

Takaaki Suishu, Seiichiro Tsuru, Tetsuro Shimo, and Kenichi Somekawa*

Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering,
Kagoshima University, Korimoto, Kagoshima 890, Japan

Received April 17, 1996

Revised March 19, 1997

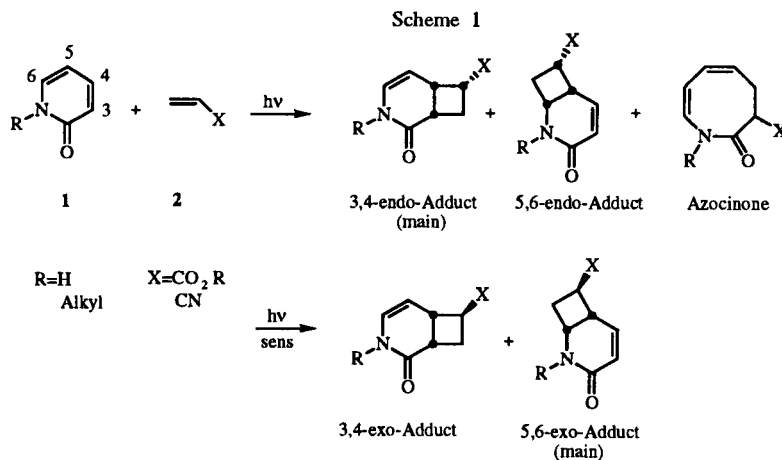
Regioselective photocycloadditions of 2-pyridones (**1**) with 2,4-pentadienoates (**3**) were analysed and compared with the reactions with propenoate (**2**), and origins of the different regioselectivities were inferred from frontier molecular orbital properties by the use of PM3-CI method.

Direct photoreactions of **1** with **3** being $\alpha,\beta,\gamma,\delta$ -unsaturated carboxylates gave four types of regioselective [2+2]cycloadducts, 3- β :4- α -**4**, **5**, 3- δ :4- γ -**6**, **7**, 5- β : 6- α -**8**, **9** and 5- δ :6- γ -[2+2]cycloadducts **10**, **11**. Sensitized photoreactions of **1** with **3** did not occur, and fluorescence of **1** was weakly quenched by **3**. Otherwise, main cycloadducts in the sensitized reactions of **1** with **2** have been obtained as 5- α :6- β -[2+2]cycloadducts, which were different from main 3- β :4- α -[2+2]cycloadducts of the direct reactions, and these site- and regio-selectivities were inferred from the different frontier molecular orbital coefficients at the 3- and 6-positions of **1** for the triplet and singlet states. Formations of **4-7** were also interpreted by both effects of frontier orbital HSOMO-LUMO interactions and of the electrostatic interaction between **1** and **3**. The other site- and regioselective adducts **8-11** were inferred to be formed by the electrostatic interactions similar to 2-pyridone photodimerization.

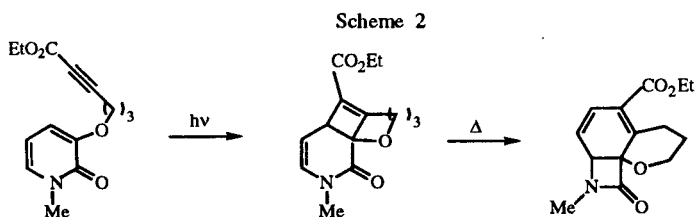
J. Heterocyclic Chem., **34**, 1005 (1997).

Inter- as well as intra-molecular [2+2]photocycloadditions have become a part of the standard repertoire of synthetic organic chemists, and this process is now one of the most widely used photoreactions in synthetic organic chemistry [1]. The typical enone [2+2]photocycloaddition reactions were recently summarized and introduced new insights into an old mechanism [2]. But there was no molecular orbital aspect on the photochemical features though molecular orbital analysis on thermal cycloaddition reactions has been successful [3]. 2-Pyridone (**1**) has a simple heterocyclic skeleton composed of 2,4-cyclohexadienone, which has many possibilities for the photocycloaddition. We have investigated photoaddition reactions of the excited singlet and triplet 2-pyridones with various ethylenes and they showed intrinsic site-, regio-, and stereo-selective photoadditions as shown in Scheme 1 in

