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PHOTOCHEMISTRY OF MESOIONIC PYRIDAZINES

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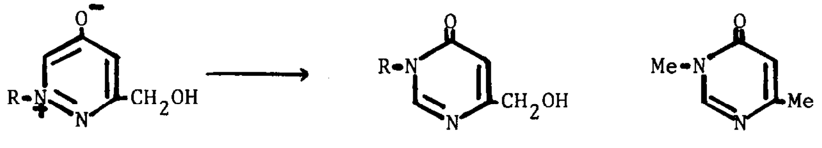
In recent years increasing attention has been directed toward the photochemistry of the mesoionic ring system.[1,2] The photochemical behavior of some five-menbered mesoionic heterocycles may be rationalized in terms of their initial valence isomerization to bicyclic systems followed by their fragmentation.[3]

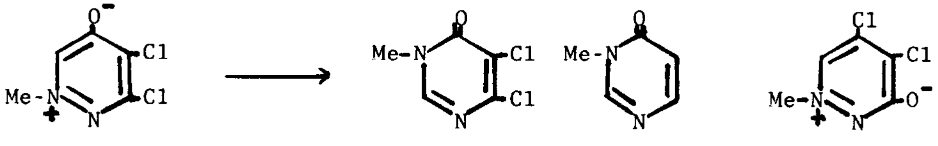
We found that irradiation of mesoionic pyridazines results in the facile formation of pyrimidones. To our best knowledge, this is the first example of the photoisomerization observed in the six-menbered mesoionic system, which has intriguing mechanistic implication.



(1) (2) (3)

a; R=Me b; R=Ph

c; R=p-Cl-Ph d; R=p-Me-Ph



(4) (5) (6) (7)

A solution of anhydro-1-substituted-3-hydroxymethyl-5-hydroxypyridazinium hydroxide(1a-d)[4](0.3 g) in ethanol(100 ml) was irradiated with a 100 W high-pressure mercury arc lamp through a Pyrex filter under nitrogen at room temperature until complete disappearance of the starting material. The reaction was followed by thin-layer chromatography and by taking NMR or UV spectra. The irradiated solution was concentrated and the residue was purified by recrystallization or, if necessary, by silica gel chromatography to obtain 3-substituted--6-hydroxymethyl-4(3H)-pyrimidones(2a); mp 118° (75%), (2b); mp 201° (55%), (2c); mp 183° (35%), and (2d); mp 203° (40%), respectively.

The UV spectrum of (1a) in ethanol during irradiation with 311 nm light changed successively with four isosbestic points at 228, 236, 269 and 292 nm, indicating a stoichiometric relation in the formation of (2a) from (1a). Comparative low yields of N-phenylpyrimidones(2b,c,d) result from that they are more light-sensitive to undergo further complicated photolysis than the N-methylpyrimidone(2a), Change of the NMR spectrum of (1b) during irradiation firmly supports this aspect.

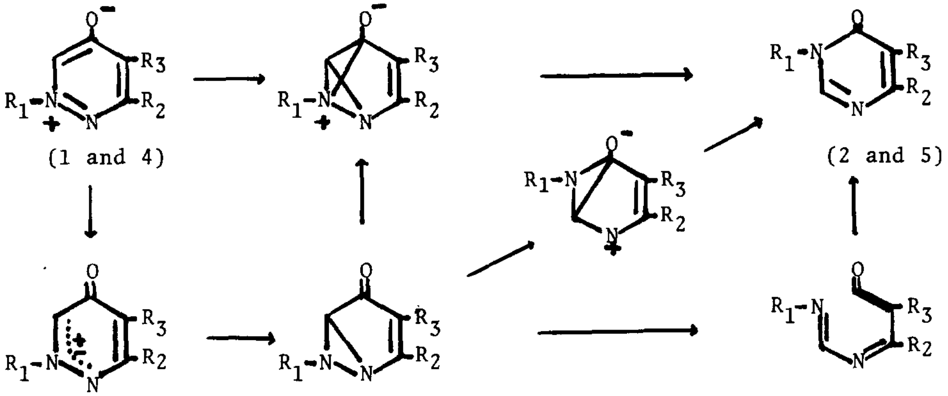
All photoproducts (2a-d)[5] showed characteristic UV absorption bands of 3-substituted-4(3H)-pyrimidones, e.g., The UV spectrum of (2a) in ethanol [λ_{max} nm(ε): 224(5600), 270(3400)] is superimposable on that of 3,6-dimethyl-4(3H)-pyrimidone(3)[6] [λ_{max}nm(ε): 224(5600), 268(3600)]. Transformation of (2a) into (3) by refluxing (2a) with Raney nickel in ethanol confirmed the structure of(2a).

