H11	121.(2)
C15	C18	H12	108.0(5)
C15	C18	H14	109.5(5)
C11	C19	C20	121.3(4)
C11	C19	C24	119.8(4)
C20	C19	C24	118.9(4)
C19	C20	C21	120.8(5)
C19	C20	H15	124.(2)
C21	C20	H15	116.(2)
C20	C21	C22	119.0(5)
C20	C21	H16	121.(2)
C22	C21	H16	120.(2)
C21	C22	C23	121.0.(5)
C21	C22	H17	119.(3)
C23	C22	H17	120.(3)
C22	C23	C24	120.0(5)
C22	C23	H18	120.(3)
C24	C23	H18	120.(3)
C19	C24	C23	120.3(5)
C19	C24	H19	118.(2)
C23	C24	H19	122.(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Torsional Angles in Degrees.

Atom 1	Atom 2	Atom 3	Atom 4	Angle	
O1	S1	N1	S2	40.09	(0.28)
O1	S1	N1	C11	-155.25	(0.29)
O2	S1	N1	S2	169.19	(0.22)
O2	S1	N1	C11	-26.15	(0.33)
C12	S1	N1	S2	-76.14	(0.27)
C12	S1	N1	C11	88.52	(0.32)
O1	S1	C12	C13	-20.16	(0.43)
O1	S1	C12	C17	163.61	(0.36)
O2	S1	C12	C13	-151.84	(0.36)
O2	S1	C12	C17	31.93	(0.43)
N1	S1	C12	C13	95.75	(0.38)
N1	S1	C12	C17	-80.49	(0.39)
C9	S2	N1	S1	78.03	(0.26)
C9	S2	N1	C11	-86.28	(0.33)
N1	S2	C9	C8	-134.84	(0.35)
N1	S2	C9	C10	42.93	(0.43)
C11	S3	C1	C2	113.52	(0.38)
C11	S3	C1	C10	-76.76	(0.41)
C1	S3	C11	N1	56.56	(0.35)
C1	S3	C11	C19	-179.32	(0.32)
S1	N1	C11	S3	-136.38	(0.25)
S1	N1	C11	C19	101.81	(0.38)
S1	N1	C11	S3	28.14	(040)
S2	N1	C11	C19	-93.67	(0.38)
S3	C1	C2	C3	167.51	(0.39)
C10	C1	C2	C3	-2.5	(0.72)
S3	C1	C10	C5	-163.61	(0.34)
S3	C1	C10	C9	17.70	(0.65)
C2	C1	C10	C5	5.56	(0.64)
C2	C1	C10	C9	-173.13	(0.45)
C1	C2	C3	C4	-2.00	(0.76)
C2	C3	C4	C5	3.16	(0.78)

Table of Torsional Angles in Degrees (continue).

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C3	C4	C5	C6	-179.66 (0.48)
C3	C4	C5	C10	0.15 (0.78)
C4	C5	C6	C7	-178.20 (0.49)
C10	C5	C6	C7	1.99 (0.74)
C4	C5	C10	C1	-4.42 (0.64)
C4	C5	C10	C9	174.41 (0.43)
C8	C7	C12	C11	-2.49 (0.29)
C8	C7	C12	H12	-178.25 (1.51)
S1	C8	C7	C1	1.21 (0.21)
S1	C8	C7	C12	179.56 (0.15)
C9	C8	C7	C1	-174.50 (0.17)
C9	C8	C7	C12	3.85 (0.27)
C10	C9	C8	S1	-178.12 (0.15)
C10	C9	C8	C7	-2.88 (0.28)
C6	C5	C10	C1	175.39 (0.43)
C6	C5	C10	C9	-5.78 (0.64)
C5	C6	C7	C8	3.54 (0.78)
C6	C7	C8	C9	-5.20 (0.76)
C7	C8	C9	S2	179.03 (0.39)
C7	C8	C9	C10	1.17 (0.72)
S2	C9	C10	C1	5.33 (0.67)
S2	C9	C10	C5	-173.36 (0.34)
C8	C9	C10	C1	-177.04 (0.45)
C8	C9	C10	C5	4.27 0.64)
S3	C11	C19	C20	-47.81 (0.53)
S3	C11	C19	C24	131.82 (0.41)
N1	C11	C19	C20	75.50 (0.54)
N1	C11	C19	C24	-104.87 (0.49)
S1	C12	C13	C14	-173.84 (0.35)
C17	C12	C13	C14	2.32 (0.67)
S1	C12	C17	C16	174.95 (0.36)
C13	C12	C17	C16	-1.25 (0.69)

Table of Torsional Angles in Degrees. (continue)

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C12	C13	C14	C15	-1.50 (0.70)
C13	C14	C15	C16	-0.39 (0.73)
C13	C14	C15	C18	177.94 (0.46)
C14	C15	C16	C17	1.52 (0.74)
C18	C15	C16	C17	-176.77 (0.48)
C15	C16	C17	C12	-0.72 (0.72)
C11	C19	C20	C21	178.12 (0.45)
C24	C19	C20	C21	-1.51 (0.73)
C11	C19	C24	C23	-178.60 (0.46)
C20	C19	C24	C23	1.03 (0.74)
C19	C20	C21	C22	0.42 (0.77)
C20	C21	C22	C23	1.20 (0.80)
C21	C22	C23	C24	-1.69 (0.83)
C22	C23	C24	C19	0.55 (0.80)

References

1) a) Achmatowicz, O.; Pietraszkiewicz, M. *J. Chem. Soc. Perkin Trans 1* **1981**, 2680; b) Melnick, M. J.; Freyer, A. J.; Weinreb, S. M. *Tetrahedron Lett.* **1988**, 29, 3891.

2) a) Albrech, R.; Kresze, G. *Chem. Ber.* **1965**, 98, 1431; b) Sisko, J.; Weinreb, S. M. *Tetrahedron Lett.* **1989**, 30, 3037.

3) a) Stetter, H.; Theisen, D. *Chem. Ber.* **1969**, 102, 1641; b) Pearce, H. L.; Bach, N. J.; Cramer, T. L. *Tetrahedron Lett.* **1989**, 30, 907; c) Sisko, J.; Weinreb, S. M. *J. Org. Chem.* **1990**, 55, 393.

4) a) Alexander, M. D.; Anderson, R. E.; Sisko, J.; Weinreb, S. M. *J. Org. Chem.* **1990**, 55, 2563; b) Ralbovsky, J. L.; Kinsella, M. A.; Sisko, J.; Weinreb, S. M. *Synth. Commun.* **1990**, 20, 573.

5) a) Lichtenburger, J.; Fleury, S.; Barrett, B. *Bull. Soc. Chim, Fr.* **1955**, 669.

6) a) Albrech, R.; Kresze, G. *Chem. Ber.* **1964**, 97, 483; b) Levchenko, E. S.; Ubarov, B. N. *Zh. Org. Khim.* **1968**, 4, 1413; c) Naddaka, V. I.; Gar'kin, V. P.; Obayashi, K. V. *Zh. Org. Khim.* **1981**, 17, 2020; d) Glass, R. S.; Hony, R. C. *Tetrahedron Lett.* **1976**, 21, 1781; e) McKay, W. R.; Proctor, G. R. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2435; f) Jennings, W. B.; Lovely, C. J. *Tetrahedron* **1991**, 47, 5561; g) Vishwakarma, L. C.; Stringer, O. D.; Davis, F. A. *Org. Synth.* Coll. Vol. VIII, 546, (1993); h) Love, B. E.; Raje, P. S.; Williams, T. C. *Synlett* **1994**, 493.

7) a) Suzuki, H.; Takeda, S.; Hanazaki, Y. *Chem. Lett.* **1985**, 679; b) Suzuki, H.; Nakaya, C.; Matano, Y.; Ogawa, T. *Chem.*

Lett. **1991**, 105; c) Trost, B. M.; Marrs, C. *J. Org. Chem.* **1991**, 56, 6468; d) Boger, D. L.; Corbett, W. L. *J. Org. Chem.* **1992**, 57, 4777.

8) a) Glass, R. S.; Andreuski, S. W.; Broeker, J. L.; Firouzabadi, H.; Steffen, L. K.; Wilson, G. S. *J. Am. Chem. Soc.* **1989**, 111, 4036; b) Glass, R. S.; Adamowicz, L.; Broeker, J. L. *ibid.* **1991**, 113, 1065; c) Fujihara, H.; Chiu, J. -J.; Furukawa, N. *Chem. Lett.* **1990**, 2217; d) Fujihara, H.; Yabe, M.; Chiu, J. -J.; Furukawa, N. *Tetrahedron Lett.* **1991**, 32, 4345; e) Furukawa, N.; Shima, H.; Kimura, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1762; f) Fujihara, H.; Yabe, M.; Furukawa, N. *J. Org. Chem.* **1993**, 58, 5291.

9) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans 2* **1981**, 341.

10) a) Robert, J.-B.; Sherfinks, J. S.; Marsh, R. E.; Roberts, J. D. *J. Org. Chem.* **1974**, 39, 1152; b) Schweizer, W. B.; Proctor, G.; Kaftory, M.; Dunitz, J. D. *Helv, Chim. Acta* **1978**, 61, 2783.

Chapter 4

One-Pot Diels-Alder Reaction of *N*-Tosylaldimines Generated by BF_3-Et_2O Catalyzed Transformation of Naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimines

Abstract

Naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimines (**16**) were prepared by the reaction of naphtho[1,8-*de*]-1,3-dithiins with chloramine-T. Treatment of **16** with dienes in the presence of boron trifluoride etherate afforded the imino Diels-Alder products *via* *N*-tosylaldimines produced *in situ*.

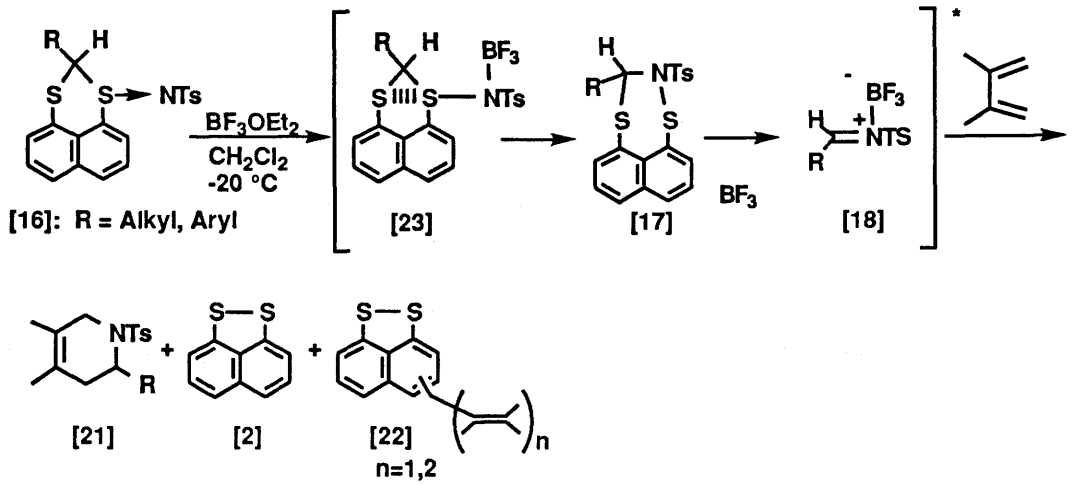
Introduction

The imino Diels-Alder reaction has been one of the useful synthetic methods for tetrahydropyridine derivatives.[1] Recently, Sisko and Weinreb have developed a new, *in situ*, procedure for effecting *N*-sulfonyl imine Diels-Alder reactions.[2, 3] The method consists of treating an aldehyde with an *N*-sulfinyl sulfonamide/boron trifluoride etherate in the presence of dienes. The cycloaddition is effective with a variety of aldehydes and 1,3-dienes. The process shows the usual high regioselectivity associated with [4+2]cycloadditions of *N*-sulfonyl imines.

1,8-Bis(alkylthio)- or 1,8-bis(alkylseleno)-naphthalene derivatives provide new reactive species or new reactions initiated by the transannular or through-space interaction between the two sulfur or selenium atoms located in close proximity.[4] As a further extension, in Chapter 4, the author describes the one-pot Diels-Alder reaction using *N*-tosylsulfilimines of naphtho[1,8-*de*]dithiin (**16**) with 1,3-dienes in the presence of boron trifluoride etherate providing the corresponding cycloadducts in high yields.

Results and Discussion

Reaction of Naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimines with Boron Trifluoride Etherate



Scheme 4-1

Table 4-1. Reaction of Naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimines **16** with BF_3-OEt_2 in the presence of 2,3-dimethyl-1,3-butadiene.[a)]

		Yield (%)[b)]		
Entry	R(16)	(21)	(22)	(2)
1	Ph(**a**)	56	8	38
2	CH_3(**c**)	73	13	45
3	Et(**d**)	81	18	41
4	$CH_3(CH_2)_5$(**e**)	83	36	30

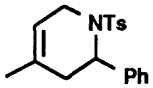
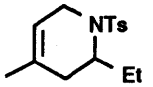
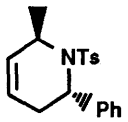
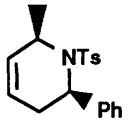
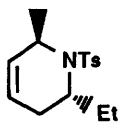
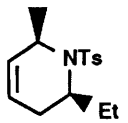
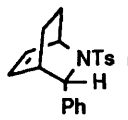
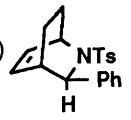
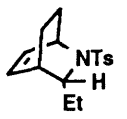
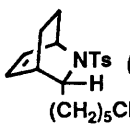
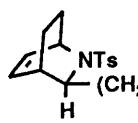
a) Substrates (0.22 mmol), Diene (0.44 mmol), BF_3-Et_2O (0.22 mmol), CH_2Cl_2 (10 ml). b) isolated yields.

Photolysis of naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimines **16** gave the corresponding *N*-tosylaldimines (**18**) quantitatively with complete recovery of naphtho[1,8-*cd*]-1,2-

dithiole (**2**) but they are thermally stable as described in Chapter 3. However, the compounds **16a** undergo the *N*-tosyl group migration from the sulfur to the 2-carbon atom to give a ring-enlargement compound (**17a**) bearing BF_3 on treatment with boron tetrafluoride etherate (BF_3-Et_2O). Furthermore, the sulfilimines (**16**) were treated with 2,3-dimethyl-1,3-butadiene in the presence of BF_3-Et_2O in dichloromethane at -20 °C to give the imino [4+2] cycloadducts (**21**) and naphtho[1,8-*cd*]-1,2-dithiole (**2**), and unexpectedly, the allylnaphto[1,8-*de*]-1,2-dithiole (**22**) (Scheme 4-1 and Table 4-1). The compound **22** was prepared by the reaction of naphtho[1,8-*cd*]-1,2-dithiole (**2**) with 2,3-dimethyl-1,3-butadiene under similar conditions. In fact, compound **17a** was obtained by liquid chromatography of the reaction mixtures by stopping the reaction of **16a**. Interestingly, the compound **17** is the same intermediate obtained from the photolysis of **16**. The results demonstrate clearly that the mechanism for the present reactions proceeds by the initial BF_3-activation of the sulfilimine to form the reactive intermediate **17** by the intramolecular migration of the *N*-tosyl group to the 2-carbon atom probably *via* the S···S initial through-space interaction, then by releasing the strain energy formed from the transient dithiiranes **23**.[5] Finally, the intermediate **17** should be converted to the corresponding reactive species, *N*-tosylaldimine-BF_3 complexes (**18**), which react with dienes to result in the cycloadducts.

The results of the Diels-Alder cycloaddition using **16** with 1,3-dienes as shown in Table 4-2 reveal that the reactions using any kind of *N*-tosylaldimines proceed the Diels-Alder reaction to afford the cycloadducts in moderate yields.

Table 4-2. Diels-Alder Cycloaddition of *N*-Tosylaldimines Generated *in situ* a)

Entry	R(16)	Diene	Product(s)	Yield(%)b)
1	Ph (a)		 (24a)	46
2	Et (d)		 (24d)	88
3	Ph (a)		 (3 : 1)c)  (25a) (26a)	52
4	Et (d)		 (2 : 1)c)  (25d) (26d)	88
5	Ph (a)		 (1 : 1.5)c)  (27a) (28a)	46
6	Et (d)		 (1 : 3)c)  (27d) (28d)	59
7	$CH_3(CH_2)_5$ (e)		 (1 : 1.7)c)  (27e) (28e)	54

a) Substrates (0.22 mmol), Dienes (0.22 mmol), BF_3-OEt_2 (0.22 mmol), CH_2Cl_2 (10 ml). b) Isolated yields. c) Stereochemistry established by ^1H NMR NOE.[2a)]

Cycloaddition reactions with unsymmetrical dienes were found to proceed highly regioselectively (Entries 1-4). Modest stereoselectivity was observed in the cases of entries 3-7. Interestingly, these reactions may be applicable to the [4+2]-cycloaddition of aliphatic aldimines derived from relatively

sensitively enolizable aldehydes, conversion of which to the corresponding aldimines is difficult by normal processes.[3)]

Experimental Section

General All melting points were uncorrected and were taken on a Yanaco micro melting point apparatus and LABORATORY DEVICES, USA, Model MRX-TEMP II. IR spectra were recorded on a JASCO FT/IR-5000 spectrometer. All NMR spectra were obtained with a JEOL LMN-EX-270 and a BRUKER MSL-400 FT-NMR spectrometer. Mass spectra were taken with a Shimadzu QP-2000 and a JEOL JMX SX102 mass spectrometer. Preparative liquid chromatography was performed on a Japan Analytical Industry Co., Ltd., Model LC-09 and LC-908. Analytical thin-layer chromatograph (TLC) was carried out on Merck precoated TLC plate (Kieselgel 60 F_{254}). Silica-gel used for column chromatography was Wako-gel C-200 and Merck kieselgel 60. Elemental analyses were carried out by Chemical Analysis Center at this University.

Materials All reagents were obtained from Wako Pure Chemical Industries, Ltd., Tokyo Kasei Kogyo, Co., Ltd., Kanto Chemicals Co., Inc., or Aldrich Chemical Co. The reagents used as reaction solvents were further purified by general methods.

General Procedure

To a well stirred solution of 0.22 mmol of sulfilimine and 0.22 mmol of diene in 10 ml of dry methylene chloride at -20 °C was added dropwise 0.22 mmol of boron trifluoride etherate. The solution was monitored by TLC. When the reaction was complete the solution was quenched with a saturated sodium hydrogen carbonate solution and extracted with dichloromethane.

