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New Consecutive Photochemical Reactions of Naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimines via the Through-Space Interaction between Two Sulfur Atoms; A Convenient Method for Preparation of *N*-Tosylaldimines

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ABSTRACT

Naphtho[1,8-de]-1,3-dithiin-1-N-tosylsulfilimines underwent facile consecutive photochemical reactions to give quantitatively the corresponding N-tosylaldimines, together with naphtho[1,8-cd]-1,2-dithiole, via a sulfur–sulfur interaction. The intermediate, 3-hydro-3-phenyl-naphtho[1,8-ef][1,4]dithia[2]-azepin, was isolated by liquid chromatography of the reaction mixtures, and its structure was determined by X-ray crystallographic analysis. The proposed mechanism for these photochemical reactions is based on quantum yield measurements, photo-intensity effects, and crossover experiments. © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:29–40, 1998

INTRODUCTION

N-Sulfonylaldimines have been widely used as important reagents in organic synthesis because they are unique electron-deficient imines that are stable enough to be isolated but still reactive enough to undergo addition reactions [1–4]. Lichtenburger first prepared aldimines by a Lewis acid-catalyzed direct condensation involving aldehydes [5,6]; however, this method appears to be limited to aromatic aldehydes. Kreze carried out the pioneering work on the imino-transfer reactions with aromatic aldehydes utilizing sulfinylsulfonamides [6a,7]. In particular, this procedure was adopted recently for Diels-Alder cycloaddition of aliphatic aldehydes with 1,3-dienes *in situ* [2b]. Disubstituted tellurium analogs and ditosyltellurodiimines have also been useful but are less convenient reagents [7].

Through-space interaction or transannular interaction has frequently been observed in organic compounds bearing more than two heteroatoms in close proximity [8–11]. These compounds usually have new chemical and physical properties, and thus exhibit unexpected reactivities. Therefore, 1,8-bis(alkylthio)- or 1,8-bis(alkylseleno)naphthalene derivatives are probably the candidates of choice for the generation of various active species and for the

Dedicated to Prof. William McEwen on the occasion of his seventy-fifth birthday.

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development of new reactions initiated by through-space interactions between two sulfur or two selenium atoms [12]. In our previous articles, we reported that the photolysis of naphtho[1,8-*de*] -1,3-dithiin-1-oxides, -1-*N*-tosylsulfilimines, and -1-bis(ethoxycarbonyl)methylides quantitatively provides the corresponding carbonyl compounds, *N*-tosylaldimines, and olefins, together with naphtho[1,8-*cd*]-1,2-dithiole [12c–e]. Furthermore, 8,13-dihydrobenzo[*g*]naphtho[1,8-*bc*]-1,5-diselenonin underwent a photo-induced cleavage of the C–Se bond to generate the corresponding *o*-quinodimethane quantitatively, together with naphtho[1,8-*cd*]-1,2-diselenole [12b]. In this article, we describe the details of the photochemical reactions of naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimines.

RESULTS

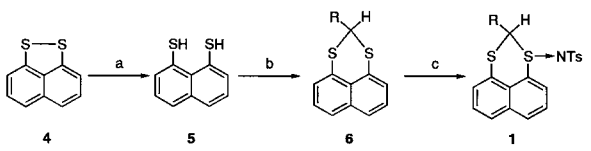
Preparation and Photochemical Reactions of Naphtho[1,8-de]-1,3-dithiin-1-N-tosylsulfilimines

2-Substituted naphtho[1,8-*de*]-1,3-dithiin-*N*-tosylsulfilimines were prepared according to the following procedures shown in Scheme 1. Reduction of naphtho[1,8-*cd*]-1,2-dithiole (**4**) [13] with sodium borohydride in THF-ethanol at room temperature almost quantitatively gave 1,8-naphthalenedithiol (**5**) [14]. Compounds **6** were prepared in high yields by the reaction of **5** with aldehydes in the presence of $SiCl_4$ in CH_2Cl_2 [15]. 2-Substituted naphtho[1,8-*de*]-1,3-dithiin-*N*-tosylsulfilimines **1** were prepared in moderate yields, as a single diasteroisomer in each case, by the reaction of **6** with chloramine-T in ethanol-CH_2Cl_2 at room temperature.

The detailed structural analyses of 3-methyl-naphtho [1,8-*de*]-1,3-dithiin-*N*-tosylsulfilimine (**1c**) and 2,2-dihydro-naphtho[1,8-*de*]-1,3-dithiin (**7**) [14] were performed by X-ray crystallographic analysis. Selected bond distances, bond angles, and torsional angles of **1c** and **7** are collected in Tables 1 and 2, respectively. The ORTEP drawings of **1c** and **7** are depicted in Figures 1 and 2, respectively. The molecular structure of **1c** is that of a *trans* isomer, with the phenyl and *N*-tosyl groups occupying the equatorial positions (R_S, S_C and S_S, R_C configurations). The S(1) ··· S(2) distance of **1c** is 2.86 Å, which is about 0.1 Å shorter than the S(1) ··· S(1)* distance of **7** and 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(2) bond angle in compound **1c** (104.4°) is smaller than the S(1)-C(7)-S(1)* bond angle of **7** (111°). The C(9)-S(2)-C(11) bond angle of 101.6° in **1c** is larger than the C(1)-S(1)-C(7) bond angle of **7** (99.4°). These observations indicate that S(1) of the sulfilimino group is positively polarized, and an attractive interaction with S(2) acts to compress the C(11) valence angle and hence to shorten the S ··· S intramolecular distance in compound **1c**.

N-Tosylsulfilimines **1** are thermally stable but decompose to the corresponding *N*-tosylaldimines **3** quantitatively with a complete recovery of naphtho[1,8-*cd*]-1,2-dithiole (**4**) on exposure to the radiation of a high-pressure mercury lamp (400 W) in benzene for 18 hours (Table 3). Interestingly, this procedure can be applied to the synthesis of the aliphatic imines **3d** (R = Et) and **3e** [R = $CH_3(CH_2)_5$] derived from enolizable aldehydes. Polar and nonpolar solvents, including acetonitrile, THF, CH_2Cl_2, $CHCl_3$, and hexane, were examined for the photoreaction of **1a**. The photodecomposition reactions gave **3a** and **4** quantitatively regardless of the solvents used. A large-scale photoreaction was also successful. Photolysis of 0.5 g of **1a** was carried out in 100 mL of CH_2Cl_2 under an Ar atmosphere using a 400 W high-pressure mercury lamp. The reaction proceeded cleanly, and subsequent evaporation of CH_2Cl_2 gave a residue that was separated to provide *N*-benzylidene-4-methylbenzenesulfonamide (**3a**) and **4** in 93 and 97% isolated yields, respectively. Furthermore, treatment of **3a** and **3d,e,** which were obtained from **1a** and **1d,e** in CH_2Cl_2, with 2,3-dimethyl-1,3-butadiene *in situ* in the presence of BF_3-Et_2O at −20°C, afforded the corresponding imino Diels-Alder products, 1-(*p*-toluenesulfonyl)-4,5-dimethyl-2-phenyl-1,2,3,6-tetrahydropyridine, 1-(*p*-toluene-sulfonyl)-4,5-dimethyl-2-ethyl-1,2,3,6-tetrahydropyridine, and 1-(*p*-toluenesulfonyl)-4,5-dimethyl-2-hexyl-1,2,3,6-tetrahydropyridine in 89, 88, and 75% yields, respectively [16]. In addition, the 2-aryl and -alkyl sulfilimines **1a** and **1c–e** were also treated with 2,3-dimethyl-1,3-butadiene in the presence of BF_3–Et_2O in CH_2Cl_2 at −20°C to give the imino [4 + 2] cycloadducts [12f].

