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REACTIONS OF CYCLIC SULFUR YLIDES

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Reactions of thiabenzene derivatives with some electrophiles were investigated in various solvents.

Reaction of 1-cyano-2-methyl-2-thianaphthalene (I) with dimethyl acetylenedicarboxylate (DMAD) in benzene gave 5,6-bis(methoxycarbonyl)-4-cyano-7-methylthio-2,3-benzonorcaradiene (II) and 5,6-bis(methoxycarbonyl)-4-cyano-7-methylthio-2,3-benzotropilidene (III) in yields of 75 % and 6 %, respectively, although in EtOH 2,3-bis(methoxycarbonyl)-1-cyanonaphthalene (IV) was formed. In sulfolane, the above reaction gave 2:1-adduct of I and DMAD with II and III. This 2:1-adduct was also given in high yield by the reaction of I and III. Compounds II and III gave IV on heating at 220°.

Reaction of I with diphenylcyclopropenone resulted in the formation of a new seven-membered cyclic ketone, while in EtOH α,β-unsaturated ester was formed. Reaction results of I with other electrophiles such as tetracyanoethylene, diethyl azodicarboxylate (DAD) were also reported with the reaction mechanisms.

Reaction of 1-benzoyl-2-methyl-2-thianaphthalene (V) with DMAD in benzene or sulfolane yielded only 4-benzoyl-5,6-bis(methoxycarbonyl)-7-methylthio-2,3-benzonorcaradiene whose structure was determined by X-ray analysis. Reaction of V with DAD in sulfolane gave a diaziridine derivative.

In order to investigate the stability and reactivity of thiaphenanthrene, 6-cyano-5-methyl-5-thiaphenanthrene (VI) was synthesized from the reaction of 6-cyano-5-methyl-5,6-dihydro-5-thiaphenanthrenium perchlorate with triethylamine, which was very stable in air but on heating in refluxing benzene underwent thermal Stevens-type 1,2-rearrangement to give 6-cyano-6-methyl-5,6-dihydro-5-thiaphenanthrene. Treatment of VI with DMAD in benzene caused a new ring expansion reaction to give a dibenzothiepin derivative. Reaction of VI with other electrophiles and their reaction mechanisms were also reported.