The organic layer was washed with water, dried with magnesium sulfate and then the solvent was removed under vaccuum. The residue was purified by preparative HPLC to give the imino[4+2]adducts (**21**), naphtho[1,8-*cd*]-1,2-dithiole (**2**), and allylnaphtho[1,8-*cd*]-1,2-dithiole (**22**).

1-(*p*-Toluenesulfonyl)-4,5-dimethyl-2-phenyl-1,2,3,6-tetrahydropyridine (21a)

mp. 80-81 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.52 (S, 3H, CH_3), 1.57 (s, 3H, CH_3), 2.22 (d, J = 17.0 Hz, 1H, CH_2), 2.35 (d, J = 17.6 Hz, 1H, CH_2), 2.40 (s, 3H, CH_3), 3.27 (d, J = 17.6 Hz, 1H, CH_2), 3.87 (d, J = 17.6 Hz, 1H, CH_2), 5.23 (d, J = 6.8 Hz, 1H, CH_2), 7.22 (d, J = 8.6 Hz, 2H, ArH), 7.23-7.27 (m, 5H, ArH), 7.65 (d, J = 8.6 Hz, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 15.98, 18.56, 21.46, 32.46, 44.89, 53.48, 122.21, 123.16, 126.99, 127.28, 127.31, 128.30, 129.34, 137.65, 139.66, 142.91; MS (m/z) 341 (M^+).

1-(*p*-Toluenesulfonyl)-4,5-dimethyl-2-methyl-1,2,3,6-tetrahydropyridine (21c)

Oil; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.98 (d, J = 7.0 Hz, 3H, CH_3), 1.55 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 1.63 (d, J = 18.0 Hz, 1H, CH_2), 2.32 (d, J = 18.0 Hz, 1H, CH_2), 2.41 (s, 3H, CH_3), 3.39 (d, J = 16.2 Hz, 1H, CH_2), 3.86 (d, J = 16.2 Hz, 1H, CH_2), 4.18-4.28 (m, 2H, CH), 7.26 (d, J = 8.3 Hz, 2H, ArH), 7.69 (d, J = 8.3 Hz, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 15.91, 16.44, 18.80, 21.42, 36.66, 44.08, 46.69, 120.54, 122.55, 127.06, 129.45, 137.32, 142.89; MS (m/z) 279 (M^+).

1-(*p*-Toluenesulfonyl)-4,5-dimethyl-2-ethyl-1,2,3,6-tetrahydropyridine (21d)

mp. 67-68°C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.87 (t, J = 7.3 Hz, 3H, CH_3), 1.29-1.43 (m, 2H, CH_2), 1.48 (s, 3H, CH_3), 1.55 (s, 3H, CH_3), 1.61 (d, J = 15.9 Hz, 1H, CH_2), 2.07 (d, J = 15.9 Hz, 1H, CH_2), 2.39 (s, 3H, CH_3), 3.42 (d, J = 17.6 Hz, 1H, CH_2), 3.84-3.92 (m, 2H, CH_2, CH), 7.25 (d, J = 8.0 Hz, 2H, ArH), 7.66 (d, J = 8.0 Hz, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 11.00, 15.82, 18.80, 21.44, 24.26, 33.34, 44.35, 52.76, 120.72, 122.84, 126.85, 129.34, 138.02, 142.73; MS (m/z) 293 (M^+).

1-(*p*-Toluenesulfonyl)-4,5-dimethyl-2-hexyl-1,2,3,6-tetrahydropyridine (21e)

Oil; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H, CH_3), 1.23-1.41 (m, 10H, CH_2), 1.49 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 1.64 (d, J = 14.9 Hz, 1H, CH_2), 2.09 (d, J = 14.9 Hz, 1H, CH_2), 2.41 (s, 3H, CH_3), 3.42 (d, J = 17.3 Hz, 1H, CH_2), 3.89 (d, J = 17.3 Hz, 1H, CH_2), 3.98-4.06 (m, 1H, CH), 7.25 (d, J = 8.6 Hz, 2H, ArH), 7.67 (d, J = 8.6 Hz, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 14.05, 15.83, 18.82, 21.45, 22.55, 26.38, 29.00, 31.18, 31.68, 33.77, 44.39, 51.23, 120.74, 122.88, 126.90, 129.34, 138.01, 142.75; MS (m/z) 349 (M^+).

1-(*p*-Toluenesulfonyl)-4-methyl-2-phenyl-1,2,3,6-tetrahydropyridine (24a)

mp. 106-107 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.66 (s, 3H, CH_3), 2.19-2.37 (m, 2H. CH_2), 2.41 (s, 3H, CH_3), 3.33 (d, J = 18.1 Hz, 1H, CH_2), 4.07 (d, J = 18.1 Hz, 1H, CH_2), 5.28 (s, 3H, CH_3), 5.31 (s, 1H, C=CH), 7.23 (d, J = 7.6 Hz, 2H, ArH), 7.26-

7.29 (m, 5H, ArH), 7.67 (d, J = 7.6 Hz, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 21.48, 23.22, 31.25, 40.81, 53.16, 117.47, 127.04, 127.28, 127.42, 128.34, 129.42, 131.41, 137.68, 139.41, 142.97; MS (m/z) 327 (M^+).

1-(*p*-Toluenesulfonyl)-4-methyl-2-ethyl-1,2,3,6-tetrahydropyridine (24d)

Oil; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.89 (t, J = 7.3 Hz, 3H, CH_3), 1.30-1.52 (m, 2H. CH_2), 1.55 (s, 3H, CH_3), 1.64 (d, J = 17.3 Hz, 1H, CH_2), 2.06 (d, J = 17.3 Hz, 1H, CH_2), 2.40 (s, 3H, CH_3), 3.97 (q, J = 7.3 Hz, 1H, CH), 4.07 (d, J = 17.8 Hz, 1H, CH_2), 5.26 (s, 1H, C=CH), 7.24 (d, J = 8.1 Hz, 2H, ArH), 7.68 (d, J = 8.1 Hz, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 11.02, 21.46, 23.43, 24.33, 32.31, 40.25, 52.49, 115.99, 126.90, 129.40, 131.05, 138.06, 142.79; MS (m/z) 279 (M^+).

(*E*)-1-(*p*-Toluenesulfonyl)-6-methyl-2-phenyl-1,2,3,6-tetrahydropyridine (25a)

Oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.41 (d, J = 6.8 Hz, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.52-2.58 (m, 1H, CH_2), 2.75-2.79 (m, 1H, CH_2), 4.55-4.61 (m, 1H, CH), 5.06-5.08 (m, 1H, CH), 5.70-5.76 (m, 1H, C=CH), 5.79-5.83 (m, 1H, C=CH), 7.07 (d, J = 8.1 Hz, 2H, ArH), 7.15-7.17 (m, 3H, ArH), 7.21-7.23 (m, 2H, ArH), 7.34 (d, J = 8.1 Hz, 2H, ArH); MS (m/z) 327 (M^+).

(*Z*)-1-(*p*-Toluenesulfonyl)-6-methyl-2-phenyl-1,2,3,6-tetrahydropyridine (26a)

Oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.76 (d, J = 7.0 Hz, 3H, CH_3), 1.90-2.10 (m, 1H, CH_2), 2.43 (s, 3H, CH_3), 2.44-2.48 (m, 1H,

CH_2), 4.35-4.40 (m, 1H, CH), 5.29-5.32 (m, 1H, CH), 5.50-5.57 (m, 2H, C=CH), 7.02 (d, J = 8.1 Hz, 2H, ArH), 7.15-7.28 (m, 5H, ArH), 7.34 (d, J = 8.1 Hz, 2H, ArH); MS (m/z) 327 (M^+).

(*E*)-1-(*p*-Toluenesulfonyl)-2-ethyl-6-methyl-1,2,3,6-tetrahydropyridine (25d)

Oil; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.94 (t, J = 7.3 Hz, 3H, CH_3), 1.20 (d, J = 7.3 Hz, 3H, CH_3), 1.63-1.74 (m, 2H, CH_2), 1.87-2.00 (m, 1H, CH_2), 2.13-2.19 (m, 1H, CH_2), 2.40 (s, 3H, CH_3), 3.68-3.78 (m, 1H, C=CH), 4.01-4.54 (m, 1H, C=CH), 5.53-5.65 (m, 1H, CH), 7.24 (d, J = 8.1 Hz, 2H, ArH), 7.71 (d, J = 8.1 Hz, 2H, ArH); MS (m/z) 279 (M^+).

(*Z*)-1-(*p*-Toluenesulfonyl)-2-ethyl-6-methyl-1,2,3,6-tetrahydropyridine (26d)

Oil; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.98 (t, J = 7.3 Hz, 3H, CH_3), 1.39 (d, J = 7.3 Hz, 3H, CH_3), 1.44-1.54 (m, 2H, CH_2), 1.87-2.00 (m, 2H, CH_2), 2.40 (s, 3H, CH_3), 3.95-3.98 (m, 1H, C=CH), 4.30-4.42 (m, 1H, C=CH), 5.53-5.65 (m, 1H, CH), 7.26 (d, J = 8.1 Hz, 2H, ArH), 7.68 (d, J = 8.1 Hz, 2H, ArH); MS (m/z) 279 (M^+).

***N*-*p*-Toluenesulfonyl-3-(exo)-phenyl-2-azabicyclo[2,2,2]oct-5-ene (27a)**

^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.84-2.23 (m, 4H, CH_2), 2.42 (s, 3H, CH_3), 2.54-2.62 (m, 1H, CH), 4.17-4.22 (m, 1H, CH), 4.63-4.69 (m, 1H, CH), 5.89-5.99 (m, 1H, C=CH), 6.18-6.24 (m, 1H, C=CH),

7.08-7.46 (m, 7H, ArH), 7.62 (d, J = 8.4 Hz, 2H, ArH); MS (m/z) 339 (M^+).

_N_-_p_-Toluenesulfonyl-3-(endo)-phenyl-2-azabicyclo[2,2,2]oct-5-ene (28a)

^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.84-2.23 (m, 4H, CH_2), 2.37 (s, 3H, CH_3), 2.76-2.83 (m, 1H, CH), 4.63-4.69 (m, 2H, CH), 5.89-5.99 (m, 1H, C=CH), 6.59-6.64 (m, 1H, C=CH), 7.08-7.46 (m, 7H, ArH), 7.58 (d, J = 8.4 Hz, 2H, ArH); MS (m/z) 339 (M^+).

_N_-_p_-Toluenesulfonyl-3-(exo)-ethyl-2-azabicyclo[2,2,2]oct-5-ene (27d)

^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 7.6 Hz, 3H, CH_3), 0.97-2.39 (m, 5H. CH), 2.41 (s, 3H, CH_3), 2.56-2.58 (m, 1H, CH), 2.85 (d,t, J_1 = 10.9 Hz, J_2 = 2.8 Hz, 1H, CH), 4.34-4.37 (m, 1H, CH), 5.79 (d, d, d, J_1 = 12.0 Hz, J_2 = 5.1 Hz, J_3 = 0.8 Hz, 1H, C=CH), 6.70 (d, d, d, J_1 = 12.0 Hz, J_2 = 5.1 Hz, J_3 = 0.8 Hz, 1H, C=CH), 7.25 (d, J = 8.4 Hz, 2H, ArH), 7.63 (d, J = 8.4 Hz, 2H, ArH); MS (m/z) 291 (M^+).

_N_-_p_-Toluenesulfonyl-3-(endo)-ethyl-2-azabicyclo[2,2,2]oct-5-ene (28d)

^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.82 (t, J = 7.5 Hz, 3H, CH_3), 0.97-2.39 (m, 5H. CH), 2.42 (s, 3H, CH_3), 2.80-2.81 (m, 1H, CH), 3.44 (d,t, J_1 = 10.4 Hz, J_2 = 2.8 Hz, 1H, CH), 4.34-4.37 (m, 1H, CH), 6.19-6.22 (m, 1H, C=CH), 6.46 (m, 1H, C=CH), 7.28 (d, J = 8.4 Hz, 2H, ArH), 7.74 (d, J = 8.4 Hz, 2H, ArH); MS (m/z) 347 (M^+).

N-p-Toluenesulfonyl-3-(exo)-hexyl-2-azabicyclo[2,2,2]oct-5-ene (27e)

^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.85-0.93 (m, 3H, CH_3), 1.23-1.39 (m, 10H. CH_2), 1.62-2.33 (m, 4H. CH_2), 2.41 (s, 3H, CH_3), 2.50-2.57 (m, 1H, CH), 2.88-2.98 (m, 1H, CH), 4.34-4.36 (m, 1H, CH), 5.79 (d, d, d, J_1 = 12.0 Hz, J_2 = 5.1 Hz, J_3 = 0.8 Hz, 1H, C=CH), 6.06 (d, d, d, J_1 = 12.0 Hz, J_2 = 5.1 Hz, J_3 = 0.8 Hz, 1H, C=CH), 7.24 (d, J = 8.5 Hz, 2H, ArH), 7.62 (d, J = 8.4 Hz, 2H, ArH); MS (m/z) 347 (M^+).

N-p-Toluenesulfonyl-3-(endo)-hexyl-2-azabicyclo[2,2,2]oct-5-ene (28e)

^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.85-0.93 (m, 3H, CH_3), 1.23-1.39 (m, 10H. CH_2), 1.62-2.33 (m, 4H. CH_2), 2.42 (s, 3H, CH_3), 2.72-2.81 (m, 1H, CH), 3.48-3.54 (m, 1H, CH), 4.34-4.36 (m, 1H, CH), 6.18-6.23 (m, 1H, C=CH), 6.45-6.50 (m, 1H, C=CH), 7.28 (d, J = 8.4 Hz, 2H, ArH), 7.74 (d, J = 8.4 Hz, 2H, ArH); MS (m/z) 347 (M^+).

Reaction of Naphtho[1,8-*cd*]-1,2-dithiole with 2,3-Dimethyl-1,3-butadiene in the Presence of Boron Trifluoride Etherate

To a well stirred solution of 0.22 mmol of naphtho[1,8-*cd*]-1,2-dithiole (**2**) and 0.22 mmol of diene in 10 ml of dry dichloromethane at -20 °C was added dropwise 0.22 mmol of boron trifluoride etherate. The solution was monitored by TLC. When the reaction was complete the solution was quenched with a saturated sodium hydrogen carbonate solution and extracted with dichloromethane. The organic layer was washed with water, dried with magnesium sulfate and the solvent was removed under

vaccum. The residue was purified by preparative HPLC to give the allylnaphtho[1,8-*cd*]-1,2-dithiole (**22**).

2,3-Dimethyl-2-butenyl-naphtho[1,8-*cd*]-1,2-dithiole

Yield 22%; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.59 (s, 3H, CH_3), 1.77 (s, 3H. CH_3), 1.81 (s, 3H, CH_3), 3.56 (s, 2H, CH_2), 7.08-7.15 (m, 2H, ArH), 7.12-7.25 (m, 1H, ArH), 7.32-7.35 (m, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ18.26, 20.78, 20.97, 39.28, 115.80, 121.29, 122.10, 123.97, 126.79, 129.15, 129.22, 129.74, 134.32, 135.11, 141.90, 143.47; MS (m/z) 272 (M^+).

Bis-(2,3-dimethyl-2-butenyl)-naphtho[1,8-*cd*]-1,2-dithiole

Yield 21%; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.59 (s, 6H, CH_3), 1.76 (s, 6H. CH_3), 1.81 (s, 6H, CH_3), 3.56 (s, 4H, CH_2), 7.06 (d, J = 8.1 Hz, 2H, ArH), 7.32 (d, J = 8.1 Hz, 2H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ18.26, 20.76, 20.94, 39.36, 121.82, 124.12, 128.10, 128.75, 129.36, 132.96, 135.40, 141.37; MS (m/z) 354 (M^+).

References

1) a) Weinreb, S. M.; Staid, R. R. *Tetrahedron* **1982**, 38, 3087; b) Weinreb, S. M. *Acc. Chem. Res.* **1985**, 18, 16; c) Boger, D. L.; Weinreb, S. M. "Hetero Diels-Alder Methodology in Organic Synthesis" Academic Press, Orlando, 1987; d) Weinreb, S. M.; Scola, P. M. *Chem. Rev.* **1989**, 89, 1525; e) Rijsenbrij, P. P. M.; Loven, R.; Wijnberg, J. B. P. A.; Speckamp, W. N.; Huisman, H. O. *Tetrahedron Lett.* **1972**, 1425; f) Krow, G.; Rodebaugh, R.; Marakowski, J. *ibid.* **1973**, 1899. g) Krow, G. R.; Pyun, C.; Rodebaugh, R.; Marakowski, J.; *Tetrahedron* **1974**, 30, 2977; h) Loven, R. P.; Zunnebeld, W. A.; Speckamp, W. N. *ibid.* **1975**, 31, 1723; i) Jung, M. E.; Shishido, K.; Light, L.; Davis, L. *ibid.* **1981**, 22, 4607; j) Larsen, S. D.; Grieco, P. A. *J. Am. Chem. Soc.* **1985**, 107, 1768; k) Holmes, A. B.; Thompson, J.; Baxter, A. J. G.; Dixon, J. J. Chem. Soc., Chem. Commun. **1985**, 37; l) Grieco, P. A.; Larsen, S. D.; Fobare, W. F. *Tetrahedron Lett.* **1986**, 27, 1975; m) Grieco, P. A.; Larsen, S. D. *J. Org. Chem.* **1986**, 51, 3553; n) Birkinshaw, T. N.; Tabor, A. B.; Holmes, A. B.; Kaye, P.; Mayne, P. M.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1988**, 1599.

2) a) Sisko, J.; Weinreb, S. M. *Tetrahedron Lett.*, **1989**, 30, 3037; b) McIntosh, M. C.; Weinreb, S. M. *J. Org. Chem.*, **1993**, 58, 4823.

3) a) Albrech, R.; Kresze, G.; Mlakar, B. *Chem. Ber.*, **1964**, 97, 483; b) Albrech, R.; Kresze, G. *ibid.*, **1965**, 98, 1431.

4) a) Glass, R. S.; Andreuski, S. W.; Broeker, J. L.; Firouzabadi, H.; Steffen, L. K.; Wilson, G. S. *J. Am. Chem.*

Soc. **1989**, 111, 4036; b) Glass, R. S.; Adamowicz, L.; Broeker, J. L. *ibid.* **1991**, 113, 1065; c) Fujihara, H.; Chiu, J. -J.; Furukawa, N. *Chem. Lett.* **1990**, 2217; d) Fujihara, H.; Yabe, M.; Chiu, J. -J.; Furukawa, N. *Tetrahedron Lett.* **1991**, 32, 4345; e) Furukawa, N.; Shima, H.; Kimura, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1762; f) Fujihara, H.; Yabe, M.; Furukawa, N. *J. Org. Chem.* **1993**, 58, 5291.

