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The Pummerer and the Thio-Claisen–Type Rearrangements of Naphtho[1,8-bc]-1,5-dithiocin Monooxide and N-p-tosylsulfilimine

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ABSTRACT

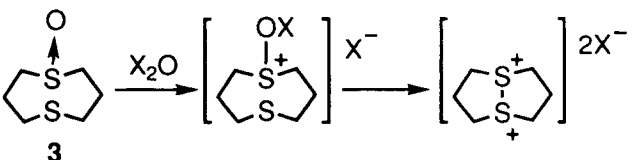
Naphtho[1,8-bc]-1,5-dithiocin N-p-tosylsulfilimine (8) and monosulfoxide (9) were prepared. On treatment with conc. H_2SO_4, both the sulfilimine (8) and sulfoxide (9) gave the dithia dication which was converted to the sulfoxide by hydrolysis. The H–D exchange reaction of (8) took place highly regioselectively to afford the monodeuterated (8–D) at the α-position of the N-tosyl group. The Pummerer rearrangement reaction of monooxide (9) with acetic anhydride gave the α-acetoxy derivative by the dication (10b), while a new thio-Claisen rearrangement of sulfilimine (8) t-BuOK in CH_2Cl_2 gave 2-allyl-naphtho[1,8-bc]-1,5-dithiole. © *1996 John Wiley & Sons, Inc.*

INTRODUCTION

The two sulfur atoms in 1,5-dithiacyclooctane (1) [1,5-DTCO] and its monosubstituted derivatives are well known to be in close proximity (within the van der Waals contact) of the two sulfur atoms (3.70 Å) [1], i.e., 3.175 Å in the monooxide (3) [2]. Recently, the X-ray crystallographic analysis of naphtho[1,8-bc]-1,5-dithiocin (2) and its derivatives has been performed by Glass and his co-workers [3], revealing that the two sulfur atoms in the compound (2) are also located in close proximity (3.000 Å); hence, the two sulfur atoms provide a transannular interaction in the molecules. In fact, the formation of dithia dications or cation radicals by a transannular interaction has been observed in the oxidation of compounds (1) and (2) [4] or in the Pummerer-type reaction of 1,5-DTCO monooxide (3) [5]. 1,5-DTCO dithia dication salt (**4a**) was actually prepared by the method shown in Scheme 1, and its structure was determined by X-ray crystallographic analysis [6].

Although the reactivities of these dithia compounds or their monooxides have been documented recently, few reports describing the reactions of their sulfilimines have been presented. The X-ray crystallographic analysis of N-p-tosylsulfilimine (5) of 1,5-DTCO has revealed that the observed internal S–S distance is 3.143 Å; hence, a strong transannular interaction exists between the two sulfur atoms [7]. When sulfilimine (5) was dissolved in conc. H_2SO_4, the formation of dithia dication (**4d**) was identified directly on the basis of ^{1}H- and ^{13}C-NMR spectroscopy [8]. Interestingly, we found that sulfilimine (5) reacts with t-BuOK in CH_2Cl_2 to produce the ring-opened products (6) and (7) in 40 and 21% yields, respectively [9] (Scheme 2).

Since the reactions of N-p-tosylsulfilimines bearing α and β protons with t-BuOK have been known to give the vinylic sulfides by the Pummerer type of reaction [10], the present reaction of N-p-tosylsulfi-



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4a : X = CF_3SO_3
4b : X = CH_3CO_2
4c : X = CF_3CO_2
4d : X= HSO_4

SCHEME 1

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limine (5) with t-BuOK seems to take place by an unusual process which could be explained in terms of the initial formation of the ylide of dithia dication (4e) prior to the β-proton elimination. Then, N-p-tosylsulfilimine (8) and monooxide (9) of naphtho[1,8-bc]-1,5-dithiocin (2) were prepared and allowed to generate the dication. Both (8) and (9) gave actually the corresponding dithia dication (10a) in conc. H_2SO_4, while the sulfilimine (8) reacted with t-BuOK in CH_2Cl_2 to afford a new thio-Claisen–type rearrangement product, 2-allyl-naphtho-[1,8-cd]-1,2-dithiole (14). This article describes the results on the formation of dithia dication (10) as a common intermediate in these reactions.

