TRANSANNULAR INTERACTIONS IN THE REACTIONS OF SULFILIMINES OF CYCLICPOLYTHIAETHERS WITH STRONG BASES

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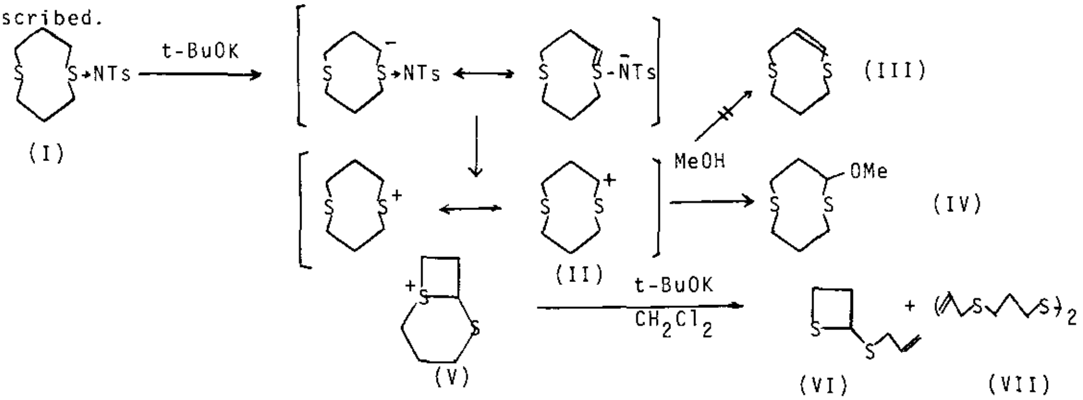
Transannular interactions by the sulfur atom to the electron deficient center have been observed accompanying with ring contraction or ring expansion.[1] N-p-Tosylsulfilimines having α-protons react with potassium hydroxide in alcohols to afford either the S-substitution product(corresponding sulfoxide) or the Pummerer type rearrangement product(corresponding α-alkoxy sulfide) or both.[2] Meanwhile, upon treatment of the sulfilimines bearing α,β-protons with strong bases such as potassium t-butoxide in an aprotic solvent such as benzene afforded the corresponding vinylic sulfides in substantial yields.[3] These sulfides are considered to be obtained via the unusual Pummerer-type rearrangemnt. However, we found that when 1-N-p-tosyl-1,5-dithiaoctanesulfilimine(1) was treated with potassium t-butoxide in an aprotic solvent such as dichloromethane, 2-allylthiothiethane(VI) and the disulfide(VII) were obtained in 40 and 21% yields respectively. The assignment for their structures were carried out by spectral analyses. Apparently, these products would be obtained via an initial formation of intermediate(V). The mechanisms for the reactions are illustrated in the scheme. This and related transannular reactions in cyclic polythia-ethers would be described.



Scheme

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