# PHOTOCHEMISTRY OF CONJUGATED NITROGEN-CARBONYL SYSTEMS

## PHOTOADDITION REACTION OF HYDROXYLAZOBENZENES AND THE RELATED THIONE ANALOGS WITH OLEFINS

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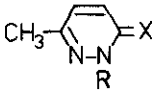
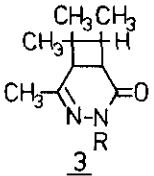
As part of systematic photochemical research on conjugated nitrogen-carbonyl systems, which stemed from our studies on nitrogen-carbonyl systems such as imides,(1) amides and nucleotides, we have started exploring photoreactions of a variety of azobenzens. In the present work photoaddition reactions of hydroxyazoaromatic compounds and their sulfur analogs with olefins were investigated.

On irradiation in acetonitrile, 3(2H)-pyridazinones 1a undergo [2+2]cycloaddition with olefins such as 2-methyl-2-butene 2 to afford cyclobutane derivatives 3 in a stereoselective manner. By contrast, the photoreaction of their sulfur analog 1b took a quite different course; namely, irradiation of 1b in the presence of 2 mainly gave rise to 4.



1a X=O
1b X=S



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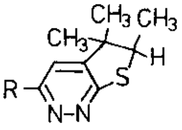

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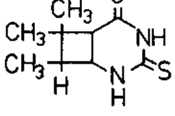
In the case of 2-thiouracil, photoaddition of 2 occured both at the $C_5$-$C_6$ double bond and the thione group leading to 5 and 6, respectively. From the parent member of the family, 2-mercaptopyridine and 2-mercaptopyrimidine, the rearranged thiol products 7 were formed under similar conditions.

Finally, 2,4-pyridinedione 8, one of the simplest conjugated nitrogen-carbonyl systems, was examined. As expected, this compound underwent either cyclobutane formation or dimerization depending upon reaction conditions.



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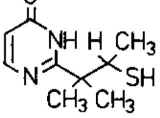

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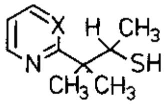

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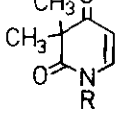

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REFERENCES

1) Y.Kanaoka, Acc.Chem.Res. 11. 407 (1978).