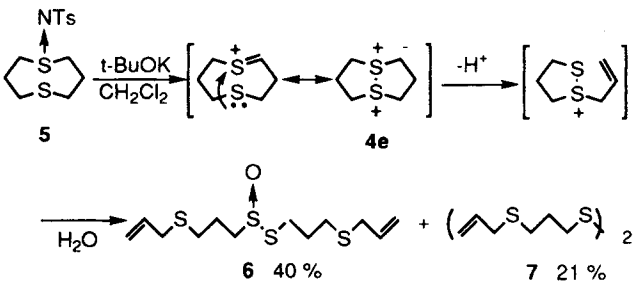
RESULTS AND DISCUSSION

Formation of the Dithia Dication from Naphtho[1,8-bc]-1,5-dithiocin N-p-tosylsulfilimine (8) with Conc. H_2SO_4

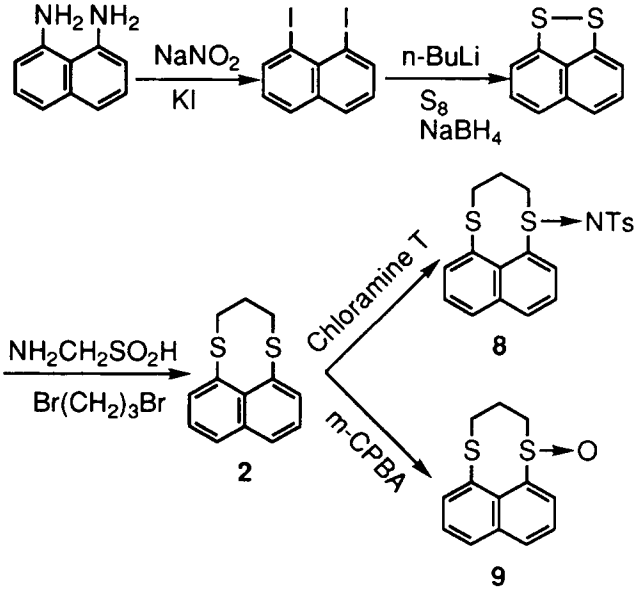
The sulfilimine (8) and sulfoxide (9) were prepared in the following ways (Scheme 3).

The structure of sulfilimine (8) was determined by the ^{1}H- and ^{13}C-NMR spectroscopy in comparison with that of sulfoxide (9) together with IR, mass, and elemental analysis. Naphtho[1,8-bc]-1,5-dithiocin (2) has been known to be composed of a rapid equilibrium mixture of chair and boat forms [3c] since the two protons attached to the central carbon in the trimethylene bridge of (2) have the same chemical shift at δ 1.82 as a multiplet peak. However, the conformation of (8) would be the chair form in solution, similar to the sulfoxide (9) because the difference in chemical shifts between the two protons attached to the central carbon in the trimethylene bridge of (8) is only 0.5 ppm. The crystal structure of (9) has been determined by X-ray crystallographic analysis to be a chair form by Glass et al. [3] Since the two sulfur atoms in the sulfoxide (9) are in close proximity in space (S–S = 3.01 Å), the formation of the dithia dication has been demonstrated as expected by treating (9) with conc. H_2SO_4. Sulfilimine (8) would also generate the dithia dication on dissolution in conc. H_2SO_4. When sulfilimine (8) was dissolved into conc. D_2SO_4 and its ^{1}H- and ^{13}C-NMR spectra were measured in situ, an NMR spectrum almost identical with that of sulfoxide (9) in conc. D_2SO_4 was obtained (Figure 1). In the ^{1}H-NMR spectrum, the chemical shifts of the central two protons appear separately at δ 1.81 and 3.16, indicating that the conformation of dithia dication (10a) would be a boat form identical to that of the dithia dication obtained from the sulfoxide (9) in conc. D_2SO_4 (Figure 2).

Furthermore, the ^{1}H-NMR chemical shifts of the four different protons at the α and γ positions in (10a) are shifted down field as two symmetrical sets



SCHEME 2



SCHEME 3

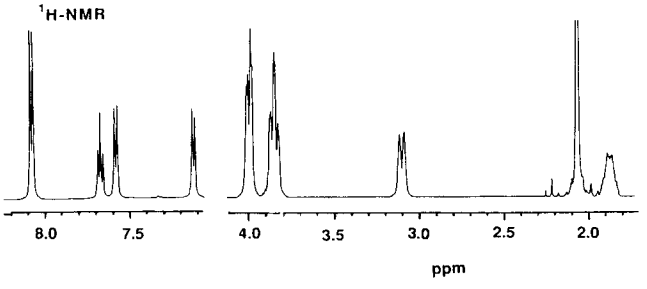


FIGURE 1 ^{1}H-NMR spectrum of **10a**.

