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Rearrangements of the Allyl Group in the Thermolysis of 1,8-Bis(allylthio)- and 1,8-Bis(allylseleno)naphthalene Monooxides *via* Through-space Interaction between Two Sulfur and Selenium Atoms

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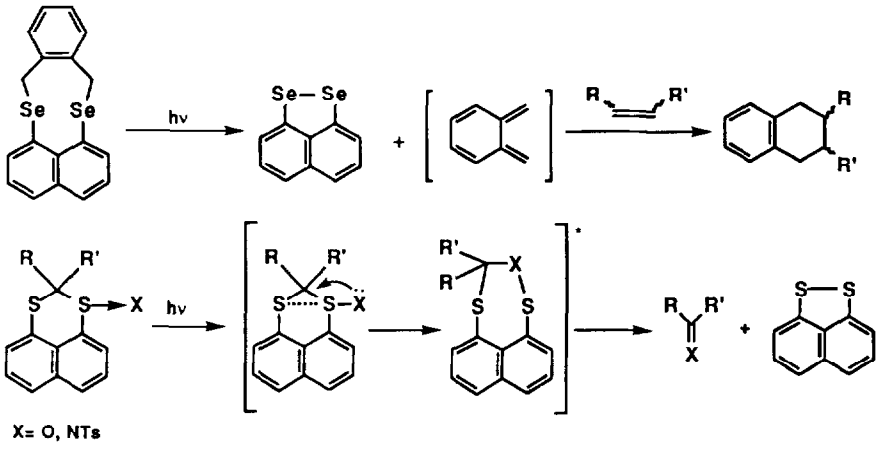
Abstract : 1,8-Bis(allylthio)- and 1,8-bis(allylseleno)naphthalene monooxides underwent facile multi-allylic rearrangements to give 2-allyl-substituted naphtho[1,8-cd]-1,2-dithioles and naphtho[1,8-cd]-1,2-diselenoles under mild conditions *via* the sulfur-sulfur and selenium-selenium through-space interaction. The mechanism for the reaction has been determined by D-tracer and cross-over experiments.

Transannular interaction between two sulfur atoms has attracted considerable attention since the pioneering works of Musker and Asmus who employed the reaction systems of 1,5-dithiacyclooctane and its related cyclic and acyclic sulfur compounds.[1] On oxidation of these compounds, the corresponding cation radicals and dications are provided as new organic species.[2,3] We have also demonstrated the generation of many dithia and diselena dications on treatment of the monooxides of both cyclic and acyclic dithia derivatives with concentrated sulfuric acid. We have succeeded in the isolation of 1,5-dithiacyclooctane dication salt [4-6], selenium analogs [7-9], and tellurium analogs [10] and determined their structures by X-ray crystallographic analysis.

These cyclic alkane systems, however, presented some limitations in the realization of our working hypothesis to create a new reactive functional group of chalcogen elements, since the alkyl compounds are stable and have an unpleasant odor. We therefore searched for potentially more reactive reaction systems which can readily be handled. For this purpose, 1,8-dichalcogen-substituted naphthalenes [11] and 1,9-dichalcogen-substituted dibenzothiophenes or selenophenes [12,13] are the appropriate candidates. One distinct proof for the existence of the proximity effect between the two sulfur and selenium atoms in 1,8-dichalcogen-substituted naphthalenes is their unusually low oxidation potentials as compared with normal sulfides and selenides, i.e., 1,8-bis(methylthio)naphthalene 0.75V, 1-(methylthio)naphthalene 0.97 V; 1,8-bis(methylseleno)naphthalene 0.57V, 1-(methylseleno)naphthalene 0.82 V; (by cyclic voltammetry measurement using $Ag/AgNO_3$ as a working electrode.[14]) Actually, the formation of dithiadication *via* a through-space interaction between the two sulfur atoms in 1,8-bis(alkyl- or arylthio)naphthalenes has been reported by us [15] and by Glass.[16]

One promising feature of the reaction systems using 1,8-bis(alkyl- or arylthio)naphthalenes is that they can provide reactive species by releasing thermodynamically stable naphtho[1,8-cd]-1,2-dithiole and naphtho[1,8-cd]-1,2-diselenole. For this purpose, we have succeeded in the generation of reactive species such as *o*-quinodimethane [17]or releasing ketones [18] or *N*-tosylaldimines [19] on photolysis of naphthalene derivatives as shown in Scheme 1.



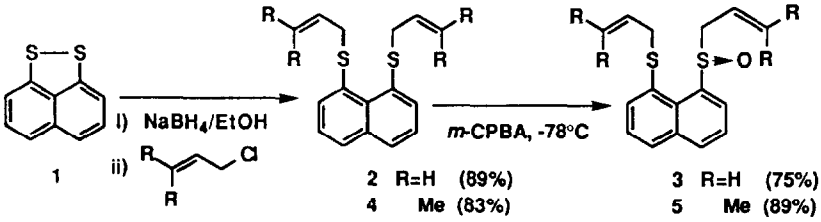
Scheme 1

Alternatively, we assume that the through-space interaction between the two sulfur and selenium atoms using allylthio- or allylseleno-substituents in the peri-positions in the naphthalene would promote the allyl-group migration. Indeed, when 1,8-bis(allylthio)naphthalene was subjected to oxidation with *m*-chloroperbenzoic acid (*m*-CPBA), multi-allylic rearrangements were found to take place, giving 2-allylnaphtho[1,8-cd]-1,2-dithiole quantitatively with simultaneous formation of allyl alcohol. [20] In this paper, we describe the details of this multi-step rearrangement of 1,8-bis(allylthio)naphthalene derivatives together with its selenium analogs.

Results and Discussion

1. Preparation of Allyl Sulfoxides 3, 15 and Deuterium-labelled Allyl Sulfoxide 3-D4

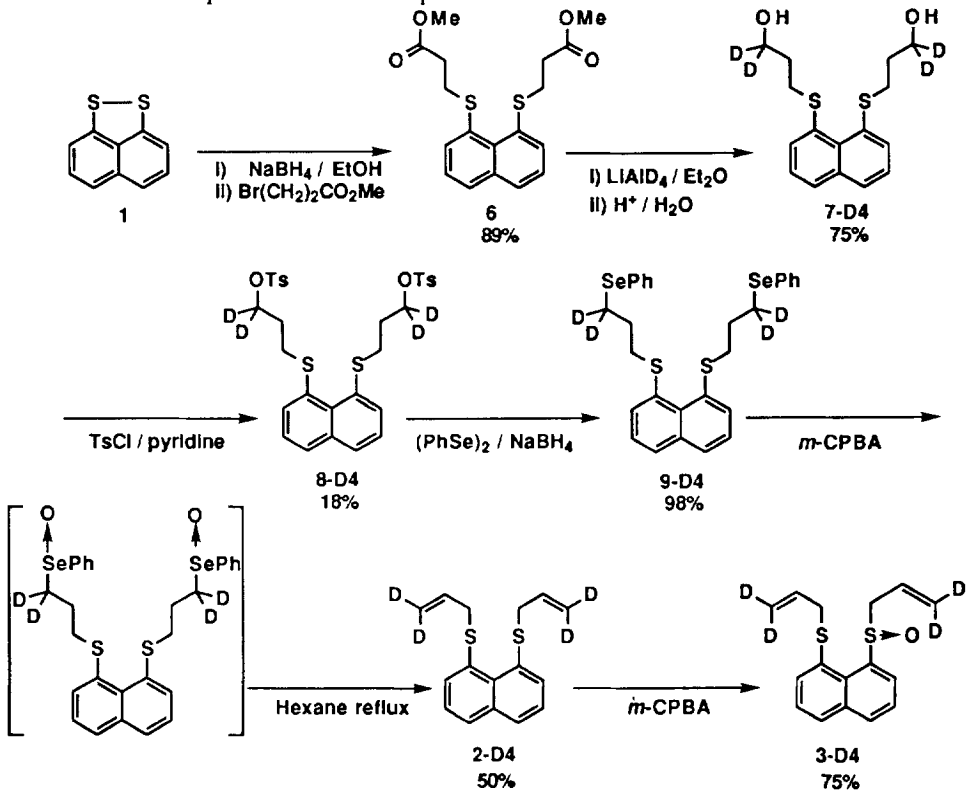
1,8-Bis(allylthio)naphthalene monooxide **3** and 1,8-bis(3,3-dimethylallylthio)naphthalene monooxide **5** were prepared according to the following procedures shown in Scheme 2.