In order to understand the mechanism of the photodecomposition of *N*-tosylsulfilimines **1,** the formation of the product and disappearance of the starting material during the photoreaction of **1a** were followed by time interval ^{1}H-NMR spectroscopy. The reaction profile for photoreaction of **1a** under irradiation with a high-pressure mercury lamp (400 W) in $CDCl_3$ is shown in Figure 3. The ^{1}H-NMR



SCHEME 1

TABLE 1 Selected Bond Distances, Bond Angles, and Torsional Angles for Compound **1c**[a]

		Bond Distances (Å)	
S(1)-N(1)	1.620(3)	C(3)-C(4)	1.350(4)
S(1)-C(1)	1.792(3)	C(4)-C(5)	1.421(5)
S(1)-C(11)	1.821(4)	C(5)-C(6)	1.413(4)
S(2)-C(9)	1.760(3)	C(5)-C(10)	1.421(4)
S(2)-C(11)	1.793(3)	C(6)-C(7)	1.363(5)
C(1)-C(2)	1.375(4)	C(7)-C(8)	1.387(5)
C(1)-C(10)	1.423(4)	C(8)-C(9)	1.363(4)
C(2)-C(3)	1.388(5)	C(9)-C(10)	1.434(4)
		Bond Angles (deg.)	
N(1)-S(1)-C(1)	103.0(1)	C(6)-C(5)-C(10)	119.8(3)
N(1)-S(1)-C(11)	105.6(2)	C(5)-C(6)-C(7)	120.7(3)
C(1)-S(1)-C(11)	99.1(2)	C(6)-C(7)-C(8)	119.8(3)
C(9)-S(2)-C(11)	101.6(1)	C(7)-C(8)-C(9)	122.0(3)
S(1)-C(1)-C(2)	115.5(2)	S(2)-C(9)-C(8)	117.8(2)
S(1)-C(1)-C(10)	123.1(2)	S(2)-C(9)-C(10)	122.0(2)
C(2)-C(1)-C(10)	121.4(3)	C(8)-C(9)-C(10)	120.0(3)
C(1)-C(2)-C(3)	120.2(3)	C(1)-C(10)-C(5)	117.3(3)
C(2)-C(3)-C(4)	120.9(3)	C(1)-C(10)-C(9)	125.2(3)
C(3)-C(4)-C(5)	120.9(3)	C(5)-C(10)-C(9)	117.5(2)
C(4)-C(5)-C(6)	120.7(3)	S(1)-C(11)-S(2)	104.4(2)
C(4)-C(5)-C(10)	119.4(3)		
		Torsional Angles (deg.)	
C(11)-S(1)-C(1)-C(10)	145.08	C(3)-C(4)-C(5)-C(6)	177.35
C(1)-S(1)-C(11)-S(2)	−67.19	C(4)-C(5)-C(6)-C(7)	179.48
C(11)-S(2)-C(9)-C(10)	−35.12	C(4)-C(5)-C(10)-C(1)	0.89
C(9)-S(2)-C(11)-S(1)	67.58	C(4)-C(5)-C(10)-C(9)	−178.90
S(1)-C(1)-C(10)-C(9)	−3.48	C(5)-C(6)-C(7)-C(8)	−1.33
C(10)-C(1)-C(2)-C(3)	−1.27	C(6)-C(7)-C(8)-C(9)	2.14
C(2)-C(1)-C(10)-C(9)	−180.00	C(7)-C(8)-C(9)-C(10)	−0.44
C(1)-C(2)-C(3)-C(4)	1.16	S(2)-C(9)-C(10)-C(1)	2.06
C(2)-C(3)-C(4)-C(5)	−0.02	C(8)-C(9)-C(10)-C(1)	178.26

[a]The atom-labeling scheme is shown in Figure 1.

TABLE 2 Bond Distances, Bond Angles, and Torsional Angles for Compound **7**[a]

		Bond Distances (Å)	
S(1)-C(1)	1.764(4)	C(2)-C(3)	1.384(6)
S(1)-C(7)	1.793(4)	C(3)-C(4)	1.354(6)
C(1)-C(2)	1.375(5)	C(4)-C(5)	1.423(4)
C(1)-C(6)	1.432(4)	C(5)-C(6)	1.434(8)
		Bond Angles (deg.)	
C(1)-S(1)-C(7)	99.4(2)	C(3)-C(4)-C(5)	121.3(4)
S(1)-C(1)-C(2)	115.7(3)	C(4)-C(5)-C(6)	119.4(3)
S(1)-C(1)-C(6)	123.5(3)	C(1)-C(6)-C*(1)	126.2(4)
C(1)-C(2)-C(3)	121.5(4)	C(1)-C(6)-C(5)	116.9(2)
C(2)-C(3)-C(4)	120.1(4)	S(1)-C(7)-S*(1)	111.3(3)
		Torsional Angles (deg.)	
C(7)-S(1)-C(1)-C(2)	−150.16	C(2)-C(1)-C(6)-C(5)	−0.42
C(7)-S(1)-C(1)-C(6)	31.40	C(1)-C(2)-C(3)-C(4)	−0.54
S(1)-C(1)-C(2)-C(3)	−177.97	C(2)-C(3)-C(4)-C(5)	0.49
C(6)-C(1)-C(2)-C(3)	0.51	C(3)-C(4)-C(5)-C(6)	−0.42
S(1)-C(1)-C(6)-C(5)	177.94	C(4)-C(5)-C(6)-C(1)	0.37

[a]The atom-labeling scheme is shown in Figure 2.

