

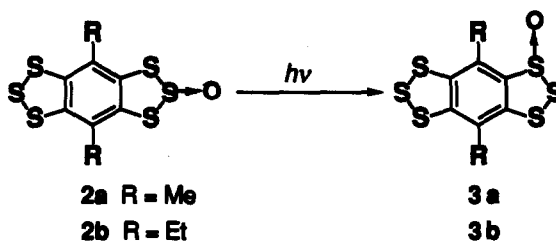
First Example of Intramolecular Photochemical Oxygen Migration from Benzotrithiole 2-Oxides to Benzotrithiole 1-Oxides

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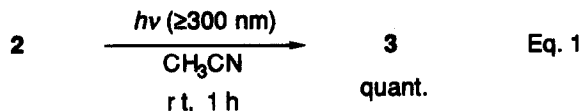
Abstract: Irradiation of 4,8-dialkylbenzo[1,2-d;4,5-d']bis[1,2,3]trithiole 2-oxides (2) in acetonitrile with a high pressure mercury lamp gave 4,8-dialkylbenzo[1,2-d;4,5-d']bis[1,2,3]trithiole 1-oxides (3) quantitatively. The present photochemical oxygen migrations of 2 and related sulfoxides were shown to proceed intramolecularly via an excited singlet state by ^{18}O -labeled, cross-over, and triplet quencher experiments.

Much attention has been drawn to the preparations, structures, and reactivities of cyclic polysulfides such as benzopentathiepins and benzotrithioles due to their biological activities, *i.e.*, *varacin* or *lissoclinotoxin A* which were isolated from the marine-natural products.¹ Although there have been many reports on the preparations and the reactions of benzopentathiepins,² a few examples of benzotrithioles have been reported.^{2a, 3} Recently, we reported the synthesis of novel benzotrithiole analogues, 4,8-dialkylbenzo[1,2-d;4,5-d']bis[1,2,3]trithioles (1), and determined their structures by X-ray crystallographic analysis.⁴ During the studies on the oxidation of the trithioles, we have found that 4,8-dialkylbenzo[1,2-d;4,5-d']bis[1,2,3]trithiole 2-oxides (2) which were obtained by the oxidation of 1 with *m*-chloroperbenzoic acid were slowly converted to 4,8-dialkylbenzo[1,2-d;4,5-d']bis[1,2,3]trithiole 1-oxides (3) on exposure to diffuse light (Scheme 1).⁵ In this communication, we wish to report these oxygen migrations in detail.



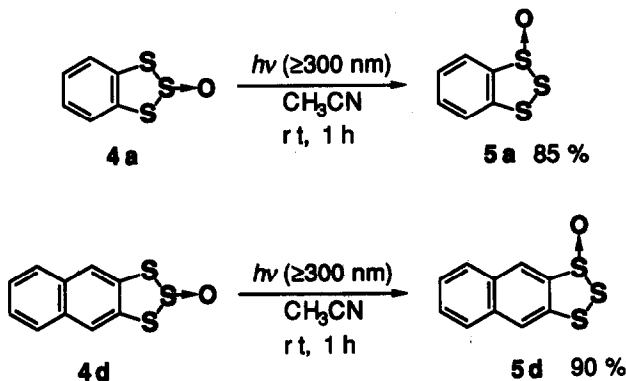
Scheme 1

When trithiole 2-oxides **2** in solid state were allowed to expose to diffuse light for 5 days, oxygen migration took place to give corresponding 1-oxides **3** in *ca.* 20% yields. Irradiation of **2a** or **2b** (1.5×10^{-4} M) in acetonitrile (CH_3CN) with a 100 W high pressure mercury lamp using a Pyrex filter for 1 h under an argon atmosphere gave **3a** or **3b** quantitatively (Eq. 1).

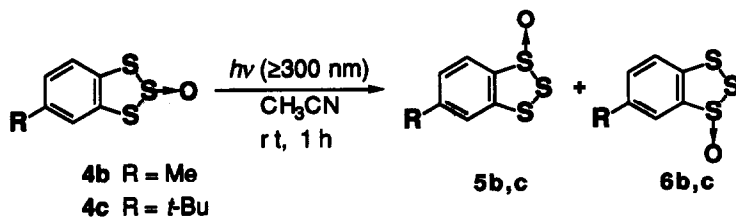


These migrations, however, did not occur thermally, treatment of **2** in CH_3CN or CHCl_3 under reflux for 5 days in the dark gave **2** unchanged. Furthermore, these reactions were not affected by the addition of a few drops of acids such as trifluoroacetic acid. On the other hand, photolysis of **3** under the same conditions resulted in the recovery of **2** quantitatively.