Scheme 2

In order to investigate the mechanism of the rearrangement, regiospecific D-labeling of **2** was carried out. At first, we tried to prepare 1,8-bis(1,1-bisdeuterioallylthio)naphthalene **2-D4'** using **1** and 1,1-bisdeuterioallyl chloride, though we found that the deuterium atoms were distributed between the 1 and 3 positions in the allyl groups of the sulfide **2-D4'** by S_N2' type reaction [21] of the allyl groups on two sulfur atoms.(see Experimental Section) Therefore, we tried alternative procedures for regiospecific D-labeling of 1,8-bis(allylthio)naphthalene **2** shown in Scheme 3. The desired 1,8-bis(3,3-bisdeuterioallylthio)naphthalene **2-D4** was obtained in totally 6% yield starting from **1** (see Experimental Section) and the deuterium content of **2-D4** was determined to be

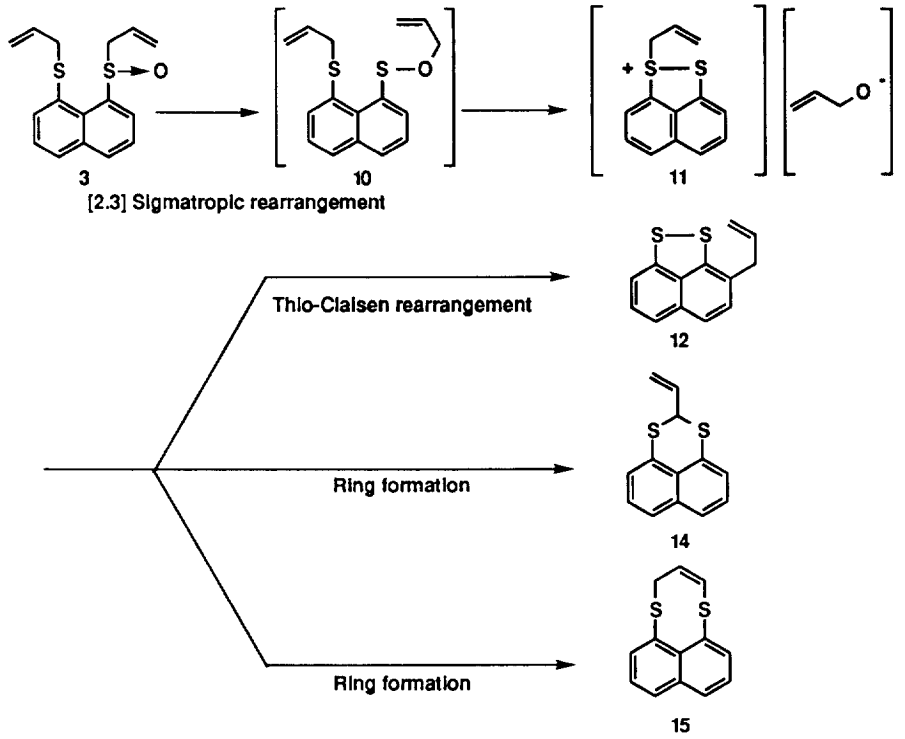
98% at the 3 positions of the allyl groups by ^{1}H-NMR and mass spectroscopy. Then, **3-D4** was also prepared on treatment of **2-D4** with 1 eq. *m*-CPBA at low temperature.



Scheme 3

2. *Reaction of Allyl Sulfoxide 3 and D-Tracer Experiment*

1,8-Bis(allylthio)naphthalene **2** was stable under reflux in toluene, however, the corresponding monosulfoxide **3** was unstable at room temperature and decomposed gradually to give 2-allylnaphtho[1,8-cd]-1,2-dithiole **12** quantitatively together with allyl alcohol **13**. But, on heating **3** at 80° C for 2 h, the decomposition of **3** proceeded rapidly to afford a mixture of three products **12**, **14**, and **15** in 23, 30, and 26% yields, respectively. The thermal reaction of the sulfoxide **3** would proceed initially *via* [2.3] sigmatropic allylic rearrangement of sulfoxide **3** to the sulfenate **10**. Mislow,[22] Evans [23] and Braverman [24] reported that the allyl group in the allyl sulfoxides undergoes facile [2.3]sigmatropic rearrangement to the corresponding sulfenates under mild conditions. They demonstrated that allyl sulfoxides and the corresponding sulfenates are in an equilibrium mixture and that the sulfoxide group is thermodynamically more favorable than the sulfenate group. The sulfenate **10** once formed may undergo facile intramolecular substitution by the remote sulfenyl sulfur atom at the 8-position of the naphthalene ring to give the thiasulfonium salt [25-28] **11** and allyl alcoholate anion. From this salt **11** finally the thio-Claisen type rearrangement [29,30] should proceed to give the compound **12** and allyl alcohol **13**, namely, the whole reaction involves at least two-step sigmatropic rearrangements. At higher temperature, several other pathways may compete with these rearrangements to result in the formation of a mixture of the products as shown in Scheme 4.

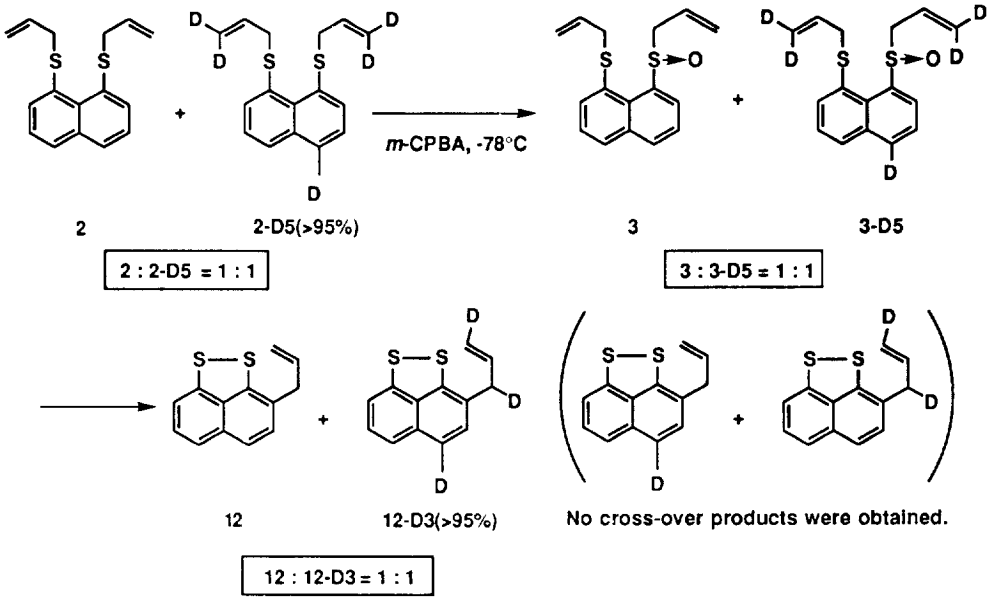


Scheme 4

Although we tried to detect the formation of sulfenate **10** and thiasulfonium salt **11** by ^{1}H-NMR spectroscopy, neither the intermediate **10** nor **11** was found in ^{1}H-NMR and hence it was assumed that **10** and **11** decompose quite rapidly under the reaction conditions. Furthermore, we tried to prepare the thiasulfonium salt **11** by using naphtho[1,8-cd]-1,2-dithiole **1** with allyl chloride in the presence of $AgBF_4$, but the preparation was unsuccessful.