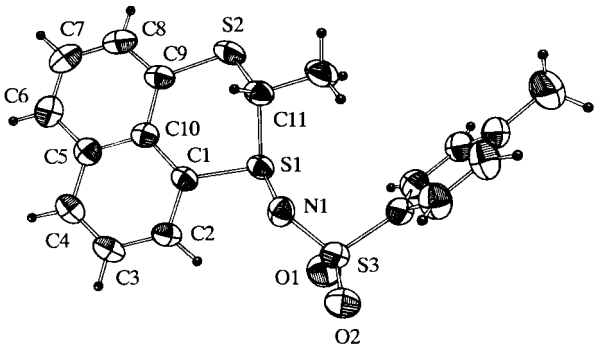


FIGURE 1 ORTEP drawing of **1c**.

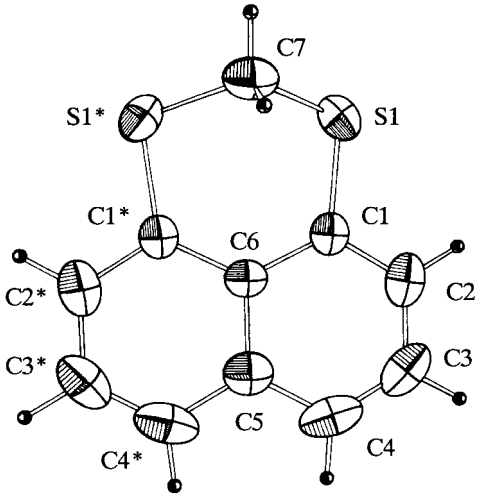
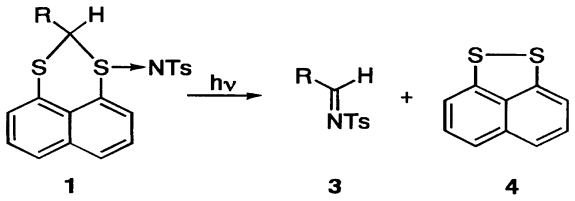


FIGURE 2 ORTEP drawing of **7**.

peaks of the starting material **1a** at δ 2.35 (s, 3H, CH_3) and 5.09 (s, 1H, CH) were gradually reduced, while the peaks of the photo-rearranged intermediate, 3-hydro-3-phenyl naphtho[1,8-*ef*][1,4]dithia[2]-azepin **2a** [δ 2.17 (s, CH_3), 6.62 (d, J = 8.4 Hz, Naph-H), 6.90 (s, CH)], together with those of the products **3a** [δ 2.44 (s, CH_3), 9.03 (s, CH)] and **1** [δ 7.14 (d, J = 7.6 Hz, Naph-H)], increased. The latter were identified by comparing the spectral data with those of authentically prepared compounds. When the photolysis of **1a** was stopped at the point of optimum conversion of **1a** to **2a,** the intermediate **2a** could be obtained in a maximum yield of 33% and could be isolated from the reaction mixture by preparative HPLC. The apparent mass balance dipped and rose again in a manner completely consistent with the formation of the intermediate **2a.** The structure of **2a** was determined by ^{1}H-, ^{13}C-NMR and mass spectroscopy, by elemental analyses and finally by X-ray crystallographic analysis as shown in Figure 4. Selected bond distances, bond angles, and torsional angles of **2a** are given in Table 4. The naphthalene ring in compound **2a** is slightly twisted about the C(5)–C(10) axis. The exocyclic bonds of S(2)–C(9) and S(3)–C(1) are splayed outward, and the sulfur atoms in the 1,8-positions of naphthalene are displaced

TABLE 3 Photolysis of **1a**[a]



1	**R**	Solvent	Yield of 3/%[b]	Yield of 4/%[b]
			>99	>99
a	Ph	C_6H_6	(98)[c]	(100)[c]
a	Ph	$CHCl_3$	>99	>99
a	Ph	CH_2Cl_2	>99	>99
a	Ph	THF	>99	>99
a	Ph	CH_3CN	>99	>99
			>99	>99
b	*p*-Tol	C_6H_6	(91)[c]	(99)[c]
c	Me	C_6H_6	—	−(91)[c]
d	Et	C_6H_6	>99	>99
			>99	>99
e	$CH_3(CH_2)_5$	C_6H_6	(93)[c]	(100)[c]
			>99	>99
f	PhCH=CH	C_6H_6	(90)[c]	(98)[c]
			>99	>99
g	2-furyl	C_6H_6	(90)[c]	(100)[c]

[a]400 W high-pressure Hg lamp, $\lambda > 300$ nm, substrates (0.1 mmol), solvent (5 ml).
[b]Yields were determined by gas chromatography and ^{1}H-NMR spectroscopy.
[c]Isolated yields.

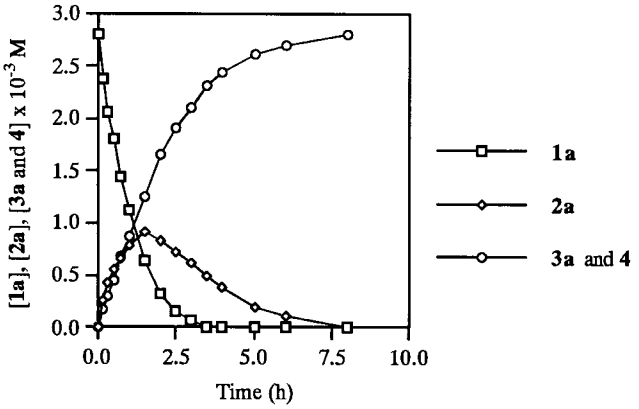


FIGURE 3 Time course of photolysis of **1a** (2.8×10^{-2} M **1a** in $CDCl_3$).

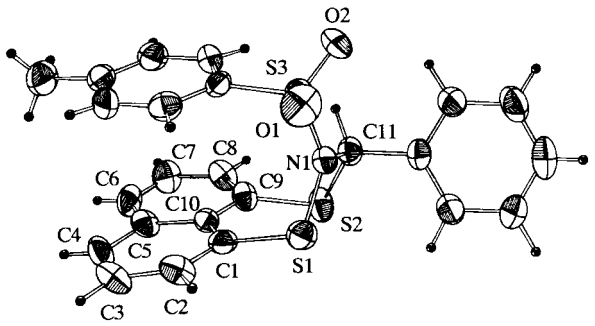


FIGURE 4 ORTEP drawing of **2a**.

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 having bulky substituents [17]. The S(1) ··· S(2) distance of **2a** is 3.11 Å, which is significantly shorter than the sum of the van der Waals radii of the two sulfur atoms (3.70 Å), but about 0.25 Å longer than the S(1) ··· S(2) distance of 2-methylnaphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimine (**1c**) (2.86 Å). These distortion patterns and the larger S ··· S intramolecular distance in compound **2a** can be explained by the presence of the repulsive interaction between the two sulfur atoms in the 1,8-positions of naphthalene.

