SYNTHESIS AND REACTIONS OF THIABENZENES

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In order to elucidate the structure of thiabenzenes, synthesis of new cyclic sulfur 1,4-ylides and their reactions with electrophiles have been studied : from 9-cyano and 9-ethoxycarbonyl-10-methylthioxanthenium salts (I and II) and base stable 9-cyano and 9-ethoxycarbonyl-10-methylthiaanthracenes (III and IV) have been synthesized. The conformation of I and II was considered by NMR spectral data.

The treatment of III (example 1) with dimethyl acetylenedicarboxylate gave 9-cyano-9-methyl-(V), 9-cyano-9-(cis-1,2-dimethoxycarbonylvinyl)-(VI), 9-cyano-9-(1,2-dimethoxycarbonylcyclopropyl)-(VII), and 9-cyano-9-(1,2-dimethoxycarbonylallyl)thioxanthene (VIII). By the reaction of III and tetracyanoethylene, V, 9-cyano-9-(dicyanomethyl)-(IX), 9-dicyanomethylidenethioxanthene (X), malononitrile (XI), and 2,2,3,3-tetracyanobutane (XII) were isolated as main products. Mechanisms of these reactions were also discussed.

In the course of the studies, the synthesis, stereochemistry and reactivity of sulfoxides, sulfones and 10-alkyl or arylsulfonium salts derived from 9-pentafluorophenyl-(XIII), 9-mesityl-(XIV), and 9-phenyl(d_5)thioxanthene (XV) were also investigated.