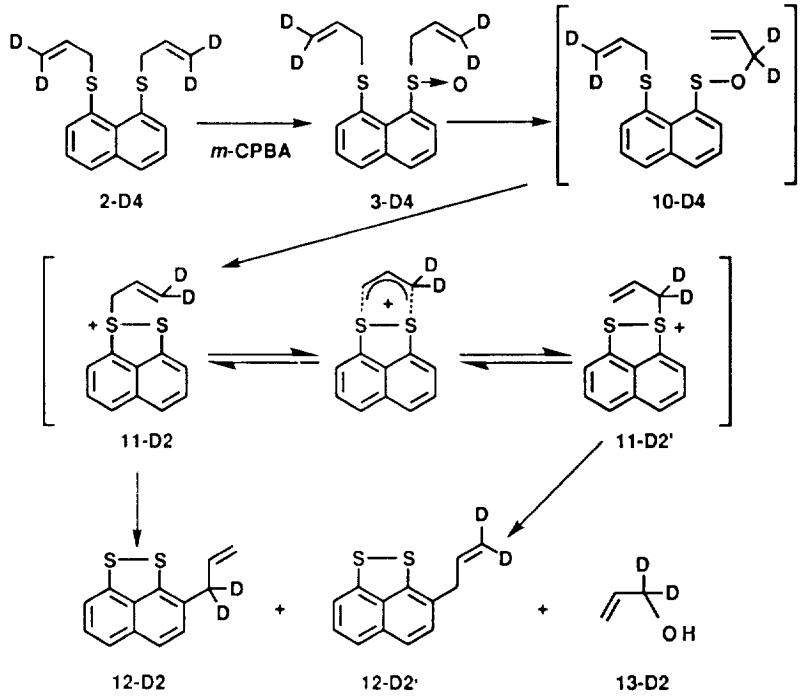
In order to know the detailed mechanism for these rearrangements, we undertook tracer-experiments using regiospecifically labelled sulfoxide **3-D4** and then the cross-over experiment. The deuterated sulfoxide **3-D4** was then subjected to the rearrangement under similar reaction conditions as described above and after separation, the distribution of deuterium atoms in the rearranged product and allyl alcohol was determined by ^{1}H-NMR spectroscopy. The deuterium distribution in the allyl group in product **12-D2** was found to be a nearly 1 : 1 ratio at both 1 and 3 positions in the allyl group, on the other hand, the D-atoms in the allyl group of the allyl alcohol **13-D2** were found only at the 1 position. The results clearly revealed that the initial [2.3]sigmatropic rearrangement of allyl sulfoxide to the sulfenate should proceed in a completely concerted manner and the allyl alcoholate serves as a leaving group by the transannular effect by the sulfenyl group located at the peri-position.

Furthermore, in order to confirm whether this rearrangement proceeds *via* an intramolecular or intermolecular process, a cross-over experiment was carried out by using an equimolar amount of **2** and **2-D5**, which was prepared from 4-deuterio-naphtho[1,8-cd]-1,2-dithiole **1-D1** (see Experimental Section), as shown in Scheme 5.



Scheme 5

Since no cross-over products were found at all, the reaction was found to proceed *via* intramolecular process. Based on a D-labelled experiment and a cross-over experiment, we suggested the reaction mechanism of the rearrangements as shown in Scheme 6.



Scheme 6

Inspection of the results reveal that the [2.3, S-S] type migration of the allyl group on the thiasulfonium salt **11** occur prior to the thio-Claisen rearrangement of **11** to **12**. Caserio and co-workers have reported a similar rearrangement of thiasulfonium salts in a concerted manner.[27]

Since the rearrangement of **3** to **12** was clean and no intermediates nor by-products could be detected by ^{1}H-NMR throughout the whole reaction at room temperature, a kinetic study of the rearrangement was conducted by monitoring of the decreasing amount of the methylene peaks in the sulfoxide **3** by the ^{1}H-NMR in $CDCl_3$ (Fig. 1).

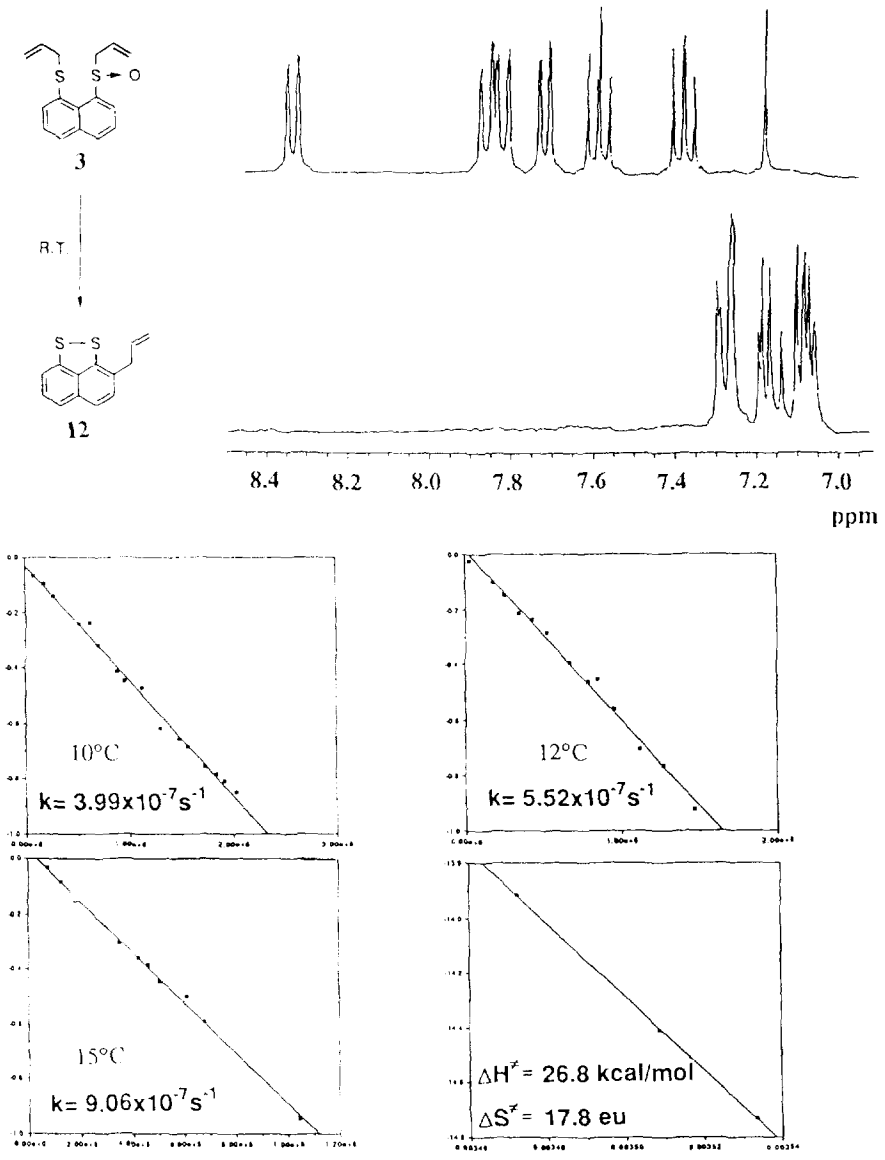
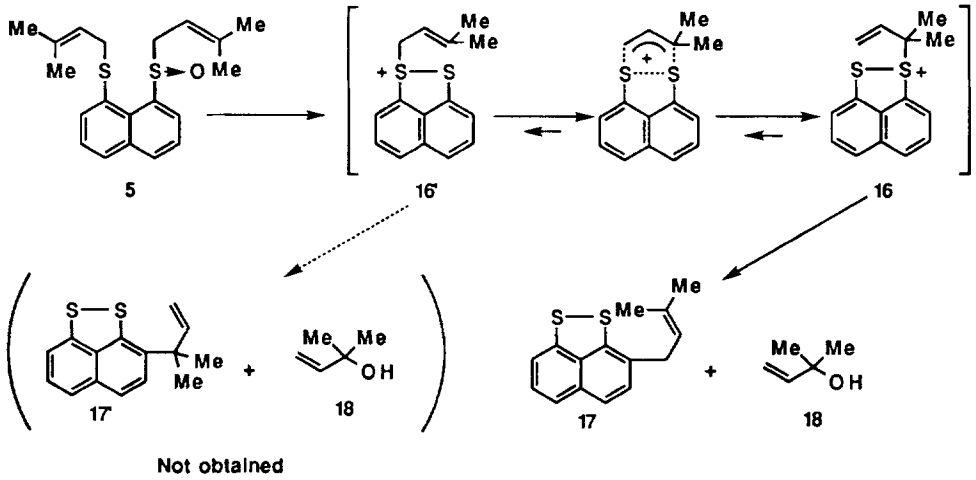