The quantum yields for the consumption of *N*-tosylsulfilimine **1a** and the formation of aldimine **3a** and naphthalene-1,8-dithiole **4** by irradiation with a high-pressure mercury lamp (500 W, 313 nm) at room temperature in deoxygenated CH_2Cl_2 were measured by fulgide actinometry [18] to be 0.74 and 0.06, respectively. These results are also indicative of the formation of an intermediate on photolysis of **1a** to **3a** and **4.** The photolysis of the photo-rearranged intermediate **2a** also provided quantitatively the corresponding **3a** and **4** under similar photolysis conditions. The quantum yields for the consumption of **2a** and the formation of **3a** and **4** were 0.32 and 0.32, respectively. The consumption of **1a** and the formation of **3a** and **4** were unaffected by the addition of benzophenone as a triplet sensitizer, or isoprene as a triplet quencher, indicating that the reaction may proceed via an excited singlet.

A crossover experiment was carried out in order to decide whether the intermediate **2** was obtained by an inter-or intramolecular process. Irradiation of a 1:1 mixture of 2-phenylnaphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimine (**1a**) and 2-*p*-tolylnaphtho[1,8-*de*]-1,3-dithiin-1-*N*-benzenesulfonylsulfilimine (**8**) was carried out under similar photolysis conditions as shown in Scheme 2. The reaction proceeded cleanly to give the aldimines **3a** and **9,** together with **4,** quantitatively. After separation of the aldimines and **4,** the ^{1}H-NMR spectra of the aldimines were found to be identical with those of a 1:1 mixture of **3a** and **9,** and hence no crossover products were detected at all, indicating clearly that their photo-migration proceeds intramolecularly. The results demonstrate that the formation of the intermediate **2** proceeds solely by an intramolecular reaction.

The effect of light intensity on photolysis of sulfilimine **1a** was studied in order to determine whether the reaction proceeds via a one-, two- or multi-photon process. The loss of **1a** was proportional to the first power of the intensity of the 313 nm light, whereas the formation of **3a** and **4** was proportional to the square of the intensity, as shown in Figure 5. These results imply that the consumption of **2a** proceeds via a one-photon process to give the intermediate **2a** in the primary photochemical step. Thereafter, the intermediate **2a** should be converted to the corresponding **3a** and **4** in a secondary photochemical step.

DISCUSSION

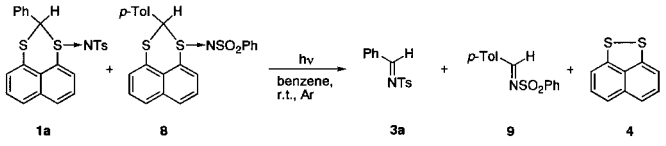
The results show that the photolysis of naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimines **1** using a high-pressure mercury lamp proceeds by the mechanism outlined in Scheme 3. The primary process is that of the photolysis of sulfilimines **1** leading to an intramolecular 1,2-migration of the nitrogen atom to give the corresponding intermediates **2** in an excited singlet state and as a one-photon process. In general, photodecompositions of sulfilimines lead to the cleavage of the nitrogen–sulfur bond to generate the nitrenes [19]. Lerch and Mattingly have reported that the photolysis of *S,S*-dimethyl-*N*-benzoylsulfilimine in methanol affords phenyl isocyanate as the photo-Curtius rearrangement product [19a]. In addition, the photolysis of dimethyl-*N*-*p*-tosylsulfilimine has produced *p*-toluenesulfonamide and ammonium *p*-toluenesulfonate [19b].

This is the first example of a carbon–sulfur bond cleavage reaction in the photolysis of sulfilimines, similar to that of acyclic and cyclic sulfoxides [20]. Because sulfilimines are not formed during the photo-Stevens–type rearrangement [21], this photorearrangement may be explained by the occurrence of a through-space interaction between the two sulfur atoms in the ground or excited state. We have no direct evidence for this interaction. However, the X-ray analysis clearly reveals that the S(1) ··· S(2) distance in the starting material **1c** (2.86 Å) is shorter than the sum of the van der Waals radii of two sulfur atoms (3.70 Å). When comparing the sulfilimine **1c**

TABLE 4 Selected Bond Distances, Bond Angles, and Torsional Angles for Compound **2a**[a]

Bond Distances (Å)			
S(1)-C(1)	1.781(4)	C(4)-C(5)	1.419(7)
S(1)-N(1)	1.696(4)	C(5)-C(6)	1.410(7)
S(2)-C(9)	1.779(4)	C(5)-C(10)	1.434(6)
S(2)-C(11)	1.812(4)	C(6)-C(7)	1.340(7)
C(1)-C(2)	1.372(7)	C(7)-C(8)	1.404(7)
C(1)-C(10)	1.427(6)	C(8)-C(9)	1.379(7)
C(2)-C(3)	1.397(7)	C(9)-C(10)	1.433(6)
C(3)-C(4)	1.348(7)	N(1)-C(11)	1.492(6)
Bond Angles (deg.)			
C(1)-S(1)-N(1)	105.4(2)	C(5)-C(6)-C(7)	122.0(4)
C(9)-S(2)-C(11)	104.0(2)	C(6)-C(7)-C(8)	119.5(5)
S(1)-C(1)-C(2)	114.4(3)	C(7)-C(8)-C(9)	121.1(5)
S(1)-C(1)-C(10)	124.8(3)	S(2)-C(9)-C(8)	115.1(3)
C(2)-C(1)-C(10)	120.8(4)	S(2)-C(9)-C(10)	123.3(3)
C(1)-C(2)-C(3)	121.7(4)	C(8)-C(9)-C(10)	120.8(4)
C(2)-C(3)-C(4)	119.1(5)	C(1)-C(10)-C(5)	116.9(4)
C(3)-C(4)-C(5)	121.9(4)	C(1)-C(10)-C(9)	126.7(4)
C(4)-C(5)-C(6)	120.8(4)	C(5)-C(10)-C(9)	116.4(4)
C(4)-C(5)-C(10)	119.3(4)	S(1)-N(1)-C(11)	120.4(3)
C(6)-C(5)-C(10)	119.9(4)	S(2)-C(11)-N(1)	111.1(3)
Torsional Angles (deg.)			
S(1)-C(1)-C(10)-C(9)	5.3	C(2)-C(3)-C(4)-C(5)	3.5
C(1)-C(10)-C(9)-S(2)	17.7	C(3)-C(4)-C(5)-C(6)	−178.2
C(10)-C(9)-S(2)-C(11)	−76.8	C(4)-C(5)-C(6)-C(7)	−179.7
C(9)-S(2)-C(11)-N(1)	56.6	C(5)-C(6)-C(7)-C(8)	3.2
S(1)-C(11)-C(12)-S(2)	−136.4	C(6)-C(7)-C(8)-C(9)	−2.0
C(1)-S(1)-N(1)-C(11)	−86.3	C(7)-C(8)-C(9)-C(10)	−2.5
N(1)-S(1)-C(1)-C(10)	42.9	C(8)-C(9)-(C10)-C(1)	−173.1
C(2)-C(1)-C(10)-C(9)	−177.0	C(1)-C(10)-C(5)-C(4)	−5.8
C(10)-C(1)-C(2)-C(3)	1.17	C(9)-C(10)-C(5)-C(4)	−4.4
C(1)-C(2)-C(3)-C(4)	−5.2		

[a]The atom-labeling scheme is shown in Figure 4.



