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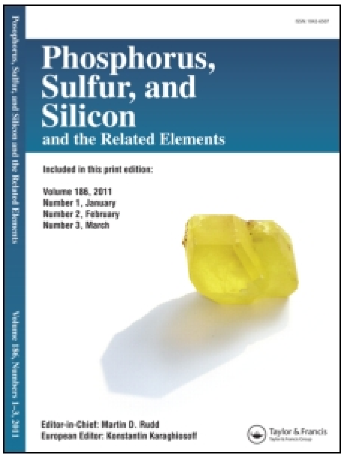

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Reaction of Cyclic Polysulfides with Alkenes in the Presence of Lewis Acid

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Reaction of Cyclic Polysulfides with Alkenes in The Presence of Lewis Acid

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Abstract Some cyclic polysulfides react stereospecifically with alkenes in the presence of Lewis acid to give cycloadducts.

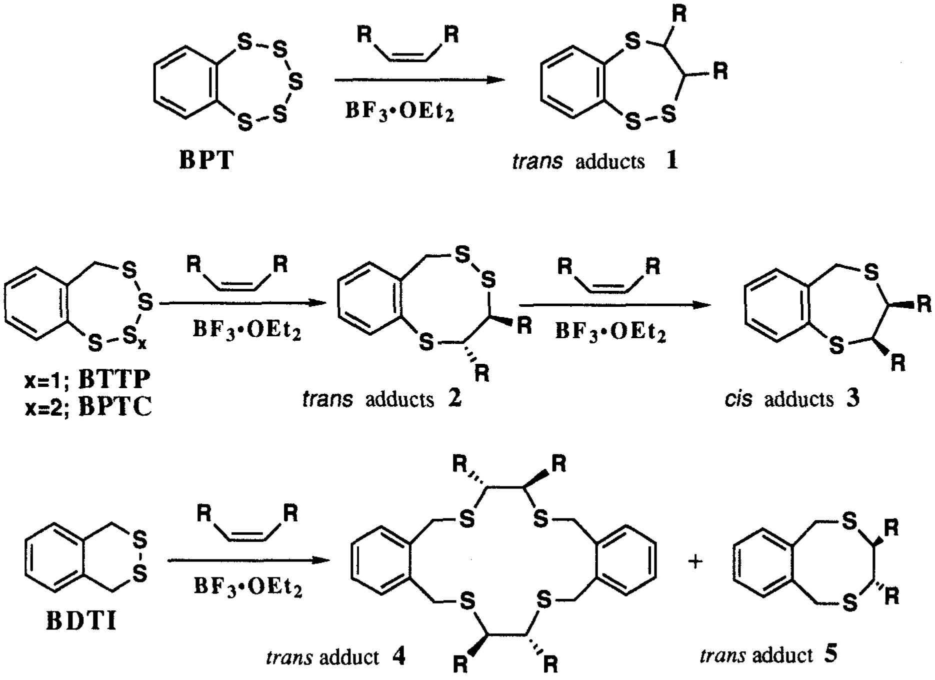
Introduction

Recently, many current interests were directed to a new field of chemistry of cyclic polysulfides involving many sulfur-sulfur linkages in the molecule such as benzopentathiepin (**BPT**) and the related compounds. Especially, it should be noted that such cyclic polysulfides are able to convert into the corresponding heterocyclic compounds containing sulfur atom. During the course of investigation of chemistry of cyclic polysulfides, we found some new cycloaddition of cyclic polysulfides to alkenes. Now, we wish to report cycloaddition of cyclic polysulfides such as **BPT**, 1)5H-benzo[f]-1,2,3,4-tetrathiepin (**BTTP**) or 6H-benzo[g]-1,2,3,4,5-pentathiocin (**BPTC**),2) and 1,4-dihydro-2,3-benzodithiin (**BDTI**) to various alkenes in the presence of Lewis acid. 3)

Results and Discussion

We could obtain the corresponding stereospecific *trans*-cycloadducts, 1,2,5-trithiepan **1**, in good yields from **BPT** with alkenes as shown in Scheme 1. This reaction was found to proceed stereospecifically through episulfonium intermediate formed from BPT activated by $BF_3 \cdot OEt_2$ with alkenes.

The treatment of **BTTP** or **BPTC** with alkenes in the presence of $BF_3 \cdot OEt_2$ at room



Scheme 1

temperature gave stereospecifically *trans*-adducts, 1,4,5-trithiocan **2**, which reacted further with alkenes under the conditions to afford cis-adducts, 1,4-dithiepan **3**. The stereospecific reaction pathway was interpreted as follows. Initially, **BTTP** or **BPTC** activated by $BF_3 \bullet OEt_2$ reacts with alkene to give trans-adduct **2** via episulfonium intermediate. The resulted trans-adduct **2** further reacts with alkene in the presence of $BF_3 \bullet OEt_2$ to afford σ–sulfurane via episulfonium intermediate. The σ–sulfurane gives cis-adduct **3** by ligand-coupling. Similarly, the formation of macrocyclic thiaether **4** together with dithiepan **5** from **BDTI** with alkenes in the presence of $BF_3 \bullet OEt_2$ is illustrated in terms of the formation of episulfonium intermediate. These methodology for the convenient synthesis of stereo-controlled 1,25-trithiepanes, 1,4-dithiepanes, and sixteen-membered thiaethers from **BPT**, **BTTP** or **BPTC**, and **BDTI** respectively is noteworthy since the resulted products have very potential versatility in the synthetic chemistry. Further investigation is now in progress in our laboratery.

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