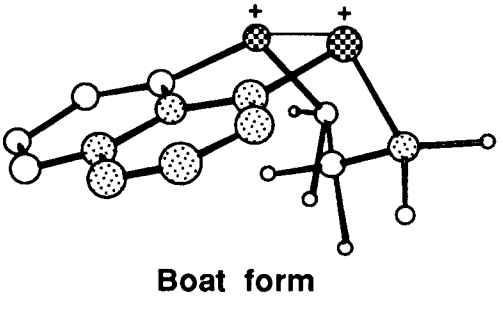
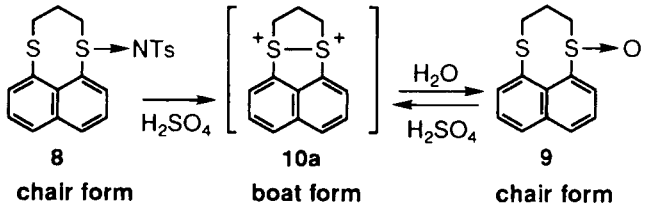


FIGURE 2 Dication (**10a**) in a boat form.

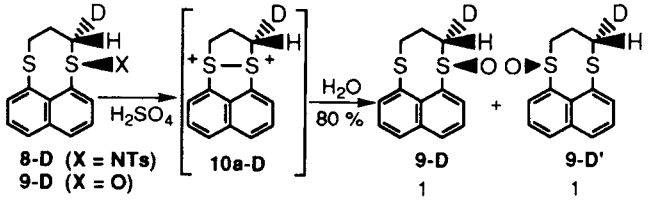
of signals at δ 3.98 and 4.15, respectively. After hydrolysis of the conc. H_2SO_4 solution of sulfilimine (**8**) with ice water, the sulfoxide (**9**) was obtained in an 80% isolated yield (Scheme 4).

In order to confirm the intermediary formation of the dithia dication (**10a**), we attempted preparation of the deuterium-labeled sulfilimine by the H–D exchange reaction of (**8**) using NaOD–D_2O in THF at 80°C for 10 minutes. Only the monodeuteration was observed at the α position to the N-p-tosyl group. In this H–D exchange reaction, only the α proton that appeared at δ 3.58 was found to be exchanged with deuterium. Although there is as yet no pertinent explanation for this specific proton exchange at the α position to the N-p-tosyl group, similar monoregioselective deuteration was also observed in the exchange reaction of sulfoxide (**9**) with CH_3Li–D_2O. According to Glass's work, the deuteration takes place exclusively at a proton α-axial to the sulfinyl oxygen atom [3b]. Since the compound (**8**) is postulated to be structurally similar to that of the sulfoxide (**9**), the deuterated site in the sulfilimine (**8**) would also most probably be at a position α-axial to the N-p-tosyl group. The deuterium content of the sulfilimine (**8**) obtained was determined to be 78% monodeuteration by its ^{1}H-NMR spectrum. The monodeuterated sulfilimine (**8–D**) was used for generation of dithia dication (**10a–D**). The dithia dication (**10a–D**) was then decomposed with ice water to afford the monodeuterated sulfoxides (**9–D**, **9–D′**) in a roughly 1:1 ratio as shown in Scheme 5.

The deuterated position in the resulting sulfoxide was consistent with that obtained by the identical treatment of the corresponding sulfoxide (**9–D**) in conc. H_2SO_4 and H_2O by Glass et al. [3b]. Accordingly, it can be concluded that the H_2O molecule attacks the dithia dication (**10a–D**) from the same side as the sulfilimino group that has been removed. This result also indicates that the H–D exchange in the sulfilimine (**8**) takes place at the α-axial position to the N-p-tosyl group. Thus, the configuration of the sulfoxide obtained in the reaction of (**8–D**) in conc. D_2SO_4 is identical with that obtained from the D-labeled sulfoxide with conc. H_2SO_4 [3]. Therefore, one can conclude that the base-catalyzed H–D exchange reaction of N-p-tosylsulfilimine (**8**) takes place in a similar stereochemical manner to that of the sulfoxide (**9**) reported by Glass et al.; hence, the proton replaced by the deuterium atom was determined to be an α-axial proton to the N-p-tosyl group.



SCHEME 4

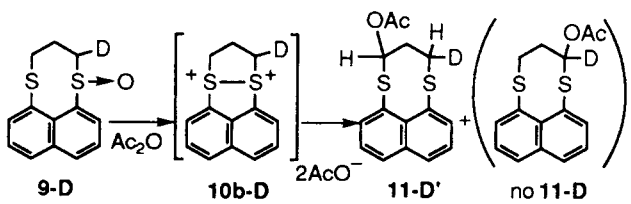


SCHEME 5

Reaction of Monooxide (**9**) *with Acid Anhydrides: The Pummerer Rearrangement and Ring Contraction Reaction*

The 1,5-DTCO monoxide (**3**) undergoes an unusual Pummerer rearrangement involving the dithia dication (**4b**) as an initially formed intermediate. The formation of intermediate (**4b**) was confirmed by using both ^{2}H- and ^{18}O-labeled compounds. The Pummerer rearrangement of naphtho[1,8-bc]-1,5-dithiocin monosulfoxide (**9**) was carried out either by treatment with acetic anhydride in situ or with trifluoroacetic anhydride. The monooxide (**9**) underwent reaction at 90°C for 6 hours to give the desired α-acetoxy derivative (**11**) in 46% yield. In order to investigate the involvement of dication (**10b**) as an intermediate, the monodeuterated sulfoxide (**9–D**) was prepared by the H–D exchange reaction using LDA–D_2O [3]. The deuterium content of the deuterated monooxide (**9–D**) was determined to be 84% at the α position. The monooxide (**9–D**) was treated in the same way as described previously, and the deuterium distribution in the product (**11**) was determined by NMR and mass spectroscopy (Scheme 6).

