Three Consecutive Allylic Sigmatropic [S–O, S–S, S–C] Rearrangements of 1,8-Bis(allylthio)naphthalene Monooxides *via* Transannular Interaction

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Oxidation of 1,8-bis(allylthio)naphthalene with *m*-chloroperbenzoic acid (*m* CPBA) gave the monooxide which undergoes three consecutive sigmatropic rearrangements to afford 2-allylnaphtho[1,8-*cd*]-1,2-dithiole; the mechanism has been studied using deuterium tracer experiments.

In the course of our studies on the transannular interaction between two sulfur atoms located in close proximity, together with the unequivocal formation of dithia dications on oxidation of 1,8-dithionaphthalenes,[1] we found that oxidation of 1,8-bis(allylthio)naphthalene **1** underwent unusually facile multistep sigmatropic rearrangements involving Evans,[2] sulfur–sulfur[3] and thio-Claisen[4] type allylic rearrangements to give 2-allylnaphtho[1,8-*cd*]-1,2-dithiole **4**. This paper describes the study of the mechanism for this new consecutive allylic rearrangement of **2** by deuterium tracer experiments.

Compound **1** is relatively stable. However, the corresponding monooxide **2** obtained on treatment of **1** with 1 equiv. of *m*-chloroperbenzoic acid (*m*CPBA) at −78 °C in $CHCl_3$ was found to decompose readily at 15 °C to give the thio-Claisen type rearranged product **4** quantitatively, together with prop-2-ene-1-ol **5**.† Apparently, **2** initially underwent the Evans rearrangement [2.3, S–O sigmatropy] to give the sulfenate **3** which could not be isolated, and rearranged to **4**.

In the sulfoxide **2** and sulfenate **3**, the second allylsulfenyl sulfur atom may attack transannularly the sulfinyl or sulfenate sulfur atom to promote the rearrangement, since the rate of this thio-Claisen rearrangement of **2** was unexpectedly rapid as compared with the normal thio-Claisen [3.3 S–C] rearrangement of allyl phenyl sulfide which requires a temperature of more than 200 °C.[4]

In order to elucidate the mechanism for this multistep allylic rearrangement reaction, regiospecifically deuteriated sulfoxide **2**-[$^2H_4$] was synthesized and subjected to the rearrangement at 15 °C (Scheme 1).‡ After isolation and purification of the two products **4**-[$^2H_2$] and **5**-[$^2H_2$], the deuterium distribution in the products was examined. In the allyl alcohol, the deuterium was found only at the 1,1-position, namely, an opposite position labelled at the starting sulfoxide **2**-[$^2H_4$] indicating clearly that the Evans rearrangement proceeds in a [2.3] sigmatropic concerted manner. On the other hand, the distribution of the deuterium atoms in the product **4** was determined by ^1H NMR and was found to be in 1 : 1 ratio at both 1 and 3 positions in the allyl group within experimental error (**4**-[$^2H_2$] and **4′**-[$^2H_2$]) revealing that the thiasulfonium salt[5] **6** involving the intermediate **7** should be produced *via* the [2.3, S–S] type migration of the allyl group prior to the rearrangement of **6** to **4**.[6]§¶

Furthermore, in order to distinguish between the intra- and inter-molecular mechanisms, we conducted a cross-over experiment using a mixture of two allylnaphthyl sulfides **1** and **1**-[$^2H_5$] under the identical conditions as described above.‖ After separation of the products, the deuterium content of **4** was examined by mass spectroscopic measurement of the parent peaks which were compared individually with those of **4** and **4**-[$^2H_3$] prepared separately. There were no parent

