

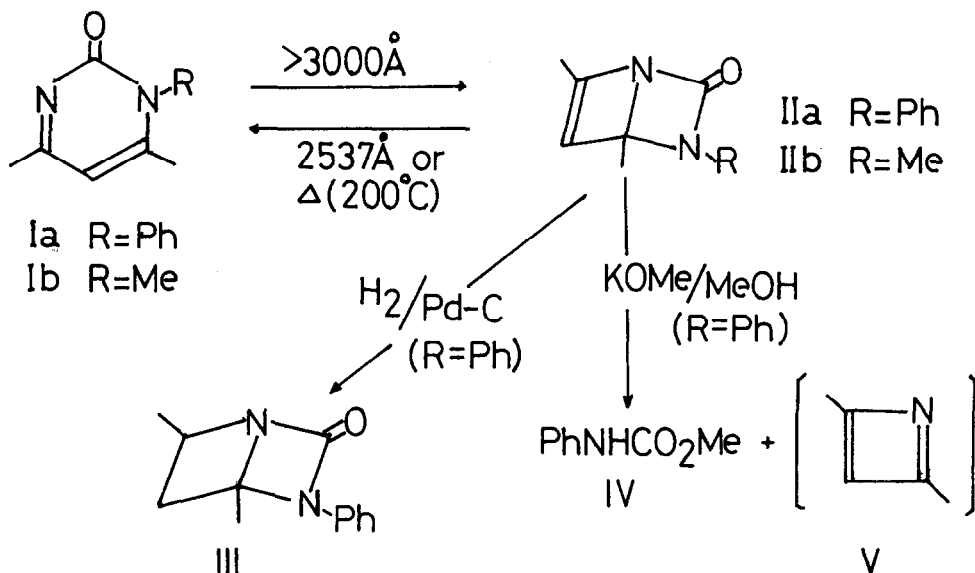
PHOTOCHEMISTRY OF 1-SUBSTITUTED-4,6-DIMETHYL-2(1H)-PYRIMIDIN-2-ONES:
SYNTHESIS OF 2-OXO-1,3-DIAZABICYCLO[2,2,0]HEX-5-ENES

Takehiko Nishio, Akira Katoh, Yoshimori Omote, and Choji Kashima
Department of Chemistry, University of Tsukuba, Sakura-mura,
Niihari-gun, Ibaraki, 300-31, Japan

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Photochemical reactions of conjugated cyclohexadienones and their aza analogues, e.g., 2-pyridones, have been extensively studied.¹⁾ However, those of diaza analogues, e.g., 2(1H)-pyrimidin-2-ones (I), draw little attention.^{2,3)} As part of a series of model studies of nucleoside bases,⁴⁾ we were interested in photochemical behaviours of pyrimidinones. In this paper we report on the photochemistry of 1-substituted-4,6-dimethyl-2(1H)-pyrimidin-2-ones (Ia and b).

Irradiation of a solution of 1-phenyl-4,6-dimethyl-2(1H)-pyrimidin-2-one (Ia) in benzene in a Pyrex vessel with a high pressure mercury lamp under argon for 15 hr at room temperature afforded in 67% yield an isomer, 3-phenyl-4,6-dimethyl-2-oxo-1,3-diazabicyclo[2,2,0]hex-5-ene (IIa), to which structure was assigned on the basis of elemental analysis as well as chemical and physical data cited below. The IR spectrum showed carbonyl absorption at 1760 cm^{-1} and the band at 1640 cm^{-1} due to C=C stretching. The NMR spectrum showed a singlet at δ 1.83 (3H), a doublet at δ 2.08 (3H, $J=1.5\text{ Hz}$), and a quartet at δ 6.00 (1H, $J=1.5\text{ Hz}$) assignable to 4-Me, 6-Me, and olefinic proton, respectively, in addition to aromatic proton peaks. The photoisomer (IIa) showed (in addition to parent mass peak) m/e peaks at 119, 81, and 80 corresponding to fragments phenyl isocyanate, 2,4-dimethyl-1-azacyclobutadiene, and 2,4-dimethyl-1-azacyclobutadienyl cation, respectively. As expected on the basis of formulation IIa, hydrogenation over palladium-charcoal of the photoisomer (IIa) gave 3-phenyl-4,6-dimethyl-2-oxo-1,3-diazabicyclo[2,2,0]hexane (III). The photoisomer (IIa) was indefinitely stable at room temperature. However, thermolysis of IIa under molten state in a sealed tube at 200°C or irradiation of IIa in methanol through quartz tube at 2537 \AA causes reversion to the starting pyrimidinone (Ia) in almost quantitative yield. Furthermore, treatment of IIa with potassium methoxide decomposed to give methyl N-phenylcarbamate (IV) and unidentified products which may be arise from 2,4-dimethyl-1-azacyclobutadiene (V).



Similarly, 3,4,6-trimethyl-2-oxo-1,3-diazabicyclo[2,2,0]hex-5-ene (IIb) was obtained in 33% yield when 1,4,6-trimethyl-2(1H)-pyrimidin-2-one (Ib) was irradiated in benzene under the same conditions as described above. Of especial interest is the photoisomer (IIa and b) as adduct of 2,4-dimethyl-1-azacyclobutadiene (V) with the stable molecule phenyl or methyl isocyanate. Removal of the stable species from IIa and b would seem to provide an approach to the synthesis of elusive azacyclobutadiene, either as an isolable substance or a metastable intermediate.

References

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- 2) K-H. Pfoertner, *Helv. Chim. Acta.*, **58**, 865 (1975).
- 3) In the photochemistry of diazacyclohexadienone system, Furrer reported that 1,3,5,6-tetramethyl-pyrazin-2-one gave an unstable photoisomer, 1,2,4,6-tetramethyl-3-oxo-2,5-diazabicyclo[2,2,0]hex-5-ene, which could not be isolated, and was trapped as dehydro derivative by hydrogenation. H. Furrer, *Chem. Ber.*, **105**, 2780 (1972).
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