Interestingly, we found that almost all the deuterium content of (**9–D**) remained in the Pummerer product (**11**), which would indicate that the Pummerer product (**11–D′**) was formed in a highly regioselective manner, the deuterium atoms being in the γ position, a position opposite that originally labeled in the sulfoxide (**9–D**). This D experiment suggests that the present Pummerer reaction may involve initial formation of the dication (**10b**) followed by proton abstraction; however, a large kinetic isotope effect would be expected in the step of proton abstraction as compared with the case of the reaction of 1,5-DTCO monooxide (**3**) with acetic anhydride (the kinetic isotope effect being roughly 1.7).



SCHEME 6

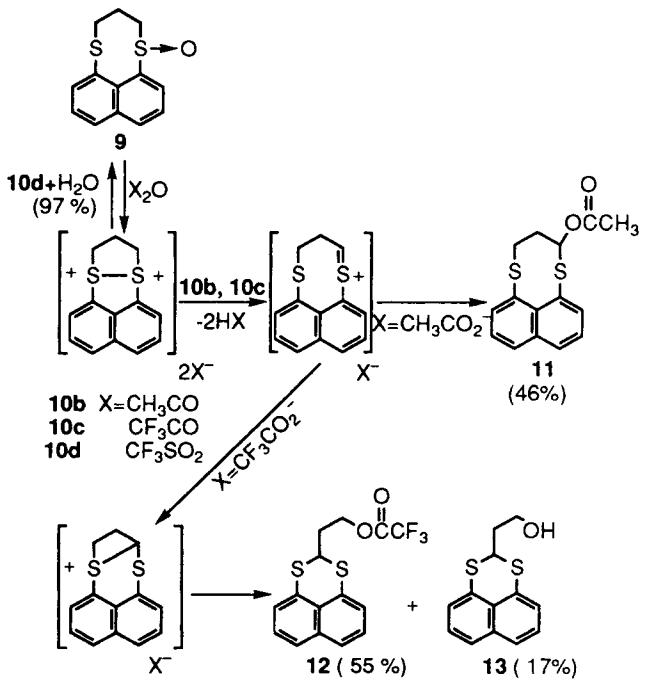
On the other hand, when we used trifluoroacetic anhydride, the Pummerer product was not obtained at all, and instead the ring contraction products (12) and (13) were produced. This result shows that the neighboring sulfur atom attacks intramolecularly the α-carbenium cation initially formed from the dication (10c) to give the bicyclic intermediate much faster than the trifluoroacetate anion does intermolecularly since CF_3CO_2- should be a weaker nucleophile than divalent sulfur. Furthermore, the reaction of sulfoxide (9) with trifluoromethanesulfonic anhydride (Tf_2O) in CH_2Cl_2 gave the dication (10d) as a yellow precipitate, which was assigned only by its ^{1}H-NMR spectrum taken at -25°C in nitromethane-d_3, due to its instability in solution. The dication (10d) was treated with H_2O to give the starting sulfoxide (9) in 95% yield similarly as in the hydrolysis reaction of the dication (10a) generated in conc. H_2SO_4.

The stability of dication (10) depends importantly on the nature of the counteranions generated in the reaction. The reactions are illustrated in Scheme 7.

