

THIACROWN ETHERS AND DERIVATIVES : PREPARATION AND APPLICATIONS FOR  
ORGANIC REACTIONS

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Recently, we found that new macrocyclic polythiaethers (V,VI) could easily be obtained in good yields via 2,2'-dithiaspiro[3,3]heptane(II).

Pentaerythrityl bromide(I), having a neopentyl type carbon skeleton, was found to be unreactive in the reactions with such nucleophiles as amine, phosphine, and cyanide anion due to the steric hindrance around the reaction center. However, the reactions of (I) with sulfur nucleophiles such as  $\text{Na}_2\text{S}_2$ , and  $\text{Na}_2\text{S}$ , and  $\text{NaSR}$  proceeded smoothly. The reaction of (I) with several sodium alkyl mercaptides gave the corresponding tetrakisulfides nearly quantitatively (Scheme). The sulfides were also readily oxidized to give the corresponding tetrakisulfoxides. When (I) was allowed to react with  $\text{Na}_2\text{S}$  in aqueous ethanol solution, an interesting key intermediate, 2,2'-dithiaspiro[3,3]heptane(II) was obtained in a good yield. New macrocyclic polythiaether(V) was prepared via (IV) starting from the compound(II) as illustrated in Scheme. Oxidation of the sulfides (V) and (VI) underwent smoothly with 30% aqueous hydrogen peroxide in acetic acid affording the corresponding sulfoxides (VII) and (VIII).

We now have prepared polysulfoxides of open chain molecules or crown thiaethers and tested their phase transfer catalytic activities. These sulfoxides [tetrakis-sulfoxides (III) and crown sulfoxide (VIII)] were found to be used as new type of phase transfer catalysts in the two-phase alkylation. Furthermore, macrocyclic polythiaethers coordinated selectively with heavy metals such as Cu, Hg, and Pd, and also formed rather stable sulfonium salts.