Fig. 1 The kinetic results

The reaction was found to follow the first-order kinetic equation with rate constants k_{obsd} =3.99 x 10^{-7} s^{-1}(10 °C), 5.52 x $10^{-7}s^{-1}$(12 °C), 9.06 x $10^{-7}s^{-1}$(15 °C). The activation parameters were calculated on the basis of the rate constants with Arrhenius and Eyring equations and the results obtained are as follows; $\Delta H^{\neq}$=26.8 kcal/mol, $\Delta S^{\neq}$=17.8 eu. The results suggest that the rate determining step of this reaction would be the [2.3]sigmatropic rearrangement of the sulfoxide to the sulfenate because the kinetic rate constants and the activation parameters obtained are relatively close to those of the rearrangement of allyl p-tolyl sulfoxide to the sulfenate ($\Delta H^{\neq}$=23.1 kcal/mol, $\Delta S^{\neq}$=-4.9 eu, and $\Delta H^{\neq}$=27.6 kcal/mol, $\Delta S^{\neq}$=-0.7 eu; in benzene and in 2,2,3,3,-tetrafluoro-1-propanol, respectively) reported by Mislow et al.[31]

3. Reaction of Allyl Sulfoxide 5

Furthermore, in order to investigate the regioselectivity of the rearrangement, 1,8-bis(3,3-dimethylallylthio)naphthalene monooxide **5** was subjected to the rearrangement under the same conditions described above. **5** was readily decomposed to give a rearranged product, 2-allylsubstituted naphtho[1,8-cd]-1,2-dithiole **17**, quantitatively together with 1,1-dimethylallyl alcohol **18**. Apparently, **5** initially underwent the [2.3]sigmatropic rearrangement of the sulfoxide to give a sulfenate, and in the sulfenate the second sulfur atom may act as a thiophile to afford **18** as in the case of the monosulfoxide **3**. Interestingly, in the reaction of **5** we found the compound **17** having 3,3-dimethylallyl group at the 2 position of naphtho[1,8-cd]-1,2-dithiole was obtained as a sole rearranged product and no regioisomer **17'**, which has 1,1-dimethylallyl group at the 2 position, was obtained . Since **17** and **17'** might be formed *via* a thiasulfonium salt **16** and **16'**, respectively, we can explain this complete regioselectivity about the rearrangement as follows: [1] the equilibrium between **16** and **16'** should be shifted to the right-hand side as shown in Scheme 7 because of a large electronic stabilization to **16** by the two methyl groups. [32]; [2] the rate of the rearrangement of **16** to **17** should be faster than that of **16'** to **17'** because of a steric hindrance in the thio-Claisen rearrangement which prevents the rearrangement from the intermediate **16'** (Scheme 8).

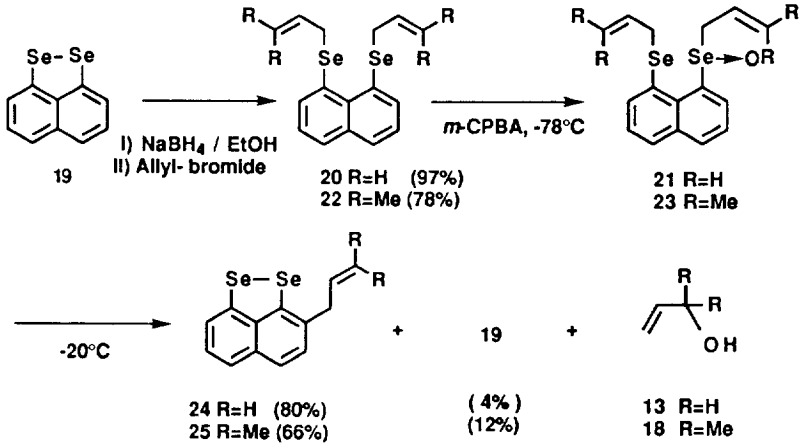


Scheme 7

4. Preparation and Reaction of Allyl Selenoxides 21, 23

1,8-Bis(allylseleno)naphthalene **20**, and 1,8-bis(3,3-dimethylallylseleno)naphthalene **22** were prepared from naphtho[1,8-cd]-1,2-diselenole **19** with the corresponding allyl halides in 97 and 78% yields, respectively. The corresponding selenoxides **21** and **23**, that would be generated on treatment of **20** and **22** with 1 eq. *m*-CPBA at -78 °C in CH_2Cl_2 (1.4×10^{-3} M), were stable at this temperature. Then we tried to compare the mode and rate of the rearrangements between the allyl sulfoxides **3** and **5** and allyl selenoxides **21** and **23**. [2.3]Sigmatropic rearrangement of allyl selenoxides to the selenenates is well known and the mechanism for the reaction has been examined kinetically by Reich. [33] A marked contrast in behavior between the sulfoxide and selenoxide is that the sulfoxide is more stable than the sulfenate, though in the case of selenoxide the rearranged selenenate is more stable than the selenoxide. On the other hand, very few studies on the seleno-Claisen rearrangement have been reported. [34] The compounds **21** and **23** are expected to react easier than the sulfur analogs **3** and **5** because of two main reasons as follows: **[1]** The bond energy of C-Se bond (58 kcal/mol) is much smaller than that of C-S bond (65 kcal/mol). **[2]** The activation energy of the [2.3]sigmatropic rearrangement of allyl 2-nitrophenyl selenoxide to the selenenate (13.5 kcal/mol) is much smaller than that of allyl 2-nitrophenyl sulfoxide to the sulfenate (19.8 kcal/mol). [33]

Actually, monoselenoxides **21** and **23** rearranged quite rapidly ($t_{1/2}$=1 min, 0°C), compared with the corresponding monosulfoxides **3** and **5** ($t_{1/2}$=7 days, 20°C), to give the rearranged products **24** and **25** in good yields together with diselenide **19** and allyl alcohol **13** and **18**, respectively. (Scheme 9)



Scheme 8

The regioselectivity of the rearrangement was found to be the same as the sulfur analogs. But in the case of the monoselenoxide **23**, when the oxidation was carried out in higher concentration (5.2×10^{-2} M), poly allylsubstituted naphtho[1,8-cd]-1,2-diselenoles were formed besides the desired products **25**. The results show that intermolecular allyl group migration would occur in part during the whole reaction, although the reaction may proceed essentially *via* the consecutive allylic [Se-O, Se-Se, Se-C] rearrangements as described on the sulfur analogs **3** and **5**. We expected that the allyl group of the allyl-selenaselenonium salts can not be strongly held on the diselenide groups, in marked contrast to the allyl-thiasulfonium salts **11** and **16**.

