CHEMISTRY LETTERS, pp. 1675-1678, 1982.

PHOTOCHEMICAL REACTIONS OF PYRIMIDIN-2(1H)-ONES: INTER- AND INTRAMOLECULAR HYDROGEN ABSTRACTION BY THE NITROGEN OF IMINO GROUP

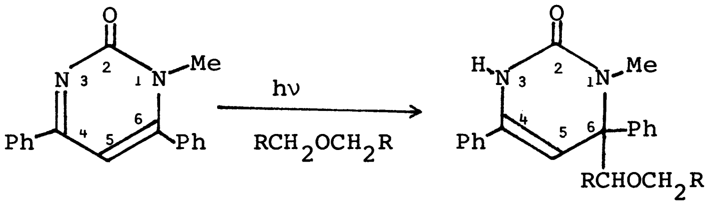
Takehiko NISHIO*, Katsuhiro KATAHIRA, and Yoshimori OMOTE
Department of Chemistry, University of Tsukuba, Sakura-mura, Niihari-gun, Ibaraki, 305

Irradiation of 1-methyl-4,6-diphenylpyrimidin-2(1H)-one (1a) in acyclic or cyclic ethers afforded the C-C bonded 1:1-adducts (2a-c) of 1a and ether via intermolecular hydrogen abstraction of the excited imino nitrogen of 1a, while irradiation of 1-phenyl-4-(3-ethoxypropyl)-6-methylpyrimidin-2(1H)-one (1g) gave 1-phenyl-4,6-dimethylpyrimidin-2(1H)-one (1d) via intramolecular hydrogen abstraction of the excited imino nitrogen of 1g, in addition to 2-oxo-1,3-diazabicyclo[2.2.0]hex-5-ene derivative (3g).

Photochemical reactions of conjugated cyclohexadienones and their aza analogues, e.g., 2-pyridones, have been studied in great detail.1) However, those of diaza analogues, e.g., pyrimidin-2(1H)-ones (1), have drawn little attention.2) It is of interest to study the photochemical behaviors of pyrimidin-2(1H)-ones (1) in relation to those of cytosine, which is one of nucleoside bases, and its derivatives.3) We previously reported the photochemical electrocyclization of 1,4,6-trisubstituted pyrimidin-2(1H)-ones to 2-oxo-1,3-diazabicyclo[2.2.0]hex-5-enes4) and photochemical ring opening of N-arylpyrimidin-2(1H)-ones to N-arylimines.5) This paper describes the photochemical addition reaction of 1-methyl-4,6-diphenylpyrimidin-2(1H)-one (1a) to acyclic and cyclic ethers and the intramolecular hydrogen abstraction of 1-phenyl-4-propyl- and 1-phenyl-4-(3-ethoxypropyl)-6-methylpyrimidin-2(1H)-ones (1f and g).

When a solution of the pyrimidin-2(1H)-one (1a) in benzene or methanol was irradiated with a high pressure mercury lamp through a Pyrex filter under an argon atmosphere at room temperature, no photoproducts could be obtained and the pyrimidin-2(1H)-one (1a) was recovered quantitatively. Meanwhile, irradiation of a solution of 1a in ether-benzene (2:1)6) under the same conditions as described above for 15 h gave the C-C bonded 1:1-adduct (2a)[m.p. 134.5-135.5 °C; IR(KBr) 3230, 1680, 1660, 1380, 1105, 760, and 700 cm^{-1}; NMR (δ in $CDCl_3$) 0.86 (t, 3H, J=

