PHOTOCHEMISTRY OF PYRIDAZINE BETAINES

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In a continuation of our study on the chemical reactivity of pyridazone derivatives, the photochemical behavior of pyridazine betaines (mesoionic pyridazines) system was investigated.

Various *anhydro*-1-substituted 5-hydroxypyridazinium hydroxides were prepared by means of known or modified methods. Irradiation of pyridazine betaines thus obtained in alcohols by Pyrex-filtered UV light resulted in the facile isomerization leading to 3-substituted 4(3*H*)-pyrimidones. The result provides a novel example demonstrating the photo-transposition of six-membered azaheterocyclic betaines. UV and NMR spectral changes during irradiation indicate that the photoisomerization occurs essentially in quantitative, regardless of the natures of the substituents at the position 3, 5 and 6 of the pyridazine ring. Thus, the present photoreaction can be utilized as a preparative method of 3-substituted 4(3*H*)-pyrimidones.

The photochemistry of some five-membered mesoionic heterocycles can be rationalized in terms of their initial valence-isomerization to bicyclic systems followed by their fragmentation with few exceptions. The photochemical ring-contraction of 3(2*H*)-pyridazinones in alcohols was also reported. In comparison with these previous photoreactions, some possible mechanisms of the present photoisomerization involving a ketene or a benzvalene-type intermediate were presented and discussed.

Pyridazine-pyrazine and pyrazine-pyrimidine photoisomerization have been well investigated. In the present case, however, the reaction sequence involving an intermediacy of pyrazine betaine can be excluded on the basis of no detection of such an intermediate and the structure of the produced 4(3*H*)-pyrimidones.

Photochemistry of isomeric pyridazine betaines, *anhydro*-1-substituted 3-hydroxypyridazinium hydroxides, will be also discussed.