SCHEME 2

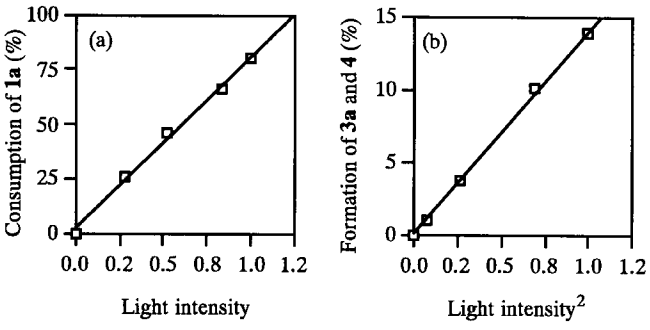
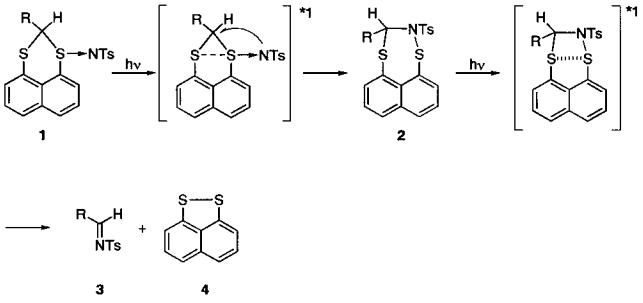


FIGURE 5 Light intensity dependence on the consumption of (a) **1a** and the formation of (b) **3a** and **4** (4.87×10^{-3} M **1a** in CH_2Cl_2).



SCHEME 3

to the corresponding sulfide **7,** we observe a shorter intramolecular S ··· S distance and a smaller S-C-S bond angle in compound **1c** than those of **7.** These observations indicate that an attractive interaction between the two sulfur atoms in the 1,8-positions of the naphthalene ring exists in the sulfilimines **1.**

In the secondary photochemical step, the intermediate **2** is presumably converted to the corre-

sponding **3** and **4** in an excited singlet state and as a one-photon process. The X-ray analysis of **2a** revealed that naphthalene is appreciably twisted, the exocyclic S–C bonds being splayed outward and the sulfur atoms in the 1,8-positions of the naphthalene being displaced above and below the average plane of the naphthalene ring, and hence the nonbonded S ··· S distance (3.11 Å) is longer than that of sulfilimine **1c** (2.86 Å), this being indicative of the repulsive interaction between the two sulfur atoms in the 1,8-positions of the naphthalene ring. The distortional pattern and the nonbonded S ··· S distance in **2a** are similar to those of the intermediate, 3-hydro-2,2-bis(ethoxycarbonyl)-3-phenylnaphtho[1,8-*ef*-][1,4]dithiepin obtained by photolysis of 2-phenyl-naphtho[1,8-*de*]-1,3-dithiin-1-bis(ethoxy-carbonyl)-methylide [12e,12h]. Recently, we carried out an ab initio calculation of an excited state (S_1) of naphtho[1,8-*ef*][1,4]dithiepin as a model compound [12h]. The result showed that the excitation to the S_1 state causes the S ··· S bonding interaction, and this is related to the clean photodecomposition of naphtho[1,8-*ef*][1,4]dithiepin. Such an interaction is also expected to play an important role in the related photochemical reactions of **2.**

CONCLUSION

Naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimines **1** were photolyzed by use of a high-pressure mercury lamp to give the corresponding *N*-tosylaldimines **3** and naphtho[1,8-*cd*]-1,2-dithiole (**4**), quantitatively. These reactions proceeded via an excited singlet state and as a two-photon process.

The advantage of our present procedure is that it is a promising method to prepare *N*-tosylaldimines in high yields without the use of a strong Lewis acid and toxic chemicals, even though it is ineffective for the preparation of ketimines. It can also be stressed that the process is "environmentally benign" for synthetic organic chemistry. Furthermore, compound **4** can be recovered completely and recycled to give the starting materials after reduction and treatment with aldehydes.

EXPERIMENTAL SECTION

Photolysis procedures, measurement of quantum yields and intensity effects, and crossover and sensitization experiments were performed by irradiation with a 400 W high-pressure mercury lamp or a 500 W ultrahigh-pressure mercury lamp equipped with a glass filter and monochromator. All photoreactions were monitored and quantified by GC, HPLC, or ^{1}H-NMR spectroscopy. X-ray data collection was performed on an Enraf-Nonius CAD4-FR computer-controlled κ-axis diffractometer [(23 ± 1)°C], and calculations for structure solution and refinement were performed on a VAX 3100 computer using SDP/VAX. Elemental analyses were carried out by Chemical Analysis Center at this University.

Naphtho[1,8-*cd*]-1,2-dithiole (**4**) was prepared according to the method reported in the literature [13]. 1,8-Naphthalenedithiole (**5**) was prepared by the reduction of **4** with $NaBH_4$ in ethanol–THF [14].

Synthesis of Naphtho[1,8-de]-1,3-dithiins **6a–d**. *General Procedure [15].* To a well-stirred solution of 5 mmol of a carbonyl compound and 5 mmol of 1,8-naphthalenedithiol (**1**) in 20 mL of CH_2Cl_2 at −20°C, tetrachlorosilane (5 mmol) was added dropwise. The solution was warmed to room temperature and the reaction was monitored by TLC. When the reaction had been completed (within 2 h), the solution was treated with 10 mL of 5% sodium bicarbonate solution and extracted with CH_2Cl_2 (3 × 100 mL). After having been dried with anhydrous magnesium sulfate and after removal of the solvent, the residue was separated by silica-gel column chromatography (eluent, tetrachloromethane), and then recrystallization of the product from ethyl acetate–hexane gave the pure product.

