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## Phosphorus, Sulfur, and Silicon and the Related Elements

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## Syntheses, Structures, and Reactivities of Sulfur-Containing Cycloalkenes

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Sulfur-containing cycloalkenes possessing disulfide units **1**, **2**, and **3** were obtained by oxidation of *cis*-disodium ethene-1,2-dithiolate, and their crystal structures were determined by the X-ray crystallographic analyses. Compound **1** was found to give the ring expansion product **3** in acetonitrile even at room temperature and also form reactive thioaldehyde under irradiation.

### INTRODUCTION

Tetrathiacyclooctadienes are considered to have some conformers similar to cyclooctadiene, however, there is little study on the synthesis and conformations. Krespan and co-workers reported the synthesis of 3,4,7,8-tetrakis(trifluoromethyl)-1,2,5,6-tetrathiacycloocta-3,7-diene.<sup>1</sup> Recently, we succeeded in synthesizing 1,2,5,6-tetrathiacycloocta-3,7-diene (1,2,5,6-tetrathiocin) (**1**) without possessing any substituent. Moreover, it was found that tetrathiocin **1** gave dimeric 16-membered cyclic compound **3** in acetonitrile solution. In this paper, syntheses, structures, and reactivities of tetrathiocin **1** and the related compounds will be reported.

### RESULTS AND DISCUSSION

Oxidation of *cis*-disodium ethene-1,2-dithiolate with iodine under dilution conditions gave tetrathiocin **1** together with bicyclic trimer **2**, monocyclic tetramer **3**, and polymeric compounds **4**. Tetrathiocin **1** was yellow prisms (m.p. 97.5-98.5°C) and the molecular structure was determined by the X-ray crystallographic analysis (Figure 1). The X-ray structure of **1** shows  $D_2$  symmetry and good agreement with the optimized structure (*ab initio* MO calculation), which is estimated to have the lowest potential energy. The crystal structures of the trimer **2** and tetramer **3** were also determined by the X-ray analyses. The crystal structure of **3** was found to have cage geometry (nearly  $D_{2d}$  symmetry) possessing a cavity. Distances between the center of the molecule and the sulfur atoms of **3** are 3.41 Å (average) and those between the center and carbon atoms are 2.53 Å (average). Compound **1** was found to be stable in non-polar solvents even in boiling *p*-xylene. However, in acetonitrile, compound **1** dimerized to the ring

expansion product 3 in moderate yield. Compound 1 was also found to be unstable toward room light and decomposed gradually to give polymeric compounds. Irradiation of 1 in benzene solution through a pyrex filter gave the bicyclic compound 2 and tricyclic compound 5 together with majority of rubberlike polymeric compounds consisted of CHS unit. When 1 was irradiated in the presence of 2,3-dimethylbutadiene, compound 6 was obtained in 44% yield. The result suggests the formation of thioaldehyde as a reactive intermediate in the photochemical reaction.

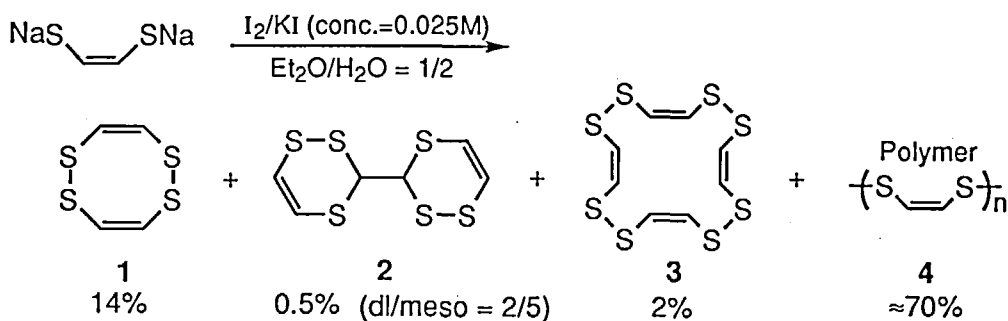
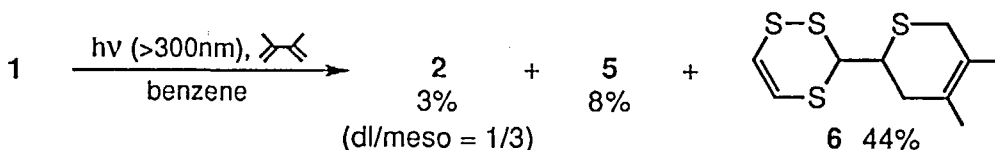
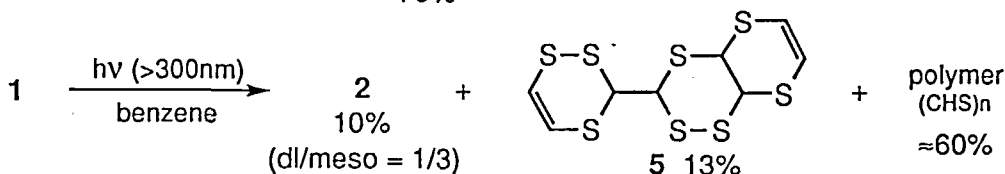
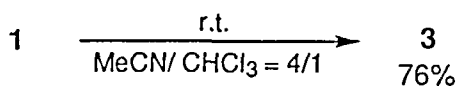
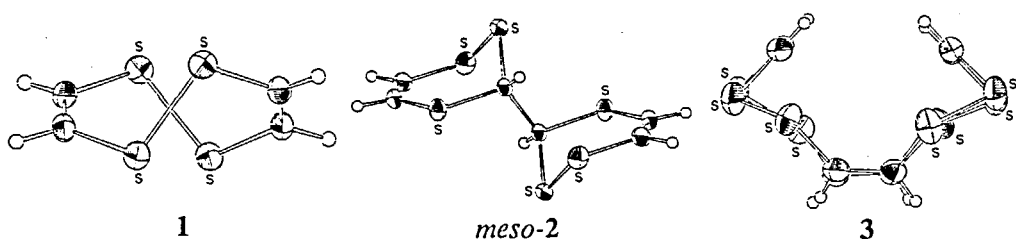


Figure 1. X-Ray structures of 1, 2, and 3.



## REFERENCES

1. Krespan, C. G.; McKusick, B. C.; Cairns, T. L. *J. Am. Chem. Soc.* 1960, 82, 1515.