33. Cashel, M.; Lazzarini, R. A.; Kalbacher, B. *J. Chromatog.* **1969**, *40*, 103.

34. Randerath, K.; Randerath, E. *J. Chromatog.* **1964**, *16*, 111.

Photocycloaddition Reaction of N¹-(4-Methyl-3-pentenyl)-uracil and -thymine

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Intramolecular [2+2] photocycloadditions of cyclic α,β-enone tethered to suitable alkenes afford the construction of carbocyclic and heterocyclic ring systems with high regio- and/or stereoselectivity.[1] When combined with the subsequent cleavage of the cyclobutane ring of the photoproducts by various chemical means, the overall transformation constitutes an annelative two-carbon ring or carbon-hetero ring expansion of original enones. This process is now the most widely used photochemical reaction in synthetic organic chemistry.[2] In conjunction with ongoing studies in our laboratories on the synthesis of heterocyclic compounds containing diaza group in analogy with previously reported routes,[3] we now report the intramolecular equivalent of this process using N¹-(4-methyl-3-pentenyl)-uracil (**1a**) and -thymine (**1b**).

N¹-alkenylpyrimidines (**1a, 1b**) were prepared by alkylation of uracil and thymine, respectively, with 5-bromo-2-methyl-2-pentene in the presence of potassium carbonate.[3a] Direct and/or Pyrex-filtered irradiation of **1** with a 200W medium pressure Hg lamp in CH_3CN at room temperature gave on distillation of the solvent and seperation by tlc the intramolecular adduct **2**.[4]

1   4   2   3

a. R=H
b. R=CH₃
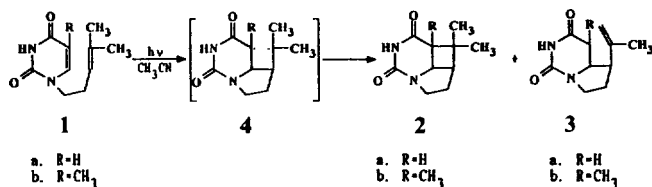
The structural assignment rests on ¹H NMR spectral data. The alternative cross adduct[2a,2b] is ruled out from consideration by careful examination of the distinguishing pattern of ¹H NMR spectrum of **2** as observed in the case of 1,3-diaza-tricyclo[5.2.1.0⁵,¹⁰]decan-2,4-dione.[3a]

In contrast to the previous study with N¹-(3-butenyl)-thymine, irradiation of **1** for 10 hr afforded not only **2** but also **3** in the ratio of 1 : 8. It appears that **3** results either from a hydrogen shift in the intermediate biradical **4** or from Type II cleavage of initially formed **2**. We could also recon-
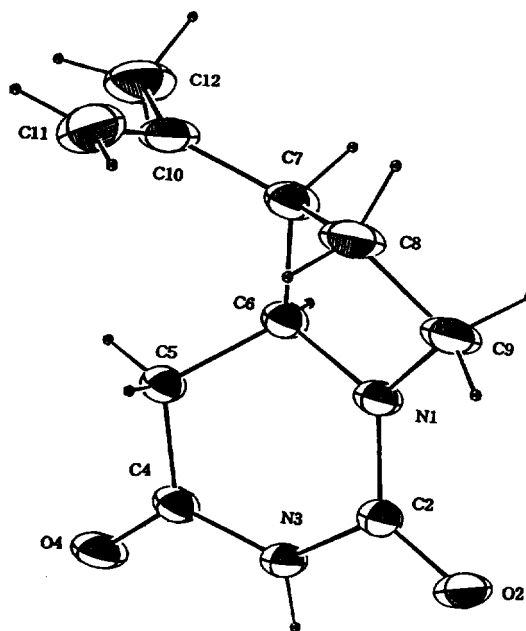
Figure 1. A Molecular Structure of 7(1-methylethenyl)-1,3-diaza-bicyclo[4.3.0]nonan-2,4-dione with atom labeling.
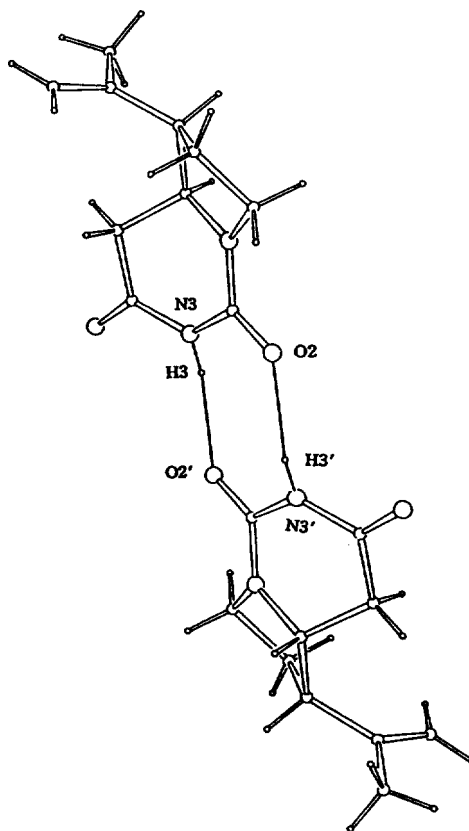
Figure 2. Hydrogen bonding interaction (thin line) between two molecules $(d(N3-O2')=2.858$ (2) Å, $\angle(N3-H3-O2')=159.83(5)°)$.

