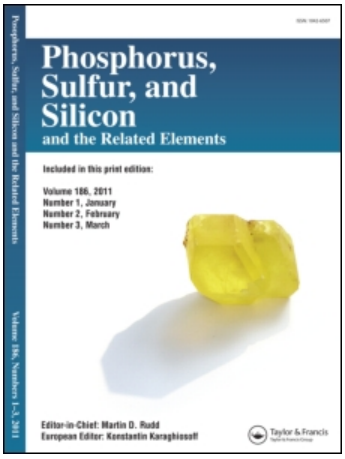



**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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

Toshio Shimizu; Kazuko Iwata; Hideyuki Murakami; Nobumasa Kamigata

**To cite this Article** Shimizu, Toshio , Iwata, Kazuko , Murakami, Hideyuki and Kamigata, Nobumasa(1997) 'Syntheses, Structures, and Reactivities of Sulfur-Containing Cycloalkenes', Phosphorus, Sulfur, and Silicon and the Related Elements, 120: 1, 457 — 458
**To link to this Article: DOI:** 10.1080/10426509708545596
**URL:** http://dx.doi.org/10.1080/10426509708545596

*Phosphorus, Sulfur, and Silicon*, 1997, Vol. 120 & 121, pp. 457–458
Reprints available directly from the publisher
Photocopying permitted by license only



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

TOSHIO SHIMIZU, KAZUKO IWATA, HIDEYUKI MURAKAMI, and NOBUMASA KAMIGATA
*Department of Chemistry, Faculty of Science, Tokyo Metropolitan University*
*Minami-ohsawa, Hachioji, Tokyo 192-03, Japan*

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.[1] 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.

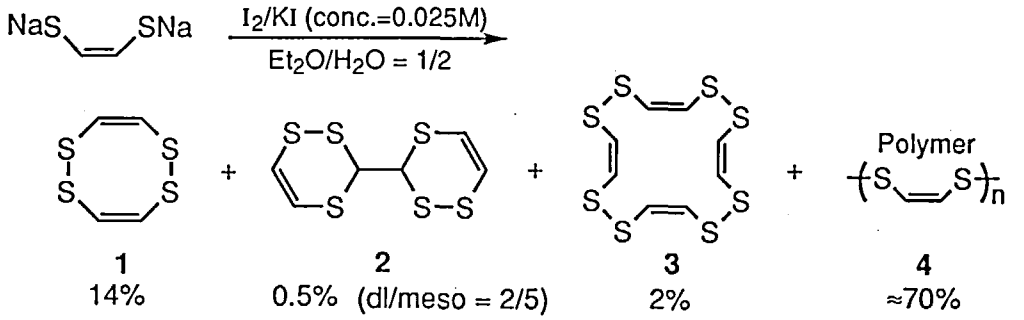
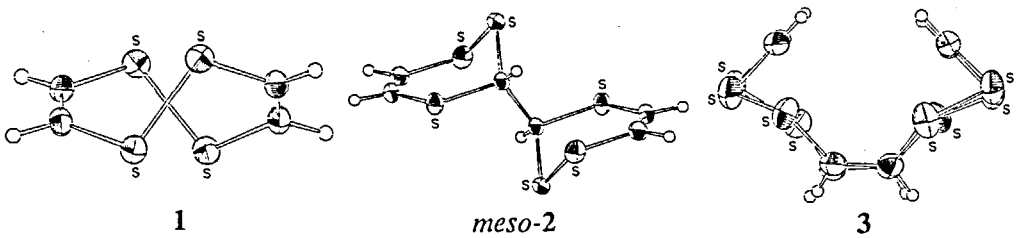
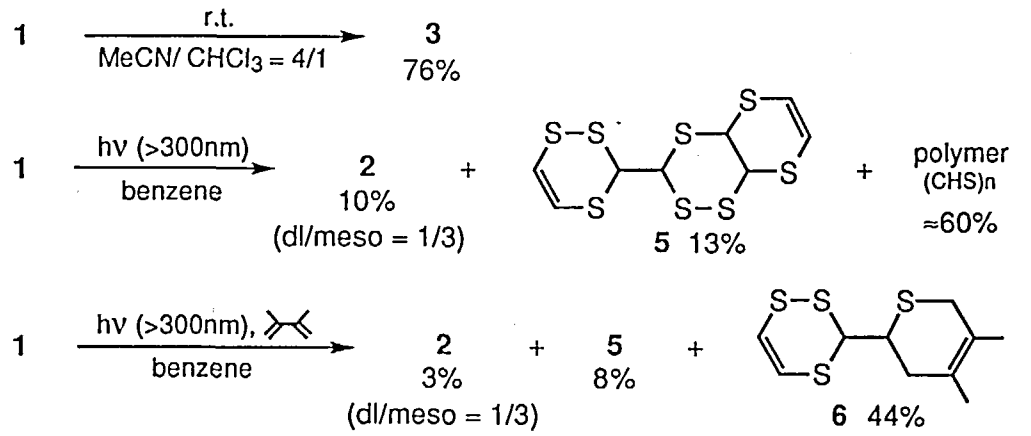



**Figure 1.** X-Ray structures of **1**, **2**, and **3**.




## REFERENCES

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