

SYNTHESES AND REACTIONS OF 8-THIABICYCLO[3.2.1]OCTENONE DERIVATIVES

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To investigate the photochemical behavior of cyclic β -ketosulfide, β -sulfoxide and β -ketosulfone, several derivatives in the 8-thiabicyclo[3.2.1]oct-3-en-2-one system were synthesized and irradiated. Among them, 6-keto, 6-exo-hydroxy, 6-endo-chloro, and 6-endo-acetoxy derivatives upon irradiation underwent 1,3-shift of the sulfur bridge and afforded the corresponding 8-thiabicyclo[4.1.1]-oct-2-en-7-one derivatives.

However, in the case of 6-endo-hydroxy derivative, hemi ketal was obtained instead of the corresponding thietanone. Contrary to these findings, β -ketosulfoxide and sulfone did not give any clear photoproduct.

It is noteworthy that such a photochemical behavior of the 8-thiabicyclo[3.2.1]-octenone derivatives is different from that of 9-thiabicyclo[3.3.1]nona-3,7-dien-2,6-dione derivatives²⁾, which was reported to exhibit a 1,3-carbon shift. In addition, attempted syntheses of 8-thiabicyclo[3.2.1]octa-3,6-dien-2-one and 8-thiabicyclo[4.1.1]octa-2,4-dien-7-one were carried out.