To confirm the reaction mechanism, we tried to observe the formation of intermediates in the rearrangements on oxidation of **20** at low temperature by following the rearrangements with ^{77}Se-NMR technique at various temperatures.(Fig. 2)

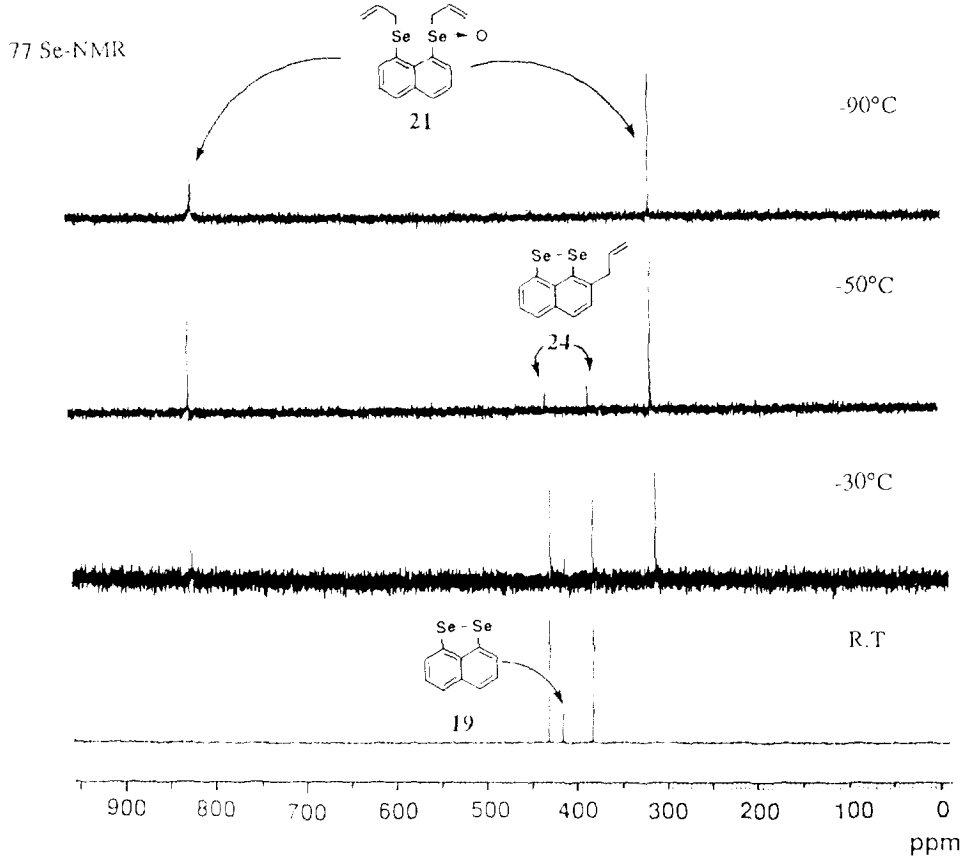


Fig. 2 The ^{77}Se-NMR spectra of **21** on elevating temperature

A ^{77}Se-NMR signal of 1,8-bis(allylseleno)naphthalene **20** was observed at δ 338 ppm as a singlet, but on addition of 1 eq. of *m*-CPBA to the solution at -90° C, the singlet of **20** disappeared and new signals assigned to monoselenoxide **21** were found at δ 312 and 818 ppm. The monoselenoxide **21** was also assigned by the ^{1}H-NMR spectrum. Above -50° C, the ^{77}Se-NMR signals of **21** gradually changed to three other signals at δ 381, 415 and 430 ppm, which were assigned to the rearranged product **24** and naphtho[1,8-cd]-1,2-diselenole **19**. Since no signals corresponding to the selenenate or allyl-selenaselenonium salts were observed during the whole reaction, the rate determining step of the reactions was expected to be selenoxide-selenenate rearrangement as the sulfur analog.

In conclusion, the three consecutive allylic sigmatropic [S-O, S-S, S-C] and [Se-O, Se-Se, Se-C] rearrangements of 1,8-bis(allylthio)- and 1,8-bis(allylseleno)-naphthalene monooxides were found to give 2-allyl-substituted naphtho[1,8-cd]-1,2-dithioles and naphtho[1,8-cd]-1,2-diselenoles in good yields under mild conditions. The rate determining step was found to be the 2,3-sigmatropy of the allyl sulfoxide and selenoxide.

Acknowledgement : This work was supported by TARA project from Tsukuba University.

EXPERIMENTAL

All the melting points were uncorrected. ^{1}H and ^{13}C-NMR spectra were measured on a JEOL JNM-EX270 or a Bruker 400 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 at Tsukuba University.

Synthesis of 1,8-bis(allylthio)naphthalene 2

To a solution of $NaBH_4$ (166 mg, 4.4 mmol) in 40 ml of EtOH, a solution of naphtho[1,8-cd]-1,2-dithiole [35] **1** (380 mg, 2.0 mmol) in 40 ml of THF was added at room temperature. After the reaction mixture was stirred for 10 min, allyl bromide (0.9 ml, 10.0 mmol) was added slowly. The reaction mixture was stirred for 1 h and extracted with CH_2Cl_2 (20 ml x 3), and dried over $MgSO_4$. The solvent was evaporated and the residue was separated and purified by column chromatography (silica gel, hexane-CCl_4 as an eluent). Yellow oil (528 mg) was obtained in 97% yield.

2: pale yellow oil. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.57~3.60 (m, 4H), 5.01~5.12 (m, 4H), 5.82~5.97 (m, 2H), 7.33 (t, J=7.8 Hz, 2H), 7.56 (d, J=7.8 Hz, 2H), 7.65 (d, J=7.8 Hz, 2H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 40.9, 118.0, 125.2, 128.2, 131.1, 133.2, 133.6, 134.1, 135.8; HRMS (DI) for $C_{16}H_{16}S_2$: Calcd 272.0693, Found 272.0678.

Synthesis of 1,8-bis(3,3-dimethylallylthio)naphthalene 4

To a solution of $NaBH_4$ (42 mg, 1.1 mmol) in 10 ml of EtOH, a solution of **1** (95 mg, 0.5 mmol) in 10 ml of THF was added at room temperature. After the reaction mixture was stirred for 10 min, 3,3-dimethylallyl chloride (0.28 ml, 2.5 mmol) was added slowly. The reaction mixture was stirred for 1 h and extracted with CH_2Cl_2 (20 ml x 3), and dried over $MgSO_4$. The solvent was evaporated and the residue was separated and purified by column chromatography (silica gel, hexane-CCl_4 as an eluent). Yellow oil (136 mg) was obtained in 83% yield.

4: pale yellow oil. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.43 (s, 6H), 1.59 (s, 6H), 3.49 (d, J=7.8 Hz, 4H), 5.25 (t, J=7.8 Hz, 2H), 7.25 (t, J=7.8 Hz, 2H), 7.47 (d, J=7.8 Hz, 2H), 7.57 (d, J=7.8 Hz, 2H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 17.7, 25.7, 36.2, 118.9, 125.2, 127.9, 130,9, 133.7, 135,3, 135.8, 136.7; HRMS (DI) for $C_{20}H_{24}S_2$: Calcd 258.0537, Found 258.0479.

Synthesis of 1-(allylsulfinyl)-8-(allylthio)naphthalene 3

To a solution of **2** (204 mg, 0.75 mmol) in 30 ml of CH_2Cl_2, a solution of 100% *m*-CPBA (129 mg, 0.75 mmol) in 20 ml of CH_2Cl_2 was added at -78 °C. After the reaction mixture was stirred for 2 h, NH_3 gas was bubbled into the solution and the precipitates (meta chlorobenzoic acid, *m*-CBA salts) formed were filtered off at -20 °C. The reaction mixture was evaporated and the residue was separated and purified by column chromatography (silica gel, CCl_4-AcOEt as an eluent) at -20 °C. Yellow oil (161 mg) was obtained in 75% yield.