5) A highly reactive intermediate **21** would be formed by the S···S interaction, see: a) References 5 and 6; b) Asmus, K. D. *Acc. Chem. Res.* **1979**, 12, 436; c) Gourcy, J.; Martigny, P.; Simonet, J.; Jaminet, G. *Tetrahedron* **1981**, 37, 1495; d) Glass, R. S.; Petsom, A.; Wilson, G. S. *J. Org. Chem.* **1986**, 51, 4337; e) Martre, A. M.; Mousset, G.; Rhlid R. B.; Veschambre, H. *Tetrahedron Lett.* **1990**, 31, 2599; f) Kiselyov, A. S.; Strekowski, L.; *Tetrahedron* **1993**, 49, 2151.

Chapter 5

Mechanism for Photodecomposition of Naphtho[1,8-*de*]-1,3-dithiin-1-bis(ethoxycarbonyl)methylides

Abstract

Naphtho[1,8-*de*]-1,3-dithiin-1-bis(ethoxycarbonyl)methylides (**29**) were prepared by the reaction of naphtho[1,8-*de*]-1,3-dithiins with diethyl diazomalonate in the presence of copper acetylacetonate. The sulfonium ylides **29** underwent photorearrangement giving olefins **33** quantitatively together with naphtho[1,8-*cd*]-1,2-dithiole.

Introduction

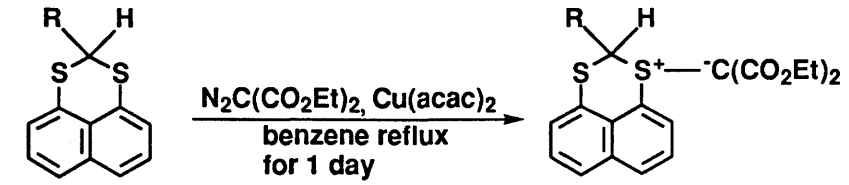
Photochemistry of sulfonium ylides has been studied a little. Trost reported that photo-irradiation of dimethylsulfonium phenacylide gives products primarily obtained from the formation of carbene in low yield which was produced propiophenone by the secondary photolysis as the Stevens rearrangement product.[1] Caserio and co-workers studied the photochemistry of some cyclic, carbonyl-stabilized sulfonium ylides and reported the formation of the products characteristic of the Stevens rearrangement.[2] Maki and Hiramitsu observed that photo-irradiation of some heterocyclic ylides gave the products derived from the Stevens rearrangement.[3] The mechanism for the photo-Stevens rearrangement has been carefully investigated by Zhang and Schuster.[4] They concluded that the direct irradiation of 9-dimethylsulfonium fluorenylide in acetonitrile or THF leads to homolysis of a carbon-sulfur bond in the $n\sigma^*$ singlet state and initial formation of the 9-(methylthio)fluorenyl and methyl radicals. Validity of this process has been supported by the product analysis, isotope tracer experiments, solvent viscosity studies.

1,8-Bis(alkylthio)- or 1,8-bis(alkylseleno)-naphthalene derivatives provide various reactive species or new reactions initiated by the through-space interaction or transannular interaction between the two sulfur or two selenium atoms.[5] Naphtho[1,8-*de*]-1,3-dithiin-1-oxides and -1-*N*-tosyl-sulfilimines undergo photo-rearrangement of oxygen and imino group to release carbonyl compounds and *N*-tosylaldimines

quantitatively together with naphtho[1,8-*cd*]-1,2-dithiole as described in Chapter 2 and 3. In further extension of these studies, the author prepared stable sulfonium ylides of naphtho[1,8-*de*]-1,3-dithiin (**5**) and found that their photolysis provides a convenient procedure to yield the corresponding olefins. In Chapter 5, the author describes the photo-Stevens type rearrangement of stable sulfonium ylides (**29**) to olefins (**33**).

Results and Discussion

Synthesis of Naphtho[1,8-*de*]-1,3-dithiin-1-bis(ethoxycarbonyl) methylides



[5a] : R=Ph
[5b] : R=*p*-Tol
[5c] : R=CH_3
[5e] : R=$CH_3(CH_2)_5$

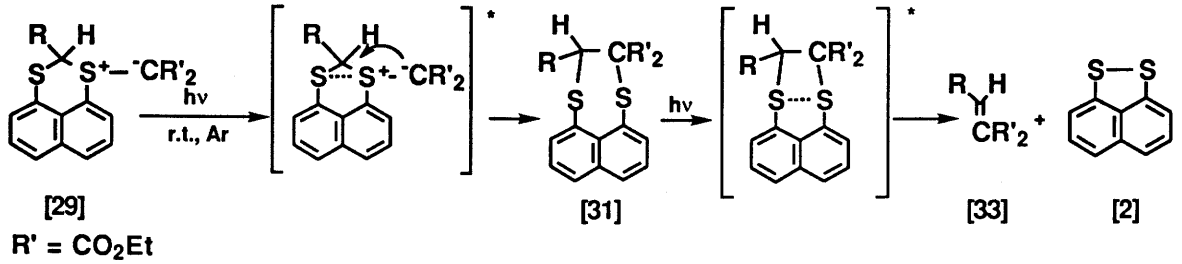
[29a] 72%
[29b] 48%
[29c] 55%
[29e] 61%

Scheme 5-1

Reduction of naphtho[1,8-*de*]-1,2-dithiole (**2**) with sodium borohydride in tetrahydrofuran-ethanol at room temperature gave almost quantitatively 1,8-naphthalene dithiol (**3**). Compound **3** was treated with aldehydes in the presence of tetrachlorosilane in dichloromethane affording the corresponding 2-substituted naphtho[1,8-*de*]-1,3-dithiins (**5**) in high yields. 2,2-Disubstituted naphtho[1,8-*de*]-1,3-dithiins (**6**) were prepared from the reaction of 2-lithiated **5** with several electrophiles. 2-Substituted naphtho[1,8-*de*]-1,3-dithiin-1-bis(ethoxycarbonyl) methylides (**29**) were prepared in moderate yields as a single diasteroisomer (R_S, S_C or S_S, R_C) in the reaction of **5** with diethyl diazomalonate in the presence of copper acetylacetonate in benzene under reflux conditions (Scheme 5-1). However, treatment of 2-phenylvinyl (**5f**), 2-furyl (**5g**), 2-methyl-2'-phenyl (**6b**), and 2-phenyl-2'-benzyl (**6h**) substituted naphtho[1,8-*de*]-1,3-dithiins with diethyl diazomalonate using the same conditions did not gave the expected compounds (**29f**,

29g, 30b, and **30h**) but instead gave the ring-expanded compounds (**31f, 31g, 32b,** and **32h**).[6] Synthesis and photolysis of these compounds are described in Chapter 6.

Photolysis of Naphtho[1,8-*de*]-1,3-dithiin-1-bis(ethoxycarbonyl) methylides



Scheme 5-2

Table 5-1. Photolysis of Stable Sulfonium Ylieds **29**.

[29]	R	Solvents	Yield of **33**/%[b]	Yield of **2**/%[b]
a	Ph	CH_2Cl_2	>99 (97)[c]	>99 (98)[c]
a	Ph	hexane	>99	>99
a	Ph	benzene	>99	>99
a	Ph	THF	>99	>99
a	Ph	CH_3CN	>99	>99
a	Ph	EtOH	>99	>99
b	*p*-Tol	CH_2Cl_2	>99 (94)[c]	>99 (99)[c]
c	CH_3	CH_2Cl_2	>99 (92)[c]	>99 (98)[c]
e	$CH_3(CH_2)_5$	CH_2Cl_2	>99 (93)[c]	>99 (97)[c]

a) 500 W high pressure Hg lamp, λ= 313 nm, Substrates (0.1 mmol), Solvents (5 ml). b) Yields were determined by HPLC and ^{1}H-NMR spectroscopy. c) Isolated yields.

Direct irradiation of stable sulfonium ylides **29** (0.1 mmol) in deoxygenated dichloromethane (5 ml) was carried out in a cylindrical quartz tube using a high pressure mercury lamp

(500 W, 313 nm) at room temperature to give the corresponding olefins **33** and naphtho[1,8-*cd*]-1,2-dithiole (**2**) quantitatively (Scheme 5-2 and Table 5-1). Polar and nonpolar solvents including ethanol, acetonitrile, tetrahydrofuran, dichrolomethane, chloroform, and n-hexane were examined on the photoreaction of **29a**. Photodecomposition reactions gave **33a** and **2** quantitatively.

The consumption of **29a** and the formation of products **33a** and **2** were unaffected by the addition of benzophenone as a triplet sensitizer, indicating that both reactions can proceed through the singlet state. The quantum yields of the consumption of sulfonium ylide **29a** and the formation of **33a** and **2** at room temperature under similar photolysis conditions were measured by comparison with fulgide actinometry[7] to be 0.84 and 0.09, respectively, being indicative of the existence of a stable intermediate on photolysis of **29a** to **33a** and **2**.

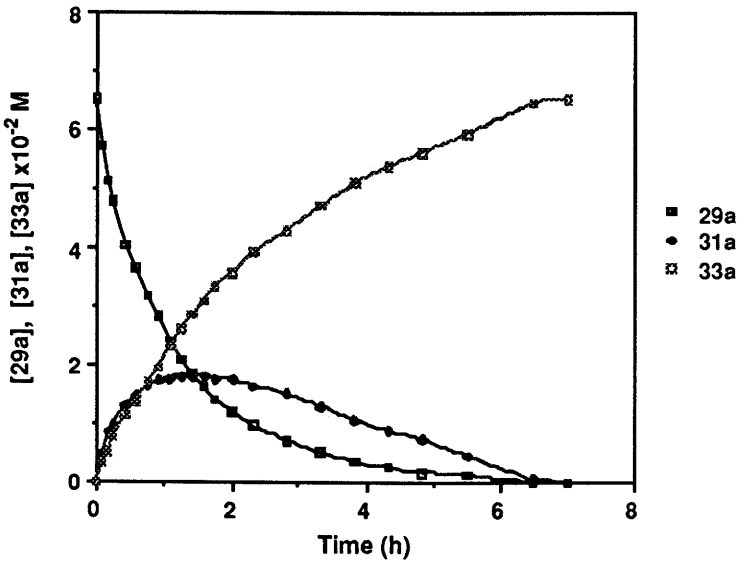


Figure 5-1. Time course of photolysis of **29a** (6.5×10^{-2} M **29a** in $CDCl_3$).

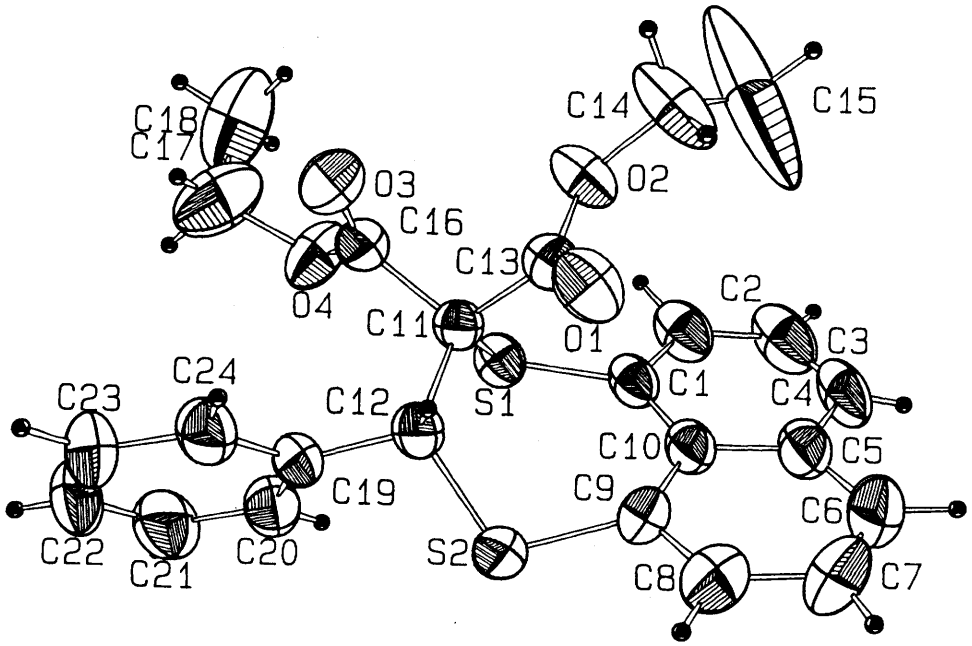
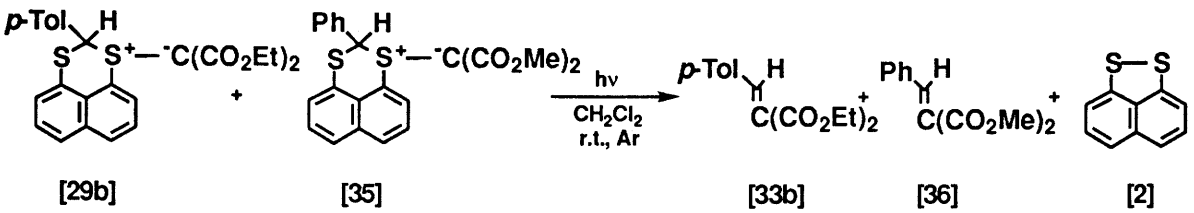


Figure 5-2. ORTEP Drawing of the Structure of **31a**

In order to understand the mechanism for the photo-decomposition of **29**, the ^{1}H-NMR spectra of the reaction of **29a** under irradiation with a high pressure Hg lamp (400 W) in $CDCl_3$ was monitored at various time intervals (Figure 5-1). When the ^{1}H-NMR signals of the starting material **29a** gradually reduced, new peaks started to appear at 0.87-0.92 (m), 3.56-3.67 (m), 3.82-3.91 (m), 5.72 ppm (s), 7.14 (d, J = 7.6 Hz), and 7.74 (S) corresponding to those of the intermediate **31a** together with other peaks from compounds **33a** and **2**, the structures of which were determined by comparing with the spectral data of the authentic compounds. The ^{1}H-NMR signals of the intermediate **31a** increased gradually but disappeared soon and the spectra were converted to those of the products

33a and **2**. Actually, the intermediate **31a** could be isolated by liquid chromatography of the reaction mixture by stopping the photolysis of **29a** at the optimum point of conversion of **29a** to **31a**. The intermediate **31a** is a solid material and its ^{1}H-, ^{13}C-NMR, IR, mass spectral data together with its elemental analysis data support the structure as shown in Scheme 5-2. Furthermore the structure of **31a** was determined by X-ray crystallographic analysis as shown in Figure 5-2. Consequently, the results demonstrate that the mechanism for the present reaction proceeds *via* an initial formation of intermediate **31**, which seems to be formed by the Stevens type rearrangement[1-4] affording the corresponding olefins **33** and naphtho[1,8-*cd*]-1,2-dithiole (**2**).

A cross-over experiment was carried out in order to decide whether the intermediate **31** was obtained by an inter- or intra-molecular process. Irradiation of a 1 : 1 mixture of **29b** and 2-phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-bis(methoxy-carbonyl) methylide (**35**) under photolysis conditions as described above gave the olefins **33b** and **36** along with **2** as shown in Scheme 5-3. The results demonstrate that formation of the intermediate **31** clearly proceeds by an intramolecular reaction.



Scheme 5-3

The effect of light intensity on photolysis of a stable sulfonium ylide **29a** was studied in order to understand whether

the reaction proceeds by a one-, two- or multi-photon process. The loss of **29a** was proportional to the first power of the 313 nm light, whereas the formation of **31a** was proportional to the square of the intensity as shown in Figure 5-3. These results imply that the consumption of sulfonium ylide **29** proceeds by a one-photon process to give an intermediate **31**, which seems to be formed by a radical or a concerted rearrangement in the primary photochemical step. Thereafter, the intermediate **31** should be converted to the corresponding olefins **33** and naphtho[1,8-*de*]-1,2-dithiole (**2**) *via* the S···S through-space interaction in the secondary photochemical step.

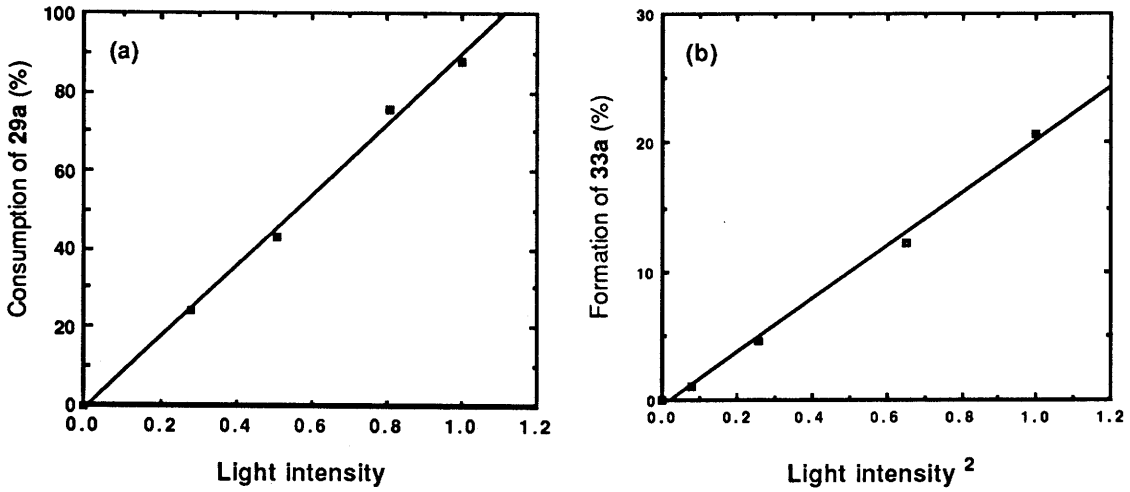


Figure 5-3. Light intensity dependence on the consumption of **29a** (a) and the formation of **33a** (b). (4.56×10^{-3} M **29a** in CH_2Cl_2).