*2-Phenyl-naphtho[1,8-de]-1,3-dithiin (***6a***).* Yield 98%; mp 124–125°C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 5.42 (s, 1H), 7.36–7.49 (m, 7H), 7.55–7.58 (m, 2H), 7.70–7.73 (m, 2H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 46.8, 125.3, 125.5, 125.9, 127.7, 128.8, 129.0, 129.1, 132.0, 135.1, 136.5; 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 (***6b***).* Yield 97%; mp 135–136°C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.37 (s, 3H), 5.37 (s, 1H), 7.21 (d, J = 7.8 Hz, 2H), 7.36 (d, J = 7.8 Hz, 2H), 7.42–7.46 (m, 4H), 7.68 (d, J = 7.8 Hz, 2H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 21.3, 46.6, 125.3, 125.5, 125.8, 127.6, 128.1, 129.7, 132.2, 133.4, 135.0, 139.0; 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-Methyl-naphtho[1,8-de]-1,3-dithiin (***6c***).* Yield 99%; mp 57–58°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.72 (d, J = 7.0 Hz, 3H), 4.38 (q, J = 7.0 Hz, 1H), 7.29 (t, J = 8.2 Hz, 2H), 7.38 (dd, J_1 = 8.2 Hz, J_2 = 1.3 Hz, 2H), 7.59 (dd, J_1 = 8.2 Hz, J_2 = 1.3 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 20.5, 37.7, 125.4, 125.6, 126.1, 127.3, 130.4, 134.9; 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 (***6d***).* Yield 94%; mp 66–67°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.16 (t, J = 7.3 Hz, 3H), 2.02 (q, J = 7.3 Hz, 2H), 4.19 (t, J = 7.3 Hz, 1H), 7.31 (t, J = 8.0 Hz, 2H), 7.40 (dd, J_1 = 8.0 Hz, J_2 = 1.3 Hz, 2H), 7.60 (dd, J_1 = 8.0 Hz, J_2 = 1.3 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 12.0, 28.2, 44.6, 125.4, 126.2, 126.5, 127.3, 130.1, 150.1; MS (*m*/*z*) 232 (M^+); anal. calcd for $C_{13}H_{12}S_2$: C, 67.20; H, 5.21. Found: C, 66.93; H, 5.20.

*2-Hexyl-naphtho[1,8-de]-1,3-dithiin (***6e***).* Yield 98%; oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.90 (t, J = 7.3 Hz, 3H), 1.28–1.38 (m, 6H), 1.57–1.66 (m, 2H), 2.02 (q, J = 7.3 Hz, 2H), 4.31 (t, J = 7.3 Hz, 1H), 7.35 (t, J = 7.6 Hz, 2H), 7.43 (dd, J_1 = 7.6 Hz, J_2 = 1.1 Hz, 2H), 7.63 (dd, J_1 = 7.6 Hz, J_2 = 1.1 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.0, 22.5, 27.0, 28.7, 31.5, 34.7, 43.0, 125.5, 126.0, 126.3, 127.3, 130.2, 135.0; MS (*m*/*z*) 232 (M^+); anal. calcd for $C_{17}H_{20}S_2$: C, 70.78; H, 6.99. Found: C, 70.58; H, 7.01.

*2-(3-Phenyl-2-propene)-naphtho[1,8-de]-1,3-dithiin (***6f***).* 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), 6.39 (dd, J_1 = 15.4 Hz, J_2 = 8.4 Hz, 1H), 6.85 (dd, J_1 = 15.4 Hz, J_2 = 1.1 Hz, 1H), 7.26–7.41 (m, 7H), 7.47 (dd, J_1 = 8.1 Hz, J_2 = 1.4 Hz, 2H), 7.69 (dd, J_1 = 8.1 Hz, J_2 = 1.4 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 43.8, 124.2, 125.6, 126.3, 126.4, 126.8, 127.7, 128.4, 128.6, 129.8, 134.4, 134.9, 135.7; 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 (***6g***).* Yield 87%; mp 67–68°C;^{1}H NMR (270 MHz, $CDCl_3$) δ 5.33 (s, 1H), 6.31 (dd, J_1 = 3.2 Hz, J_2 = 1.9 Hz, 1H), 6.35 (d, J = 3.2 Hz, 1H), 7.36–7.40 (m, 3H), 7.47 (dd, J_1 = 8.1 Hz, J_2 = 1.1 Hz, 2H), 7.70 (dd, J_1 = 8.1 Hz, J_2 = 1.1 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 38.6, 109.0, 110.8, 125.5, 125.6, 126.3, 127.8, 129.8, 134.9, 142.7, 150.1; 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.

*2,2-Dihydro-naphtho[1,8-de]-1,3-dithiin (***7***) [14].* Yield 71%; mp 121–122°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.13 (s, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 27.9, 125.3, 125.9, 126.2, 127.6, 129.3, 135.1; MS (*m*/*z*) 204 (M^+). The crystal data for **7:** orthorhombic, Pnma, a = 7.511(1) 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(MoKα) = 4.8 cm^{-1}, R = 0.037 (R_w = 0.038), 512 unique reflections with $Fo^2 > 3.0\sigma(Fo^2)$. The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Center. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK.

Synthesis of 2-Substituted Naphtho[1,8-de]-1,3-dithiin-1-N-tosylsulfilimines **1**. *General Procedure.* 2-Substituted naphtho[1,8-*de*]-1,3-dithiins **6** (1 mmol) and chloramine-T (281 mg, 1 mmol) were dissolved in 20 mL of ethanol-CH_2Cl_2 and stirred for 12 hours under an Ar atmosphere. To this solution was added a 1M NaOH solution. The precipitates were collected, washed with water, and recrystallized from CH_2Cl_2-ethanol to give the pure products **1.**

*2-Phenyl-naphtho[1,8-de]-1,3-dithiin-1-N-tosylsulfilimine (***1a***).* Yield 70%; mp 192–193°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.35 (s, 3H), 5.09 (s, 1H), 6.97 (d, J = 8.2 Hz, 2H), 6.96–7.25 (m, 3H), 7.26–7.37 (m, 4H), 7.52 (t, J = 7.8 Hz, 1H), 7.63 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 1H), 7.76 (t, J = 7.8 Hz, 1H), 7.90 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 1H), 8.80 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 1H), 8.47 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 1H); ^{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, 64.12; 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 (***1b***).* Yield 75%; mp 200–201°C (decomp.); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.37 (s, 3H), 2.38 (s, 3H), 5.04 (s, 1H), 6.96–7.03 (m, 4H), 7.16–7.23 (m, 2H), 7.35–7.38 (m, 2H), 7.52 (t, J = 7.8 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.76 (t, J = 7.8 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 8.08 (d, J = 7.8 Hz, 1H), 8.48 (d, J = 7.8 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.40, 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, 64.77; H, 4.57; N, 3.02. Found: C, 64.48; H, 4.47; N, 2.99.