3: pale yellow oil. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.19~3.48 (m, 3H), 3.98~4.05 (m, 1H), 4.63~5.28 (m, 4H), 5.67~5.82 (m, 2H), 7.42 (t, J=7.6 Hz, 1H), 7.64 (t, J=7.6 Hz, 1H), 7.77 (d, J=7.6 Hz, 1H), 7.89 (d, J=7.6 Hz, 1H), 7.94 (d, J=7.6 Hz, 1H), 8.44 (d, J=7.6 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, 0°C) δ 41.8,

61.9, 118.5, 123.3, 125.5, 125.6, 125.8, 126.7, 128.2, 130.9, 131.5, 132.2, 132.4, 135.6, 138.9, 141.3; HRMS (DI) for $C_{16}H_{16}OS_2$ (M^+): Calcd 288.0643, Found 288.0628; IR (nujol) 1038 cm^{-1}(SO).

Synthesis of 1-(3,3-dimethylallylsulfinyl)-8-(3,3-dimethylallylthio)naphthalene 5

To a solution of **4** (58 mg, 0.18 mmol) in 15 ml of CH_2Cl_2, a solution of 100% *m*-CPBA (31 mg, 0.18 mmol) in 15 ml of CH_2Cl_2 was added at -78 °C. After the reaction mixture was stirred for 2 hr, NH_3 gas was bubbled into the solution and the precipitates (*m*-CBA salts) formed were filtered off at -20 °C. The reaction mixture was evaporated and the residue was separated and purified by column chromatography (silica gel, CCl_4-AcOEt as an eluent) at -20 °C. Yellow oil (54 mg) was obtained in 89% yield.

5: pale yellow oil. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.83 (s, 3H), 1.12 (s, 3H), 1.41 (s, 3H), 1.55 (s, 3H), 3.20 (d, J=8.0 Hz, 2H), 3.27 (dd, J=8.0, 13.0 Hz, 1H), 3.88 (dd, J=8.0, 13.0 Hz, 1H), 5.06 (t, J=8.0 Hz, 1H), 5.18 (t, J=8.0 Hz, 1H), 7.31 (t, J=7.6 Hz, 1H), 7.54 (t, J=7.6 Hz, 1H), 7.64 (d, J=7.6 Hz, 1H), 7.83 (t, J=7.6 Hz, 2H), 8.33 (d, J=7.6 Hz, 1H); ^{13}C-NMR (68 MHz, $CDCl_3$, -40°C) δ 16.9, 18.0, 25.6, 26.1, 36.6, 57.0, 112.4, 117.7, 125.3, 125.4, 125.6, 128.3, 130.8, 131.8, 132.1, 135.3, 137.5, 139.4, 141.5, 141.7; MS m/z 344 (M^+): HRMS (DI) for $C_{20}H_{24}OS_2$ (M^+): Calcd 344.1269, Found 344.1248; IR (nujol) 1031 cm^{-1}(SO).

Thermolysis of sulfoxide 3 at room temperature

Sulfoxide **3** (288 mg, 1.0 mmol) was dissolved in 20 ml of CH_2Cl_2 and stood for 2 weeks at room temperature. The reaction mixtutre was evaporated, and the residue was separated and purified by column chromatography (silica gel, CCl_4 as an eluent). Red oil (230 mg, 1.0 mmol) and allyl alcohol were obtained in quantitative yields (isolated and NMR yields).

12: red oil. ^{1}H-NMR (270 MHz ,$CDCl_3$) δ 3.32~3.35 (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 (t, 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.

13: allyl alcohol. colorless liquid. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.96~4.00 (m, 2H), 4.23~4.48 (bt, 1H), 4.97~5.19 (m, 2H), 5.79~5.91 (m, 1H).

Thermolysis of sulfoxide 3 at 80 °C

Sulfoxide **3** (98 mg, 0.34 mmol) was dissolved in 20 ml of CCl_4 and refluxed for 8 h at 80°C. The reaction mixtutre was evaporated, and the residue was separated and purified by column chromatography (silica gel, CCl_4 as an eluent). **12** (14 mg), yellow oil **14** (18 mg) and yellow crystals **15** (20 mg) were obtained in 18, 23, 26 % yields, respectively.

14: 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=7.6, 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) for $C_{13}H_{10}S_2$: Calcd 230.0224, Found 230.0195.

15: yellow crystals. mp. 110-111°C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.20~3.70 (bs, 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.

Thermolysis of sulfoxide 5 at room temperature

Sufoxide **5** (344 mg, 1.0 mmol) was dissolved in 20 ml of CH_2Cl_2 and standed for 2 weeks at room temperature. The reaction mixtutre was evaporated, and the residue was separated and purified by column chromatography (silica gel, CCl_4 as an eluent). Red oil (258 mg, 1.0 mmol) and 1,1-dimethylallyl alcohol were obtained in quantitatively yield (isolated and NMR yields).

17: red oil. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.77 (s, 6H), 3.29 (d, J=7.3 Hz, 2H), 5.27 (t, J=7.3 Hz, 1H), 7.14 (t, J=7.8 Hz, 2H), 7.21 (t, J=7.8 Hz, 1H), 7.33 (d, J=7.8 Hz, 2H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 18.1, 25.8, 33.7, 115.8, 115.9, 120.0, 121.3, 122.2, 126.8, 129.0, 130.1, 134.3, 135.3, 141.7, 143.5; MS m/z 258 (M^+); HRMS (DI) for $C_{15}H_{14}S_2$: Calcd 258.0537, Found 258.0479.

18: 3,3 dimethy allyl alcohol. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.32 (s, 6H), 4.80 (bs, 1H), 5.00 (d, J=10.8 Hz, 1H), 5.21 (d, J=17.0 Hz, 1H), 6.00 (dd, J=10.8, 17.0Hz, 1H).

Synthesis of 1,8-bis(1,1-deuterioallylthio)naphthalene 2-D4'

Tetradeuterated **2-D4'** was synthesized by the same methods as **2** in 80% yield, using **1** and 1,1-bisdeuterioallyl chloride which was prepared by known method.[35] The labelled position of **2-D4'** was determined by ^{1}H-NMR to be 25% in 3 position and 75% in 1 position.

Synthesis of 1,8-bis[2-(1-methoxycarbonyl)ethylthio]naphthalene 6

To a solution of $NaBH_4$ (166 mg, 4.4 mmol) in 20 ml of anhydrous EtOH, a solution of **1** (380 mg, 2.0 mmol) in 20 ml of anhydrous THF was added at room temperature. After the reaction mixture was stirred for 10 min, methyl 3-bromopropionate (1.48 ml, 10.0 mmol) was added slowly. The reaction mixture was allowed to be stirred for 1 h and extracted with CH_2Cl_2 (20 ml x 3), and dried over $MgSO_4$. The solvent was evaporated and the residue was separated and purified by column chromatography (silica gel, AcOEt-CH_2Cl_2 as an eluent). Pale yellow oil (645 mg) was obtained in 89% yield.

6: pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.61 (t, J=7.6 Hz, 4H), 3.18 (t, J=7.6 Hz, 4H), 3.65 (s, 6H), 7.37 (t, J=7.2 Hz, 2H), 7.61 (d, J=7.2 Hz, 2H), 7.70 (d, J=7.2 Hz, 2H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 32.3, 33.2, 51.7, 125.4, 128.7, 131.5, 133.3, 133.5, 135.9, 172.2; HRMS (DI) for $C_{18}H_{20}O_4S_2$: Calcd 364.0803, Found 364.0843.

Synthesis of 1,8-bis[3-(1-hydroxy)propylthio]naphthalene 7

To a solution of $LiAlH_4$ (43 mg, 1.07 mmol) [* $LiAlD_4$ was used for **7-D4**] in 10 ml of anhydrous Et_2O, a solution of **6** (328 mg, 0.9 mmol) in 10 ml of anhydrous Et_2O was added dropwise at 0 °C. After the reaction mixture was refluxed for 30 min, 1.5 ml of H_2O was added slowly at 0 °C. The reaction mixture was dried over Na_2SO_4. The solvent was evaporated and the residue was separated and purified by column chromatography (silica gel, CH_2Cl_2-MeOH as an eluent). White crystals (208 mg) were obtained in 75% yield.

