PHOTOCHEMICAL REACTIONS OF PYRIMIDIN-2-ONES

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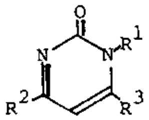
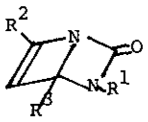
Photochemistry of nucleoside bases and their derivatives is an area of significant importance for understanding the photo-reactivity of nucleic acids. We have investigated the photochemical reactions of 2(1H)-pyrimidin-2-ones (1) related to cytosine, which is one of the nucleoside bases.

Irradiation of a solution of 1,4,6-trisubstituted-2(1H)-pyrimidin-2-one (1) in benzene afforded the isomer, 3,4,6-trisubstituted-2-oxo-1,3-diazabicyclo[2,2,0]hex-5-ene (2), in fair yields via the excited singlet state of (1). 4,6-Dialkyl-2-oxo-1,3-diazabicyclo[2,2,0]hex-5ene (2: R^1=R^2=alkyl) is stable up to about 150°C and converted back to the starting 2(1H)-pyrimidin-2-one (1) when (2) was heated in DMF at reflux temperature or in a sealed tube at 200°C. On the other hand, 3,4,6-triaryl-2-oxo-1,3-diazabicyclo[2,2,0]hex-5-ene (2: R^1,R^2,R^3=aryl) was heated in benzene at reflux temperature to give 2,4-diarylquinoline derivative (3). Irradiation of a solution of N-aryl-2(1H)-pyrimidin-2-one (1: R^2=R^3=H) in benzene-alcohol gave the product initiated by Type I cleavage, 1=(3-alkoxycarbonylamino-2-propene)-N-arylimine (4), which was hydrolyzed to afford 3-alkoxycarbonylaminoprop-2-en-1-one (5). When (1) was irradiated in the presence of alkoxide, di-imine derivative (6) was obtained in good yields. 1-Methyl-4,6-diphenyl-2(1H)-pyrimidin-2-one (1j: R^1=Me, R^2=R^3=Ph) was inert to the photolysis in benzene or methanol, however, irradiation of (1j) in acyclic or cyclic ethereal solution gave the 1:1-adduct (7) of (1j) and solvent, which was presumed to arise via intermolecular hydrogen abstraction by the nitrogen of imine functional group of (1j) followed by radical combination.



(1)



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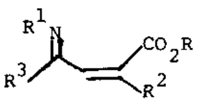

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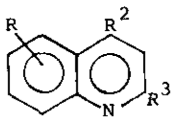

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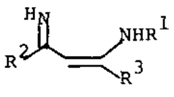

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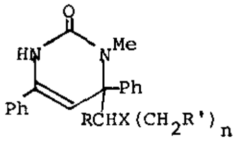

(7)