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PHOTOCHEMISTRY OF N-ARYL-2(1H)-PYRIMIDIN-2-ONES

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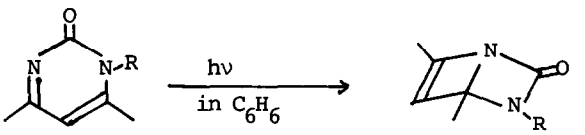
Summary: Irradiation of N-aryl-2(1H)-pyrimidin-2-ones (3a-c) in a mixed benzene-alcohol solution afforded the products initiated by Type I cleavage, 1-(3-alkoxycarbonylamino-2-propene)-N-arylimines (4a-c, 5, and 6) in 45-51% yields.

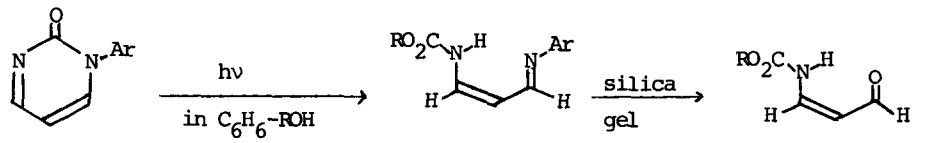
Because of their biological importance, the photochemistry of nucleoside bases has been extensively studied.[1] It is also of interest to study the photochemical behaviors of 2(1H)-pyrimidin-2-ones in relation to those of cytosine, which is one of nucleoside bases, and its derivatives. Furthermore, the 2(1H)-pyrimidin-2-one system is particulary attractive to study since the analogous ketone system, the conjugated cyclohexadienone, has been studied in such great detail[2] and can be used for comparison. We previously reported the photochemical synthesis of a stable 3-substituted-4,6-dimethyl-2-oxo-1,3-diazabicyclo[2,2,0]hex-5-ene (2) by the internal photoaddition reaction of 1-substituted-4,6-dimethyl-2(1H)-pyrimidin-2-one (1).[3]



1 2

This paper describes the photochemical reactions of N-aryl-2(1H)-pyrimidin-2-ones (3a-c). Irradiation of N-phenyl-2(1H)-pyrimidin-2-one (3a) in a mixed benzene-methanol solution in a Pyrex vessel with a high pressure mercury lamp under an argon atmosphere for 15 h at room temperature afforded a mixture containing 1-(3-methoxycarbonylamino-2-propene)-N-phenylimine (4a)[4], which was purified through a silica gel column chromatography to give 3-methoxycarbonylamino-2-propene-1-one (7) and aniline in 51 and 54% yields, respectively, and a starting pyrimidin-2-one (3a). When a solution of 3a in benzene-ethanol or benzene-2-propanol was irradiated under the same conditions, 1-(3-ethoxycarbonylamino-2-propene)-N-phenylimine (5)[5] [mp. 158-160°C; ν_{max}^{KBr} 3180, 1720, 1630,1260, 1170, 750, and 680 cm^{-1}; $\delta(CD_3OD\text{-}CDCl_3)$ 1.24(t, 3H),

4.71(q, 2H), 6.01(dd, 1H, J=9.4, 14.8 Hz), 6.9-7.6(m, 6H), 8.13(d, 1H, J=9.4 Hz)] and 1-(3-isopropoxycarbonylamino-2-propene)-N-phenylimine (6)[5] [mp. 160-161°C; ν_{max}^{KBr} 3450, 3180, 1715, 1635, 1265, 1170, 755, and 690 cm^{-1}; $\delta(CD_3OD\text{-}CDCl_3)$ 1.30(d, 6H), 5.0(m, 1H), 6.01(dd, 1H, J=9.4, 13.8 Hz), 7.05-7.7(m, 6H), 8.15(d, 1H, J=9.4 Hz)] was obtained in 45 and 51% yields, respectively.

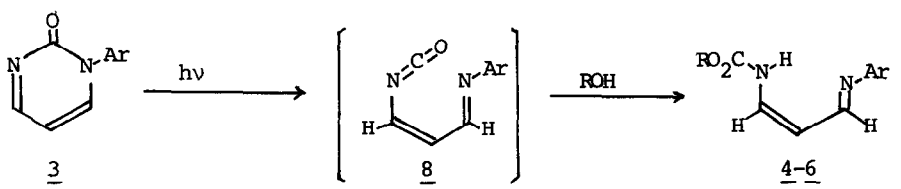


3a Ar=C_6H_5
3b Ar=p-MeC_6H_4
3c Ar=p-$MeOC_6H_4$

4a [Ar=C_6H_5 R=Me][4]
4b Ar=p-MeC_6H_4 R=Me
4c Ar=p-$MeOC_6H_4$ R=Me
5 Ar=C_6H_5 R=Et
6 Ar=C_6H_5 R=Pr^i

7 R=Me

Similarly, 1-(alkoxycarbonylamino-2-propene)-N-arylimines (4b-c)[5] were obtained in 45-51% yields when N-aryl-2(1H)-pyrimidin-2-ones (3b-c) were irradiated in benzene-methanol under the same conditions as described above. A reasonalble mechanism for the formation of the products (4-6) is proposed in Scheme 1, in which an unstable isocyanate intermediate (8), formed initially by Type I cleavage, traps an alcohol to give the final product.



3 8 4-6

Scheme 1

References

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2) G. Quinkert, B. Bronstert, D. Egert, P. Michaelis, P. Jürges, G. Presher, A. Syldark, and H-H. Perkampus, Chem. Ber., 109, 1332 (1976). G. Quinkert, Angew. Chem. Internat. Edn., 14, 790 (1975).

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4) The product (4a) could not be isolated, but the formation of 4a was detected by nmr spectrum.

5) Satisfactory elemental analyses were obtained on all new compounds.

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