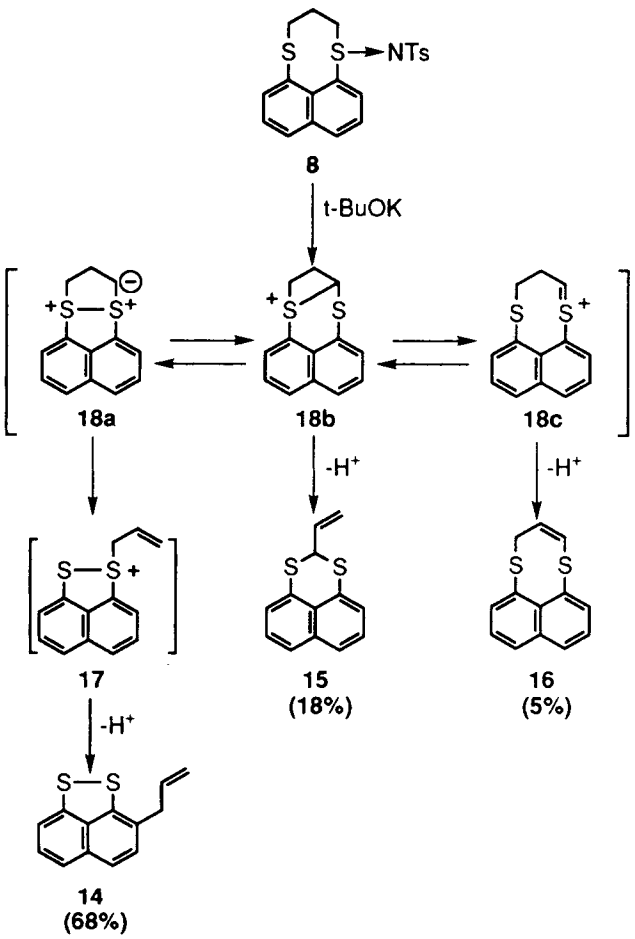
Reaction of Sulfilimine (8) with t-BuOK in CH_2Cl_2: Thio-Claisen Rearrangement and Ring Opening Reaction

The reactions of N-p-tosylsulfilimines having α and β protons with strong bases such as $NaOCH_3$ or NaOBu-t have been reported to give the Pummerer-type products [11], i.e., either hemithio acetals or vinyl sulfides depending upon the base and solvent employed in the reactions. When sulfilimine (8) was treated with t-BuOK in CH_2Cl_2 at 20°C, three products, (14), (15), and (16) were obtained in 68, 18, and 5% yields, respectively (Scheme 8).

When monodeuterated sulfilimine (8–D) prepared by the previously described method was treated similarly as above, the products (14), (15), and (16) contained no deuterium atom at all, indicating that the reaction may proceed by an initially rapid α-proton abstraction by a base. Three cationic species (18a–c) would be generated which finally provide the three products (14), (15), and (16), respectively, by the processes (a), (b), (c). Recently, we found that (14) was generated from allyl thiasulfonium salt (17) in the thermolysis of 1,8-bisallylthionaphthalene monooxide [12]. While no one can give a clear-cut mechanism for the formation of (14) in the reaction of (8) with t-BuOK, the most conceivable process would involve the same thio-Claisen-type rearrangement from an intermediary formation of (17). Both the products (15) and (16) should be provided by the E2-type elimination in the presence of a base [10] (either t-BuOK or TsNH anion), in which sulfide groups serve as good leaving groups.



SCHEME 7



SCHEME 8

In conclusion, N-p-tosylsulfilimine (**8**) gives the corresponding dithia dication (**10**) by the removal of the N-p-tosyl group either on treatment with conc. H_2SO_4 and acid anhydrides, or on treatment of (**8**) with t-BuOK in CH_2Cl_2.

EXPERIMENTAL

All the melting points are uncorrected. ^{1}H- and ^{13}C-NMR spectra were measured on a JEOL JNM-EX270 or a Bruker AM-500 spectrometer. Mass spectra were obtained with a Shimadzu QP-2000 or a JEOL JMX SX102 mass spectrometer. All the reagents used in the experiments were obtained from Wako Pure Chemical Co. or Aldrich Chemical Co. Solvents were purified before use. All the elemental analyses were performed in the Analytical Center of Tsukuba University.

Preparation of Naphtho[1,8-bc]-1,5-dithiocin (**2**)

Naphtho[1,8-cd]-1,2-dithiole [13] (200 mg, 1.06 mmol), aminomethane sulfinic acid (204 mg, 1.88 mmol), and cetylammonium bromide (40 mg, 0.1 mmol) were dissolved into 110 mL aq. 40% NaOH (3.7 M, 20 mL)-THF solution. The solution was refluxed at 100°C and 1,3-dibromopropane (212 mg, 1.06 mmol in 30 mL THF) was added. After having been refluxed for 1 hour, the solution was cooled to room temperature, extracted with CH_2Cl_2, and dried over $MgSO_4$. The solvent was evaporated and the residue was separated and purified by column chromatography (silica gel, CCl_4 as an eluent). Yellow crystals (207 mg) were obtained in 89% yield.

2: mp. 82–84°C (lit. [3a] 82°C); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.80–1.84 (m, 2H), 3.08–3.12 (m, 4H), 7.39 (t, J = 8.1 Hz, 2H), 7.89 (d, J = 8.1 Hz, 2H), 7.99 (d, J = 8.1 Hz, 2H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 24.5, 37.0, 125.6, 131.4, 131.5, 135.9, 138.0, 139.4; Ms m/z 232 (M^+).

