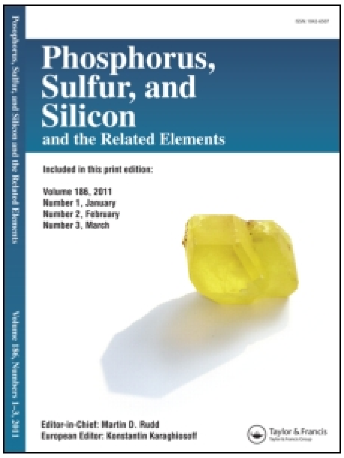

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Synthesis and Reactions of 1,2-Dithiete and Related Compounds

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Bis(methoxycarbonyl)-1,2-dithiete **1**, the cyclic dimer **2**, and the tetramer **3** were obtained by oxidation of titanocene dithiolene complex with sulfuryl chloride, and the crystal structures of **1** and **2** were determined by X-ray crystallographic analysis. Novel ring conversion reaction among the compounds was found under various conditions, such as in non-polar solvent, in polar solvent, and in the presence of silica-gel.

INTRODUCTION

Unsaturated cyclic compounds possessing disulfide unit have received much attention. Previously, we reported the oxidation of *cis*-disodium ethene-1,2-dithiolate gave 1,2,5,6-tetrathiocin and the dimeric macrocycle without any substituent.[1] Recently, we succeeded in synthesizing bis(methoxycarbonyl)-1,2-dithiete (**1**) together with small amount of the related cyclic compounds **2** and **3** by oxidation of titanocene dithiolene complex with sulfuryl chloride. In this paper, synthesis, crystal structures, and novel ring conversion reaction of the 1,2-dithiete and the related compounds will be reported.

RESULTS AND DISCUSSION

Oxidation of titanocene dithiolene complex with sulfuryl chloride in benzene under dilution conditions yielded bis(methoxycarbonyl)-1,2-dithiete (**1**) as pale yellow plates in 66% yield together with small amount of larger cyclic compounds **2** (1.6%) and **3** (2.0%). 1,2,5,6-Tetrathiocins **4**, **5**, and **6** and sixteen-membered cyclic compound **7** were also obtained by similar oxidation of corresponding titanocene dithiolene complexes in 22, 17, 21, and 10% yields, respectively. The crystal structures of **1** and **2** were determined by X-ray analysis, and the crystal structure of **1** was found to have planar geometry and that of **2** shows twisted geometry, as shown in Figure 1. 1,2-Dithiete **1** was found to underwent tetramerization selectively to give sixteen-membered cyclic compound **3** in chloroform or benzene solution even at room temperature, whereas compounds **2** and **3** were stable under the conditions. In acetonitrile solution, the compounds **1**, **2**, and **3** reacted to form ring-conversion products each other. Chloroform solution of **1**, **2**, and **3** also afforded the ring-conversion products in the presence of silica-gel, and long reaction time caused further reaction to give a bicyclic product. However, corresponding twelve-membered cyclic compound could not be obtained in any reaction. The ring-size selectivity of the reactions was found to be controlled by the conformation of the intermediate in the ring closure reactions on the basis of *ab initio* molecular orbital calculations.

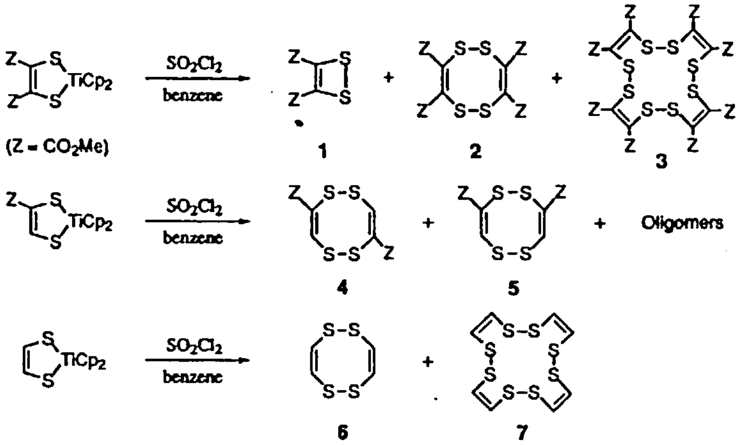
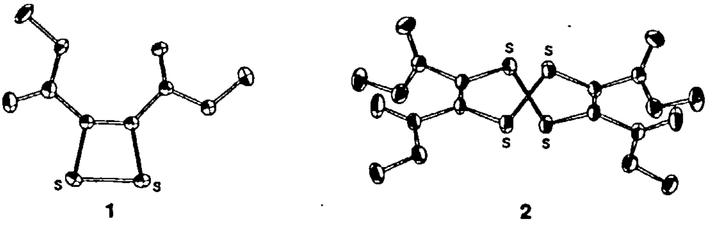
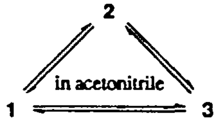


Figure 1. Crystal structures of 1 and 2.



$$1 \xrightarrow[\text{benzene or chloroform}]{\text{r.t.}} 2 + 3$$

$$2 \text{ or } 3 \xrightarrow[\text{chloroform}]{\text{r.t.}} \textit{no reaction}$$



$$1 \rightleftharpoons 2 \rightleftharpoons 3$$

in the presence of silica-gel

References

[1] Shimizu, T.; Iwata, K.; Kamigata, N. *Angew. Chem., Int. Ed. Engl.* 1996, *35*, 2357.