Japanese [4]. We also previously reported intramolecular [2+2]photocycloadditions of 2-pyridones and the derivations of the adducts to a new type of tricyclic β -lactam etc. (Scheme 2) [5]. Kaneko et al. have reported many photocycloadditions of **1** and 2-quinolones with lots of ethylenes and derivations of the adducts to some interesting and natural compounds [6]. Kanaoka et al. also reported that **1b** photochemically reacted with cyclopentadiene to give a 3,4-[2+2]cycloadduct via [1,3] sigmatropy of the photo[4+4]cycloadducts [7]. Mechanistic investigations of the photoadditions and the molecular orbital aspect have not been extended beyond our reports [4,8]. Houk's theoretical prediction of regioselectivity in the bond-forming step in cyclohexenone photocycloadditions [9] is also in contrast to Weedon's experimental implication of no selectivity in α or β attack in cyclopentenone



photocycloadditions [10]. We recently suggested that the photoexcited state [2+2]cycloaddition regioselectivities of the cyclic conjugated enones are mainly determined in the initial biradical producing steps of these processes but that they can be altered by partitioning of the biradical intermediates to products vs. ground state reactants [11]. Accumulation of these informations for basic photocycloadditions is now necessary.



We now report interesting photocycloadditions between **1** and 2,4-pentadienoates **3**, and compare the results with those [4] between **1** and propenoate **2**, and the main factor in the photoexcited addition reactions is also analysed by use of frontier molecular orbital methods. Photochemical Products. A solution of 2-pyridone (**1a**) and methyl sorbate (**3b**) in acetonitrile was irradiated with a 400 W high-pressure mercury lamp under nitrogen to afford eight types of [2+2]cycloadducts, **4ab-11ab**. The results of photoreactions between 2-pyridones **1**, **1a**, or **1b** and 2,4-pentadienoates **3**, **3a**, or **3b** are summarized in Scheme 3 and Table 1. The direct photoreactions gave four types of site- and regio-selective [2+2]photoadducts **4-11**. Acetonitrile as a solvent is more satisfactory for the addition reactions than methanol. The product-separation methods were similar to those used in our previous studies [4,5] and the chemical structures were mainly elucidated through ^1H nmr spectral data including ^1H NOE effects and H-H COSY (2D) mainly in the cyclobutane protons. For example, the structures of **4ab** and **5ab** obtained from the reaction of **1a** with **3a** were inferred as head-to-head [2+2]cycloadducts across the $\text{C}_3\text{-C}_4$ double bond in **1a** with α,β -double bond in **3b** *ie*, 3- β :4- α bond formation. Configuration at the exocyclic ethene bonds of **4ab** and **5ab** were first determined from the vicinal *trans*-CH=CH spin couplings. **4ab** have relatively higher field signals of 5-H and lower field one of 6-H than those of **5ab**. They are inferred to be sterically caused from 7-endo- CO_2Me of **4ab** and 7-exo- CO_2Me of **5ab**.

Table 1

Results of Photoreactions between 2-Pyridones and 2,4-Pentadienoates

Entry	Pyridone (R ¹)	Dienoate (R ²)	(subcript)	Product (%)							
				4	5	6	7	8	9	10	11
1	1a (H)	3b (Me)	ab	6	3	2	1	4	2	4	5
2	1b (Me)	3b (H)	ba	5	3	6		22	32		
3	1b (Me)	3b (Me)	ba	11	3	3	5	15	15	12	

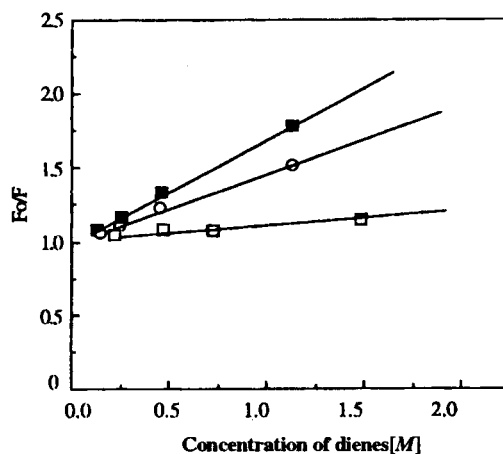


Figure 1. Fluorescence Stern-Volmer plots of 2-pyridone with dienes **1**: $3.0 \times 10^{-5} \text{ M}$ in methanol $k_q \tau (\text{M})^{-1}$

