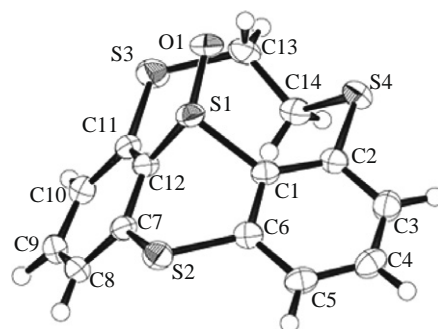


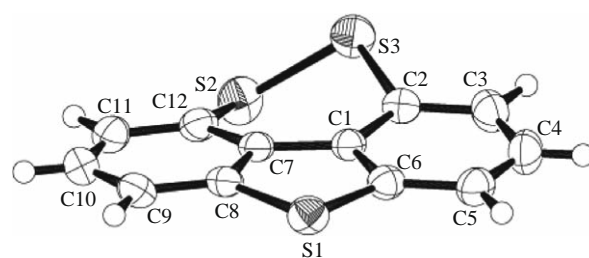
**Figure 1.** An ORTEP drawing of **2ax** (50% probability ellipsoids). Selected bond lengths (Å) and angles (°). S(1)–O(1), 1.492(1); S(1)–C(1), 1.776(1); S(2)–C(6), 1.760(2); S(3)–C(2), 1.772(2); S(4)–C(13), 1.821(2); O(1)–S(1)–C(1), 107.70(7); O(1)–S(1)–C(12), 107.12(6); C(1)–S(1)–C(12), 93.97(6); C(2)–S(4)–C(13), 101.96(8).



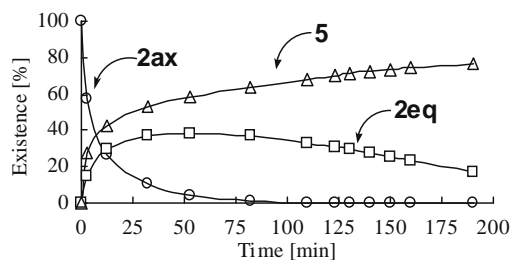
**Figure 2.** An ORTEP drawing of **2eq** (50% probability ellipsoids). Selected bond lengths (Å) and angles (°). S(1)–O(1), 1.457(2); S(1)–C(1), 1.81(1); S(1)–C(12), 1.781(3); S(2)–C(6), 1.78(1); S(4)–C(14), 1.847(7); O(1)–S(1)–C(1), 113.5(1); C(1)–S(1)–C(12), 94.4(3); C(11)–S(3)–C(13), 110.1(2); S(3)–C(11)–C(12), 129.8(2).

a Pyrex filter. As shown in Table 2 (entry 1), S–O inversion product **2eq** was obtained in 27% yield after irradiation for 3 h, and interestingly 1,9-dithiadibenzothiophene (**5**)<sup>7</sup> was formed in 47% yield. The structures of **2eq** and **5** were finally determined by the single crystal X-ray crystallographic analyses as shown in Figures 2<sup>10,310</sup>, respectively.

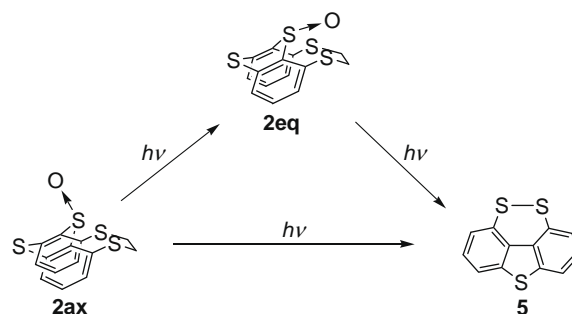
Further, in order to obtain a clue of reaction pathway, the time-course dependence of products was carried out by <sup>1</sup>H NMR spectroscopy. The observation of the formation of **5** at very early stage of the photoreaction and the slower reaction rate of **2eq** to **5** compared to the disappearance of **2ax** seems to suggest the existence of the direct path from **2ax** to **5** in Figure 4 and Scheme 1. Additionally, in the measurement of <sup>1</sup>H NMR spectra, gradual increase of a singlet peak around 5.40 ppm was observed. This peak was confirmed to be ethylene when compared with the <sup>1</sup>H NMR spectra of the sample prepared authentically. Further, several mechanistic studies for the formation of **5** were carried out as follows: Since SO trapping experiments were reported using diene and acetylene derivatives,<sup>8</sup> the photolysis of **2ax** was carried out in the presence of 2,3-dimethyl-1,3-butadiene, and the formation of the SO-trapped product, that is, 3,4-dimethyl-2,5-dihydrothiophene S-oxide (**6**), was observed in 73% yield (Scheme 2). It is reported that SO exists as the triplet state (biradical state) at ground state and can be excited to the singlet state by UV irradiation.<sup>8a</sup> Therefore, it is interesting to obtain the information about the electronic state of SO formed in the photolysis. Additionally, we carried out the photolysis of **2ax** in the presence of 2,4-hexadiene (contains three isomers). As a result, SO-trapped products, 2,5-dimethyl-3-thiolenes S-oxides **7a** (11%), **7b** (22%), and **7c** (13%) were observed (Scheme 3 and Fig. 5). This result may suggest the possibility of generation of the triplet SO by the photolysis of **2ax** forming ethylene and **5**, as similarly reported in the literature.<sup>8a,e,f</sup> Further, in order to make clear the ethylene formation step, we synthesized