Preparation of Naphtho[1,8-bc]-1,5-dithiocin N-p-tosylsulfilimine (**8**)

Naphtho[1,8-bc]-1,5-dithiocin (**2**) (100 mg, 0.43 mmol) and chloramine-T (147 mg, 0.52 mmol) were dissolved in 5 mL of EtOH and stirred for 6 hours under an argon atmosphere. To this solution was added a 1 M NaOH solution, and the aq. solution was extracted with $CHCl_3$. The solution was dried ($MgSO_4$), and the solvent was removed. The residue was purified by column chromatography (silica-gel, EtOAc) to give naphtho[1,8-bc]-1,5-dithiocin-1-N-tosylsulfilimine (**8**) (142 mg) in 82% yield.

8: colorless crystals. mp 150°C (dec.); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.40–1.57 (m, 1H), 1.96–2.35 (m, 4H), 2.68–2.79 (m, 1H), 2.99–3.15 (m, 2H), 3.51–3.62 (m, 1H), 7.18 (d, J = 7.6 Hz, 2H), 7.50 (t, J = 7.6 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.82 (d, J = 7.6 Hz, 2H), 7.88 (d, J = 7.6 Hz, 1H), 7.97 (d, J = 7.6 Hz, 2H), 8.75 (d, J = 7.6 Hz, 1H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 21.3, 24.6, 37.9, 57.9, 126.1, 126.2, 126.8, 126.9, 128.5, 129.0, 130.7, 131.3, 132.9, 134.9, 136.3, 138.8, 141.2, 141.8; IR (KBr) 1141, 1276, (SO_2): Ms m/z 401 (M^+); Anal. calcd. for $C_{20}H_{19}NO_2S_3$: C, 59.82; H, 4.77%. Found: C, 59.43; H, 4.81%.

The Reaction of Naphtho[1,8-bc]-1,5-dithiocin-1-N-p-tosylsulfilimine (**8**) *with Conc.* H_2SO_4

The sulfilimine (**8**) (100 mg, 0.25 mmol) was dissolved in 6 mL of commercial conc. H_2SO_4 (95%). The solution turned to deep red soon to form the dication which was identified by ^{1}H- and ^{13}C-NMR spectroscopy [^{1}H-NMR (500 MHz, D_2SO_4), δ 1.70–1.85 (m, 1H), 3.14–3.17 (m, 1H), 3.96–4.00 (m, 2H), 4.13–4.16 (m, 2H), 7.62 (d, J = 8.0 Hz, 2H), 8.02 (d, J = 8.0 Hz, 4H); ^{13}C-NMR (125 MHz, D_2SO_4) δ 36.6, 63.9, 122.5, 133.9, 134.3, 137.7, 138.0, 138.2]. The red-colored solution was decomposed with ice water, and the aq. solution was extracted with CH_2Cl_2. The solution was dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography to give naphtho[1,8-bc]-1,5-dithiocin-1-oxide (**9**) (49 mg) in 80% yield.

Preparation of Naphtho[1,8-bc]-1,5-dithiocin-1-oxide [3b](**9**)

This sulfoxide was prepared by a known method starting from naphtho[1,8-bc]-1,5-dithiocin (**2**) and m-CPBA in 97% yield. White crystals. mp 134°C (lit. [3b] 134–135°C). ^{1}H- and ^{13}C-NMR spectra were obtained identical with the literature values.

H-D Exchange Reaction of Sulfilimine (**8**)

A typical example of H–D exchange reaction of **8** is as follows: metallic Na (360 mg, 15.6 mmol) was dissolved in D_2O (0.9 mL, 45 mmol). To this solution was added N-p-tosylsulfilimine (**8**) (100 mg, 0.25 mmol/THF 6 mL), and the solution was refluxed for 10 minutes and then stirred for 6 hours at room temperature. The alkaline solution was neutralized with aq. 1 M HCl and was extracted with $CHCl_3$. After purification of the sulfilimine, the deuterated (**8–D**) was recovered in 67% yield (67 mg). The ratio of H–D exchange was determined by ^{1}H-NMR spectroscopy to be 78% monodeuteration only in the proton a-axial to the N-p-tosyl group.

The Reaction of Sulfoxide (**9**) *with Acetic Anhydride*

The sulfoxide (**9**) was dissolved in 5 mL of freshly distilled acetic anhydride and heated at 90°C for 6 hours. After excess acetic anhydride had been removed under reduced pressure, the reaction mixture was purified by column chromatography (CH_2Cl_2)

and liquid chromatography to give the Pummerer product (11) in 46% yield.