7: white crystals. mp. 70-70.5°C; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.86 (quint, J=6.2 Hz, 4H), 2.57 (bs, 2H), 3.01 (t, J=6.2 Hz, 4H), *3.71 (t, J=6.2 Hz, 4H), 7.33 (t, J=7.8 Hz, 2H), 7.57 (d, J=7.8 Hz, 2H), 7.64 (d, J=7.8 Hz, 2H) * The signal disappeared in deuterated compound **7-D4**; ^{13}C-NMR (68 MHz, $CDCl_3$) δ 30.9, 34.2, 61.3, 125.4, 128.1, 130.5, 133.3, 134.5. 135.8; MS m/z 308 (M^+); Anal. Calcd for $C_{16}H_{20}O_2S_2$: C, 62.30, H, 6.54. Found: C, 62.10, H, 6.44.

Synthesis of 1,8-bis[3-(1-p-tolylsulfonyl)propylthio]naphthalene 8

To a solution of **7** (50 mg, 0.16 mmol) [* **7-D4** was used for **8-D4**] in 5 ml of anhydrous pyridine, a solution of tosyl chloride (68 mg, 0.36 mmol) in 10 ml of anhydrous pyridine was added dropwise at -5 °C. After the reaction mixture was stirred for 2 h, 1.0 ml of H_2O was added slowly at 0 °C. The solvent was evaporated and the reaction mixture was extracted with CH_2Cl_2 (20 ml x 3) and dried over $MgSO_4$. The solvent was evaporated and the residue was separated and purified by HPLC. Pale yellow oil (11 mg) was obtained in 18% yield.

8: pale yellow oil. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.91 (quint, J=7.0 Hz, 4H), 2.41 (s, 6H), 2.91 (t, J=7.0 Hz, 4H), *4.14 (t, J=7.0 Hz, 4H), 7.29 (d, J=8.1 Hz, 4H), 7.35 (t, J=7.3 Hz, 2H), 7.50 (d, J=7.3 Hz, 2H), 7.69 (d, J=7.3 Hz, 2H), 7.75 (d, J=8.1 Hz, 4H) * The signal disappeared in deuterated compound **8-D4**; ^{13}C-NMR (68 MHz, $CDCl_3$) δ 21.6, 27.8, 33.4, 69.0, 125.5, 127.9, 128.5, 129.9, 131.0, 132.9, 133.4, 133.7, 136.0, 144.9; MS m/z 616 (M^+); Anal. Calcd for $C_{30}H_{32}O_6S_4$: C, 57.93, H, 5.18. Found: C, 58.42, H, 5.23.

Synthesis of 1,8-bis[3-(1-phenylseleno)propylthio]naphthalene 9

To a solution of $NaBH_4$ (49 mg, 1.30 mmol) in 10 ml of anhydrous EtOH, a solution of diphenyl diselenide (200 mg, 0.64 mmol) in 10 ml of anhydrous EtOH, was added at room temperature. After the reaction mixture was stirred for 30 min, a solution of **8** (200 mg, 0.32 mmol) [* **8-D4** was used for **9-D4**] in 10 ml of anhydrous benzene was added slowly to the mixture. The reaction mixture was stirred for 12 h and extracted with CH_2Cl_2 (20 ml x 3), and dried over $MgSO_4$. The solvent was evaporated and the residue was separated and purified by HPLC. Pale yellow oil (188 mg) was obtained in 98% yield.

9: pale yellow oil. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.97 (quint, J=7.0 Hz, 4H), *3.00 (q, J=7.0 Hz, 8H), 7.17~7.22 (m, 6H), 7.30 (t, J=7.6 Hz, 2H), 7.40~7.44 (m, 4H), 7.51 (d, J=7.6 Hz, 2H), 7.63 (d, J=7.6 Hz, 2H) *Integral value of the signal decreased from 8H to 4H in deuterated compound **9-D4**; ^{13}C-NMR (68 MHz, $CDCl_3$) δ 26.7, 28.6, 32.3, 125.4, 126.7, 128.1, 128.9, 129.9, 130.5, 132.5, 133.4, 134.4, 135.8; ^{77}Se-NMR (76 MHz) δ 310.3; MS m/z 588 (M^+); Anal. Calcd for $C_{28}H_{28}S_2Se_2$: C, 57.34, H, 4.81. Found: C, 57.29, H, 4.76.

Oxidation of 1,8-bis[3-(1-phenylseleno)propylthio]naphthalene 9

To a solution of **9** (142 mg, 0.24 mmol) [* **9-D4** was used for **2-D4**] in 30 ml of CH_2Cl_2, a solution of 100% *m*-CPBA (42 mg, 0.24 mmol) in 30 ml of CH_2Cl_2 was added at -78 °C and the mixture was stirred for 2 h. The solution was added in one portion into a boiling hexane solution (100 ml) containing triethylamine (49 mg, 0.38 mmol), then the solution was rufluxed for 2 h.[36,37] The reaction mixture was cooled to room temperature and washed with aq. $NaHCO_3$ solution, and dried over $MgSO_4$. The solvent was evaporated and the residue was separated and purified by HPLC. Yellow oil (36 mg, 0.13 mmol) was obtained in 55 % yield.

The positions of the deuterium atoms and the deuterium contents were determined to be 100% in 3 position by ^{1}H-NMR and the deuterium content was determined to be 98 % by mass spectrometry.
2: ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.57~3.60 (m, 4H), *5.01~5.12 (m, 4H), 5.82~5.97 (m, 2H), 7.33 (t, J=7.8 Hz, 2H), 7.56 (d, J=7.8 Hz, 2H), 7.65 (d, J=7.8 Hz, 2H).*The signal disappeared in deuterated compound **2-D4**.

Synthesis of 4-deuterio-naphtho[1,8-cd]-1,2-dithiole 1-D1

To a solution of 4-bromo-naphtho[1,8-cd]-1,2-dithiole (140 mg, 0.5 mmol) in 10 ml of anhydrous THF, which was prepared by known method [38] a solution of n-butyllithium (0.9 ml, 1.5 mmol) was added at -78°C. After the reaction mixture was stirred for 1 h, the reaction mixture was warmed to 0 °C and 1.0 ml of H_2O [* D_2O was used for **26-D1**] was added. The reaction mixture was allowed to be warmed to room temperature and dried over $MgSO_4$. The solvent was evaporated and the residue was separated and purified by column chromatography (hexane as an eluent). 1,8-Bis(butylthio)naphthalene (103 mg) **26** was obtained as pale yellow oil in 67% yield.
26: pale yellow oil. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.91 (t, J=7.4 Hz, 6H), 1.45 (sext, J=7.4 Hz, 4H), 1.64 (quint, J=7.4 Hz, 4H), 2.94 (t, J=7.4 Hz, 4H), *7.34 (d, J=7.8 Hz, 2H), 7.55 (d, J=7.8 Hz, 2H), **7.64 (d, J=7.8 Hz, 2H). *The signal changed to δ 7.34 (d, t, J=7.8 Hz, 1H) in deuterated compound **26-D1**, **The signal changed to δ 7.64 (d, J=7.8 Hz, 1H) in deuterated compound **26-D1**; ^{13}C-NMR (68 MHz, $CDCl_3$) δ 13.7, 22.3, 30.5, 37.4, 125.3, 127.7, 129.9, 133.3, 135.6, 135.8; MS m/z 304 (M^+); Anal. Calcd for $C_{18}H_{24}S_2$: C, 70.99, H, 7.94. Found: C, 70.86, H, 7.98.

26 (36 mg, 0.12 mmol) [* **26-D1** was used for **1-D1**] was sealed in a glass tube and heated with free flame for 10 min. The reaction mixture was separated and purified by column choromatography (hexane as an eluent). Red crystals (20 mg) were obtained in 83 % yield.
1: red crystals. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.15 (d, J=7.6 Hz, 2H), *7.27 (t, J=7.6 Hz, 2H), 7.35 (d, J=7.6 Hz, 1H) *The signal written changes to δ 7.27 (d, t, J=7.6 Hz, 1H) in deuterated compound **1-D1**.

