PHOTOCHEMICAL AND THERMAL REACTIONS OF SOME BICYCLIC δ-THIA-α,β-UNSATURATED KETONES

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It has been reported that 9-thiabicyclo[3.3.1]nona-3,7-dien-2,6-dione (1) which contains β-keto-sulfide and δ-thia-α,β-unsaturated ketone moieties undergoes photo-1,3-carbon shift to give 2-thiabicyclo[3.3.1]nona-3,7-dien-6,9-dione (2), whereas the analogous compound, 8-thiabicyclo[3.2.1]octa-3-en-2-one (3), upon irradiation, affords the photo-1,3-sulfur shift product, 8-thiabicyclo[4.1.1]-octa-2-en-4,7-dione (4). However, there is no generalized mechanistic interpretation to account for those two different types of photoreactions. In order to gain some insight into the mechanism of the photochemistry of δ-thia-α,β-unsaturated ketones, the photochemistry of 6-acetoxy-9-thiabicyclo-[3.3.1]nona-3,7-dien-2-one (5) has been investigated.

The starting material (5) was prepared by monoacethylation of 2,6-dihydroxy-9-thiabicyclo[3.3.1]-nona-3,7-diene (6) followed by the oxidation. Irradiation of (5) in benzene with 350 nm light afforded the following four photo-products, 6-*exo*-acetoxy-2-thiabicyclo[3.3.1]nona-3,7-dien-9-one (7)(12-13%), 9-*endo*-acetoxy-2-thiabicyclo[3.3.1]nona-3,7-dien-6-one (8)(4-5%), 7-*exo*-acetoxy-2-thiabicyclo[4.3.0]nona-4,8-dien-3-one (9)(10-26%) and 7-*endo*-acetoxy-2-thiabicyclo[4.3.0]nona-4,8-dien-3-one (10)(17-20%), whereas in methanol irradiation of (5) resulted in the formation of (7) and (8). Of these products, the formation of (8) can be formally accomodated by 1,3-carbon shift, but the other products (7, 9 and 10) can not be explained by the previously proposed mechanisms. The most likely mechanism for the formation of these products involves ketene intermediates (11 and 12) which were detected by the appearance of the ir absorption maximum at 2150 cm^{-1} during irradiation of (5) in 2-Me-THF at 77°K.

In addition to the photochemical skeletal rearrangement of (5) to (7), the base-catalyzed skeletal rearrangement of 6-hydroxy-9-thiabicyclo[3.3.1]nona-3,7-dien-2-one (13) leading to 6-hydroxy-2-thiabicyclo[3.3.1]nona-3,7-dien-9-ones (14 and 15) with epimerization of the hydroxyl group was found. In connection with their mass spectra, the pyrolyses of 9-thiabicyclo[3.3.1]nona-3,7-dien-2,6-dione-9-oxide (16) and 9,9-dioxide (17) have been also studied.