11: pale yellow crystals. mp 125–126°C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.78 (ddd, J = 3.0, 13.2, 13.2 Hz, 1H), 2.07 (s, 3H), 2.11 (dd, J = 3.0, 13.2 Hz, 1H), 2.82 (ddd, J = 3.0, 13.2, 13.2 Hz, 1H), 3.26 (ddd, J = 3.0, 3.0, 13.2 Hz, 1H), 6.06 (dd, J = 3.0, 13.2 Hz, 1H), 7.38–8.00 (m, 6H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 21.3, 29.0, 32.7, 79.4, 125.5, 125.8, 126.0, 130.3, 131.7, 132.4, 135.7, 138.7, 139.6, 141.3, 169.5; HRMS (DI) calcd. for $C_{15}H_{14}O_2S_2$: 290.0435. Found: 290.0395.

The Reaction of Sulfoxide (9–D) *with Acetic Anhydride*

The H–D exchange reaction of sulfoxide (9) was carried out as follows. To a solution of sulfoxide (9) (177 mg, 0.71 mmol) in THF (20 mL), LDA solution (1.42 mmol, 0.40 mmol) in THF (15 mL) was added at −78°C under an argon atmosphere. The reaction mixture was stirred for 3 hours, then treated with D_2O (1 mL). The aq. solution was extracted with CH_2Cl_2, and the extract was dried over anhydrous $MgSO_4$. The reaction mixture was separated by column chromatography (silica-gel, EtOAc) to give the sulfoxide (9) (142 mg, 80%). The ratio of H–D exchange was determined by ^{1}H-NMR spectroscopy to be 84% monodeuteration in the α-axial proton to the sulfinyl group.

The sulfoxide (9–D) was treated with acetic anhydride in the same manner as described previously, and the Pummerer product (11) was obtained in 45% yield. The deuterium content of (11) was determined by ^{1}H-NMR and mass spectroscopy to be 80%.

The Reaction of Sulfoxide (9) *with Trifluoroacetic Anhydride*

To a solution of sulfoxide (9) (100 mg, 0.40 mmol) in benzene (10 mL), trifluoroacetic anhydride (57 μL, 0.40 mmol) was added at room temperature under an argon atmosphere. The reaction was completed in 6 hours, and the reaction mixture was washed with H_2O, then dried over $MgSO_4$. The reaction mixture was separated by column chromatography (silica-gel, CCl_4-EtOAc) to give the ring contraction products (12) (76 mg, 55%) and (13) (17 mg, 17%).

12: pale yellow oil; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.37 (ddd, J = 6.4, 6.4, 7.6 Hz, 2H), 4.33 (t, J = 7.6 Hz, 1H), 4.54 (t, J = 6.4 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.42 (d, J = 7.6 Hz, 2H), 7.66 (d, J = 7.6 Hz, 2H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 34.4, 38.3, 65.4, 125.7, 125.8, 127.1, 127.5, 128.0, 134.9, 158.0: HRMS (DI) calcd. for $C_{15}H_{11}O_2F_3S_2$: 344.0153. Found: 344.0135.

13: pale yellow oil; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.23 (ddd, J = 5.9, 5.9, 7.3 Hz, 2H), 2.61 (s, 1H), 3.91 (t, J = 5.9 Hz, 1H), 4.51 (t, J = 7.3 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.43 (d, J = 7.6 Hz, 2H), 7.66 (d, J = 7.6 Hz, 2H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 37.9, 39.4, 60.0, 125.7, 126.7, 127.1, 127.6, 129.0, 135.0; HRMS (DI) calcd. for $C_{15}H_{12}OS_2$: 248.0330. Found: 248.0291.

The Reaction of Sulfoxide (9) *with Trifluoromethanesulfonic Anhydride* (Tf_2O)

To a solution of sulfoxide (9) (100 mg, 0.40 mmol) in CH_2Cl_2 (10 mL), a solution of Tf_2O (68 μL, 0.40 mmol) in CH_2Cl_2 (10 mL) was added at −78°C under an argon atmosphere. The mixture was stirred for 30 minutes at −78°C, then warmed to −20°C and kept standing for 1 hour. A yellow precipitate was identified as the dication (**10d**) only by ^{1}H-NMR measurement, because in nitromethane-d_3, the dication (**10d**) readily decomposed within a minute at −25°C. In the solid state, the dication (**10d**) was stable in the ambient atmosphere.

Yellow solids. ^{1}H-NMR (270 MHz, CD_3NO_2, −25°C) δ 2.30–2.50 (m, 1H), 3.50–3.70 (m, 1H), 4.70–4.90 (m, 4H), 8.11 (t, J = 7.8 Hz, 2H), 8.54 (d, J = 7.8 Hz, 2H), 8.70 (d, J = 7.8 Hz, 2H).

When 3 mL of H_2O was added to (**10d**), the solid immediately changed to the starting sulfoxide (9) soluble in CH_2Cl_2 in 95% yield.