To examine the generality of these photochemical oxygen migrations, benzotrithiole 2-oxide (**4a**), 5-methylbenzotrithiole 2-oxide (**4b**), 5-*tert*-butylbenzotrithiole 2-oxide (**4c**), and naphthotrithiole 2-oxide (**4d**) were prepared by the reactions of the corresponding dithiols with SOCl_2 (**4a**, 76%; **4b**, 78%; **4c**, 85%; **4d**, 82%).^{5,6} Photolysis of symmetrical trithiole 2-oxides **4a** and **4d** (5.0×10^{-3} M) under the same conditions provided benzotrithiole 1-oxide (**5a**) and naphthotrithiole 1-oxide (**5d**) in 85 and 90% yields, respectively (Scheme 2). A similar treatment of unsymmetrical trithiole 2-oxides **4b** and **4c** gave an unseparable mixture of the corresponding 1-oxides **5b,c** and 3-oxides **6b,c** quantitatively (Scheme 3).

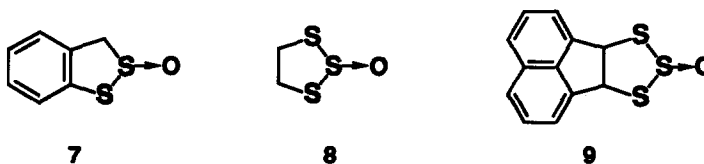


Scheme 2

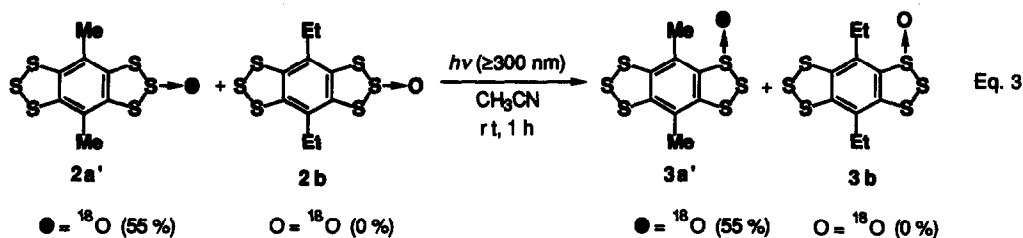
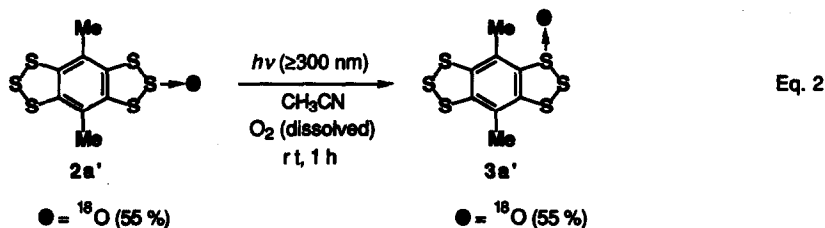


Scheme 3

It seems that the aromatic ring fused to the trithiole 2-oxide ring plays an important role for these oxygen migrations because 3*H*-1,2-benzodithiole 2-oxide (7), 1,2,3-trithiolane 2-oxide (8), and 6*b*,9*a*-dihydroacenaphtho[1,2-*d*][1,2,3]trithiolane 2-oxide (9) were not converted to the corresponding 1-oxides by irradiation at all.



To estimate whether the oxygen migrations proceed intra- or inter-molecularly, we carried out ¹⁸O-labeled and cross-over experiments. ¹⁸O-Labeled 2*a*' (¹⁸O contents: 55%) was prepared by the treatment of 1*a* with 1 equiv of *N*-iodosuccinimide followed by hydrolysis with H₂¹⁸O. Photolysis of ¹⁸O-labeled 2*a*' in CH₃CN containing dissolving oxygen for 1 h gave 3*a*' without loss of its ¹⁸O contents (Eq. 2).⁷ Furthermore, the cross-over photolysis experiment using a 1:1 mixture of ¹⁸O-labeled 2*a*' and non-labeled 2*b* in CH₃CN under an argon atmosphere gave 3*a*' without loss of initial ¹⁸O contents and 3*b* with no ¹⁸O-incorporation (Eq. 3). These results clearly indicate that the photochemical oxygen migration proceeded intramolecularly.



Furthermore, these reactions were not quenched under the irradiation in the presence of some triplet quenchers such as oxygen, 1,3-cyclohexadiene, and 1,3-pentadiene. These results suggest that the oxygen migration proceeded via an excited singlet state. Trithiole 2-oxides 2 and 4 in CH₃CN showed a strong UV absorption band in the range from 245 to 285 nm ($\epsilon = 8000$) which could be assigned as a π - π^* transition of the aromatic ring fused to the trithiole 2-oxide ring. It appears attractive to assume that the reaction started from their

π - π^* transition since photolysis of 4 in a quartz tube increased the yields of 5 and 6, but detailed excitation mechanism is still unclear at this time.

In conclusion, we have demonstrated, to the best of our knowledge,⁸ first photochemical oxygen migration which proceeded intramolecularly via excited singlet state of benzotrithiole 2-oxide and their analogues. Further investigation on these reactions are now in progress.

Acknowledgement.

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References and Notes

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