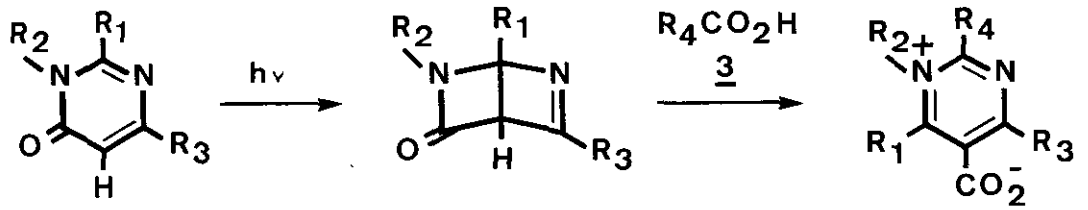
A NOVEL PHOTOCHEMICAL RING TRANSFORMATION OF 4-PYRIMIDINONES. FORMATION OF 5-CARBOXYPYRIMIDINIUM BETAINES

Tamiko TAKAHASHI,[a] Shun-ichi HIROKAMI,[a] Masanori NAGATA,[a] and Takao YAMAZAKI[b]

(a) Laboratory of Chemistry, Toyama Medical and Pharmaceutical University, Toyama 930-01, Japan; (b) Faculty of Pharmaceutical Sciences, Toyama Medical and Pharmaceutical University, Toyama 930-01, Japan

The photochemical ring transformation of 4-pyrimidinones to 5-carboxypyrimidinium betaines has been studied. Irradiation of the 4-pyrimidinones (1: R_1, R_2, R_3= alkyl or aryl) in acetic acid or in acetic acid-acetonitrile solution gave the betaines (4: R_1, R_2, R_3= alkyl or aryl; R_4= CH_3) in 27-57% yields. The starting materials 1 were recovered in 31-62% yields. The betaines 4 were obtained from the thermal reaction of acetic acid with the Dewar 4-pyrimidinones 2,[1] which were photochemically produced from 1. The result indicated that the Dewar 4-pyrimidinone 2 is the photochemical intermediate in the betaine formation. To investigate the mechanism and synthetic application of the reaction, the steric effect of α-substitution of the carboxylic acid 3 on the betaine formation was studied.



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1) (a) Hirokami, S.; Takahashi, T.; Nagata, M.; Hirai, Y.; Yamazaki, T. J. Org. Chem. 1981, 46, 1769. (b) Takahashi, T.; Hirokami, S.; Kato, K.; Nagata, M.; Yamazaki, T. ibid. 1983, 48, in press.