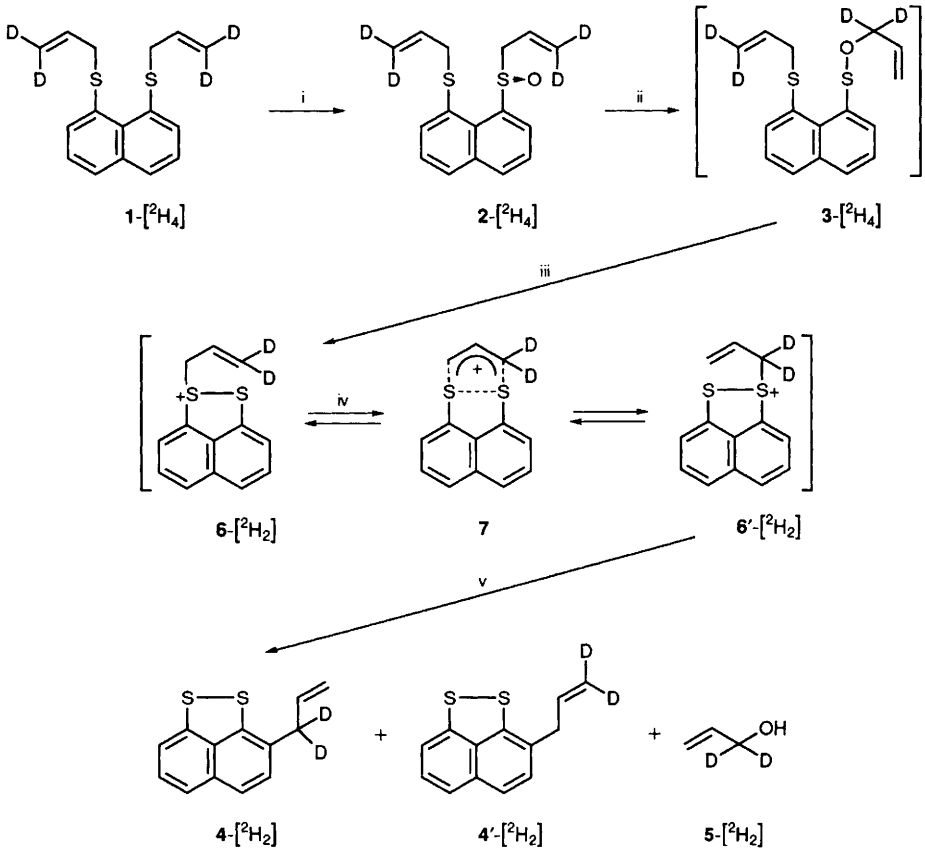
† **2**: Pale-yellow liquid; ^1H NMR (270 MHz, $CDCl_3$) δ 3.20 (dd, *J* 12.9, 8.6 Hz, 1 H, SCH–H), 3.27 (dd, *J* 12.7, 8.1 Hz, 1 H, SOCH–H), 3.37 (dd, *J* 12.9, 6.7 Hz, 1 H, SCH–H), 4.01 (dd, *J* 12.7, 7.4 Hz, 1 H, SOCH–H), 4.60 (d, *J* 16.7 Hz, 1 H, SCH_2CH=CH–H), 4.82 (d, *J* 10.0 Hz, 1 H, SCH_2CH=CH–H), 5.15 (d, *J* 17.3 Hz, 1 H, $SOCH_2CH$=CH–H), 5.28 (d, *J* 10.0 Hz, 1 H, $SOCH_2CH$=CH–H), 5.71 (dddd, *J* 16.7, 10.0, 8.6, 6.7 Hz, 1 H, SCH_2C–H), 5.74 (dddd, *J* 7.3, 10.0, 8.1, 7.4 Hz, 1 H, SCH_2C–H), 7.42 (t, *J* 7.6 Hz, 1 H), 7.64 (t, *J* 7.6 Hz, 1 H), 7.77 (d, *J* 7.6 Hz, 1 H), 7.89 (d, *J* 7.6 Hz, 1 H), 7.94 (d, *J* 7.6 Hz, 1 H), 8.44 (d, *J* 7.6 Hz, 1 H); IR (Nujol) 1038 cm^{-1} (SO); HRMS calc. for $C_{16}H_{16}OS_2$: 288.0643, found 288.0628.

‡ The regiospecific labelled sulfoxide **2**-[$^2H_4$] was prepared from the oxidation and thermolysis of 1,8-bis(3,3-dideuteriated 3-phenylselenylpropylthio)naphthalene and then oxidation of the sulfide **1**-[$^2H_4$] with *m*CPBA.

§ Preparation of thiasulfonium salts **6**[4] has been attempted using disulfide and allyl bromide but was unsuccessful.

¶ Sigmatropic allyl group rearrangement using allyl methyl sulfide and methanesulfenyl chloride have been reported.[5]

‖ **1**-[$^2H_5$] ([^2H] content >98%) was prepared from 4-deuteriated naphtho[1,8-*cd*]-1,2-dithiole and 1,1-dideuteriated allyl chloride. The deuterium atoms were distributed between the 1 and 3 positions of the allyl group.



Scheme 1 i, *m*CPBA in CH_2Cl_2; ii, [2.3] sigmatropy (S–O); iii, [2.3] sigmatropy (S–S); iv, [2.3] sigmatropy (S–S); v, [3.3] sigmatropy (S–C), **4**-[$^2H_2$]:**4'**-[$^2H_2$] = 1:1

peaks corresponding to the rearranged products **4**-[^{2}H] and **4**-[$^2H_2$] which should be obtained *via* an intermolecular process. Thus, the deuterium tracer experiment reveals unambiguously that the current rearrangement of **2** involves three consecutive multistep [S–O, S–S, S–C] pathways *via* a discrete intramolecular mechanism. More detailed studies on this new type of multi-allylic rearrangement in 1,8-dithionaphthalenes are underway in this laboratory.**

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** 1,8-bis(crotylthio)- and 1,8-bis(metallylthio)-naphthalene monooxides gave the corresponding 2-allylsubstituted naphthalenethioles as sole rearranged products.

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