X-ray Crystallographic Analysis of 3-Hydro-2,2-bis(ethoxycarbonyl)-3-phenyl-naphtho [1,8-*ef*][1,4]dithiepin (31a)

The detailed structural analysis of **31a** was performed by X-ray crystallographic analysis. Selected bond distances, bond angles, and torsional angles of **31a** are collected in Table 5-2,

Table 5-2. Selected Bond Distances (Å) for 3-Hydro-2,2-bis (ethoxycarbonyl)-3-phenyl-naphtho[1,8-*ef*][1,4]dithiepin (31a).[a)]

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
S1	C1	1.774(4)	O2	C14	1.446(7)
S1	C11	1.830(4)	O3	C16	1.195(5)
S2	C9	1.782(4)	O4	C16	1.317(6)
S2	C12	1.819(3)	O4	C17	1.476(6)
O1	C13	1.188(5)	C11	C12	1.562(5)
O2	C13	1.329(4)			

a) Numbers in parentheses are estimated standard deviations in the least significant digits. The atoms-labeling scheme is shown in Figure 5-2.

Table 5-3. Selected Bond Angles (deg) for 3-Hydro-2,2-bis(ethoxycarbonyl)-3-phenyl-naphtho[1,8-*ef*][1,4]dithiepin (31a)[a)].

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C1	S1	C11	103.0(2)	C7	C8	C9	120.5(5)
C9	S2	C12	108.0(2)	S2	C9	C8	114.8(3)
C13	O2	C14	116.6(3)	S2	C9	C10	124.0(3)
C16	O4	C17	117.6(4)	C8	C9	C10	120.3(4)
S1	C1	C2	112.8(3)	C1	C10	C5	116.6(4)
S1	C1	C10	126.3(3)	C1	C10	C9	126.5(4)
C2	C1	C10	120.9(4)	C5	C10	C9	117.0(4)
C2	C3	C4	119.9(4)	S1	C11	C12	111.8(2)
C3	C4	C5	122.0(4)	S1	C11	C13	112.0(2)
C4	C5	C6	121.4(5)	S1	C11	C16	109.4(3)
C4	C5	C10	118.8(4)	S2	C12	C11	112.8(2)
C6	C5	C10	119.8(4)	S2	C12	C19	106.1(2)
C5	C6	C7	122.1(5)	S2	C12	H12	111.(2)
C6	C7	C8	120.3(5)				

a) Numbers in parentheses are estimated standard deviations in the least significant digits. The atoms-labeling scheme is shown in Figure 5-2.

5-3, and 5-4. The ORTEP drawing of **31a** is depicted in Figure 5-2. The naphthalene ring in compound **31a** is slightly twisted about the C(5)-C(10) axis. The exocyclic bonds of S(1)-C(1)

Table 5-4. Selected Torsional Angles (deg) for 3-Hydro-2,2-bis(ethoxycar-bonyl)-3-phenyl-naphtho[1,8-*ef*][1,4] dithiepin (31a).[a)]

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C11	S1	C1	C2	-131.82 (0.29)
C11	S1	C1	C10	48.83 (0.36)
C1	S1	C11	C12	-92.04 (0.27)
C1	S1	C11	C13	31.87 (0.29)
C1	S1	C11	C16	149.01 (0.25)
C12	S2	C9	C8	117.41 (0.35)
C12	S2	C9	C10	-73.82 (0.36)
C9	S2	C12	C11	47.37 (0.31)
C9	S2	C12	C19	172.68 (0.25)
S1	C1	C2	C3	-179.08 (0.35)
S1	C1	C10	C5	-177.21 (0.29)
S1	C1	C10	C9	2.22 (0.57)
C1	C2	C3	C4	-2.27 (0.68)
C4	C5	C10	C1	-5.35 (0.54)
C4	C5	C10	C9	175.17 (0.36)
C6	C5	C10	C1	176.01 (0.39)
C6	C5	C10	C9	-3.47 (0.57)
C7	C8	C9	S2	166.29 (0.41)
S2	C9	C10	C1	17.06 (0.57)
S2	C9	C10	C5	-163.51 (0.30)
C8	C9	C10	C1	-174.76 (0.41)
C8	C9	C10	C5	4.67 (0.58)
C7	C8	C9	S2	166.29 (0.41)
C8	C9	C10	C1	-174.76 (0.41)
S1	C11	C12	S2	36.49 (0.33)

a) Numbers in parentheses are estimated standard deviations in the least significant digits. The atoms-labeling scheme is shown in Figure 5-2.

and S(2)-C(9) are splayed outwards and the sulfur atoms in 1,8-positions of naphthalene are displaced above and below the average plane of the naphthalene ring. More substantial twisting of the naphthalene ring has been observed in 1,8-

disubstituted derivatives with bulky substituents.[8] The S(1)···S(2) distance of **31a** is 3.132 Å, which is significantly shorter than the sum of van der Waals radii (3.70 Å), being indicative of the existence of the through-space interaction between the two sulfur atoms at the 1,8-positions of naphthalene.

Experimental Section

General All melting points were uncorrected and were taken on a Yanaco micro melting point apparatus and LABORATORY DEVICES, USA, Model MRX-TEMP II. IR spectra were recorded on a JASCO FT/IR-5000 spectrometer. All NMR spectra were obtained with a JEOL LMN-EX-270 and a BRUKER MSL-400 FT-NMR spectrometer. Mass spectra were taken with a Shimadzu QP-2000 and a JEOL JMX SX102 mass spectrometer. Ultraviolet-visible spectra were recorded on a Hitachi U-3000. X-ray crystallographic analysis was performed on an Enraf-Nonius CAD4 automatic diffractometer. Preparative liquid chromatography was performed on a Japan Analytical Industry Co., Ltd., Model LC-09 and LC-908. High performance liquid chromatography (HPLC) data were collected with a Shimadzu LC-10A system, using a TSK gel ODS-ST column (length, 250 mm; internal diameter, 4.6 mm) and methanol-water as an eluent with monitoring at 254 nm. Photolyses were carried out in a Pyrex round-bottomed flask using a 400 W high pressure mercury lamp. Quantum yield, the sensitization, a cross over, and intensity effect experiments were performed by irradiation with a 500 W ultrahigh pressure mercury lamp equipped with a glass filter and a monochromator. All photo-reactions were monitored and quantified by HPLC or ^{1}H-NMR. Analytical thin-layer chromatograph (TLC) was carried out on Merck precoated TLC plate (Kieselgel 60 F_{254}). Silica-gel used for column chromatography was Wako-gel C-200 and Merck kieselgel 60. Elemental analyses were carried out by Chemical Analysis Center at this University.

Materials All reagents were obtained from Wako Pure Chemical Industries, Ltd., Tokyo Kasei Kogyo, Co., Ltd., Kanto Chemicals Co., Inc., or Aldrich Chemical Co. The reagents used as reaction solvents were further purified by general methods.

General Procedure of Sulfonium Ylide

A mixture of 2-substituted naphtho[1,8-*de*]-1,3-dithiins (**5**) (1 mmol) and diazomalonate (1 mmol) in benzene (5 ml) was refluxed for 12 h in the presence of 15 mg copper acetylacetonate. After cooling, the solvent was evaporated. The residues were purified by silica-gel column chromatography (eluent, ethylacetate-hexane) and recrystallization from dichloromethane-hexane to give the pure sulfonium ylides (**29**).

2-Phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-bis(ethoxycarbonyl) methylide (29a)

Yield 72%; mp. 179-180 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.01-1.12 (br, 3H, CH_3), 1.16 (t, 6.7 Hz, 3H, CH_3), 3.94-4.01 (m, 3H, CH_2), 4.12-4.14 (m, 1H, CH_2), 6.35 (s, 1H, CH), 7.41-7.44 (m, 3H, ArH), 7.45-7.51 (m, 3H, ArH), 7.57-7.62 (m, 2H, ArH), 7.88 (d, J = 8.2 Hz, 1H, ArH), 8.00 (d, J = 8.2 Hz, 1H, ArH), 8.01 (d, J = 8.2 Hz, 1H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) Broad peaks; IR (KBr) 1626, 1288, 1089 cm^{-1} (CO_2); MS (m/z) 438 (M^+); Anal. Calcd for $C_{24}H_{22}O_4S_2$: C, 65.73, H, 5.06. Found: C, 65.43, H, 4.95.

2-*p*-Tolyl-naphtho[1,8-*de*]-1,3-dithiin-1-bis(ethoxycarbonyl) methylide (29b)

Yield 48%; mp. 160-161 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.07-1.18 (br, 6H, CH_3), 2.38 (s, 3H, CH_3), 3.90-4.00 (br, 3H, CH_2), 4.10-4.21 (br, 1H, CH_2), 6.31 (s, 1H, CH), 7.22 (d, J = 8.0 Hz, 2H, ArH), 7.36 (d, J = 8.0 Hz, 2H, ArH), 7.50 (t, J = 7.8 Hz, 1H, ArH), 7.58-7.62 (m, 2H, ArH), 7.87 (dd, J_1 = 7.8 Hz, J_2 = 0.8 Hz, 1H, ArH), 7.99-8.00 (m, 2H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) Broad peaks; IR (KBr) 1628, 1290, 1083 cm^{-1} (CO_2); MS (m/z) 452 (M^+); Anal. Calcd for $C_{25}H_{24}O_4S_2$: C, 66.35, H, 5.34. Found: C, 66.35, H, 5.28.

2-Methyl-naphtho[1,8-*de*]-1,3-dithiin-1-bis(ethoxycarbonyl) methylide (29c)

Yield 55%; mp. 126-127 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.01-1.42 (br, 6H, CH_3), 1.83 (d, J = 7.0 Hz, 3H, CH_3), 3.95-4.39 (br, 4H, CH_2), 5.38 (q, J = 7.0 Hz, 1H, CH), 7.47 (t, J = 7.7 Hz, 1H, ArH), 7.55-7.59 (m, 2H, ArH), 7.83 (d, J = 7.7 Hz, 1H, ArH), 7.93-7.97 (m, 2H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) Broad peaks; IR (KBr) 1676, 1303, 1064 cm^{-1} (CO_2); MS (m/z) 376 (M^+); Anal. Calcd for $C_{19}H_{20}O_4S_2$: C, 60.62, H, 5.35. Found: C, 60.76, H, 5.34.

2-Hexyl-naphtho[1,8-*de*]-1,3-dithiin-1-bis(ethoxycarbonyl) methylide (29e)

Yield 61%; mp. 76-77 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.871-0.98 (m, 3H, CH_3), 1.05-1.43 (m, 12H, CH_3, CH_2), 1.51-1.59 (m, 1H, CH_2), 1.63-1.76 (m, 1H, CH_2), 1.94-2.04 (m, 1H, CH_2), 4.04-4.35 (br, 4H, CH_2), 5.34 (dd, J_1 = 9.1 Hz, J_2 = 2.1 Hz, 1H, CH), 7.47 (t, J = 7.8 Hz, 1H), 7.56 (t, J = 7.8 Hz, 1H), 7.58 (d, J = 7.8 Hz, 1H, ArH), 7.83 (d, J = 7.8 Hz, 1H, ArH), 7.94 (d, J =

7.8 Hz, 1H, ArH), 7.95 (d, J = 7.8 Hz, 1H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) Broad peaks; IR (KBr) 1690, 1299, 1069 cm^{-1} (CO_2); MS (m/z) 446 (M^+); Anal. Calcd for $C_{24}H_{30}O_4S_2$: C, 64.54, H, 6.77. Found: C, 64.54, H, 6.90.

2-Phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-bis(methoxycarbonyl) methylide (35)

Yield 70%; mp. 201-202 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.59 (s, 6H, CH_3), 6.40 (s, 1H, CH), 7.43-7.50 (m, 5H, ArH), 7.53 (d, J = 8.0 Hz, 1H, ArH), 7.59-7.64 (m, 2H, ArH), 7.89 (d, J = 8.0 Hz, 1H, ArH), 7.98 (d, J = 8.0 Hz, 1H, ArH), 8.02 (d, J = 8.0 Hz, 1H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) Broad peaks; IR (KBr) 1628, 1301, 1083 cm^{-1} (CO_2); MS (m/z) 410 (M^+); Anal. Calcd for $C_{22}H_{18}O_4S_2$: C, 64.37, H, 4.42. Found: C, 64.18, H, 4.37.

General Photolysis Procedure

A solution of sulfonium ylides (0.1 mmol) in solvent (5 ml) was placed in a cylindrical quartz tube equipped with a stirrer bar and a silicon septum. The solution was bubbled with Ar for 30 min to remove O_2. Irradiation of samples was carried out using the output of a 500 W high pressure mercury lamp filtered through a Toshiba UVD33S filter and a monochromator set at 313 nm under conditions of complete light absorption. The reaction progress was monitored by HPLC or ^{1}H-NMR spectroscopy. After irradiation, the solvent was evaporated and the residue was purified by preparative HPLC, and the products were characterized by NMR and GC-MS spectroscopies.

Diethyl-benzalmalonate (33a)

Oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.29 (t, J = 7.1 Hz, 3H, CH_3), 1.34 (t, J = 7.1 Hz, 3H, CH_3), 4.28-4.37 (m, 4H, CH_2), 7.37-7.40 (m, 3H, ArH), 7.44-7.47 (m, 2H, ArH), 7.74 (s, 1H, C=CH); MS (m/z) 248 (M^+).

Diethyl-4-methyl-benzenemethylidenemalonate (33b)

Oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.31 (t, J = 7.1 Hz, 3H, CH_3), 1.33 (t, J = 7.1 Hz, 3H, CH_3), 2.37 (s, 3H, CH_3), 4.30 (q, J = 7.1 Hz, 2H, CH_2), 4.35 (q, J = 7.1 Hz, 2H, CH_2), 7.18 (d, J = 8.1 Hz, 2H, ArH), 7.35 (d, J = 8.1 Hz, 2H, ArH), 7.70 (s, 1H, C=CH); MS (m/z) 262 (M^+).

Diethyl-methylidenemalonate (33c)

Oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.29 (t, J = 7.1 Hz, 3H, CH_3), 1.34 (t, J = 7.1 Hz, 3H, CH_3), 1.96 (d, J = 7.4 Hz, 3H, CH_3), 4.24 (q, J = 7.1 Hz, 2H, CH_2), 4.31 (q, J = 7.1 Hz, 2H, CH_2), 7.09 (q, J = 7.4 Hz, 2H, C=CH); MS (m/z) 262 (M^+).

Diethyl-heptylidenemalonate (33e)

Oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H, CH_3), 1.24-1.34 (m, 12H, CH_2, CH_3), 1.44-1.50 (m, 2H, CH_2), 2.29 (q, J = 7.8 Hz, 2H, CH_2), 4.23 (q, J = 7.8 Hz, 2H, CH_2), 4.30 (q, J = 7.8 Hz, 2H, CH_2), 6.98 (t, J = 7.8 Hz, 1H, C=CH); MS (m/z) 256 (M^+).

Reaction intermediate **31a** was isolated by silica-gel chromatography and liquid chromatography of the reaction mixture by stopping the photolysis of **29a** at the optimum point

of conversion of **29a** to **31a**. Compound **31a** was stable, solid material.

3-Hydro-2,2-bis(ethoxycarbonyl)-3-phenyl-naphtho[1,8-*ef*][1,4] dithiepin (31a)

mp. 139-140 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.87-0.92 (m, 6H, CH_3), 3.56-3.67 (m, 1H, CH_2), 3.82-3.91 (m, 3H, CH_2), 5.72 (s, 1H, CH), 7.25-7.33 (m, 5H, ArH), 7.44-7.47 (m, 2H, ArH), 7.70-7.79 (m, 4H, ArH), 7.25-7.33 (m, 5H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 13.29, 13.65, 59.43, 62.25, 74.56, 125.63, 125.81, 128.11, 128.20, 128.89, 129.58, 129.95, 131.27, 133.67, 133.82, 134.08, 135.67, 135,83, 137.25, 165.68, 167.65; IR (KBr) 1742, 1721, 1241, 1218 cm^{-1} (CO_2); MS (m/z) 438 (M^+); Anal. Calcd for $C_{24}H_{22}O_4S_2$: C, 65.73, H, 5.06. Found: C, 65.63, H, 5.03.

Benzophenone Dependence on the Photolysis of 2-Phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-bis(ethoxycarbonyl)methylides

A solution of 2-phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-bis(ethoxycarbonyl)methylide (**29a**) (10 mg, 0.023 mmol) and benzophenone (0.024, 0.048, and 0.23 mmol, respectively) in dichloromethane was placed in a cylindrical quartz tube equipped with a stirrer bar and a silicon septum. The solution was bubbled with Ar for 30 min to remove O_2. Irradiation of samples was carried out using the output of a 500 W high pressure mercury lamp filtered through a Toshiba UVD33S filter and a monochromator set at 366 nm. Quantification was done with HPLC. Maleic anhydride was used as an external standard for HPLC. Yields were determined from solutions and irradiation times were kept under 1 h. The

measurement of yields was repeated several times by HPLC detection.

Cross-over Experiment of 2-*p*-Tolyl-naphtho[1,8-*de*]-1,3-dithiin-1-bis (ethoxycarbonyl)methylide (29b) and 2-Phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-bis(methoxycarbonyl)methylide (35)

2-*p*-Tolyl-naphtho[1,8-*de*]-1,3-dithiin-1-bis(ethoxycarbonyl) methylide (**29b**) (10.4 mg, 0.023 mmol) and 2-phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-bis(methoxycarbonyl)methylide (**35**) (9.4 mg, 0.023 mmol) were dissolved in 10 ml of deoxygenated dichloromethane. The solution was irradiated with a high pressure mercury lamp (500 W) until the sulfonium ylides completely disappeared. The products were determination with GC-MS and ^{1}H-NMR spectroscopies.

Dimethyl-benzalmalonate (36)

Oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3H, CH_3), 3.86 (s, 3H, CH_3), 7.38-7.44 (m, 5H, ArH), 7.78 (s, 1H, C=CH); MS (m/z) 220 (M^+).

Quantum Yields

The measurement of the quantum yield was carried out using the output of a 500 W high pressure mercury lamp filtered through a Toshiba UVD33S filter and a monochromator set at 313 nm under conditions of complete light absorption. The fulgide, (E)-α-(2,5-dimethyl-3-furyl-ethylidene)(isopropylidene)succinic anhydride, which has a quantum yield of 0.20 for its photocolouration at 313 nm in toluene was used as an actinometer. Quantification was done with HPLC. Maleic

anhydride was used as an external standard for HPLC. Sample and actinometer cells were sequentially irradiated. The actinometer cell was used to determine the photo flux, which was then used to convert the rate of loss of the material into a quantum yield. All quantum yields were determined from the solutions that began at concentration of 3-6 mM, and conversions were kept under 5%. The measurement of quantum yields was repeated several times by HPLC detection.