*2-Methyl-naphtho[1,8-de]-1,3-dithiin-1-N-tosylsulfilimine (***1c***).* Yield 73%; mp 164–165°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.69 (d, J = 7.2 Hz, 3H), 2.43 (s, 3H), 4.13 (q, J = 7.2 Hz, 1H), 7.30 (d, J = 7.9 Hz, 2H), 7.49 (t, J = 7.2 Hz, 1H), 7.57 (d, J = 7.2 Hz, 1H), 7.61 (t, J = 7.2 Hz, 1H), 7.83 (d, J = 7.2 Hz, 1H), 7.92 (d, J = 7.9 Hz, 2H), 8.01 (d, J = 7.2

Hz, 1H), 8.06 (d, J = 7.2 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.7, 21.5, 52.8, 126.0, 126.3, 126.4, 126.8, 127.7, 128.2, 128.4, 129.4, 129.5, 130.9, 132.8, 134.6, 141.2, 142.1; 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. The crystal data for **1c:** triclinic, P$\bar{1}$, a = 10.158(1) Å, b = 12.257(1) Å, c = 8.390(1) Å, α = 105.0 (3)°, β = 109.1 (3)°, γ = 67.8 (3)°, V = 903.3 Å^3, z = 2, ρ = 1.42 g/cm^3, μ(MoKα) = 4.1 cm^{-1}, R = 0.043 (R_w = 0.046), 2483 unique reflections with $Fo^2 > 3.0\ \sigma(Fo^2)$. Lists of fractional atomic coordinates, thermal parameters, bond lengths, and angles have been deposited at the Cambridge Crystallographic Data Center [12f].

*2-Ethyl-naphtho[1,8-de]-1,3-dithiin-1-N-tosylsulfilimine (***1d***).* Yield 73%; mp 158–159°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.10 (t, J = 7.6 Hz, 3H), 1.83–1.95 (m, 1H), 2.35–2.41 (m, 1H), 2.45 (s, 3H), 4.09 (dd, J_1 = 8.8 Hz, J_2 = 3.5 Hz, 1H), 7.30 (d, J = 8.1 Hz, 2H), 7.49 (t, J = 7.7 Hz, 1H), 7.57–7.63 (m, 2H), 7.83 (d, J = 7.7 Hz, 1H), 7.92 (d, J = 8.1 Hz, 2H), 7.99–8.05 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 9.9, 21.5, 21.7, 59.7, 126.0, 126.3, 126.4, 126.9, 128.1, 128.2, 128.6, 129.4, 129.5, 131.3, 132.8, 134.6, 141.2, 142.1; 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 (***1e***).* Yield 70%; mp 167–168°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3H), 1.21–1.37 (m, 6H), 1.59–1.71 (m, 3H), 2.15–2.21 (m, 1H), 2.43 (s, 3H), 4.10 (dd, J_1 = 9.6 Hz, J_2 = 3.5 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.49 (t, J = 7.8 Hz, 1H), 7.59 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 1H), 7.64 (t, J = 7.8 Hz, 1H), 7.84 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 1H), 7.92 (d, J = 8.4 Hz, 2H), 8.02 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 1H), 8.14 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 1H); ^{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, 5.95; 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 (***6f***).* Yield 68%; mp 193–194°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.19 (s, 3H), 4.85 (d, J = 8.9 Hz, 1H), 5.92 (dd, J_1 = 15.7 Hz, J_2 = 8.9 Hz, 1H), 6.85 (d, J = 15.7 Hz, 1H), 6.91 (d, J = 7.8 Hz, 2H), 7.22–7.25 (m, 2H), 7.34–7.35 (m, 3H), 7.53 (t, J = 7.7 Hz, 1H), 7.64 (d, J = 7.7 Hz, 1H), 7.72–7.77 (m, 3H), 7.89 (d, J = 7.7 Hz, 1H), 8.07 (d, J = 7.7 Hz, 1H), 8.39 (d, J = 7.7 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.42, 60.1, 115.9, 126.1, 126.3, 126.6, 126.7, 127.3, 128.0, 128.4, 128.6, 129.2, 129.4, 133.0, 133.5, 134.6, 134.7, 137.1, 141.0, 141.7, 141.9, 143.8; 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 (***6g***).* Yield 42%; mp 170–171°C (decomp); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.19 (s, 3H), 6.40 (dd, J_1 = 3.2 Hz, J_2 = 1.8 Hz, 1H), 6.56 (d, J = 3.2 Hz, 1H), 6.66 (d, J = 8.2 Hz, 2H), 6.98 (s, 1H), 7.15 (d, J = 8.2 Hz, 2H), 7.20 (t, J = 7.7 Hz, 1H), 7.31 (t, J = 7.7 Hz, 1H), 7.44 (d, J = 1.8 Hz, 1H), 7.49 (dd, J_1 = 7.7 Hz, J_2 = 1.1 Hz, 1H), 7.59 (dd, J_1 = 7.7 Hz, J_2 = 1.1 Hz, 1H), 7.69 (dd, J_1 = 7.7 Hz, J_2 = 1.1 Hz, 1H), 7.82 (dd, J_1 = 7.7 Hz, J_2 = 1.1 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.3, 68.0, 108.9, 110.8, 125.3, 126.2, 126.8, 128.4, 128.8, 129.4, 129.7, 131.8, 132.7, 135.1, 135.7, 136.2, 136.4, 137.7, 143.2, 150.2; 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, 59.83; H, 3.88; N, 3.05.

*2-p-Tolyl-naphtho[1,8-de]-1,3-dithiin-1-N-benzenesulfonylsulfilimine (***8***).* **6b** (294 mg, 1 mmol) and chloramine-B (267 mg, 1 mmol) were dissolved in 20 mL of ethanol-CH_2Cl_2 and the mixture was stirred for 12 hours under an Ar atmosphere. To this solution a 1M NaOH solution was added. The precipitates were filtered off, washed with water, and recrystallized from CH_2Cl_2-ethanol to give the *N*-benzenesulfonylsulfilimine **8** in 69% yield. Mp 198–199°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.35 (s, 3H), 5.05 (s, 1H), 7.01 (d, J = 8.2 Hz, 2H), 7.15–7.20 (m, 4H), 7.36 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 8.09 (d, J = 7.6 Hz, 1H), 8.47 (d, J = 7.6 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.42, 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, 64.12; H, 4.26; N, 3.12. Found: C, 64.02; H, 4.24; N, 3.07.

General Photolysis Procedure. A solution of naphtho[1,8-*de*]-1,3-dithiin-1-*N*-tosylsulfilimines **1** (0.1 mmol) in a suitable solvent (5 mL) was placed in a cylindrical quartz tube equipped with a stirrer bar

and a silicon septum. Ar was bubbled through the solution for 30 minutes to remove O_2. Irradiation of samples was carried out using the output of a 400 or 500 W high-pressure mercury lamp under conditions of complete light absorption. The reaction progress was monitored by GC 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.

