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SYNTHESIS AND REACTIONS OF THIAAZULENIUM SALTS

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In the course of our studies on 6-thiaazulenylium salts, called dream compounds, synthesis and reactions of thiaazulencyclone (I) and thiaazulenium derivatives (II) have been reported.

By the reaction of 10,11-dihydrodibenzo[b,f]thiepin-10,11-dione with dibenzyl ketone, I has been synthesized in good yield. The reactivities of I were discussed by the comparison of Diels-Alder reactions and other behavior with those of phencyclone : from I with acetylene derivatives, electron defficient olefins (N-phenylmaleinimide, maleic anhydride and so on), electron rich olefins (norbornadiene and acenaphthene) and benzyne, 1,4-diphenyl-2,3-R or R'tribenzo[b,d,f]thiepin (III), two endo [4+2] adducts (IVa, IVb), the sole endo [4+2] adduct (V) and 1,6-diphenylnaphto-[2,3-d]dibenzo[b,f]thiepin (VI) were, respectively, obtained. The treatment of I with bromine in carbon tetrachloride, phenyllithium (or phenylmagnesium bromide) and lithium aluminum hydride-aluminum chloride etc. gave cis adduct (VII) as main product besides trans adduct, the corresponding dienol derivative (VIII) and cyclopentadiene derivative (IX), respectively.

IX reacted with methyl iodide-silver perchlorate to give II which was converted into a novel cyclic sulfur ylide (X) using strong base, such as sodium hydride, in tetrahydrofuran. Heating X afforded Stevens type rearrangement product (XI).

In connection with the Stevens type rearrangement reaction of the sulfur ylides, the mechanisms for the interesting reactions of IX with methyl iodide or deuterium oxide in the presence of sodium hydride were proposed. 8-Arylthiaazulenium derivatives were also investigated.