Effect of Light Intensity

The measurement of the light intensity effect was carried out using the output of a 500 W high pressure mercury lamp filtered through a Toshiba UVD33S filter and a monochromator set at 313 nm under conditions of complete light absorption. The light intensity was attenuated by using a quartz filter (313 nm; 27%, 52%, and 83%). Quantification was done with HPLC. Maleic anhydride was used as an external standard for HPLC. Yields were determined from the solutions that began at concentration 6 mM, and irradiation times were kept under 1 h. The measurement of yields was repeated several times by HPLC detection.

Detailed Information of the X-ray Crystal Analysis of 3-Hydro-2,2-bis(ethoxycarbonyl)-3-phenyl-naphtho[1,8-*ef*][1,4]dithiepin (31a)

Crystal Data

$C_{24}H_{22}O_4S_2$

F.W. 438.57 F(000)=920

crystal dimensions: 0.50x0.50x0.30 mm

peak width at half-height=0.00

Mo Kα radiation (λ=0.71073 Å)

temperature=23±1 °C

orthorhombic space group P21/c

a=9.460(2) Å b=15.673(6) Å c=14.933(3) Å

β=105.05(2) Å

V=2138.0 $Å^3$

Z=4 ρ=1.36 g/cm^3

μ=2.7 cm^{-1}

Intensity Measurements

Instrument:	Enraf-Nonius CAD4 diffractometer
Monochromator:	Graphite crystal, incident beam
Attenuator:	Zr foil, factor 13.4
Take-off angle:	2.8°
Detector aperture:	1.5 to 1.7 mm horizontal
	4.0 mm vertical
Crystal-detector dist.:	21 cm
Scan type:	ω–2θ
Scan rate:	2-20 °/min (in omega)
Scan width, deg:	0.5+0.460tan θ

Maximum 2θ: 50.0°

No. of refl. measured: 4056 total, 3903 unique

Corrections: Lorentz-polarization
Linear decay (from 1.000 to 1.013 on I)
Emprical absorption (from 0.97 to 1.00 on I)

Structure Solution and Refinement

Solution:	Direct methods
Hydrogen atoms:	Included as fixed contribution to the structure factor
Refinement:	Full-matrix least-squares
Minimization function:	$\Sigma w(\|Fo\|-\|Fc\|)^2$
Least-squares weights:	$4Fo^2/\sigma^2(Fo^2)$
Anomalous dispersion:	All non-hydrogen atoms
Reflection included:	2836 with $Fo^2>3.0\sigma(Fo^2)$
Parameter refined:	271
Unweighted agreement factor:	0.056
Weighted agreement factor:	0.053
Esd of obs. of unit weight:	1.25
Convergence, large shifts:	0.02σ
High peak in final diff. map:	0.45 (5) e/Å^3
Low peak in final diff. map:	-0.11 (0) e/Å^3
Computer hardware:	VAX
Computer software:	MolEn (Enraf-Nonius)

Table of Positional Parameters and Their Estimated Standard Deviations.

Atom	x	y	z	B(A2)
S1	0.2324(1)	0.10230(6)	0.84753(7)	3.65(2)
S2	0.4618(1)	0.24353(7)	0.93353(7)	4.30(2)
O1	0.4640(3)	0.1923(2)	0.6993(2)	5.13(7)
O2	0.3023(3)	0.0861(2)	0.6610(2)	4.82(6)
O3	0.1088(4)	0.2497(2)	0.6335(2)	5.77(8)
O4	0.0031(3)	0.1941(2)	0.7379(2)	5.94(8)
C1	0.3966(4)	0.0422(2)	0.8696(2)	3.84(8)
C2	0.3717(5)	-0.0446(3)	0.8578(3)	5.1(1)
C3	0.4854(6)	-0.1022(3)	0.8724(3)	6.6(1)
C4	0.6228(6)	-0.0745(3)	0.8944(3)	6.6(1)
C5	0.6579(5)	0.0147(3)	0.9041(3)	5.3(1)
C6	0.8023(6)	0.0431(4)	0.9240(4)	7.3(1)
C7	0.8365(5)	0.1248(4)	0.9355(4)	7.9(2)
C8	0.7253(5)	0.1868(3)	0.9299(4)	6.2(1)
C9	0.5820(4)	0.1630(3)	0.9123(3)	4.33(9)
C10	0.5413(4)	0.0752(3)	0.8949(3)	4.09(9)
C11	0.2621(4)	0.1867(2)	0.7696(2)	3.18(7)
C12	0.3307(4)	0.2682(2)	0.8240(2)	3.37(8)
C13	0.3574(4)	0.1562(2)	0.7071(2)	3.57(8)
C14	0.3829(6)	0.0504(3)	0.5998(3)	7.4(1)
C15	0.4191(9)	-0.0228(5)	0.6096(5)	22.6(2)
C16	0.1152(5)	0.2126(3)	0.7044(3)	4.16(9)
C17	-0.1411(6)	0.2293(5)	0.6892(4)	8.9(2)
C18	-0.2223(7)	0.1678(5)	0.6403(6)	11.1(2)
C19	0.2192(4)	0.3278(2)	0.8473(3)	3.56(8)
C20	0.1531(5)	0.3122(3)	0.9181(3)	4.6(1)
C21	0.0471(5)	0.3670(3)	0.9330(3)	6.0(1)
C22	0.0055(5)	0.4366(3)	0.8766(4)	6.7(1)
C23	0.0685(5)	0.4530(3)	0.8059(4)	5.9(1)
C24	0.1761(5)	0.3995(3)	0.7921(3)	4.7(1)
H2	0.260(4)	-0.065(2)	0.830(2)	4.0*

Table of Positional Parameters and Their Estimated Standard Deviations (continue).

Atom	x	y	z	B(A2)
H3	0.470(4)	-0.163(2)	0.870(2)	4.0*
H4	0.695(4)	-0.102(2)	0.908(2)	4.0*
H6	0.877(4)	-0.004(2)	0.931(2)	4.0*
H7	0.919(4)	0.151(2)	0.947(2)	4.0*
H8	0.746(4)	0.241(3)	0.945(2)	4.0*
H12	0.379(4)	0.295(2)	0.781(2)	4.0*
H14	0.4720	0.0833	0.6049	4.0*
H14'	0.3263	0.0560	0.5360	4.0*
H15	0.4727	-0.0449	0.5701	4.0*
H15'	0.4799	-0.0327	0.6743	4.0*
H15"	0.3342	-0.0600	0.6053	4.0*
H17	-0.1343	0.2772	0.6494	4.0*
H17'	-0.1940	0.2522	0.7333	4.0*
H18	-0.3174	0.1848	0.6061	4.0*
H18'	-0.1723	0.1454	0.5953	4.0*
H18"	-0.2319	0.1204	0.6791	4.0*
H20	0.177(4)	0.266(2)	0.955(2)	4.0*
H21	0.003(4)	0.353(2)	0.980(2)	4.0*
H22	-0.058(4)	0.467(2)	0.886(2)	4.0*
H23	0.041(4)	0.503(2)	0.765(3)	4.0*
H24	0.219(4)	0.414(2)	0.746(2)	4.0*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)* B(1,3) + bc(cos alpha)*B(2,3)]

Table of General Displacement Parameter Expressions - B's.

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	Beqv
S1	4.33(4)	2.91(3)	3.92(3)	0.03(3)	1.43(3)	0.23(3)	3.65(2)
S2	4.33(4)	3.60(4)	4.30(4)	0.56(4)	-0.07(4)	-0.79(4)	4.30(2)
O1	6.0(1)	4.5(1)	5.8(1)	-0.5(1)	3.12(9)	-0.3(1)	5.13(7)
O2	7.0(1)	3.5(1)	4.8(1)	-0.4(1)	2.95(9)	-0.9(1)	4.82(6)
O3	6.9(2)	5.8(1)	4.1(1)	1.7(1)	0.4(1)	0.9(1)	5.77(8)
O4	3.5(1)	7.6(2)	6.1(2)	0.6(1)	0.1(1)	1.1(1)	5.94(8)
C1	5.5(2)	3.0(1)	3.2(1)	1.0(1)	1.5(1)	0.4(1)	3.84(8)
C2	7.8(2)	3.1(2)	4.8(2)	1.0(2)	2.4(2)	0.6(1)	5.1(1)
C3	11.3(3)	3.8(2)	5.4(2)	2.7(2)	3.4(2)	1.2(2)	6.6(1)
C4	10.0(2)	5.6(2)	4.1(2)	5.3(2)	1.9(2)	1.1(2)	6.6(1)
C5	6.1(2)	6.3(2)	3.3(2)	3.0(2)	0.8(1)	0.3(2)	5.3(1)
C6	6.2(2)	8.8(3)	6.1(2)	4.0(2)	0.2(2)	-0.7(2)	7.3(1)
C7	3.3(2)	10.9(4)	8.5(3)	1.0(2)	-0.1(2)	-1.5(3)	7.9(2)
C8	4.5(2)	6.6(3)	6.7(3)	0.3(2)	0.1(2)	-1.2(2)	6.2(1)
C9	3.6(2)	4.8(2)	4.1(2)	1.1(1)	0.2(1)	-0.1(2)	4.33(9)
C10	5.1(2)	4.0(2)	3.0(1)	1.8(1)	0.8(1)	0.3(1)	4.09(9)
C11	3.7(1)	2.6(1)	3.1(1)	0.1(1)	0.7(1)	0.1(1)	3.18(7)
C12	2.7(2)	3.0(2)	2.4(2)	-0.9(2)	0.1(2)	0.1(2)	2.69(9)
C13	4.7(2)	2.9(1)	3.2(1)	0.4(1)	1.1(1)	0.5(1)	3.57(8)
C14	11.9(3)	4.4(2)	8.1(2)	-0.2(2)	6.9(2)	-1.5(2)	7.4(1)
C15	39.4(4)	10.9(4)	29.9(4)	13.6(3)	31.3(2)	10.1(3)	22.6(2)
C16	4.9(2)	3.6(2)	3.6(2)	0.7(1)	0.3(1)	-0.3(1)	4.16(9)
C17	5.1(2)	12.1(5)	8.0(3)	-1.1(3)	-0.9(2)	0.5(3)	8.9(2)
C18	6.4(3)	11.4(5)	14.8(5)	2.0(3)	1.8(3)	4.3(4)	11.1(2)
C19	3.8(2)	2.8(1)	4.0(1)	0.2(1)	0.8(1)	-0.3(1)	3.56(8)
C20	5.1(2)	4.3(2)	4.5(2)	0.6(2)	1.4(1)	0.2(2)	4.6(1)
C21	5.7(2)	6.8(3)	6.3(2)	0.8(2)	2.7(2)	-1.1(2)	6.0(1)
C22	5.2(2)	5.9(2)	8.7(3)	2.5(2)	1.4(2)	-1.6(2)	6.7(1)
C23	6.5(2)	3.8(2)	6.8(2)	2.0(2)	0.8(2)	0.3(2)	5.9(1)
C24	5.9(2)	3.3(2)	4.7(2)	0.6(2)	1.3(2)	0.2(2)	4.7(1)

The form of the anisotropic displacement parameter is: exp[-0.25{h2a2B(1,1) + k2b2B(2,2) + l2c2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3)}]where a, b, and c are reciprocal lattice constants.

Table of Refined Displacement Parameter Expressions - Beta's.

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
S1	0.0130(1)	0.00296(3)	0.00472(4)	0.0001(1)	0.0054(1)	0.00051(7)
S2	0.0130(1)	0.00366(4)	0.00517(5)	0.0019(1)	-0.0003(1)	-0.00174(8)
O1	0.0180(4)	0.0046(1)	0.0069(1)	-0.0018(4)	0.0119(4)	-0.0006(3)
O2	0.0209(4)	0.0035(1)	0.0058(1)	-0.0013(4)	0.0112(4)	-0.0020(2)
O3	0.0205(5)	0.0059(2)	0.0049(2)	0.0058(5)	0.0016(4)	0.0019(3)
O4	0.0105(4)	0.0077(2)	0.0073(2)	0.0021(5)	0.0005(4)	0.0024(3)
C1	0.0164(5)	0.0031(2)	0.0039(2)	0.0036(5)	0.0057(5)	0.0009(3)
C2	0.0233(7)	0.0032(2)	0.0058(2)	0.0036(6)	0.0093(6)	0.0014(3)
C3	0.0339(9)	0.0039(2)	0.0065(2)	0.0094(7)	0.0127(7)	0.0027(4)
C4	0.0299(8)	0.0057(2)	0.0050(2)	0.0185(6)	0.0073(7)	0.0023(4)
C5	0.0182(6)	0.0064(2)	0.0040(2)	0.0104(6)	0.0029(6)	0.0007(4)
C6	0.0186(7)	0.0090(3)	0.0073(3)	0.0138(7)	0.0007(8)	-0.0015(5)
C7	0.0099(6)	0.0111(4)	0.0102(4)	0.0034(8)	-0.0004(8)	-0.0034(7)
C8	0.0134(6)	0.0067(3)	0.0081(3)	0.0011(7)	0.0003(7)	-0.0026(5)
C9	0.0109(5)	0.0049(2)	0.0049(2)	0.0037(5)	0.0007(5)	-0.0001(4)
C10	0.0153(5)	0.0041(2)	0.0037(2)	0.0063(5)	0.0031(5)	0.0008(3)
C11	0.0111(4)	0.0027(1)	0.0037(2)	0.0004(4)	0.0028(4)	0.0002(3)
C12	0.0115(4)	0.0026(1)	0.0044(2)	0.0007(4)	0.0033(5)	0.0004(3)
C13	0.0141(5)	0.0029(1)	0.0038(2)	0.0014(5)	0.0043(5)	-0.0001(4)
C14	0.0358(8)	0.0045(2)	0.0097(2)	-0.0008(7)	0.0262(6)	-0.0034(4)
C15	0.118(1)	0.0111(4)	0.0359(4)	0.047(1)	0.1189(9)	0.0224(7)
C16	0.0147(5)	0.0037(2)	0.0043(2)	0.0025(5)	0.0013(5)	-0.0007(3)
C17	0.0151(7)	0.0123(5)	0.0096(4)	-0.004(1)	-0.0036(9)	0.0011(8)
C18	0.0192(9)	0.0117(5)	0.0178(6)	0.007(1)	0.007(1)	0.0094(9)
C19	0.0114(5)	0.0028(1)	0.0048(2)	0.0008(5)	0.0029(5)	-0.007(3)
C20	0.0152(6)	0.0044(2)	0.0054(2)	0.0022(6)	0.0054(5)	0.0004(4)
C21	0.0170(6)	0.0069(3)	0.0076(3)	0.0026(7)	0.0103(6)	-0.0024(4)
C22	0.0156(6)	0.0060(2)	0.0105(3)	0.0087(6)	0.0053(7)	-0.0036(5)
C23	0.0195(7)	0.0038(2)	0.0082(3)	0.0069(6)	0.0029(8)	0.0006(4)
C24	0.0178(6)	0.0034(2)	0.0057(2)	0.0023(6)	0.0048(6)	0.0005(3)

The form of the anisotropic displacement parameter is: exp[-(B(1,1)*h2 + B(2,2)*k2 + B(3,3)*l2 + B(1,2)*hk + B(1,3)*hl + B(2,3)*kl)].

Table of General Displacement Parameter Expressions - U's.

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
S1	0.0548(5)	0.0369(4)	0.0497(4)	0.0004(4)	0.0181(4)	0.0029(4)
S2	0.0549(5)	0.0455(5)	0.0544(5)	0.0070(5)	-0.0009(5)	-0.0100(5)
O1	0.076(2)	0.057(2)	0.073(2)	-0.007(1)	0.040(1)	-0.004(1)
O2	0.088(2)	0.044(1)	0.061(1)	-0.005(1)	0.037(1)	-0.011(1)
O3	0.087(2)	0.074(2)	0.052(2)	0.021(2)	0.005(1)	0.011(2)
O4	0.044(1)	0.096(2)	0.077(2)	0.008(2)	0.002(1)	0.014(2)
C1	0.069(2)	0.038(2)	0.041(2)	0.013(2)	0.019(2)	0.005(2)
C2	0.099(3)	0.040(2)	0.061(2)	0.013(2)	0.031(2)	0.008(2)
C3	0.143(4)	0.049(2)	0.069(2)	0.034(3)	0.042(2)	0.016(2)
C4	0.126(3)	0.071(2)	0.053(2)	0.067(2)	0.024(2)	0.013(2)
C5	0.077(3)	0.079(3)	0.042(2)	0.038(2)	0.010(2)	0.004(2)
C6	0.079(3)	0.112(4)	0.077(3)	0.050(3)	0.002(3)	-0.009(3)
C7	0.042(2)	0.138(5)	0.107(4)	0.012(3)	-0.001(3)	-0.019(4)
C8	0.057(3)	0.083(3)	0.085(3)	0.004(3)	0.001(2)	-0.015(3)
C9	0.046(2)	0.061(2)	0.052(2)	0.014(2)	0.002(2)	-0.001(2)
C10	0.065(2)	0.051(2)	0.038(2)	0.023(2)	0.010(2)	0.004(2)
C11	0.047(2)	0.033(2)	0.039(2)	0.002(2)	0.009(1)	0.001(1)
C12	0.048(2)	0.033(2)	0.046(2)	0.003(2)	0.011(2)	0.002(2)
C13	0.060(2)	0.036(2)	0.041(2)	0.005(2)	0.014(2)	0.006(2)
C14	0.151(3)	0.056(3)	0.103(3)	-0.003(3)	0.087(2)	-0.019(2)
C15	0.499(5)	0.138(5)	0.379(5)	0.172(4)	0.397(3)	0.128(4)
C16	0.062(2)	0.046(2)	0.045(2)	0.009(2)	0.004(2)	-0.004(2)
C17	0.064(3)	0.153(6)	0.101(4)	-0.014(4)	-0.012(3)	0.006(4)
C18	0.081(4)	0.145(6)	0.188(7)	0.025(4)	0.023(4)	0.054(5)
C19	0.048(2)	0.035(2)	0.050(2)	0.003(2)	0.010(2)	-0.004(2)
C20	0.064(2)	0.055(2)	0.057(2)	0.008(2)	0.018(2)	0.002(2)
C21	0.072(3)	0.086(3)	0.080(3)	0.010(3)	0.034(2)	-0.014(3)
C22	0.072(3)	0.086(3)	0.111(4)	0.032(2)	0.018(2)	-0.021(3)
C23	0.082(3)	0.048(2)	0.086(3)	0.025(2)	0.010(3)	0.003(2)
C24	0.075(3)	0.042(2)	0.060(2)	0.008(2)	0.016(2)	0.003(2)

The form of the anisotropic displacement parameter is: exp[-2pI2{h2a2U(1,1) + k2b2U(2,2) + l2c2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)}] where a, b, and c are reciprocal lattice constants.

