PHOTOCHEMICAL RING OPENING OF PYRIMIDIN-2(1H)-ONES

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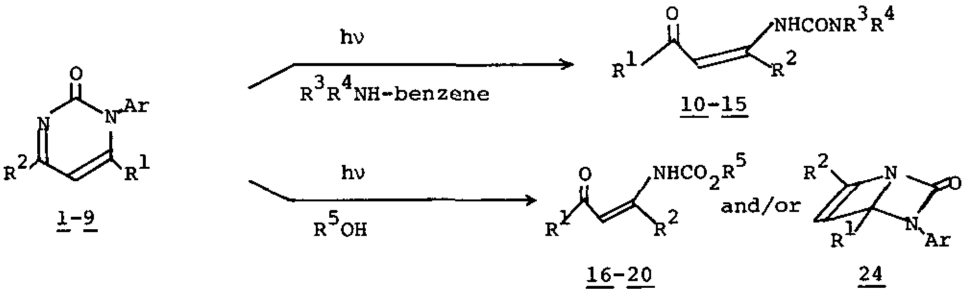
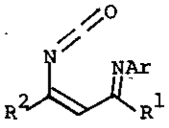
Recently, we have reported the photochemical electrocyclization of 1,4,6-trisubstituted pyrimidin-2(1H)-ones to the 2-oxo-1,3-diazabicyclo[2.2.0]hex-5-enes and the photochemical ring opening of N-arylpyrimidin-2(1H)-ones to the N-arylimines. In this context, we report herein the photochemical reactions of the pyrimidin-2(1H)-ones (1-9) in the presence of nucleophiles such as amine and alcohol. When 1,4,6-triphenylpyrimidin-2(1H)-one (1) was irradiated in benzene in the presence of propylamine, 1-propylaminocarbonylamino-1,3-diphenyl-3-phenyliminoprop-1-ene (10a)[1] was obtained in 81% yield. The product (10a) was treated with HCl in MeOH to convert back to the starting pyrimidin-2(1H)-one (1), while 10a was treated with KOH to give 1-propyl-4,6-diphenylpyrimidin-2(1H)-one (25). Similarly, irradiation of 1-aryl-4,6-disubstituted pyrimidin-2(1H)-ones (2-6) in the presence of amine gave the corresponding arylimines (11-15). However, irradiation of the pyrimidin-2(1H)-ones (1, 4-9) in alcohol gave the arylimines (16-20) and/or the 2-oxo-1,3-diazabicyclo-[2.2.0]hex-5-enes(24).





26

The mechanism for the formation of the arylimines (10-20) was proposed in Scheme, in which an unstable isocyanate intermediate (26), formed initially by Norrish Type I cleavage of the ArN-CO bond of the pyrimidin-2(1H)-ones (1-9) upon irradiation, was trapped with nucleophiles such as amine and alcohol to give the arylimines (10-20).