THE PHOTOCHEMISTRY OF FIVE-MEMBERED DIHYDROHETEROAROMATICS

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The photochemical reactions of certain five-membered dihydroheteroaromatics, including 2-thiazolines and 2-isoxazolines were investigated. 2-Thiazolines isomerize photochemically (2537Å) to N-alkenylthioamides. For example, both 2,4,4- and 2,5,5-trimethyl-2-thiazolines in acetonitrile gave a 5 : 6 mixture of N-(2-methyl-1-propenyl)thioacetamide and N-(2-methylallyl)thioacetamide, suggesting the intermediary formation of an N-thioacylaziridine which was experimentally proved. 2-Isoxazolines undergo photochemical valence tautomerization and fragmentation reactions giving 3-oxazolines, nitriles, nitrile oxides and olefins. For example, 3,5-diphenyl-2-isoxazoline in acetonitrile (2537Å) gave 2-phenylquinoline, benzonitrile, benzaldehyde and styrene, in addition to the previously reported products, 4,5-diphenyl-3-oxazoline and β-aminochalcone. The ratio of products was found to be substituent-dependent. Most of the reactions can be interpreted as formal [2 + 2] reactions. Mechanisms involved are discussed in some detail.