Table of Root-Mean-Square Amplitudes of Anisotropic Displacement in Angstroms.

Atom	Min.	Int'med.	Max.
S1	0.190	0.215	0.238
S2	0.198	0.209	0.284
O1	0.216	0.237	0.303
O2	0.189	0.229	0.308
O3	0.206	0.268	0.324
O4	0.200	0.286	0.322
C1	0.182	0.196	0.272
C2	0.190	0.234	0.320
C3	0.191	0.246	0.394
C4	0.161	0.226	0.415
C5	0.195	0.214	0.344
C6	0.206	0.275	0.399
C7	0.198	0.322	0.395
C8	0.228	0.270	0.333
C9	0.190	0.233	0.272
C10	0.181	0.201	0.287
C11	0.182	0.198	0.212
C12	0.179	0.216	0.222
C13	0.178	0.208	0.246
C14	0.188	0.260	0.420
C15	0.206	0.289	0.855
C16	0.202	0.207	0.273
C17	0.225	0.354	0.403
C18	0.265	0.352	0.476
C19	0.182	0.216	0.235
C20	0.224	0.235	0.263
C21	0.216	0.293	0.311
C22	0.181	0.296	0.365
C23	0.186	0.286	0.326
C24	0.200	0.246	0.279

Table of Bond Distances in Angstroms.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
S1	C1	1.774(4)	C12	H12	0.97(4)
S1	C11	1.830(4)	C14	C15	1.196(9)
S2	C9	1.782(4)	C14	H14	0.975(6)
S2	C12	1.819(3)	C14	H14'	0.967(4)
O1	C13	1.188(5)	C15	H15	0.938(9)
O2	C13	1.329(4)	C15	H15'	1.000(7)
O2	C14	1.446(7)	C15	H15"	0.981(8)
O3	C16	1.195(5)	C17	C18	1.33(1)
O4	C16	1.317(6)	C17	H17	0.970(7)
O4	C17	1.476(6)	C17	H17'	0.992(7)
C1	C2	1.382(5)	C18	H18	0.951(6)
C1	C10	1.420(6)	C18	H18'	0.981(9)
C2	C3	1.378(7)	C18	H18"	0.961(8)
C2	H2	1.08(4)	C19	C20	1.383(6)
C3	C4	1.328(8)	C19	C24	1.390(5)
C3	H3	0.96(4)	C20	C21	1.381(7)
C4	C5	1.435(6)	C20	H20	0.90(4)
C4	H4	0.79(4)	C21	C22	1.372(7)
C5	C6	1.393(7)	C21	H21	0.93(4)
C5	C10	1.434(6)	C22	C23	1.364(8)
C6	C7	1.321(9)	C22	H22	0.81(4)
C6	H6	1.00(4)	C23	C24	1.376(7)
C7	C8	1.419(8)	C23	H23	0.98(4)
C7	H7	0.85(4)	C24	H24	0.92(4)
C8	C9	1.365(6)			
C8	H8	0.88(4)			
C9	C10	1.434(6)			
C11	C12	1.562(5)			
C11	C13	1.533(6)			
C11	C16	1.531(5)			
C12	C19	1.515(5)			

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Bond Angles in Degrees.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C1	S1	C11	103.0(2)	C1	C10	C9	126.5(4)
C9	S2	C12	108.0(2)	C5	C10	C9	117.0(4)
C13	O2	C14	116.6(3)	S1	C11	C12	111.8(2)
C16	O4	C17	117.6(4)	S1	C11	C13	112.0(2)
S1	C1	C2	112.8(3)	S1	C11	C16	109.4(3)
S1	C1	C10	126.3(3)	C12	C11	C13	110.0(3)
C2	C1	C10	120.9(4)	C12	C11	C16	107.4(3)
C1	C2	H2	118.(2)	C13	C11	C16	105.9(3)
C3	C2	H2	120.(2)	S2	C12	C11	112.8(2)
C2	C3	C4	119.9(4)	S2	C12	C19	106.1(2)
C2	C3	H3	122.(2)	S2	C12	H12	111.(2)
C4	C3	H3	118.(2)	C11	C12	C19	113.8(3)
C3	C4	C5	122.0(4)	C11	C12	H12	102.(2)
C3	C4	H4	128.(3)	C19	C121	H12	111.(3)
C5	C4	H4	110.(3)	O1	C13	O2	124.9(4)
C4	C5	C6	121.4(5)	O1	C13	C11	124.0(3)
C4	C5	C10	118.8(4)	O2	C13	C11	111.1(3)
C6	C5	C10	119.8(4)	O2	C14	C15	118.3(6)
C5	C6	C7	122.1(5)	O2	C14	H14	109.4(4)
C5	C6	H6	114.(2)	O2	C14	H14'	109.8(5)
C7	C6	H6	124.(2)	C15	C14	H14	106.5(6)
C6	C7	C8	120.3(5)	C15	C14	H14'	106.1(5)
C6	C7	H7	132.(3)	C14	C15	H15	117.5(8)
C8	C7	H7	108.(3)	C14	C15	H15'	110.0(7)
C7	C8	C9	120.5(5)	C14	C15	H15"	111.1(8)
C7	C8	H8	122.(2)	O3	C16	O4	125.6(4)
C9	C8	H8	117.(2)	O3	C16	C11	121.5(4)
S2	C9	C8	114.8(3)	O4	C16	C11	112.8(3)
S2	C9	C10	124.0(3)	O4	C17	C18	109.2(6)
C8	C9	C10	120.3(4)	O4	C17	H17	113.1(5)
C1	C10	C5	116.6(4)	O4	C17	H17'	111.7(5)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Bond Angles in Degrees (continue).

Atom 1	Atom 2	Atom 3	Angle
C18	C17	H17	110.3(6)
C18	C17	H17'	108.0(6)
C17	C18	H18	115.0(7)
C17	C18	H18'	108.9(7)
C17	C18	H18"	111.2(7)
C12	C19	C20	123.1(3)
C12	C19	C24	118.5(4)
C20	C19	C24	118.3(4)
C19	C20	C21	120.3(4)
C18	C20	H20	122.(3)
C21	C20	H20	118.(3)
C20	C21	C22	120.0(5)
C19	C24	H24	122.(2)
C23	C24	H24	117.(2)
C20	C21	H21	118.(2)
C22	C21	H21	122.(2)
C21	C22	C23	120.8(5)
C21	C22	H22	119.(3)
C23	C22	H22	121.(3)
C22	C23	C24	119.3(4)
C22	C23	H23	122.(3)
C24	C23	H23	119.(3)
C24	C23	H23	119.(3)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Torsional Angles in Degrees.

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C11	S1	C1	C2	-131.82 (0.29)
C11	S1	C1	C10	48.83 (0.36)
C1	S1	C11	C12	-92.04 (0.27)
C1	S1	C11	C13	31.87 (0.29)
C1	S1	C11	C16	149.01 (0.25)
C12	S2	C9	C8	117.41 (0.35)
C12	S2	C9	C10	-73.82 (0.36)
C9	S2	C12	C11	47.37 (0.31)
C9	S2	C12	C19	172.68 (0.25)
C14	O2	C13	O1	2.36 (0.54)
C14	O2	C13	C11	-179.59 (0.31)
C13	O2	C14	C15	125.43 (0.61)
C17	O4	C16	O3	-6.51 (0.66)
C17	O4	C16	C11	169.59 (0.41)
C16	O4	C17	C18	104.30 (0.60)
S1	C1	C2	C3	-179.08 (0.35)
C10	C1	C2	C3	0.31 (0.61)
S1	C1	C10	C5	-177.21 (0.29)
S1	C1	C10	C9	2.22 (0.57)
C2	C1	C10	C5	3.49 (0.54)
C2	C1	C10	C9	-177.08 (0.38)
C1	C2	C3	C4	-2.27 (0.68)
C2	C3	C4	C5	0.21 (0.70)
C3	C4	C5	C6	-177.69 (0.45)
C3	C4	C5	C10	3.69 (0.64)
C4	C5	C6	C7	-178.12 (0.49)
C10	C5	C6	C7	0.48 (0.74)
C4	C5	C10	C1	-5.35 (0.54)
C4	C5	C10	C9	175.17 (0.36)
C1	C5	C10	C1	176.01 (0.39)
C6	C5	C10	C9	-3.47 (0.57)
C5	C6	C7	C8	1.45 (0.85)

Table of Torsional Angles in Degrees (continue).

Atom 1	Atom 2	Atom 3	Atom 4	Angle	
C6	C7	C8	C9	-0.22	(0.82)
C7	C8	C9	S2	166.29	(0.41)
C7	C8	C9	C10	-2.93	(0.70)
S2	C9	C10	C1	17.06	(0.57)
S2	C9	C10	C5	-163.51	(0.30)
C8	C9	C10	C1	-174.76	(0.41)
C8	C9	C10	C5	4.67	(0.58)
S1	C11	C12	S2	36.49	(0.33)
S1	C11	C12	C19	-84.53	(0.32)
C13	C11	C12	S2	-88.53	(0.30)
C13	C11	C12	C19	150.44	(0.30)
C16	C11	C12	S2	156.60	(0.25)
C16	C11	C12	C19	35.58	(0.39)
S1	C11	C13	01	-127.81	(0.34)
S1	C11	C13	O2	54.12	(0.35)
C12	C11	C13	O1	-2.84	(0.49)
C12	C11	C13	O2	179.09	(0.28)
C16	C11	C13	O1	112.97	(0.40)
C16	C11	C13	O2	-65.09	(0.36)
S1	C11	C16	O3	-160.79	(0.33)
S1	C11	C16	O4	22.93	(0.40)
C12	C11	C16	O3	77.58	(0.44)
C12	C11	C16	O4	-98.70	(0.37)
C13	C11	C16	O3	-39.93	0.47)
C13	C11	C16	O4	143.08	(0.33)
S2	C12	C19	C20	-48.07	(0.43)
S2	C12	C19	C24	135.18	(0.33)
C11	C12	C19	C20	76.62	(0.45)
C11	C12	C19	C24	-100.12	(0.40)
C12	C19	C20	C21	-176.90	(0.39)
C24	C19	C20	C21	-0.16	(0.61)
C12	C19	C24	C23	175.74	(0.39)

Table of Torsional Angles in Degrees (continue).

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C20	C19	C24	C23	-1.15 (0.62)
C19	C20	C21	C22	1.01 (0.70)
C20	C21	C22	C23	-0.57 (0.77)
C21	C22	C23	C24	-0.72 (0.77)
C22	C23	C24	C19	1.60 (0.70)

References

1) Trost, B. M. *J. Am. Chem. Soc.* **1966**, 88, 1587; **1967**, 89, 138.

2) Fish, R. H.; Chow, L. C.; Caserio, M. C. *Tetrahedron Lett.* **1969**, 1259.

3) Maki, Y.; Hiramitsu, T. *Chem. Pharm. Bull.* **1977**, 25, 292.

4) Zhang, J.-J.; Schuster, G. B. *J. Org. Chem.* **1988**, 53, 716.

5) a) Glass, R. S.; Andreuski, S. W.; Broeker, J. L.; Firouzabadi, H.; Steffen, L. K.; Wilson, G. S. *J. Am. Chem. Soc.* **1989**, 111, 4036; b) Glass, R. S.; Adamowicz, L.; Broeker, J. L. *ibid.* **1991**, 113, 1065; c) Fujihara, H.; Chiu, J. -J.; Furukawa, N. *Chem. Lett.* **1990**, 2217; d) Fujihara, H.; Yabe, M.; Chiu, J.-J.; Furukawa, N. *Tetrahedron Lett.* **1991**, 32, 4345; e) Furukawa, N.; Shima, H.; Kimura, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1762; f) Fujihara, H.; Yabe, M.; Furukawa, N. *J. Org. Chem.* **1993**, 58, 5291.

6) Ando, W.; Kondo, S.; Nakayama, K.; Ichibori, K.; Kohoda, H.; Yamamoto, H.; Imai, I.; Nakaido, S.; Migita, T. *J. Am. Chem. Soc.* **1972**, 94, 3870-3876.

7) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans 2,* **1981**, 341.

8) a) Robert, J.-B.; Sherfinks, J. S.; Marsh, R. E.; Roberts, J. D. *J. Org. Chem.* **1974**, 39, 1152; b) Schweizer, W. B.; Proctor, G.; Kaftory, M.; Dunitz, J. D. *Helv, Chim. Acta* **1978**, 61, 2783.

Chapter 6

Evidence of Through-space Interaction between the Two Sulfur Atoms on Photolysis of Naphtho[1,8-*ef*][1,4]dithiepins

Abstract

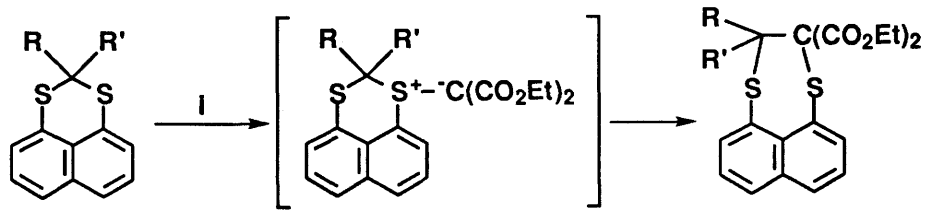
Irradiation of naphtho[1,8-*ef*][1,4]dithiepins at 313 nm gave the corresponding olefins and naphtho[1,8-*cd*]-1,2-dithiole quantitatively. Experimental results and *ab initio* calculations suggest that this photodecomposition proceeds *via* the S_1 state, and that a through-space interaction between the two sulfur atoms induced upon photo-excitation plays an important role.

Introduction

Transannular interaction or through-space interaction has often been observed between two or more heteroatoms that are arranged appropriately in one molecule.[1] The author described that photodecomposition of naphtho[1,8-*de*]-1,3-dithiin-1-oxides, 1-*N*-tosyl-sulfilimines, and 1-bis(ethoxycarbonyl)methylides provided quantitatively the corresponding carbonyl compounds, *N*-tosylaldimines, and olefins, respectively, together with naphtho[1,8-*cd*]-1,2-dithiole in Chapters 2, 3, and 5. Furthermore, the author suggested that the photodecomposition of these compounds proceeded by a through-space interaction between the two sulfur atoms at the 1,8-positions of naphthalene. However, direct experimental evidence of the S···S interaction has hardly been presented so far. In further extension of these studies, the author prepared and photolyzed 2-substituted- and 2,2-disubstituted-3,3-bis(ethoxycarbonyl)-naphtho[1,8-*ef*][1,4] dithiepins (**31** and **32**) and carried out *ab initio* calculations of naphtho[1,8-*ef*][1,4]dithiepin (**37**) as a model compound. The author describes evidence of the through-space interaction between the two sulfur atoms on photolysis of **31** and **32**.

Results and Discussion

Synthesis of Naphtho[1,8-*ef*][1,4]dithiepins



[5a] : R=Ph, R'=H
[5b] : R=*p*-Tol, R'=H
[5f] : R=PhCH=CH, R'=H
[5g] : R=2-fryl, R'=H
[6b] : R=Ph, R'=CH_3
[6h] : R=Ph, R'=$C_6H_5CH_2$

[29] or [30]

[31a] 66%
[31b] 72%
[31f] 72%
[31g] 68%
[32b] 82%
[32h] 66%

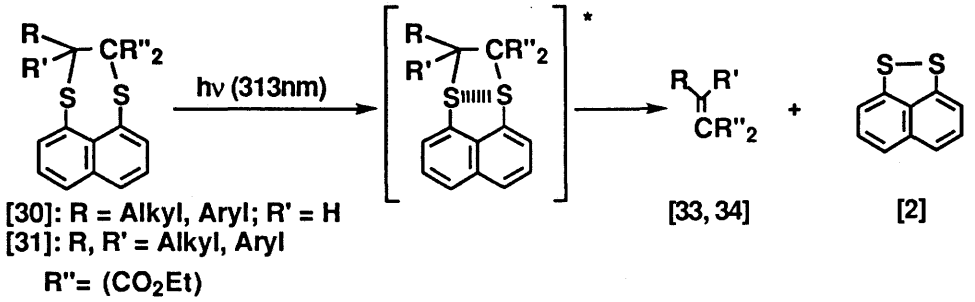
I: $N_2C(CO_2Et)_2$, $Cu(acac)_2$, benzene reflux

Scheme 6-1

Treatment of 2-substituted naphtho[1,8-*de*]-1,3-dithiins (**5**) or 2,2-disubstituted naphtho[1,8-*de*]-1,3-dithiins (**6**) with diethyl diazomalonate in the presence of copper acetylacetonate in benzene under reflux conditions gave the corresponding 2-substituted 3,3-bis(ethoxycarbonyl)-naphtho[1,8-*ef*][1,4] dithiepins (**31**), or 2,2-disubstituted 3,3-bis(ethoxycarbonyl)-naphtho[1,8-*ef*][1,4]dithiepins (**32**) which may be formed from the sulfonium ylides by the Stevens type rearrangement[2] (Scheme 6-1). The sulfonium ylides **29a** and **29b** could be isolated and underwent thermal-Stevens type rearrangement to give the corresponding ring-expanded compounds **31a** and **31b**. However compounds **29f**, **29g**, **30b**, and **30h** were not obtained on similar conditions. Interestingly, similar treatment of **5f** with diethyl diazomalonate did not yield the allylic rearrangement compund[3] but gave the Stevens type rearrangement

compound **31f**. The structure of **31a** was determined by X-ray crystallographic analysis as described in Chapter 5 (Figure 5-2).

Photolysis of Naphtho[1,8-*ef*][1,4]dithiepins



Scheme 6-2

Table 6-1. Photolysis of **31** and **32**.