firm that extensive photolysis of **2** (CH_3CN/Pyrex) leads to **3** by Type II cleavage of the bond in the cyclobutane ring initiated by a hydrogen abstraction of carbonyl group as shown in **5**. Thus, irradiation of **2** in CH_3CN with 200W

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medium pressure Hg lamp for 6 hr furnished a 5.5 : 4.5 mixture of **2** and **3** in more than 99% yield, together with negligible other products.
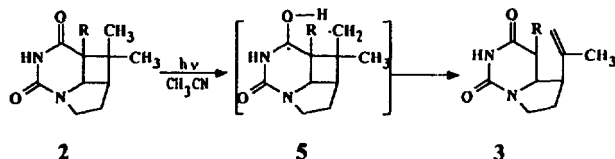
Irradiation of **1** with a 12W low pressure Hg lamp gave the same result. The detailed consequence of the resulting photocycloaddition will be published in a forthcoming paper. Unambiguous assignment of the structure of **3a** was performed by single-crystal X-ray diffraction techniques.[5]

The structure was proved to be fused by a N^1-C6 bond of 5- and 6- membered ring and to have a butterfly conformation with an almost planar pyrimidone part (Figure 1). Two molecules are held together by an inversion center through two hydrogen bonding interactions between N and O atoms of pyrimidine moiety (Figure 2).

References

1. (a) Schuster, D. I.; Len, G.; Kaprinidins, N. A. *Chem. Rev.* **1993**, *93*, 3. (b) Becker, D.; Haddad, N. *Org. Photochem.* **1989**, *10*, 1. (c) Crimmins, M. T. *Chem. Rev.* **1988**, *88*, 1453. (d) Carless, H. A. *Photochemistry in Organic Synthesis*; Coyle, J. D.; Royal Soc. Chem: London. **1986**; p 95-117. (e) Weeden, A. C. *Synthetic Org. Chemistry*; Horspool, W. M., Ed., Plenum Press; New York, **1984**, p 61-144. (f) Oppolzer, W. Acc. *Chem. Res.* **1982**, *15*, 135. (g) Boldwin, S. W. *Org. Photochem.* **1981**, *5*, 23.

2. (a) Ikeda, M.; Uchiro, T.; Takahashi, M.; Ishibashi, H.; Tamura, Y.; Kido, M. *Chem. Pharm. Bull.* **1985**, *33*, 3279. (b) Ikeda, M. ; Takahashi, H. Uchiro, T.; Ohro, K.; Tamura, Y.; Kido, M. *J. Org. Chem.* **1982**, *47*, 3597. (c) Coates, R. M.; Senter, P. D.; Baker, W. R. *J. Org. Chem.* **1983**, *47*, 3597. (d) Begley, M. J.; Mellor, M.; Pattender, G. *J. Chem. Soc., Chem. Commun.* **1979**, 235. (e) Tamura, Y.; Ishibashi, H.; Hirai, M.; Kita, Y.; Iketa, M. *J. Org. Chem.* **1975**, *40*, 2702. (f) Tamura, Y.; Kita, Y. Isibashi, H.; Keta, M. *J. Chem. Soc., Chem. Commun.* **1971**, 1167.

3. (a) Ahn, C. I.; Choi, H.; Hahn, B. S. *Heterocycles.* **1990**, *31*, 1737. (b) **1a**: yield 42%; mp 118-119 °C ; ¹H NMR (80 MHz, CDCl₃) δ 1.56 (s, 3H), 1.72 (s, 3H), 2.38 (q, J=6.8 Hz, 2H), 3.70 (t, J=7.2 Hz, 2H), 4.97-5.18 (m, 1H), 5.64 (d, J=8.8 Hz, 1H), 8.86 (s, 1H); IR (KBr), 1690, 1638 cm⁻¹ ($v_{C=O}$); EIMS m/z 194 (M⁺). **1b**: yield 46%; mp 159-160 °C ; ¹H NMR (80 MHz, CDCl₃) δ 1.59 (s, 3H), 1.71 (s, 3H), 1.88 (s, 3H), 2.35 (q, J=12.4 Hz, 2H), 3.67 (t, J=6.8 Hz, 2H), 4.93-5.17 (m, 1H), 6.83 (s, 1H), 8.70 (s, 1H); IR (KBr), 1685, 1643 cm⁻¹ ($v_{C=O}$); EIMS m/z 208 (M⁺).