**Figure 3.** An ORTEP drawing of **5** (50% probability ellipsoids). Selected bond lengths (Å) and angles (°). S(1)–C(6), 1.749(2); S(1)–C(8), 1.751(2); S(2)–S(3), 2.066(1); S(2)–C(12), 1.773(3); S(3)–C(2), 1.775(2); C(1)–C(7), 1.435(3); C(6)–S(1)–C(8), 91.7(1); S(3)–S(2)–C(12), 102.43(8); S(2)–S(3)–C(2), 101.94(8).



**Figure 4.** Time course of photolysis of **2ax**.



**Scheme 1.** Photoreaction pathway of **2ax** under irradiation of high pressure mercury lamp with a pyrex filter.

**Table 2**  
Photolysis of **2ax**–**4ax** under irradiation of high pressure mercury lamp with a Pyrex filter

Entry	<i>n</i>	Time (min)	Yield (%)	
			Equatorial isomer	<b>5</b>
1	2	180	27	47
2	3	20	95	—
3	4	20	98	—

1,9-dithiaethylene-bridged dibenzothiophene **8**, by the reaction of **2ax** with *n*-BuLi (1.5 equiv) following the reported procedure,<sup>9</sup> and carried out the photolysis of **8** under the same conditions as shown in Scheme 3. This result indicated clearly that the photolysis of **2ax** proceeded to form **8** eliminating SO (probably triplet state)

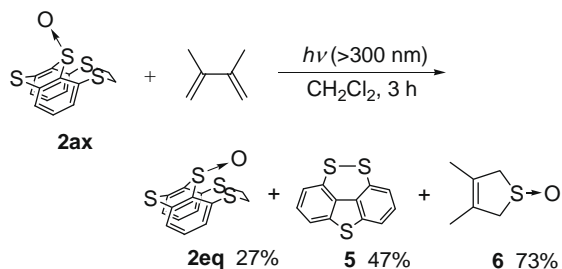
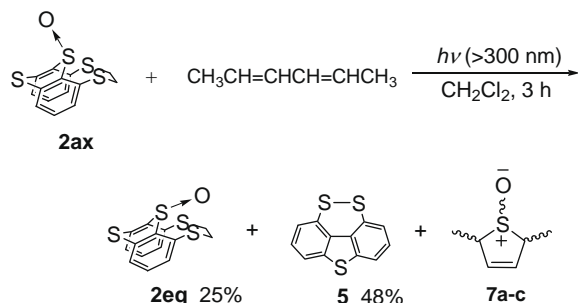
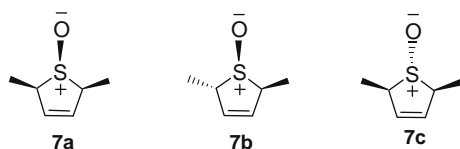
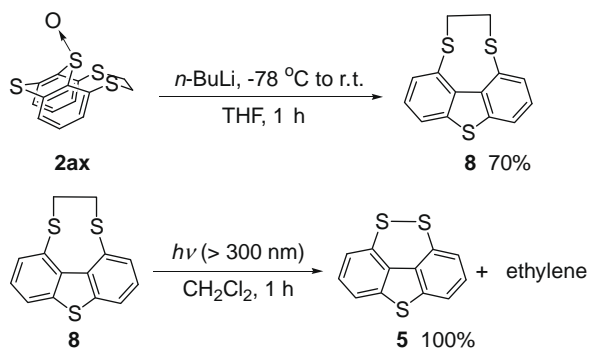
Scheme 2. Photoreaction of **2ax** with 2,3-dimethyl 1,3-butadiene.Scheme 3. Photoreaction of **2ax** with 2,4-hexadiene.

Figure 5. Isomers of 2,5-dimethyl-3thiolenesulfoxide.

Scheme 4. Synthesis of **8** and its photolytic behavior.

and successively, **8** was photolyzed secondarily to form **5** and ethylene exclusively and very rapidly, (Scheme 4) because no initial formation of **8** was observed in the photolysis of **2ax**.

