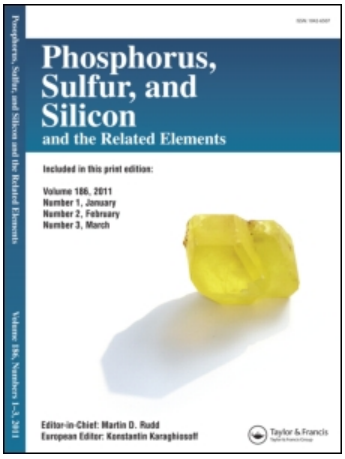

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Naomichi Furukawa[a]; Hidetaka Shima[a]
[a] Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki, Japan

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THREE CONSECUTIVE ALLYLIC SIGMATROPIC [S-O, S-S, S-C] REARRANGEMENTS OF 1,8-BIS(ALLYLTHIO)NAPHTHALENE MONOOXIDES VIA TRANSANNULAR INTERACTION

NAOMICHI FURUKAWA* AND HIDETAKA SHIMA
Department of Chemistry, University of Tsukuba , Tsukuba, Ibaraki 305, Japan

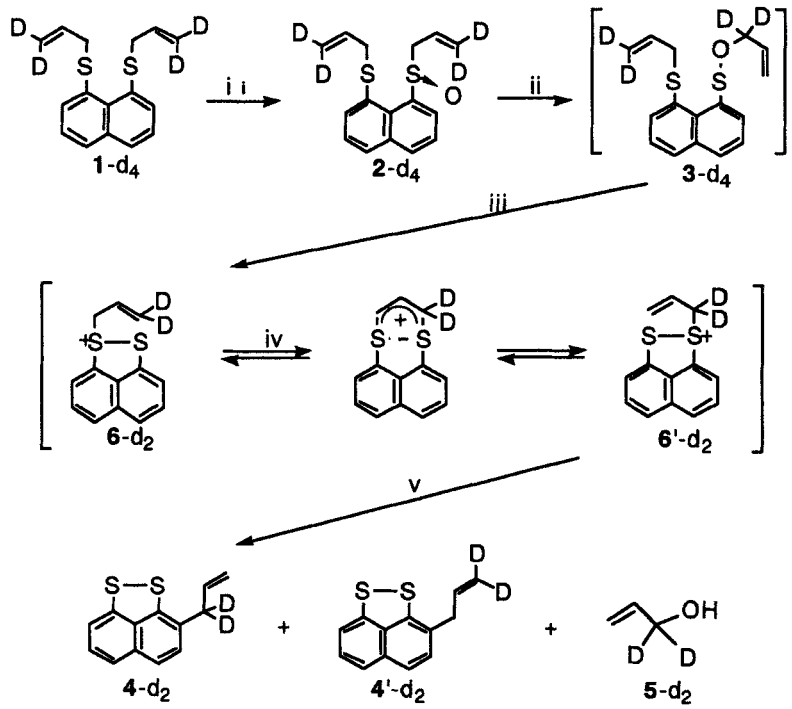
Abstract Oxidation of 1,8-bis(allylthio)naphthalene (**1**) with *m*CPBA gave the monooxide (**2**) which underwent three consecutive sigmatropic rearrangements, namely the Mislow-Evans, [2.3] S-S and the thio-Claisen rearrangements to afford 2-allyl-naphtho[1,8-*cd*]-1,2-dithiole (**4**) and prop-2-enol (**5**) quantitatively. 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 rapid as compared with that of the normal thio-Claisen rearrangement of allyl phenyl sulfide which requires a temperature of more than 200 °C.

Recently, we found that oxidation of 1,8-bis(allylthio)naphthalene (**1**) underwent unusually facile multistep sigmatropic rearrangements involving Mislow-Evans, [2.3] S-S and thio-Claisen type allylic rearrangements at room temperature to give 2-allylnaphtho[1,8-*cd*]-1,2-dithiole (**4**) and allyl alcohol (**5**) in quantitative yields. Similarly, **1** underwent multistep sigmatropic rearrangement on treatment with chloramine-T to give finally **4** and N-allyl-p-toluene sulfonyl amide (**7**) in also quantitative yields (Scheme 1).

Compound **1** is relatively stable. However, the sulfoxide **2** obtained by the oxidation of **1** with m-chloroperbenzoic acid (*m*CPBA) was found to decompose even at room temperature to give the thio-Claisen type rearrangement product (**4**) quantitatively together with prop-2-enol (**5**). The mechanism for the rearrangement could be explained in terms of the initial [2.3]sigmatropic rearrangement of S-O to C-S bond. The sulfoxide (**2**) may give initially the sulfenate (**3**) as a reaction intermediate from which the S-S transannular interaction may take place readily to give the thiasulfonium salt (**6**). Finally [2.3]sigmatropic rearrangement of the allyl group from the sulfur atom to the 2-position in the naphthalene ring. The mechanism for this multi-step rearrangements has been elucidated using regiospecifically deuterated sulfoxide (**2**-D_4).

After the reaction, the deuterated products **4**-D_2, **4'**-D_2 and **5**-D_2 were separated and their deuterium distribution was determined by ^{1}H-NMR and mass spectroscopy. In the allyl alcohol (**5**-D_2), the deuterium was found at only 1,1-position, indicating clearly that the Evans-Mislow rearrangement proceeds in a [2.3]sigmatropic concerted manner. On the other hand, the distribution of the deuterium atoms in the product (**4**) was found to be in 1: 1 ratio at both the 1- and 3-positions in the allyl group. These results reveal that the thiasulfonium salt **6** should be formed via a [2.3] S-S type migration of the allyl group prior to the rearrangement of **6** to **4**. The reaction was also elucidated to proceed via an intramolecular mechanism and not via an intermolecular process by the cross-over experiments. The whole scheme of the mechanism of this multi-step sigmatropic rearrangements is illustrated in Scheme 1.

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**-d_2:**4'**-d_2=1:1

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