Analogous photoisomerization leading to 3-methyl-5,6-dichloro-4(3H)-pyrimidone(5) was observed when anhydro-1-methyl-3,4-dichloro-5-hydroxypyridazinium hydroxide(4)[7] was irradiated in methanol under the conditions similar to the case of (2a-d). Concentration of the reaction mixture gave simply (5), mp 108°, as crystals almost quantitatively. Structure proof of (5) follows from its transformation into 3-methyl-4(3H)-pyrimidone(6)[8] by catalytic dechlorination.

The above results suggest that this type of the photoconversion is general in the anhydro-1-substituted-5-hydroxypyridazinium hydroxide system, regardless of the natures of the substituents. It is also noticeable that the photoproduct(5) is a versatile intermediate for synthesis of various fused pyrimidones.

The photochemical ring-contraction of 3(2H)-pyridazinones in alcohols to 1-amino-5-alkoxy-Δ^3-pyrrolin-2-ones has been well accounted for by reaction sequence analogous to the photoreaction of 2,4-cyclohexadienones, which involves a ketene intermediate.[9] It has been proposed that the photoisomerization of hexafluorocinnoline into hexafluoroquinazoline could proceed via a diazabenzvalene intermediate.[10]

Some possible mechanisms involving a ketene or a valene-type intermediate can be written for the present photoreaction as outlined below.



We are unable at present to obtain evidence favoring any one over the others. Work is underway in an effort to clarify the course of this photoisomerization.

Irradiation of isomeric anhydro-1-methyl-3-hydroxy-4,5-dichloropyridazinium hydroxide(7)[7] under the similar conditions to the previous cases gave only resinous products.

Acknowledgement

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References and Footnotes

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3 Only few examples of the photoisomerization, in which two atoms in the heterocyclic ring exchange simply their positions, have been reported in the five menbered mesoionic system. (cf. H. Kato, T. Shiba, H. Yoshida, and S. Fujimori, *Chem. Commun.* **1970**, 1591; O. Buchardt, J. Domanus, N. Harrit, A. Holm, G. Isaksson, and J. Sandstrom, *J. C. S. Chem. Commun.*, **1974**, 376)

4 Mesoionic pyridazines(1a-d) were readily prepared by condensation of calcium 2,5-diketogluconate with monosubstituted hydrazines(cf. K. Imada, *J. C. S.Chem. Commun.*, **1973**, 796)

5 All new compounds gave satisfactory microanalytical results and spectral data consistent with their structures.

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7 *Anhydro*-3,4-dichloro-5-hydroxy-1-methylpyridazinium hydroxide(4), mp 217°, was prepared in 60% yield by refluxing a mixture of 2,3-dichloro-4-hydroxypyridazine and dimethyl sulfate in toluene for 1 hr.(cf. German Patent, 2003461). NMR(CD_3OD) δ : 4.26($-C\underline{H}_3$), 8.52(ring-$\underline{H}$) IR(KBr)cm^{-1}: 3025, 1615, 1580 UV(EtOH) nm(ε); 273(5200), 324(6200).

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