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### CHEMISTRY OF CYCLIC POLYSULFIDES. OXIDATION OF BENZOBISTRITHIOLE AND THE RELATED REACTIONS

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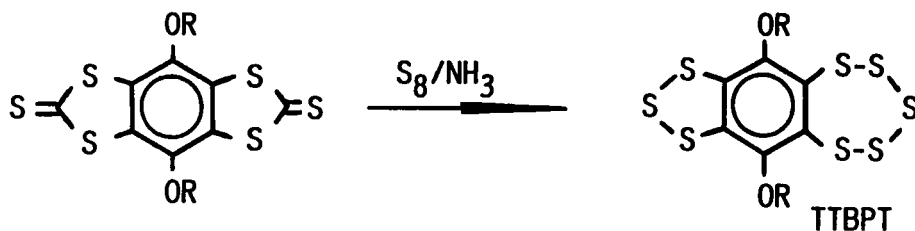
## CHEMISTRY OF CYCLIC POLYSULFIDES. OXIDATION OF BENZOBISTRITHIOLE AND THE RELATED REACTIONS

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**Abstract:** A new type of compound, 4,8-dialkylbenzo[1,2-d;4,5-d']bis-1,2,3-trithiole, was synthesized in satisfactory yields by novel reaction of 1,4-dialkyl-2,3,5,6-tetrabromobenzenes with elemental sulfur in liquid ammonia. Some interesting chemical behaviors of the obtained compounds were observed upon treating with reducing and oxidizing agents.

Some natural products containing many sulfur-sulfur linkages in the molecule such as lenthionine have attracted much attention of organosulfur chemists.<sup>1</sup> On the other hand, cyclic polysulfides e.g. sporidesmine have also been characterized to have antivacterial activity.<sup>2</sup> In these viewpoints, many reports on synthesis and reactions of cyclic polysulfides have appeared.<sup>3</sup> Recently, we have reported synthesis of many cyclic polysulfides from the corresponding  $\alpha$ ,  $\omega$ -alkanedithiols and the related compounds with elemental sulfur in liq-

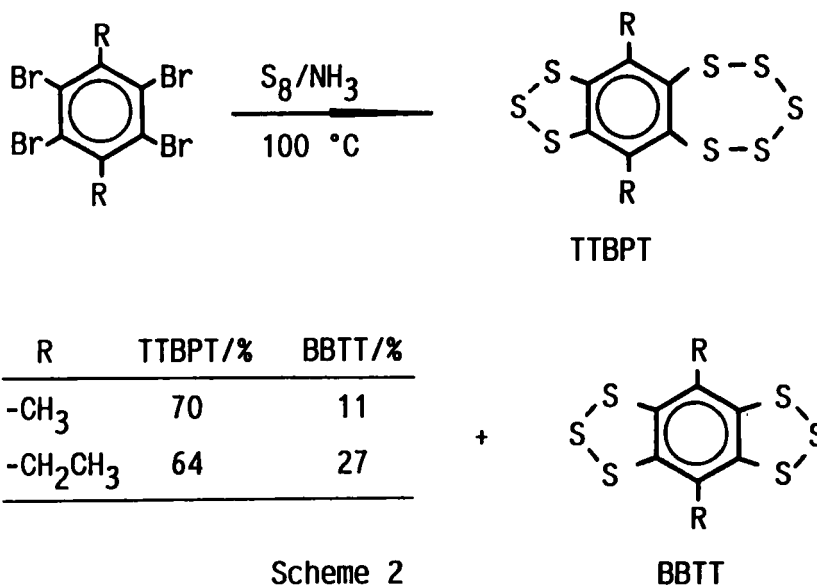
uid ammonia.<sup>4</sup> Based on the above results, we have challenged to synthesis of new types of cyclic polysulfides. Consequently, we succeeded in synthesis of novel cyclic polysulfide, 6,10-dialkoxy[1,2,3]trithiolo[5,4-h]benzopentathiepin (TTBPT), bearing both trithiole and pentathiepin rings on benzene ring from the corresponding benzobisdithiole-2-thiones with elemental sulfur in liquid ammonia (Scheme 1).<sup>5</sup>



R	Yield/%	R	Yield/%
-CH <sub>3</sub>	82	-CH(CH <sub>3</sub> ) <sub>2</sub>	99
-CH <sub>2</sub> CH <sub>3</sub>	99	-CH <sub>2</sub> Ph	62

Scheme 1

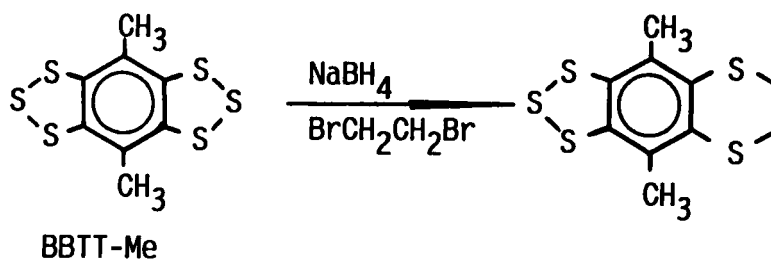
Four TTBPT were obtained in good yields as stable reddish brown crystals (62-99%) and were shown to be cis conformation for all substituents by X-ray crystallography. Furthermore, we have tried to synthesize directly such cyclic polysulfides from polyhalobenzenes. When 1,4-dialkyl-2,3,5,6-tetrabromobenzenes were treated with elemental sulfur in liquid ammonia at 100 °C, two interesting products, 6,10-dialkyl[1,2,3]trithiolo[5,4-h]benzopentathiepins (TTBPT) and 4,8-dialkylbenzo[1,2-d;4,5-d']bis[1,2,3]trithioles (BBTT), were obtained in satisfactory yields as shown in Scheme 2.<sup>6</sup> The X-ray crystallography of these compounds clearly demonstrated



Scheme 2

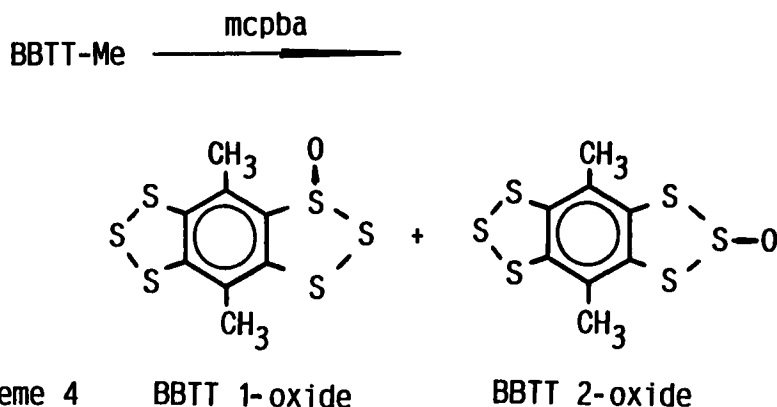
that the structure of TTBPT is cis conformation for all substituents, whereas BBTT is trans.

A reduction of trithiole ring of BBTT-Me followed by alkylation with 1,2-dibromoethane gave benzodithiane derivative (Scheme 3).



Scheme 3

An oxidation of BBTT-Me with mcpba at room temperature afforded preferentially BBTT 1-oxide as shown in Scheme 4. BBTT 2-oxide was formed as a minor product.



Moreover, a slow conversion of BBTT 2-oxide to BBTT 1-oxide was observed in  $\text{CH}_2\text{Cl}_2$  at room temperature.

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