In order to study the photolytic behavior on the S–O bond isomerization depending on the size of 1,9-dithiaalkane-bridged linkages, the photoreactions of **3ax** and **4ax** were carried out under the same conditions. The results are summarized in Table 2 (entries 2 and 3). In the photoreaction of **3ax** and **4ax**, no degraded product **5** was formed, and S–O inversion products **3eq** and **4eq** were formed in 95% and 98% yields, respectively. The photoreactions of the photo-isomerized products **3eq** and **4eq** (equatorial isomers), thus obtained, were carried out. However, the photo-S–O inversion to axial isomers in reverse way was not observed,

**Table 3**  
Thermal reaction of **3eq–4eq** in sealed tube

**3eq-4eq**  $\xrightarrow[\text{1,2-dichloroethane in sealed tube}]{\Delta (85 \text{ }^\circ\text{C})}$  **3ax-4ax**

Entry	<i>n</i>	Time (day)	Yield (%)
1	3	5	100
2	4	5	100

resulting in the recovery of **3eq** and **4eq**. Comparing the UV spectral data of the isomers, **3ax** and **4ax**, were found to have a weak UV absorption around 330–350 nm ( $\epsilon = \text{ca. } 0.5$ ), while nothing in the equatorial isomers of **3eq** and **4eq**. This evidence is also one of the reasons for the one-way photo isomerization from **3ax–4ax** to **3eq–4eq**, together with the steric restriction between S–O bond and the side of chain linkages. The structures of **3eq–4eq** were finally determined by a single crystal X-ray crystallographic analysis. As already mentioned earlier, since sulfoxides are known to invert thermally, it is interesting to study the thermal behavior of **3ax** and **4ax**, and **3eq** and **4eq**. In both cases of axial (**3ax** and **4ax**) and equatorial isomers (**3eq** and **4eq**), the decomposition reactions proceeded and resulted in the formation of the complex product mixtures. Under milder conditions in sealed tube at 85 °C for 20 h, the axial isomers **3ax** and **4ax** afforded the complete recovery of the starting material. However, the equatorial isomers **3eq** and **4eq** were revealed to afford the isomerized products **3ax** and **4ax** in high yield at the same temperatures for five days (Table 3). As the results in the 1,9-dithiaalkane-bridged thianthrene 10-oxides **3ax** and **4ax**, we first demonstrated the reversible change of S–O configuration by photolytical axial to equatorial and thermal equatorial to axial ways.

In summary, the irreversible photochemical axial to equatorial change (**3ax–4ax**→**3eq–4eq**) and the irreversible thermal equatorial to axial change (**3eq–4eq**→**3ax–4ax**) of the S–O configuration were first observed. Meanwhile, in the photolysis of **2ax**, S–O inversion product **2eq** and 1,9-dithiadibenzothiophene **5** were obtained.

### Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.12.116.

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10. *Crystal data* **2ax**:  $C_{14}H_{10}OS_4$ ,  $M = 322.47$ , monoclinic,  $a = 10.527(4)$ ,  $b = 11.625(3)$ ,  $c = 11.231(1)$  Å,  $\beta = 96.46(2)^\circ$ ,  $V = 1365.7(5)$  Å<sup>3</sup>,  $T = 296.2$  K, space group  $P2_1/n$ ,  $Z = 4$ ,  $\mu(\text{MoK}\alpha) = 6.81$  cm<sup>-1</sup>, 4175 reflection measured, 3345 unique ( $R_{\text{int}} = 0.015$ ),  $R_i[I > 2s(I)] = 0.031$ ,  $R_w(\text{all data}) = 0.099$ ; **2eq**:  $C_{14}H_{10}OS_4$ ,  $M = 322.47$ , monoclinic,  $a = 9.38(8)$ ,  $b = 26.15(9)$ ,  $c = 11.14(6)$  Å,  $\beta = 107.8(5)^\circ$ ,  $V = 2600(28)$  Å<sup>3</sup>,  $T = 233.2$  K, space group  $P2_1/c$ ,  $Z = 8$ ,  $\mu(\text{MoK}\alpha) = 7.16$  cm<sup>-1</sup>, 8250 reflection measured, 8074 unique ( $R_{\text{int}} = 0.022$ ),  $R_i[I > 2s(I)] = 0.034$ ,  $R_w(\text{all data}) = 0.099$ ; **5**:  $C_{12}H_6S_3$ ,  $M = 246.36$ , monoclinic,  $a = 12.003(1)$ ,  $b = 10.990(1)$ ,  $c = 16.392(1)$  Å,  $\beta = 109.296(6)^\circ$ ,  $V = 2040.7(3)$  Å<sup>3</sup>,  $T = 296.2$  K, space group  $P2_1/a$ ,  $Z = 8$ ,  $\mu(\text{MoK}\alpha) = 6.81$  cm<sup>-1</sup>, 6216 reflection measured, 4096 unique ( $R_{\text{int}} = 0.013$ ),  $R_i[I > 2s(I)] = 0.042$ ,  $R_w(\text{all data}) = 0.139$ .