4. **2a**: yield 37%; mp 168-170 °C ; ¹H NMR (200 MHz, CDCl₃) δ 0.90 (s, 3H), 1.28 (s, 3H), 1.84-1.94 (m, 2H), 2.63 (td, J=6.2, 5.7 Hz, 1H), 2.83 (d, J=5.8 Hz, 1H), 3.13 (ddd, J=12.2, 8.7, 8.7 Hz, 1H), 3.91 (dd, J=5.7, 5.6 Hz, 1H), 4.05-4.17 (m, 2H), 7.18 (s, 1H); IR (KBr), 1713, 1683 cm⁻¹

($v_{C=O}$); EIMS m/z 194 (M⁺). **2b**: yield 33%; mp 204-206 °C ; ¹H NMR (200 MHz, CDCl₃) δ 0.90 (s, 3H), 1.05 (s, 3H), 1.34 (s, 3H), 1.82-1.93 (m, 2H), 2.61 (td, J=6.1, 5.6 Hz, 1H), 3.16 (ddd, J=12.2, 8.7, 8.7 Hz, 1H), 3.55 (d, J=6.2 Hz, 1H), 4.06-4.19 (m, 1H), 7.20 (s, 1H); IR (KBr), 1703 cm⁻¹ ($v_{C=O}$); EIMS m/z 208 (M⁺). **3a**: yield 45%; mp 148-150 °C ; ¹H NMR (200 MHz, CDCl₃) δ 1.67 (d, J=0.7 Hz, 3H), 1.90-2.11 (m, 2H), 2.22-2.47 (m, 2H), 2.85-2.94 (m, 1H), 3.41-3.53 (m, 1H), 3.61-3.75 (m, 1H), 3.85-3.98 (m, 1H), 4.72 (s, 1H), 4.92 (dd, J=1.31, 1.1 Hz, 1H), 7.78 (s, 1H); IR (KBr), 1713, 1693 cm⁻¹ ($v_{C=O}$); EIMS m/z 194 (M⁺). **3b**: yield 41%; mp 220-222 °C ; ¹H NMR (200 MHz, CDCl₃) δ 1.10 (d, J=6.7 Hz, 3H), 1.67 (s, 3H), 1.90-2.18 (m, 2H), 2.32-2.42 (m, 1H), 2.89 (dd, J=6.3, 6.2 Hz, 1H), 3.45 (dd, J=12.7, 5.8 Hz, 1H), 3.54-3.62 (m, 2H), 4.70 (s, 1H), 4.86 (d, J=1.3 Hz, 1H), 7.17 (s, 1H); IR (KBr), 1721, 1691 cm⁻¹ ($v_{C=O}$); EIMS m/z 208 (M⁺).

5. Data for crystallographic studies were measured on a MAC sciences MXC³ four-circle diffractometer. The unit cell and other related parameters of compound (3a) are as follows: F.W=194.23; Coloress plate; Crystal dimension=$1.0 \times 1.0 \times 0.2$ mm³; Space group P2₁/n (No. 14); a= 14.456 (5) Å, b=7.999 (3) Å, c=8.858(3) Å, β=100.58 (3)°, V=1006.9 (5) Å³; Z=4; D_{calc}=1.28 mg/m³; Radiation= MoKα, λ=0.71069 Å; μ=0.091 mm⁻¹; F(000)=416; Temperature=293 K; Final R=0.0367; Number of unique reflections=1582.

Prediction of Asymmetric Resonances in the Predissociation of the $A^2\Sigma^+$ State of OH

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Photodissociation to open-shell atomic fragments has yielded valuable informations on the nonadiabatic interactions among electronically excited states.[1,2] When the fragments have nonvanishing angular momenta, there may be more than one electronic state correlating with an atomic term limit. Nonadiabatic interactions among these states can affect the dissociation processes since these interactions can be equal to or larger than the separations between the electronic states at intermediate and asymptotic internuclear distances. Freed and coworkers[2-5] have shown for direct dissociation processes that the nonadiabatic couplings could affect the outcomes of the dissociation processes, such as the population ratios of the atomic fine structure components and the anisotropy parameters.

When there is an explicit curve crossing between states correlating with different atomic term limits, as in predissociating systems, *two* different kinds of nonadiabatic interactions must be considered. The influence of the interactions