Synthesis of 4-deuterio-1,8-bis(3,3-deuterioallylthio)naphthalene 2-D5

Pentadeuterated **2-D5** was synthsized by the same methods as 1,8-bis(allylthio)naphthalene **2** in 80% yield, using **1-D1** and 1,1-bisdeuterioallyl chloride.[39]

Synthesis of 1,8-bis(allylseleno)naphthalene 20

To a solution of $NaBH_4$ (42 mg, 1.1 mmol) in 10 ml of anhydrous EtOH, a solution of naphtho[1,8-cd]-1,2-diselenole [40] **19** (144 mg, 0.5 mmol) in 10 ml of anhydrous THF was added at room temperature. After the reaction mixture was stirred for 10 min, allyl bromide (0.22 ml, 2.5 mmol) was added slowly. The reaction mixture was allowed to stir for 30 min and extracted with CH_2Cl_2 (20 ml x 3), and dried over $MgSO_4$. The solvent was evaporated and the residue was separated and purified by HPLC. Pale yellow oil (178 mg) was obtained in 97% yield.
20: pale yellow oil. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.48-3.53 (m, 4H), 4.88-4.98 (m, 4H), 5.82-5.98 (m, 2H), 7.31 (t, J=7.6 Hz, 2H), 7.68 (d, J=7.6 Hz, 2H), 7.75 (d, J=7.6 Hz, 2H); ^{13}C-NMR (68 MHz,$CDCl_3$) δ

35.6, 117.3, 125.6, 128.7, 130.5, 133.7, 133.9, 135.6, 136.4; ^{77}Se-NMR (76 MHz) δ 337.7; MS m/z 368 (M^+); HRMS (DI) for $C_{16}H_{16}Se_2$: Calcd 367.9585, Found 367.9622.

Synthesis of 1,8-bis(3,3-dimethylallylseleno)naphthalene 22

To a solution of $NaBH_4$ (166 mg, 4.4 mmol) in 10 ml of anhydrous EtOH, a solution of **19** (568 mg, 2.0 mmol) in 10 ml of anhydrous THF was added at room temperature. After the reaction mixture was stirred for 10 min, 3,3-dimethylallyl chloride (0.5 ml, 4.4 mmol) was added slowly. The reaction mixture was stirred for 30 min and extracted with CH_2Cl_2 (20 ml x 3), and dried over $MgSO_4$. The solvent was evaporated and the residue was separated and purified by HPLC. Colorless crystals (658 mg,1.6 mmol) were obtained in 78% yield.

22: colorless crystals. mp. 42.5-43.0°C. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.45 (s, 6H), 1.63 (s, 6H), 3.50 (d, J=8.4 Hz, 4H), 5.33 (t, J=8.4 Hz, 2H), 7.27 (t, J=7.6 Hz, 2H), 7.66 (d, J=7.6 Hz, 2H), 7.71 (d, J=7.6 Hz, 2H); ^{13}C-NMR (68 MHz, $CDCl_3$) δ 17.4, 25.6, 30.9, 119.3, 125.4, 128.3, 131.6, 133.9, 135.5, 136.2, 136.5; ^{77}Se-NMR (76 MHz) δ 329.4; MS m/z 424 (M^+); Anal. Calcd for $C_{20}H_{24}Se_2$; C, 56.88, H, 5.73. Found: C, 56.65, H, 5.71.

Oxidation of 1,8-bis(allylseleno)naphthalene 20

To a solution of **20** (110 mg, 0.3 mmol) in 10 ml of CH_2Cl_2, a solution of 100% *m*-CPBA (52 mg, 0.3 mmol) in 10 ml of CH_2Cl_2 was added at -78 °C. The selenoxide **21** was assigned by ^{1}H-NMR at -50°C:

21: pale yellow solution in $CDCl_3$; ^{1}H-NMR (270 MHz, $CDCl_3$, -60°C) δ 3.33 (dd, J=10.0, 10.0 Hz, 1H), 3.48 (dd, J=10.0, 10.0 Hz, 1H), 3.73 (dd, J=10.0, 10.0 Hz, 1H), 4.06 (dd, J=10.0, 10.0 Hz, 1H), 4.49 (d, J=16.7 Hz, 1H), 4.77 (d, J= 9.7 Hz, 1H), 5.03 (d, J=16.7 Hz, 1H), 5.22 (d, J=9.7 Hz, 1H), 5.61 (dddd, J=9.7, 10.0, 10.0, 16.7 Hz, 1H), 5.78 (dddd, J=9.7, 10.0, 10.0, 16.7 Hz, 1H), 7.46 (t, J=7.3 Hz, 1H), 7.70 (t, J=7.3 Hz, 1H), 7.88 (d, J=7.3 Hz, 1H), 7.97 (d, J=7.3 Hz, 2H), 8.61 (d, J=7.3 Hz, 1H); ^{77}Se-NMR (76 MHz, -60°C) δ 311.9, 818.1.

After stirring for 1 h at -20°C, the reaction mixture was washed with aq. $NaHCO_3$ solution and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was separated and purified by HPLC. Purple oil (77 mg) was obtained in 80% yield together with diselenide **19** (3 mg, 4%).

24: purple oil. ^{1}H-NMR (270 MHz, $CDCl_3$) δ 3.34-3.37 (m, 2H), 5.18-5.25 (m, 2H), 5.86-6.00 (m, 1H), 7.16 (d, J=7.8 Hz, 1H), 7.21 (t, J=7.8 Hz, 1H), 7.34 (d, J=7.8 Hz, 1H), 7.46 (d, J=7.8 Hz, 1H), 7.51 (d, J=7.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 41.1, 117.8, 121.2, 123.4, 124.7, 126.7, 128.8, 132.9, 133.7, 136.4, 137.6, 140.0, 140.5; ^{77}Se-NMR (76 MHz) δ 385.6, 432.8; MS m/z 328 (M^+); HRMS (DI) for $C_{13}H_{10}Se_2$: Calcd 325.9115, Found 325.9124.

Oxidation of 1,8-bis(3,3-dimethylallylseleno)naphthalene 22

To a solution of **22** (121 mg, 0.29 mmol) in 100 ml of CH_2Cl_2, a solution of 100% *m*-CPBA (50 mg, 0.29 mmol) in 100 ml of CH_2Cl_2 was added at -78 °C. After the reaction mixture was stirred for 30 min at -78°C and 60 min at -20°C, the reaction mixture was washed with aq. $NaHCO_3$ solution and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was separated and purified by HPLC. Purple oil (67 mg, 0.19 mmol) was obtained in 67% yield, together with diselenide **19** (10 mg, 0.03 mmol) in 12% yield.

25: purple oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.78 (d, J=1.4 Hz, 3H), 1.79 (d, J=1.4 Hz, 3H), 3.20 (d, J=7.3 Hz, 2H), 5.28 (ddd, J=1.4, 1.4, 7.3 Hz, 1H), 7.15 (d, J=7.6 Hz, 1H), 7.19 (t, J=7.6 Hz, 1H), 7.34 (d, J=7.6 Hz, 1H), 7.44 (d, J=7.6 Hz, 1H), 7.48 (d, J=7.6 Hz, 1H); ^{13}C-NMR (100 MHz,$CDCl_3$) δ 18.3, 25.8, 35.5, 120.1, 121.3, 123.3, 124.5, 126.5, 128.8, 134.8, 136.3, 136.7, 137.8, 139.8, 139.9; ^{77}Se-NMR (76 MHz) δ 389.1, 424.3; MS m/z 356 (M^+); HRMS (DI) for $C_{15}H_{14}Se_2$: Calcd 353.9429, Found 353.9473.

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