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Preparation of *N-p*-Tosylaldimines by the Intramolecular Photo-Imino Group Migration of Naphtho[1,8-*de*]dithiin-1-*N*-tosylsulfilimines

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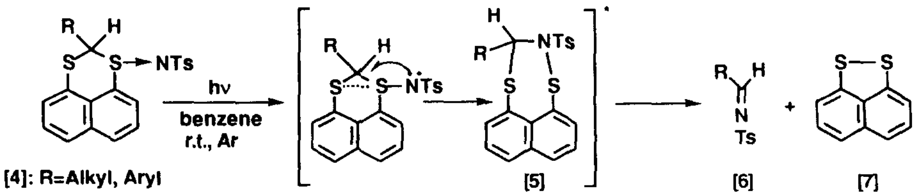
Abstract. Naphtho[1,8-*de*]dithiin-1-*N*-tosylsulfilimines (4) were prepared by the reaction of naphtho[1,8-*de*]dithiins with chloramine-T. Photolysis of 4 undergoes intramolecular imino group rearrangement to give *N*-tosylaldimines quantitatively together with naphthalene-1,8-dithiole.

N-Sulfonylaldimines normally prepared by condensation of *N*-sulfinyl sulfonamide with a variety of aliphatic and aromatic aldehydes in the presence of a Lewis acid[1, 2] have been widely used in organic synthesis undergoing addition reactions.[3-6]

1,8-Dithia or -diselena naphthalene derivatives are presumably candidates for generation of various active species initiated by the through space interaction between the two sulfur or two selenium atoms.[7] In fact, naphtho[1,8-*de*]dithiin monooxides undergo photo-oxygen rearrangement to release carbonyl compounds quantitatively together with naphthalene-1,8-dithiole.[8] *o*-Quinodimethane is readily generated from photolysis of 8,13-dihydrobenzo[*g*]naphtho[1,8-*bc*][1,5]diselenonin.[9] In further extension of these studies, we prepared *N-p*-tosylsulfilimines of naphtho[1,8-*de*]dithiin (4) and found that their photolysis provides a convenient procedure to yield the corresponding *N*-sulfonylaldimines. In the present paper we wish to report the intramolecular photo-migration of the imino group to *N*-tosylaldimines (6) using *N*-tosylsulfilimines (4).

1,8-Naphthalene dithiol (1) was treated with aldehydes in the presence of $SiCl_4$ in CH_2Cl_2 affording the corresponding 2-substituted naphtho[1,8-*de*]1,3-dithiins (2) in high yields.[10] 2-Substituted naphtho[1,8-*de*]1,3-dithiin-1-*N*-tosylsulfilimines (4) were prepared in moderate yields in the reaction of 2 with chloramine-T



Scheme-1

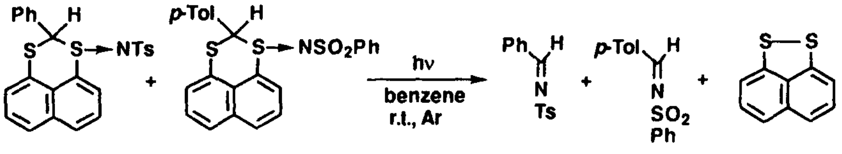
Table 1. Photolysis of 1,3-Dithiin-1-*N*-tosylsulfilimines [4] in Benzene a)

[4]	R	Yield of **6** (%) b)	Yield of **7** (%) b)
a	Ph	>99 (98) c) (m.p. 112-3 °C)[1a]	>99 (100) c)
b	*p*-Tol	>99 (91) (m.p. 118-9 °C)[1a]	>99 (98)
c	Et	>99	>99
d	$CH_3(CH_2)_5$	>99 (93) d)	>99 (100)
e	PhCH=CH	>99 (90) (m.p.113-114 °C)[2d]	>99 (98)
f		>99 (90) (m.p. 102-103 °C)[1a]	>99 (100)

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

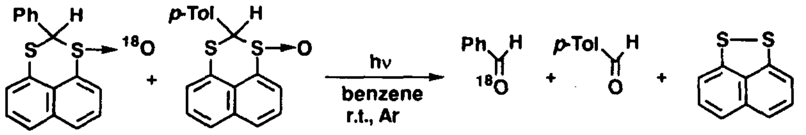
in ethanol-CH_2Cl_2 at room temperature.[10] However, 2,2'-disubstituted naphtho[1,8-*de*]1,3-dithiin-1-*N*-tosylsulfilimines were not obtained on similar treatment of 2,2'-disubstituted naphtho[1,8-*de*]1,3-dithiins (**3**) with chloramine-T. Compounds **4** were thermally stable but decomposed to the corresponding *N*-tosylaldimines quantitatively with a complete recovery of naphthalene-1,8-dithiole (**7**) on exposure to a high pressure mercury lamp (400 W) in benzene for 18 h (Scheme 1). After evaporation of the benzene and usual work-up, the residue was chromatographed to give **6** and **7** quite readily as shown in Table 1. Interestingly, this procedure can be applied to the synthesis of aliphatic imines **6c** and **6d** derived from enolizable aldehydes.