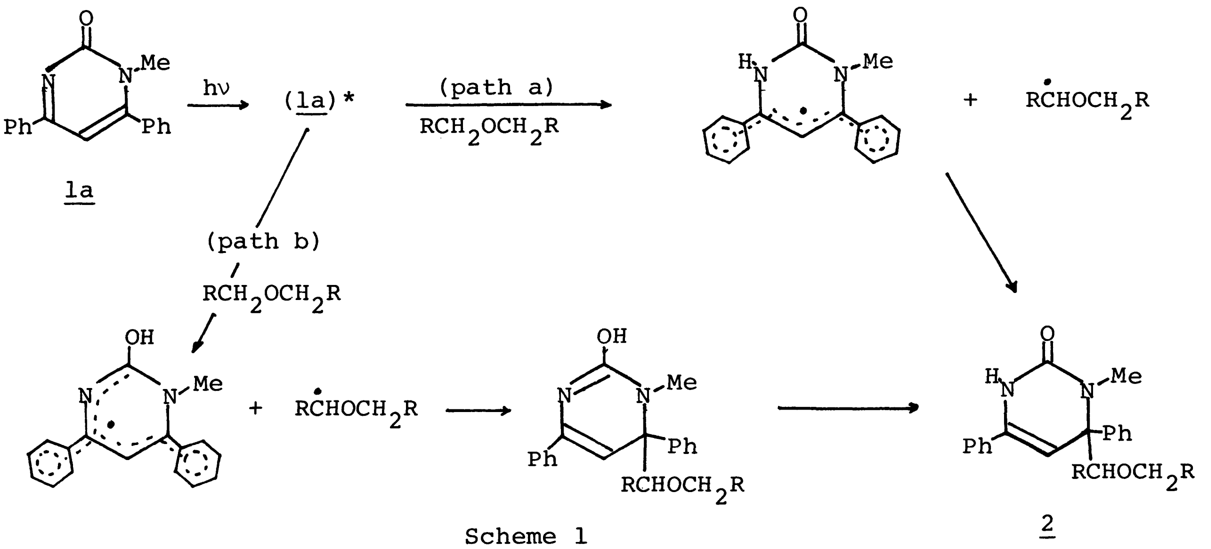
6.8 Hz, $C\underline{H}_3CH_2-$), 1.30 (d, 3H, J=6.4 Hz, $C\underline{H}_3\overset{|}{C}H-$), 2.85 (s, 3H, $>NC\underline{H}_3$), 2.90 and 3.37 (AB of ABX_3 pattern, J=6.8, 8.1 Hz, $CH_3C\underline{H}_2-$), 3.70 (q, 1H, J=6.4 Hz, $CH_3\overset{|}{C}\underline{H}-$), 4.92 (d, 1H, J=2.0 Hz, $=C\underline{H}-$), 5.72 (br s, 1H, $>N\underline{H}$, exchangeable with D_2O), and 7.18-7.48 (m, 10H, aromatic protons)] of 1a and ether in 56% yield. The structure of 2a was confirmed on the basis of spectroscopic and elemental analyses.[7] The ethoxy protons appear as ABX_3 pattern in the NMR spectrum. The site of ether in the C-C bonded 1:1-adduct (2a) was assigned to 6-position since the NMR spectrum of 2a showed the long-range coupling (J=2.0 Hz) between the amino proton and olefinic proton at C-5.[8]



1a 2

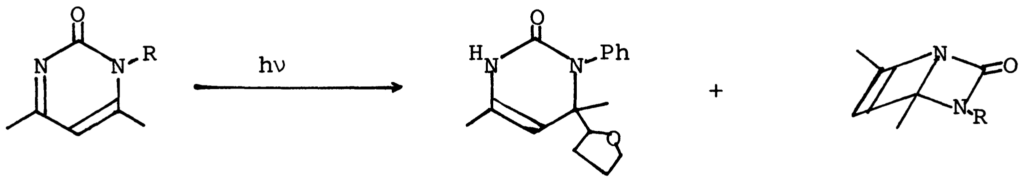
a; R=Me (56%)
b; R=$-(CH_2)_2-$ (45%)
c; R=$-CH_2OCH_2-$ (65%)

Similarly, irradiation of the pyrimidin-2(1H)-one (1a) in tetrahydrofuran or dioxane under the same conditions for 15 h gave the C-C bonded 1:1-adducts, (2b; m.p. 208-209 °C) (45%) and (2c; m.p. 188-189 °C) (65%). The possible mechanism for the formation of the C-C bonded 1:1-adducts (2a-c) of the pyrimidin-2(1H)-one (1a) and ethers is presented in Scheme 1, in which the excited pyrimidin-2(1H)-one (1a) might abstract α-hydrogen atom of ether by the nitrogen of the imino group (path a) or by the carbonyl oxygen of the ureide group (path b) followed by radical recombination to give the C-C bonded 1:1-adduct (2). Photochemical reactions of 1-phenyl- and 1-propyl-4,6-dimethylpyrimidin-2(1H)-ones (1d and e) and 1-phenyl-4-propyl- and 1-phenyl-4-(3-ethoxypropyl)-6-methylpyrimidin-2(1H)-ones (1f and g) were studied in order to gain some evidence for the formation of the C-C bonded 1:1-adduct (2). Irradiation of 1-phenyl-4,6-dimethylpyrimidin-2(1H)-one (1d) in tetrahydrofuran under the similar condition gave the C-C bonded 1:1-adduct (2d; m.p. 152-154 °C) and the 2-oxo-1,3-diazabicyclo[2.2.0]hex-5-ene (3d; m.p. 64.5-66 °C) in 6 and 45% yields, respectively. Irradiation of the pyrimidin-2(1H)-one (1e) in benzene gave the sole product, 2-oxo-1,3-diazabicyclo[2.2.0]hex-5-ene derivative (3e; b.p. 85 °C/2 mmHg) (35%) and 4,6-dimethylpyrimidin-2(1H)-one, which might be formed via intramolecular γ-hydrogen abstraction by carbonyl oxygen of ureide group