Product Identification. The products **3a–g** were identified on the basis of a comparison of the respective GC, GC-mass, HPLC, and/or ^{1}H-NMR data with those of the authentic samples and those obtained from literature [6a,7c] values.

3a: Mp 112–113°C (Ref. [6a] 107°C); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.44 (s, 3H), 7.35 (d, J = 8.1 Hz, 2H), 7.52 (t, J = 7.6 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.89 (d, J = 8.1 Hz, 2H), 7.93 (t, J = 7.6 Hz, 2H) 9.03 (s, 1H); MS (*m/z*) 259 (M^+).

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

3d: Melting point was unmeasurable; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.17 (t, J = 4.1 Hz, 3H), 2.44 (s, 3H), 2.55 (oct, J = 4.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 8.63 (t, J = 4.1 Hz, 1H); MS (*m/z*) 211 (M^+).

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

3f: Mp 113–114°C (Ref. [7c] 109–110°C); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.44 (s, 3H), 6.99 (dd, J_1 = 15.7 Hz, J_2 = 9.5 Hz, 1H), 7.31 (d, J = 8.1 Hz, 2H), 7.36–7.46 (m, 3H), 7.52–7.57 (m, 3H), 7.86 (d, J = 8.1 Hz, 2H), 8.78 (d, J = 9.5 Hz, 1H); MS (*m/z*) 285 (M^+).

3g: Mp 102–103°C (Ref. [6a] 100–102°C); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.43 (s, 3H), 6.64 (dd, J_1 = 3.8 Hz, J_2 = 1.7 Hz, 1H), 73.1 (d, J = 3.8 Hz, 1H), 7.35 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 1.7 Hz, 1H), 7.87 (d, J = 8.1 Hz, 2H), 8.81 (s, 1H); MS (*m/z*) 249 (M^+).

*3-Hydro-3-phenyl-naphtho[1,8-ef][1,4]dithia-[2]azepin (***2a***).* Mp 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, 64.12; H, 4.26; N, 3.12, Found: C, 64.10; H, 4.18; N, 3.07. The crystal data for **2a:** orthorhombic, 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, μ(MoKα) = 3.6 cm^{-1}, R = 0.041 (R_w = 0.043), 1911 unique reflections with $Fo^2 > 3.0\sigma(Fo^2)$. Lists of fractional atomic coordinates, thermal parameters, bond lengths, and angles have been deposited at the Cambridge Crystallographic Data Center [12f].

Imino Diels-Alder Reaction. After the photoreaction of **1a, 1d,** and **1e** (0.5 g) had been completed, 2,3-dimethyl-1,3-butadiene (1.0 eq.) was added to the reaction mixture. To this solution maintained at −20°C, BF_3-Et_2O (1.0 eq.) was added dropwise. The reaction was monitored by TLC. When the reaction was complete, the solution was treated with a saturated sodium hydrogen carbonate solution and extracted with CH_2Cl_2. The organic layer was washed with water, dried with magnesium sulfate, and then the solvent was removed under vacuum. The residue was purified by preparative HPLC to give the imino[4 + 2]adducts, naphtho[1,8-*cd*]-1,2-dithiole (**4**), and 2,3-dimethyl-2-butenyl-naphtho[1,8-*cd*]-1,2-dithiole.

1-(p-Toluenesulfonyl)-4,5-dimethyl-2-phenyl-1,2,3,6-tetrahydropyridine. ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.52 (s, 3H), 1.57 (s, 3H), 1.58 (d, J = 17.0 Hz, 1H), 2.22 (d, J = 17.0 Hz, 1H), 2.40 (s, 3H), 3.27 (d, J = 17.6 Hz, 1H), 3.87 (d, J = 17.6 Hz, 1H), 5.23 (d, J = 6.8 Hz, 1H), 7.22 (d, J = 8.6 Hz, 2H), 7.23–7.27 (m, 5H), 7.65 (d, J = 8.6 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 16.0, 18.6, 21.5, 32.5, 44.9, 53.5, 122.2, 123.2, 127.0, 127.3, 127.31, 128.30, 129.3, 137.7, 139.7, 142.9; MS (*m/z*) 341 (M^+).

1-(p-Toluenesulfonyl)-4,5-dimethyl-2-ethyl-1,2,3,6-tetrahydropyridine. ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.87 (t, J = 7.3 Hz, 3H), 1.29–1.43 (m, 2H), 1.48 (s, 3H), 1.55 (s, 3H), 1.61 (d, J = 15.9 Hz, 1H), 2.07 (d, J = 15.9 Hz, 1H), 2.39 (s, 3H), 3.42 (d, J = 17.6 Hz, 1H), 3.84–3.92 (m, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 11.0, 15.8, 18.8, 21.4, 24.3, 33.3, 44.4, 52.8, 120.7, 122.8, 126.9, 129.3, 138.0, 142.7; MS (*m/z*) 293 (M^+).

1-(p-Toluenesulfonyl)-4,5-dimethyl-2-hexyl-1,2,3,6-tetrahydropyridine. ^{1}H NMR (270 MHz,

$CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.23–1.41 (m, 10H), 1.49 (s, 3H), 1.57 (s, 3H), 1.64 (d, J = 14.9 Hz, 1H), 2.09 (d, J = 14.9 Hz, 1H), 2.41 (s, 3H), 3.42 (d, J = 17.3 Hz, 1H), 3.89 (d, J = 17.3 Hz, 1H), 3.98–4.06 (m, 1H), 7.25 (d, J = 8.6 Hz, 2H), 7.67 (d, J = 8.6 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.1, 15.8, 18.8, 21.5, 22.6, 26.4, 29.0, 31.2, 31.7, 33.8, 44.4, 51.2, 120.7, 122.9, 126.9, 129.3, 138.0, 142.8; MS (*m*/*z*) 349 (M^+).

2,3-Dimethyl-2-butenyl-naphtho[1,8-cd]-1,2-dithiole. ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.59 (s, 3H), 1.77 (s, 3H), 1.81 (s, 3H), 3.56 (s, 2H), 7.08–7.15 (m, 2H), 7.12–7.25 (m, 1H), 7.32–7.35 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 18.26, 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^+).

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*)-a-(2,5-dimethyl-3-furylethylidene)(isopropylidene)succinic anhydride, which has a quantum yield of 0.20 for its photocoloration at 313 nm in toluene, was used as an actinometer [16]. 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. The quantum yield was determined from the solutions starting at a concentration of 6 mM, and the 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 achieved by HPLC. Maleic anhydride was used as an external standard for HPLC. Yields were determined from the solutions starting at a concentration 6 mM, and the irradiation times were kept under 1 hour. The measurement of yields was repeated several times by HPLC detection.

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