	R	R'	Solvents	Yield of **33** and **34**/%[b]	Yield of **2**/%[b]
[**31a**]	Ph	H	CH_2Cl_2	>99 (92)[c]	>99 (100)[c]
[**31a**]	Ph	H	hexane	>99	>99
[**31a**]	Ph	H	benzene	>99	>99
[**31a**]	Ph	H	THF	>99	>99
[**31a**]	Ph	H	CH_3CN	>99	>99
[**31a**]	Ph	H	EtOH	>99	>99
[**31b**]	*p*-Tol	H	CH_2Cl_2	>99 (91)[c]	>99 (97)[c]
[**31f**]	PhCH=CH	H	CH_2Cl_2	>99 (91)[c]	>99 (99)[c]
[**31g**]	2-fury	H	CH_2Cl_2	>99 (96)[c]	>99 (98)[c]
[**32b**]	Ph	CH_3	CH_2Cl_2	>99 (96)[c]	>99 (99)[c]
[**32h**]	Ph	$PhCH_2$	CH_2Cl_2	>99 (97)[c]	>99 (98)[c]

a) 500 W high pressure Hg lamp, λ= 313 nm, Substrates (0.1 mmol), Solvents (5 ml). b) Yields were determined by HPLC and ^{1}H-NMR spectroscopy. c) Isolated yields.

Direct irradiation of compounds **31** and **32** (0.1 mmol) in deoxygenated dichloromethane (5 ml) was carried out in a cylindrical quartz tube using a high pressure mercury lamp (500

W, 313 nm) at room temperature to give the corresponding olefins **33** and **34** quantitatively with complete recover of naphtho[1,8-*cd*]-1,2-dithiole (**2**) (Scheme 6-2 and Table 6-1). Polar and nonpolar solvents including ethanol, acetonitrile, tetrahydrofuran, dichloromethane, chloroform, and hexane were examined on a photoreaction of **31a**. Photodecomposition reactions gave **33a** and **2** quantitatively.

The consumption of **31a** and formation of products **33a** and **2** were unaffected by the addition of benzophenone as a triplet sensitizer, indicating that both reactions may proceed *via* an excited singlet state, perhaps the lowest excited singlet (S_1) state. The quantum yields of the consumption of compound **31a** and the formation of **33a** and **2** at room temperature under similar photolysis conditions were measured by comparison with fulgide actinometry[4] to be 0.34, respectively.

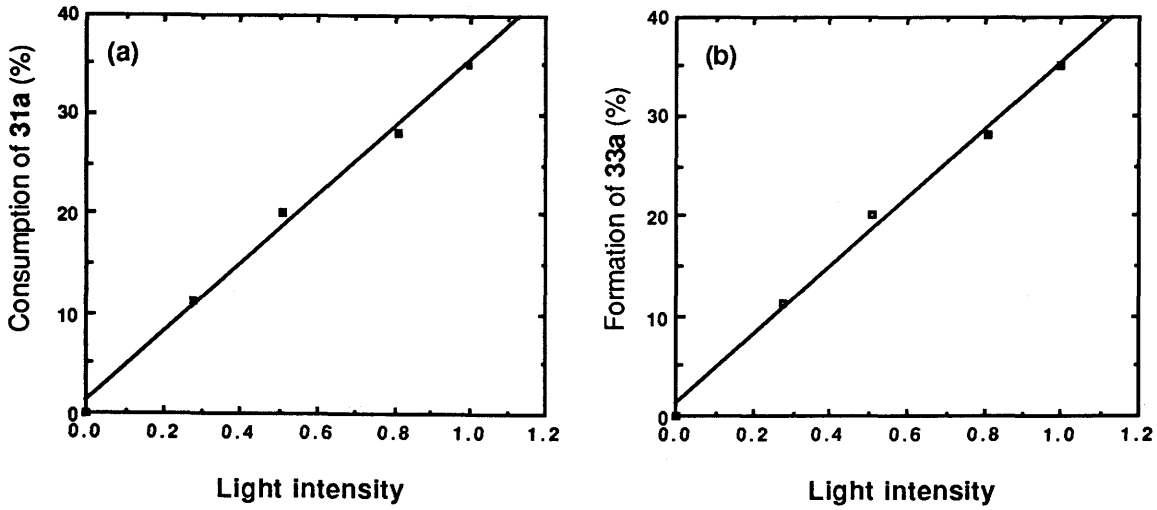


Figure 6-1. Light intensity dependence on the consumption of **31a** (a) and the formation of **33a** (b). (4.61×10^{-3} M **31a** in CH_2Cl_2).

The effect of light intensity on photolysis of compound **31a** was studied in order to understand whether the reaction proceeds by a one-, two-, or multi-photon process. The loss of **31a** and the formation of **33a** was proportional to the first power of the 313 nm light as shown in Figure 6-1. These results imply that the overall reaction proceeds by a one-photon process.

Ab Initio Calculation of Naphtho[1,8-*ef*][1,4]dithiepins

As it was suggested that the photodecomposition of **31** and **32** proceeds *via* the S_1 state, the *ab initio* calculations was carried out by using a model compound **37** (R, R', R"= H) in the S_1 state as well as in the ground state (S_0). The RHF method was applied to the S_0 state, and the CIS method to the S_1 state, using the STO-3G* basis set.[5] The geometry was optimized for both states, respectively.

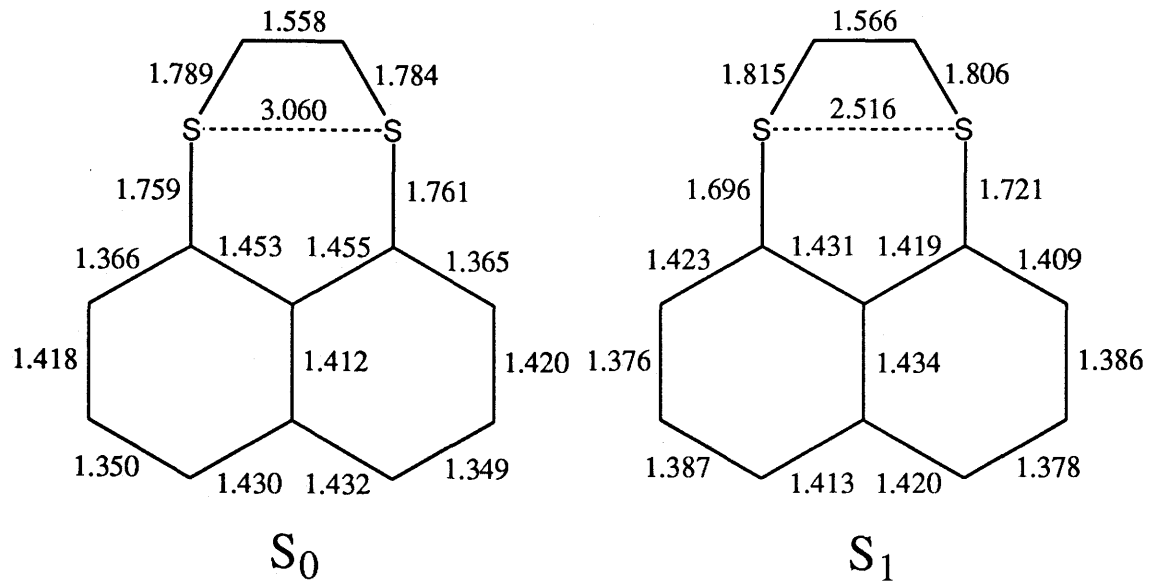


Figure 6-2. RHF optimized S_0 structure (left) and CIS optimized S_1 structure (right) of **37**. Only the bond lengths (Å) in the skelton are shown.

Figure 6-2 shows the RHF optimized S_0 structure and the CIS optimized S_1 structure. The S···S distance in S_0 was calculated to be 3.06 Å, which is very close to the corresponding value of **31a**: 3.13 Å described in Chapter 5 (Figure 5-2). As shown in Figure 6-3, the HOMO of **37** is essentially an out-of-phase combination of the so-called σ^*_{S-S} orbital and the HOMO of naphthalene, and the LUMO of **37** is essentially the LUMO of naphthalene. As expected, the S_1 state calculated at the S_0 geometry is mainly (72%) composed of the HOMO→LUMO single excitation. Four low-lying singlet excited states were calculated at the S_0 geometry; the oscillator strength for S_1 was the largest among these states, and it is plausible that the photodecomposition proceeds *via* the S_1 state. Since the σ^*_{S-S} orbital is anti-bonding between the two sulfur atoms, the excitation to S_1 causes a bonding character between them. Indeed, the geometry optimization for S_1 resulted in a shortening of the S···S distance by *ca.* 0.5 Å (Figure 6-2).

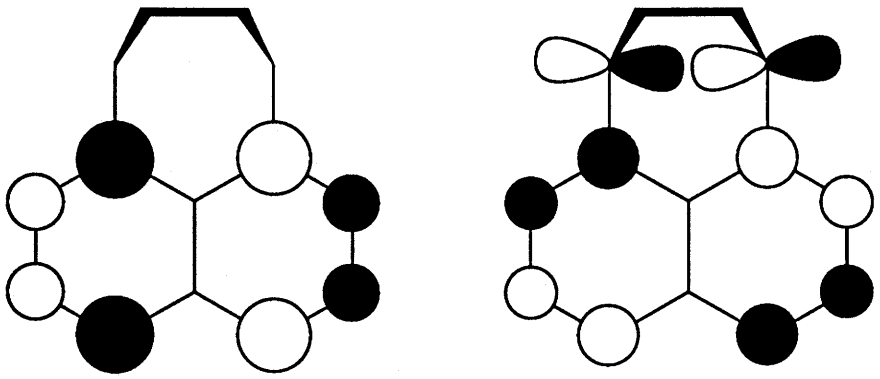


Figure 6-3. Schematic representation of HOMO and LUMO of **37**.

The shortening of the S···S distance upon excitation to S_1 can be associated with the reactivity as follows. As shown in Figure 6-4, the decomposition of the $-SCH_2CH_2-$ moiety to give ethylene is symmetry-forbidden whithin C_s symmetry; the reaction will proceed effectively if the electrons in the σ^*_{S-C} orbital are doubly excited to the σ^*_{S-C} orbital. However, the S_1 state of **37** does not correspond to such an excitation, though the elongation of the two S-C bonds is expected to ultimately make the $\sigma^*_{S-C}{}^- \rightarrow \sigma^*_{S-C}{}^+$ doubly excited state the lowest one. The situation is illustrated in Figure 6-5 where

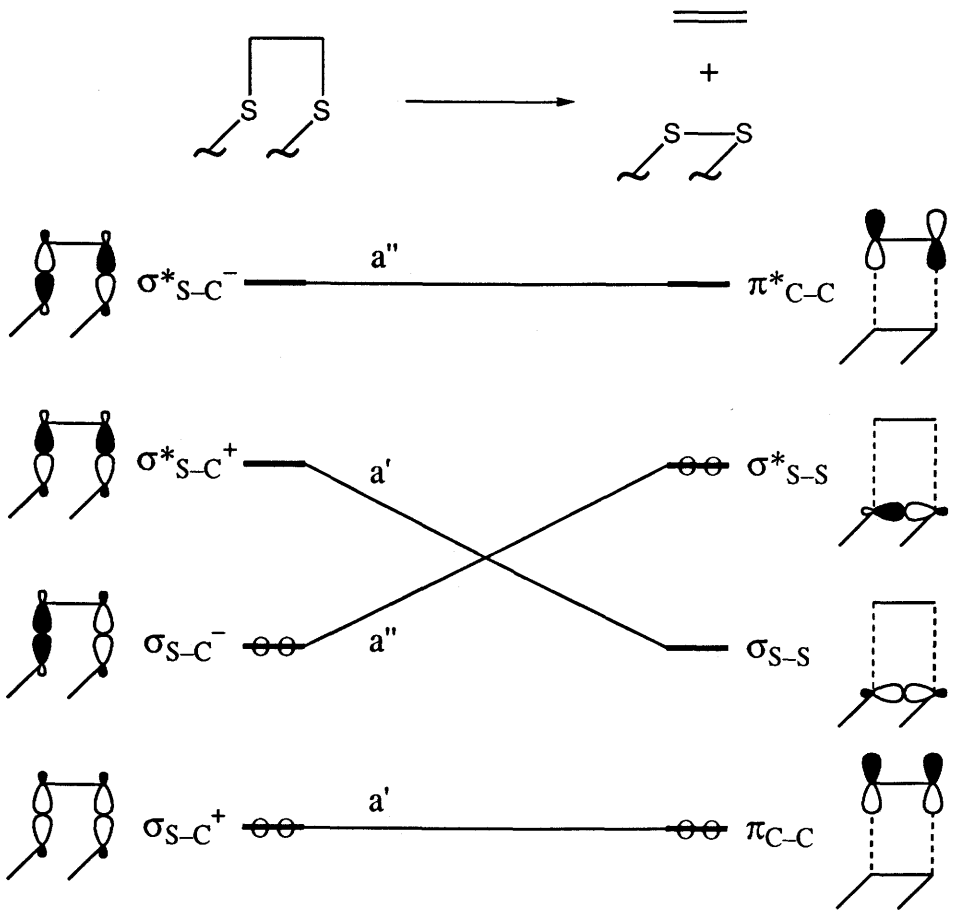


Figure 6-4. An MO correlation diagram which explains that the decomposition of a $-S-CH_2-CH_2-S-$ moiety to give $-S-S-$ and ethylene is symmetry forbidden (a C_s symmetry is assumed).

"Sn" represents an excited state which has a $\sigma^*_{s-c^-} \rightarrow \sigma^*_{s-c^+}$ doubly excited character. As may be seen from Figure 6-5, the barrier on the S_1 potential energy surface is expected to be much lower than in S_0. The observed quantumn yield, 0.34, is in consistent with the proposed pathway shown in Figure 6-5. Moreover, it should be noted that the shortening of the S···S distance radii, the energy level of $\sigma^*_{s-c^-}$ and lowers that of $\sigma^*_{s-c^+}$, making the S-C bonds breaking easier. Thus, it has been shown that the excitation of **31** and **32** causes the S···S bonding interaction, and that this is related to the clean photodecomposition of **31** and **32**. Such an interaction is also expected to play an important role also in the related photochemical reactions as described in Chapter 2, 3, and 5.

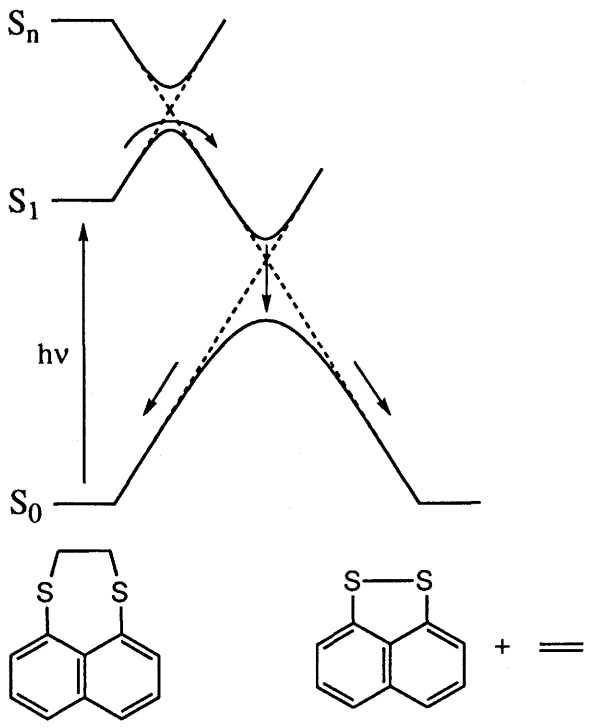


Figure 6-5. A schematic state correlation diagram between **37** and **2** + ethylene. The proposed photodecomposition pathway is also shown.

Experimental Section

General All melting points were uncorrected and were taken on a Yanaco micro melting point apparatus and LABORATORY DEVICES, USA, Model MRX-TEMP II. IR spectra were recorded on a JASCO FT/IR-5000 spectrometer. All NMR spectra were obtained with a JEOL LMN-EX-270 and a BRUKER MSL-400 FT-NMR spectrometer. Mass spectra were taken with a Shimadzu QP-2000 and a JEOL JMX SX102 mass spectrometer. Ultraviolet-visible spectra were recorded on a Hitachi U-3000. Preparative liquid chromatography was performed on a Japan Analytical Industry Co., Ltd., Model LC-09 and LC-908. High performance liquid chromatography (HPLC) data were collected with a Shimadzu LC-10A system, using a TSK gel ODS-ST column (length, 250 mm; internal diameter, 4.6 mm) and methanol-water as an eluent with monitoring at 254 nm. Photolyses, quantum yield, the sensitization, and intensity effect experiments were performed by irradiation with a 500 W ultrahigh pressure mercury lamp equipped with a glass filter and a monochromator. All photo-reactions were monitored and quantified by HPLC or ^{1}H-NMR. Analytical thin-layer chromatograph (TLC) was carried out on Merck precoated TLC plate (Kieselgel 60 F_{254}). Silica-gel used for column chromatography was Wako-gel C-200 and Merck kieselgel 60. Elemental analyses were carried out by Chemical Analysis Center at this University.

Materials All reagents were obtained from Wako Pure Chemical Industries, Ltd., Tokyo Kasei Kogyo, Co., Ltd., Kanto

Chemicals Co., Inc., or Aldrich Chemical Co. The reagents used as reaction solvents were further purified by general methods.

Synthesis of 2-Benzyl-2-phenyl-naphtho[1,8-*de*]-1,3-dithiin (6h)

n-Butyllithium (1.3 ml of 1.67 N solution in hexane, 2.2 mmol) was added dropwise at -78 °C to a solution of 2-phenyl-naphtho[1,8-*de*]-1,3-dithiin (**5a**) (408 mg, 2.0 mmol) in tetrahydrofuran (20 ml) and stirred for 1 h. To this solution was added benzylbromide (2.2 mmol) for 1 h at -78 °C with stirring then warmed up to room temperature and monitored by TLC. After the reaction and usual work-up process, the products were separated by silica-gel column chromatography using carbon tetrachloride as an eluent and then recrystallization from ethylacetate-hexane to give the pure product **6h**.

2-Benzyl-2-phenyl-naphtho[1,8-*de*]-1,3-dithiin (6h)

Yield 84 %; mp. 137-138 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.55 (s, 2H, CH_2), 6.73 (d, J = 7.1, 2H, ArH), 7.12 (t, J = 7.1, 2H, ArH), 7.16-7.22 (m, 4H, ArH), 7.34 (t, J 7.3 Hz, 2H, ArH), 7.48 (dd, J_1 = 7.3 Hz, J_2 = 1.0 Hz, 2H, ArH), 7.61-7.66 (m, 4H, ArH); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 49.33, 57.32, 125.73, 126.42, 126.52, 126.97, 127.46, 127.55, 127.98, 128.05, 128.46, 130.05, 130.80, 134.61, 134.86, 140.54; MS (m/z) 370 (M^+); Anal. Calcd for $C_{24}H_{18}S_2$: C, 77.80, H, 4.90. Found: C, 77.66, H, 4.78.