Scheme 1

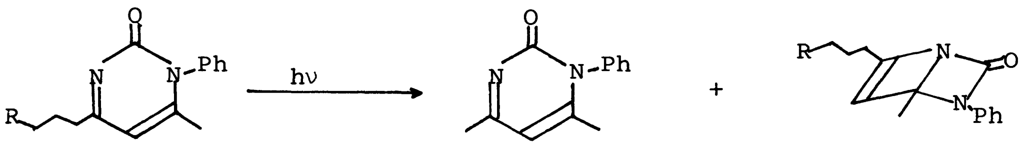
followed by the Type II photoelimination, was not observed. These observations suggest that the formation of the C-C bonded 1:1-adduct (2) of the pyrimidin-2(1H)-one (1) and ether is presumed to arise via intermolecular α-hydrogen abstraction of the ether by the nitrogen of the imino group of 1 followed by recombination of the radicals thus formed (path a). On the other hand, irradiation of the pyrimidin-2(1H)-ones (1f and g) in benzene afforded 1-phenyl-4,6-dimethylpyrimidin-2(1H)-one



1d R=Ph
1e R=Pr^n

2d (6%)

3d R=Ph (45%)
3e R=Pr^n (35%)



1f R=H
1g R=EtO

1d (trace)
1d (10%)

3f R=H (25%)
3g R=EtO (25%)

(1d) and 2-oxo-1,3-diazabicyclo[2.2.0]hex-5-enes (3f; b.p. 110 °C/2 mmHg and 3g; b.p. 165 °C/2 mmHg). The formation of 1d upon irradiation of 1f and 1g can be explained in terms of intramolecular γ-hydrogen abstraction by the nitrogen of imino group followed by the Type II photoelimination.9)

Acknowledgment. We thank Dr. H. Aoyama for his useful suggestion. This work is supported by a grant from the Ministry of Education, Science and Culture, No 56410.

References

1) D. Bryce-Smith, "Photochemistry", The Chemical Society, London, Vol. 1-11, 1970-1980. O. Buchardt, "Photochemistry of Heterocyclic Compounds", John Wiley & Sons, New York, 1976.

2) K-H. Pfoertner, Helv. Chim. Acta, 58, 865 (1975). Y. Kanaoka, M. Hasebe, and Y. Hatanaka, Heterocycles, 13, 263 (1979).

3) K.I. Ekpenyong, R.B. Meyer Jr., and M.D. Shetler, Tetrahedron Lett., 1978, 1619.

4) T. Nishio, A. Kato, Y. Omote, and C. Kashima, Tetrahedron Lett., 1978, 1543. T. Nishio, A. Kato, C. Kashima, and Y. Omote, J. Chem. Soc. Perkin I, 1980, 607.

5) T. Nishio, K. Katahira, A. Kato, C. Kashima, and Y. Omote, Tetrahedron Lett., 1979, 4211. T. Nishio, K. Katahira, and Y. Omote, J. Chem. Soc. Perkin I, 1981, 943.

6) 1-Methyl-4,6-diphenylpyrimidin-2(1H)-one (1a) was insoluble in ether.

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

8) L.M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press Ltd., Oxford, 2nd ed., 1969, p.338. When the signal of the amine proton at δ 5.72 was irradiated, the signal of the olefinic proton at δ 4.92 (d) changed into singlet.

9) Analogous hydrogen abstraction reactions by the nitrogen of imino group have been observed in the photochemistry of keto imino ether10) and N-acylimine,11) however, those reactions have not yet observed in the pyrimidin-2(1H)-one photochemistry.

10) T.H. Koch, R.J. Sluski, and R.H. Mosely, J. Am. Chem. Soc,. 95, 3957 (1973).

11) M. Saeki, N. Toshima, and H. Hirai, Bull. Chem. Soc. Jpn, 48, 476 (1975).

(Received August 9, 1982)