The photolysis of **4** presumably proceeds by the initial photo-excitation of the sulfilimine to form the reactive intermediate **5** by the intramolecular migration of the *N*-tosyl group to the 2-carbon atom *via* the S-S through space interaction. Finally, the intermediate **5** should be converted to the corresponding *N*-tosylimines (**6**) and naphthalene-1,8-dithiole (**7**).



[4a] [8] [6a] [9] [7]

Scheme-2



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

Scheme-3

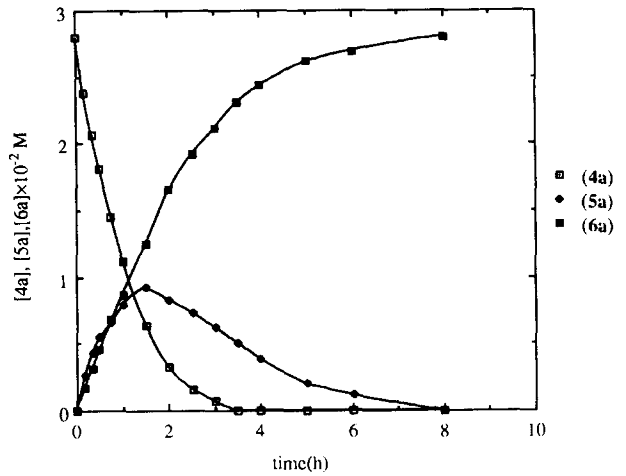


Figure 1. Time course of photolysis of 1-phenyl-naphtho[1,8-*de*] 1,3-dithiane-1-*N*-tosylsulfilimine **4a** (2.8×10^{-2} M **4a** in $CDCl_3$).

In order to determine whether the nitrogen migration is intra- or intermolecular, a cross-over experiment using a 1 : 1 mixture of **4a** and *N*-benzenesulfonyl naphtho[1,8-*de*]dithiin sulfilimine **8** was carried out under a similar photolysis condition as shown in Scheme 2. The reaction proceeded cleanly to give the aldimines **6a** and **9**, and compound **7** quantitatively. After separation of the aldimines and **7**, the ^{1}H- and ^{13}C-NMR spectra of the aldimines were found to be identical with those of a 1 : 1 mixture of **6a** and **9**, and hence no cross-over products were detected at all indicating clearly that their photo-migration proceeds intramolecularly. The photo-oxygen migration of the corresponding sulfoxides under similar conditions has been also confirmed to proceed *via* an intramolecular pathway as shown in Scheme 3.[8] Therefore, it can be concluded that the photochemical migration of the sulfoxides and sulfilimines proceeds *via* an intramolecular process.

In order to understand the mechanism for decomposition of **4**, the ^{1}H-NMR spectra of the reaction of **4a** under irradiation with a high pressure Hg lamp in $CDCl_3$ was monitored at various time intervals (Figure 1). When the ^{1}H NMR signals of the starting material **4a** gradually reduced, new peaks started to appear at 2.17 ppm (s), 6.62 ppm (d, J = 8.4 Hz) and 6.90 ppm (s) corresponding to that of intermediate **5a** together with other peaks from compounds **6a** and **7** by comparing with their spectral data of the authentically prepared compounds. The ^{1}H-NMR signals of the intermediate **5a** increased gradually but disappeared soon and the spectra were converted to that of the products **6a** and **7**. Actually, this intermediate **5a** could be isolated by liquid chromatography of the reaction mixtures by stopping the photolysis of **4a** at the highest conversion of **4a** to **5a**. The intermediate **5a** is a solid material of which ^{1}H-, ^{13}C-NMR, IR, mass spectra and elemental analysis data support the structure (see Scheme 1).[11] Consequently, the results demonstrate clearly that the mechanism for the present reaction proceeds *via* an initial formation of intermediate **5** affording the corresponding *N*-tosylaldimines (**6**) and naphthalene-1, 8-dithiole (**7**)

The advantage of our present procedure is that it promises a method to prepare *N*-tosylaldimines in high yields without use of a strong Lewis acid, though it is ineffective for the preparation of ketimines. Furthermore, the starting material naphthalene-1,8-dithiole (**8**) can be recovered completely and recycled after the reactions. We are currently exploring extension and applications of these reactions.

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10. The compounds **2**, **3**, and **4** were prepared and their structures were determined by ^{1}H- , ^{13}C-NMR, and mass spectrometries. They gave satisfied elemental analysis.
11. Compound **5a**: 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 (68 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$_2$S$_3$: C, 64.11; H, 4.26; N, 3.12; Found: C, 64.10; H, 4.18; N, 3.07.

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