General Procedure of Naphtho[1,8-*ef*] [1,4]dithiepins

A mixture of 2-substituted naphtho[1,8-*de*]dithiins (**5**) or 2,2-substituted naphtho[1,8-*de*]dithiins (**6**)(1 mmol) and

diazomalonate (1 mmol) in benzene (5 ml) was refluxed for 48 h in the presence of 15 mg copper acetylacetonate. After cooling, the solvent was evaporated. The residues were purified by silica-gel column chromatography (eluent, ethylacetate-hexane) and recrystallization from dichloromethane-hexane to give the pure products **31** and **32**.

3-Hydro-2,2-bis(ethoxycarbonyl)-3-*p*-tolyl-naphtho[1,8-*ef*][1,4] dithiepin (31b)

Yield 72%; mp. 144-145 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88-0.95 (m, 6H, CH_3), 3.21 (s, 3H, CH_3), 3.65-3.69 (m, 1H, CH_2), 3.83-3.91 (m, 3H, CH_2), 5.69 (s, 1H. CH), 7.10 (d, J = 8.0 Hz, 2H, ArH), 7.26-7.32 (m, 2H, ArH), 7.35 (d, J = 8.0 Hz, 2H, ArH), 7.71-7.86 (m, 4H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ13.40, 13.71, 21.12, 59.14, 62.30, 62.33, 74.65, 125.67, 125.90, 127.75, 128.85, 129.78, 129.97, 131.27, 133.74, 133.92, 134.19, 134.26, 135.67, 135.90, 138.10, 165.80, 167.77; IR (KBr) 1738, 1301, 1238, 1195 cm^{-1} (CO_2); MS (m/z) 452 (M^+); Anal. Calcd for $C_{25}H_{24}O_4S_2$: C, 66.35, H, 5.34. Found: C, 66.38, H, 5.30.

3-Hydro-2,2-bis(ethoxycarbonyl)-3-(3-phenyl-2-propene)-naphtho [1,8-*ef*][1,4]dithiepin (31f)

Yield 72%; Oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.12 (t, J = 7.1 Hz, 3H, CH_3), 1.31 (t, J = 7.1 Hz, 3H, CH_3), 4.09-4.16 (m, 2H, CH_2), 4.29-4.37 (m, 2H, CH_2), 4.76 (d, J = 8.7 Hz, 1H, CH), 6.43 (d, J = 15.6 Hz, 1H, C=CH), 6.50 (dd, J_1 = 15.6 Hz, J_2 = 8.7 Hz, 1H, C=CH), 7.18-7.38 (m, 7H, ArH), 7.69-7.71 (m, 2H, ArH), 7.83-7.86 (m, 2H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ13.94, 14.00, 59.01, 62.30, 62.57, 70.06, 124.51, 125.45, 125.96,

126.58, 127.89, 128.39, 128.44, 128.62, 131.67, 132.24, 133.48, 133.91, 135.42, 136.19, 136.31, 137.48, 166.29, 168.53; IR (KBr) 1735, 1272, 1241, 1218 cm^{-1} (CO_2); MS (m/z) 464 (M^+); Anal. Calcd for $C_{26}H_{24}O_4S_2$: C, 67.22., H, 5.21. Found: C, 67.34, H, 5.33

3-Hydro-2,2-bis(ethoxycarbonyl)-3-(2-furyl)-naphtho[1,8-*ef*] [1,4]dithiepin (31g)

Yield 68%; mp. 91-92 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.16 (t, J = 7.2 Hz, 3H, CH_3), 1.17 (t, J = 7.2 Hz, 3H, CH_3), 4.05-4.09 (m, 1H, CH_2), 4.13-4.23 (m, 3H, CH_2), 5.47 (s, 1H. CH), 6.28-6.30 (m, 1H, 2-furylH), 7.30-7.37 (m, 3H, 2-furylH, ArH), 7.71-7.77 (m, 3H, ArH), 7.85 (d, J = 8.0 Hz, 1H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 13.71, 13.96, 53.80, 62.41, 62.76, 70.64, 108.94, 110.58, 125.51, 125.97, 128.04, 129.06, 132.23, 132.31, 133.63, 135.19, 132.26, 137.43, 141.97, 150.00, 165.80, 167.96; IR (KBr) 1742, 1721, 1255, 1195 cm^{-1} (CO_2); MS (m/z) 428 (M^+); Anal. Calcd for $C_{22}H_{20}O_4S_2$: C, 61.66, H, 4.70. Found: C, 61.65, H, 4.61.

2,2-Bis(ethoxycarbonyl)-3-methyl-3-phenyl-naphtho[1,8-*ef*][1,4] dithiepin (32b)

Yield 82%; mp. 139-140 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.76 (t, J = 7.1 Hz, 3H, CH_3), 0.98 (t, J = 7.1 Hz, 3H, CH_3), 2.52 (s, 3H, CH_3), 3.48-3.67 (m, 4H, CH_2), 7.295-7,39 (m, 5H, ArH), 7.77-7.83 (m, 4H, ArH), 7.99-8.01 (m, 2H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 13.41, 13.70, 25.10, 61.50, 62.11, 63.76, 78.95, 125.34, 125.35, 126.01, 127.78, 128.29, 128.73, 130.53, 131.24, 132.10, 134.38, 135.81, 141.38, 165.04, 165.68 ; IR (KBr) 1729,

1238, 1185 cm^{-1} (CO_2); MS (m/z) 452 (M^+); Anal. Calcd for $C_{25}H_{24}O_4S_2$: C, 66.35, H, 5.34. Found: C, 66.23., H, 5.32.

2,2-Bis(ethoxycarbonyl)-3-benzyl-3-phenyl-naphtho[1,8-*ef*][1,4] dithiepin (32h)

Yield 66%; mp. 176-177 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.70 (t, J = 6.9 Hz, 3H, CH_3), 1.03 (t, J = 6.9 Hz, 3H, CH_3), 3.39-3.43 (m, 2H, CH_2), 3.83 (d, J = 15.0, 1H, CH_2), 3.90-4.05 (br s, 2H, CH_2), 4.54 (d, J = 15.0, 1H, CH_2), 7.13-7.20 (m, 5H, ArH), 7.21-7.32 (m, 5H, ArH), 7.72-7.78 (m, 4H, ArH), 7.90-7.92 (m, 2H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ13.12, 13.75, 42.12, 61.82, 62.27, 69.59, 80.29, 125.37, 126.08, 126.17, 127.17, 127.43, 127.52, 130.24, 130.39, 130.80, 130.93, 131.88, 131.97, 133.84, 135.09, 133.35, 134.55, 137.43, 139.65, 165.40, 165.99; IR (KBr) 1744, 1717, 1241, 1212 cm^{-1} (CO_2); MS (m/z) 528 (M^+); Anal. Calcd for $C_{31}H_{28}O_4S_2$: C, 70.43, H, 5.34. Found: C, 70.19, H, 5.25.

General Photolysis Procedure

A solution of naphtho[1,8-*ef*][1,4]dithiepins (0.1 mmol) in solvent (5 ml) was placed in a cylindrical quartz tube equipped with a stirrer bar and a silicon septum. The solution was bubbled with Ar for 30 min to remove O_2. Irradiation of samples was carried out using the output of a 500 W high pressure mercury lamp filtered through a Toshiba UVD33S filter and a monochromator set at 313 nm under conditions of complete light absorption. The reaction progress was monitored by HPLC or ^{1}H-NMR spectroscopy. After irradiation, the solvent was evaporated and the residue was purified by preparative HPLC,

and the products were characterized by NMR and GC-MS spectroscopies.

1-[Bis(ethoxycarbonyl)]-4-phenyl-1,3-butadiene (33f)

Oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.27-1.41 (m, 12H, CH_3), 4.23-4.40 (m, 8H, CH_2), 6.62-6.67 (m, 1H, C=CH), 7.00-7.07 (m, 2H, C=CH), 7.23-7.42 (m, 8H, C=CH, ArH), 7.49-7.54 (m, 4H, C=CH, ArH), 7.79-7.82 (C=CH); MS (m/z) 274 (M^+).

Diethyl-2-furylmethylidenemalonate (33g)

Oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.32 (t, J = 7.1 Hz, 3H, CH_3), 1.37 (t, J = 7.1 Hz, 3H, CH_3), 4.28 (q, J = 7.1 Hz, 2H, CH_2), 4.40 (q, J = 7.1 Hz, 2H, CH_2), 6.50 (dd, J_1 = 3.5 Hz, J_2 = 1.7 Hz, 1H, 2-furylH), 6.70 (d, J = 3.5 Hz, 1H, 2-furylH), 7.45 (s, 1H, C=CH), 7.52 (d, J = 1.7 Hz, 1H, 2-furylH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.09, 14.13, 61.56, 61.62, 112.58, 117.89, 122.01, 127.51, 146.04, 149.03, 164.18, 166.30; MS (m/z) 238 (M^+).

Diethyl-1-methyl-benzylidenemalonate (33b)

Oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.95 (t, J = 7.1 Hz, 3H, CH_3), 1.32 (t, J = 7.1 Hz, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.96 (q, J = 7.1 Hz, 2H, CH_2), 4.29 (q, J = 7.1 Hz, 2H, CH_2), 7.23-7.26 (m, 2H, ArH), 7.32-7.37 (m, 3H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 13.58,14.09, 22.80, 22.82, 60.94, 61.09, 126.15, 126.56, 128.24, 128.46, 141.60, 155.75, 164.77, 161.18; MS (m/z) 262 (M^+).

Diethyl-1-benzyl-benzylidenemalonate (33h)

Oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.93 (t, J = 7.1 Hz, 3H, CH_3), 1.32 (t, J = 7.1 Hz, 3H, CH_3), 3.94 (q, J = 7.1 Hz, 2H, CH_2), 4.16 (s, 2H, CH_2), 4.32 (q, J = 7.1 Hz, 2H, CH_2), 7.10-7.14 (m, 2H, ArH), 7.15-7.20 (m, 3H, ArH), 7.22-7.26 (m, 3H, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 13.57, 14.08, 41.09, 61.03, 61.36, 126.42, 126.90, 127.30, 127.94, 128.24, 128.25, 129.26, 136.82, 139.50, 156.93, 164.69, 165.91; MS (m/z) 338 (M^+).

Benzophenone Dependence on the Photolysis of 3-Hydro-2,2-bis(ethoxycarbonyl)-naphtho[1,8-*ef*][1,4]dithiepin (31a)

A solution of 3-hydro-2,2-bis(ethoxycarbonyl)-naphtho[1,8-*ef*][1,4]dithiepin (**31a**) (10 mg, 0.023 mmol) and benzophenone (349 mg, 1.91 mmol) in dichloromethane was placed in a cylindrical quartz tube equipped with a stirrer bar and a silicon septum. The solution was bubbled with Ar for 30 min to remove O_2. Irradiation of samples was carried out using the output of a 500 W high pressure mercury lamp filtered through a Toshiba UVD33S filter and a monochromator set at 366 nm. Quantification was done with HPLC. Maleic anhydride was used as an external standard for HPLC. Yields were determined from solutions and irradiation times were kept under 30 min. The measurement of yields was repeated several times by HPLC detection.

Quantum Yields

The measurement of the quantum yield was carried out using the output of a 500 W high pressure mercury lamp filtered through a Toshiba UVD33S filter and a monochromator set at 313 nm under conditions of complete light absorption. The

fulgide, (E)-α-(2,5-dimethyl-3-furyl-ethylidene)(isopropylidene)succinic anhydride, which has a quantum yield of 0.20 for its photocolouration at 313 nm in toluene was used as an actinometer. Quantification was done with HPLC. Maleic anhydride was used as an external standard for HPLC. Sample and actinometer cells were sequentially irradiated. The actinometer cells were used to determined the photo flux, which was then used to convert the rate of loss of the material into a quantum yield. All quantum yields were determined from the solutions that began at concentration of 3-6 mM, and conversions were kept under 5%. The measurement of quantum yields was repeated several times by HPLC detection.

Effect of Light Intensity

The measurement of the light intensity effect was carried out using the output of a 500 W high pressure mercury lamp filtered through a Toshiba UVD33S filter and a monochromator set at 313 nm under conditions of complete light absorption. The light intensity was attenuated by using a quartz filter (313 nm; 27%, 52%, and 83%). Quantification was done with HPLC. Maleic anhydride was used as an external standard for HPLC. Yields were determined from the solutions that began at concentration 6 mM, and irradiation times were kept under 1 h. The measurement of yields was several times by HPLC detection.

***Ab Initio* Calculations**

Ab initio calculations were carried out on a HP735/125 workstation. Sparutan 3.0[6] was used for the RHF calculation, and Gaussian 92[7] for the CIS calculations using Spartan 3.0 as

an interface. The STO-3G* basis set which includes d polarization functions on S was employed.

References

1) a) Glass, R. S.; Andreuski, S. W.; Broeker, J. L.; Firouzabadi, H.; Steffen, L. K.; Wilson, G. S. *J. Am. Chem. Soc.* **1989**, 111, 4036; b) Glass, R. S.; Adamowicz, L.; Broeker, J. L. *ibid.* **1991**, 113, 1065; c) Fujihara, H.; Chiu, J.-J.; Furukawa, N. *Chem. Lett.* **1990**, 2217; d) Fujihara, H.; Yabe, M.; Chiu, J.-J.; e) Furukawa, N. *Tetrahedron Lett.* **1991**, 32, 4345; Furukawa, N.; Shima, H.; Kimura, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1762; f) Fujihara, H.; Yabe, M.; Furukawa, N. *J. Org. Chem.* **1993**, 58, 5291.

2) a) Thompson, T.; Stevens, T. S. *J. Chem. Soc.* **1932**, 69; b) Ando, W,; Yagihara, T.; Migata, T. *Tetrahedron Lett.* **1969**, 1425.

3) Ando, W.; Kondo, S.; Nakayama, K.; Ichibori, K.; Kohoda, H.; Yamamoto, H.; Imai, I.; Nakaido, S.; Migita, T. *J. Am. Chem. Soc.* **1972**, 94, 3870.

4) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans 2* **1981**, 341.

5) Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1976**, 64, 5142.

6) Hehre, W. J. et al. Wavefunction, Inc., Irvine, CA.

7) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkey, J.; Stewart, J. J. P.; Pole, J. A.; Gaussian, Inc., Pittsburgh, PA, 1992.

List of Publications

1) "The Simple Preparation of Aldehydes and Ketones by the Photo-Oxygen Rearrangement of Naphtho[1,8-*de*]dithiin Monooxides";
Furukawa, N.; Fujii, T.; Kimura, T.; Fujihara, H.
Chemistry Lett. **1994**, 1007.

2) "Preparation of *N*-Tosylaldimines by the Intramolecular Photo-Imino Group Migration of Naphtho[1,8-*de*]dithiin-1-*N*-tosylsulfilimines ";
Fujii, T.; Kimura, T.; Furukawa, N.
Tetrahedron Lett. **1995**, 36, 1075.

3) "One-Pot Diels-Alder Reaction of *N*-Tosylaldimines Generated by BF_3-Et_2O Catalyzed Transformation of Naphtho[1,8-*de*]dithiin-1-*N*-tosylsulfilimines";
Fujii, T.; Kimura, T.; Furukawa, N.
Tetrahedron Lett. **1995**, 36, 4813.

4) "Mechanism for Photodecomposition of Naphtho[1,8-*de*][1,3] dithiin-1-bis(ethoxycarbonyl)methylides";
Fujii, T.; Sakuragi, H.; Furukawa, N.
Tetrahedron Lett., **1995**, 36, 8039.

5) "Evidence of Through-space Interaction between the Two Sulfur Atoms on Photolysis of Naphtho[1,8-*ef*][1,4] dithiepins";
Fujii, T.; Takahashi, O.; Furukawa, N.

Submitted for Publication.

6) "Photochemical Studies on Through-space S···S Interaction of Naphtho[1,8-*de*]-1,3-dithiin-1-oxides"
Submitted for Publication.

7) "Comparison of Photolysis of Naphtho[1,8-*de*]-1,3-dithiin-1-oxides, Dibenzo[*bc,hi*][1,5,7]trithiaazulene-5-oxides, and Dibenzo[*d,f*]-1,3-dithiepan-1-oxides";
Submitted for Publication.

Others

1) "Synthesis and Application of Quinine-Bearing Clay";
Moriguchi, T.; Fujii, T.; Koike, T.; Yoshihara, M.; Maeshima, T.
J, Oil Chemistry, **1993**, 42, 134.

2) "Synthesis of γ-Zirconium Phosphate Immobilized by Pyridoxal and Application for Transaminatiion";
Kaku, G.; Fujii, T.; Matubara, Y.; Asakura, J.; Yoshihara, M.; Maeshima, T.
Chemistry Express, **1993**, 3, 805.

3) "Synthesis and Application of Pyridoxal-Bearing γ-Zirconium Phosphate";
Kaku, G.; Fujii, T.; Ito, S.; Yoshihara, M.; Maeshima, T.
J, Color Material, **1993**, 66, 643.

Acknowledgement

The author wishes to express sincerest gratitude to Professor Naomichi Furukawa of Tsukuba University for his continuing valuable suggestion and warm encouragement throughout the course of doctor.

The author also wishes to thank Professor Masakuni Yoshihara of Kinki University for his numerous advice and discussions in this study.

The author wishes to express much appreciation to Professor Akira Yabe of National Institute of Materials and Chemical Research and Associate Professor Hirochika Sakuragi of Tsukuba University for their constant advice and discussions during this work.

The author would like to thank Associate Professor Hisashi Fujihara of Kinki University and Associate Professor Tatsuya Nabeshima of Tsukuba University and Dr. Takeshi Kimura of Iwate University for their constant advice and discussions during this work.

The author would like to thank Professor Ernst Horn of Tsukuba Advanced Research Alliance Center for the measurement of X-ray crystallographic analysis and his constant advice.

The author also would like to thank Dr. Ohgi Takahashi for his computational work and discussions in this study.

The author wishes to his gratitude to Dr. Souichi Sato and Dr. tetsushi Maruyama for the measurement of Mass spectrometry and NMR spectroscopy.

The author gratefully thanks to the members of Furukawa's group, especially, Mr. Hidetaka Shima and Mr. Hiroki Kusanagi for their collaborations.

Finally, the author express his deep appreciation to his parents for their constant assistance and encouragement.

January, 1996

Takayoshi Fujii