Reaction of Naphtho[1,8-b,c]-1,5-dithiocin-1-N-tosylsulfilimine (8) *with t-BuOK in* CH_2Cl_2

Naphtho[1,8-bc]-1,5-dithiocin-1-N-tosylsulfilimine (8) (100 mg, 0.25 mmol) and t-BuOK (84 mg, 0.75 mmol) were dissolved in 10 mL of CH_2Cl_2 at 20°C under an argon atmosphere. The solution was stirred for 5 hours and then treated with 1 M HCl. The aq. solution was extracted with CH_2Cl_2 and the extract was dried over anhydrous $MgSO_4$. The crude products were separated by column chromatography (silica-gel, CCl_4) to give 2-allyl-naphtho[1,8-cd]1,2-dithiole (14) (37 mg, 65%), 2-vinyl-naphtho[1,8-de]1,3-dithiin (15) (10 mg, 18%) and naphtho[1,8-bc]1,5-dithiocin-6-ene (16) (3 mg, 5%).

14: red oil. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.3–3.35 (m, 2H), 5.13–5.21 (m, 2H), 5.84–5.98 (m, 1H), 7.14 (d, J = 8.0 Hz, 1H), 7.15 (d, J = 8.0 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 39.2, 115.9, 117.4, 121.4, 122.4, 127.0, 128.2, 129.3, 133.8, 134.5, 134.9, 142.3, 143.7; Ms m/z 230 (M^+); Anal. calcd. for $C_{13}H_{10}S_2$: C, 67.78, H, 4.38%. Found: C, 67.46, H, 4.32%.

15: pale yellow oil. ^{1}H-NMR (270 MHz, $CDCl_3$), δ 4.89 (d, J = 7.6 Hz, 1H), 5.29 (d, J = 10.0 Hz, 1H), 5.51 (d, J = 17.0 Hz, 1H), 6.07 (ddd, J = 7.3, 10.0, 17.0 Hz, 1H), 7.36 (t, J = 8.1 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 7.67 (d, J = 8.1 Hz, 2H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 43.7, 119.4, 125.6, 125.7, 126.4, 127.6, 129.5, 133.6, 134.9; Ms m/z 230 (M^+); HRMS(DI) calcd. for $C_{13}H_{10}S_2$: 230.0224, Found: 230.0195.

16: yellow crystals. mp 110–111.5°C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.20–3.70 (brs, 2H), 6.05–6.12 (m, 1H), 6.55–6.60 (m, 1H), 7.29 (t, J = 7.3 Hz, 1H), 7.33 (t, J = 7.3 Hz, 1H), 7.72 (d, J = 7.3 Hz, 1H), 7.79 (d, J = 7.3 Hz, 1H), 7.84 (d, J = 7.3 Hz, 1H), 7.88 (d, J = 7.3 Hz, 1H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 37.7, 125.0, 126.1, 127.0, 129.1, 129.8, 130.4, 131.8, 134.9, 135.3, 135.6, 136.2, 139.1; Ms *m/z* 230 (M^+); Anal. calcd. for $C_{13}H_{10}S_2$: C, 67.78, H, 4.38%. Found: C, 67.57, H, 4.48%.

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N-p-Tosylsulfilimine (**5**) (200 mg, 0.63 mmol) was treated with t-BuOK (353 mg, 3.15 mmol) in CH_2Cl_2 at −5°C under an argon atmosphere. After 6 hours, the reaction mixture was filtered and the solvent was removed from the filtrate under reduced pressure. The products were separated with silica-gel column (CH_2Cl_2:EtOH = 99:1) to afford 39 mg of thiolsulfinate (**6**) and 20 mg of disulfide (**7**) in 40 and 21% yields, respectively.
6: oil. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 2.0 (q, J = 6.0 Hz, 4H, CH_2), 2.57 (t, J = 6.0 Hz, 4H, CH_2), 3.14 (m, 8H, CH_2), 6.20–4.90 (m, 6H, CH_2=CH); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 22.7, 28.9, 29.0, 29.9, 31.6, 34.3, 34.4, 54.5, 117.0, 117.2, 133.8, 134.0; MS (DI) 146; IR (neat) 1080 (S=O); Anal. calcd. for $C_{12}H_{22}OS_4$: C, 46.41; H, 7.14. Found: C, 46.65; H, 7.19.
7: ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.94 (q, J = 6.0 Hz, 4H, CH_2), 2.57 (t, J = 6.0 Hz, 4H, CH_2), 2.78 (t, J = 6.0 Hz, 4H, CH_2), 3.13 (d, J = 6.0 Hz, 4H, CH_2), 6.20–4.90 (m, 6H, CH_2=CH–); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 24.8, 29.1, 34.7, 37.3, 117.0, 134.2; MS (DI) 294 (M^+).

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