- ; **1b** with **3a**: 2.0
- ; **1a** with **3b**: 5.1
- ; **1b** with **3b**: 7.4

Those effects were similar to that of photoadducts of methyl acrylate (**2**) [4]. The NOE data for **4ab** also showed a short distance between the 5-H and 7- CO_2Me , *etc*. Other cycloadducts **6** and **7**, **8** and **9**, and **10** and **11** were similarly inferred to be 3- δ :4- γ , 5- β :6- α and 5- δ :6- γ bonded products, respectively. The endo- CO_2Me configurations in **4**, **6**, and **9** were also inferred from the ^1H nmr data at the cyclobutane protons and the NOE observations. The main products were found to be **4**, **8**, and **9** which were monitored by gc and ^1H nmr and checked that the product signals became large as time went on. It means that the photoreactions of **1** with **3** directly gave the regioselective [2+2]cycloadducts, **4-11**. It is in contrast to the result that gave a [4+4]cycloadduct in the reaction of **1** with cyclopentadiene [7]. The formation of photo[4+4]cycloaddition is explained from the interaction of larger frontier molecular orbital coefficients at the both diene terminal carbons of 2-pyridones (Figure 2 as described later) and symmetric cyclopentadiene. The [2+2]cycloadducts of **1** with **3** may be inferred from the more stable *s*-transoid conformation (the value of $\Delta\Delta G = -0.78 \text{ kcal/mol}$ was calculated), the frontier molecular orbital asymmetric coefficients of **3**, and electrostatic interactions shown in Figure 3 and Scheme 4.

The benzophenone sensitized photoreactions of **1** ($E_T = 60 \text{ kcal/mol}$) [5] with **3** gave no photoadduct. The photoreactivity is not same as those with ethylenes [4] and that of the intramolecular photoadditions [5].

Fluorescence of **1** and the Quenching.

We have reported that 2-pyridones show fluorescence unless they have electron-withdrawing substituents, and some electron-poor ethylenes quench the fluorescence to give photocycloadducts. The photoadditions were

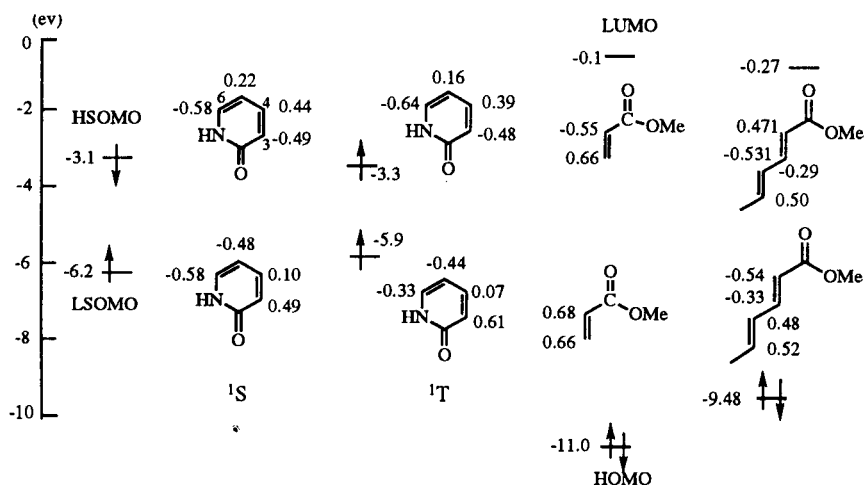


Figure 2. Estimated frontier-orbital energies and coefficients of 2-pyridone (1a) singlet 1S , triplet 1T , and methyl acrylate (2) 0S and methyl 2,4-pentadienoate (3b) 0S

concluded to occur when the quenching constants ($k_{q\tau}$) have the values of $0 < k_{q\tau} < 7.6$, and to occur *via* singlet excited states of 1 [4]. Then, quenching effect of 3 for the fluorescence of 1 was measured, and it gave the Stern-Volmer plots as shown in Figure 1. The values of $k_{q\tau}$ between 1b and 3a, 1a and 3b, and 1b and 3b were 2.0, 5.1 and 7.4, respectively. As they are within the range ($0 < k_{q\tau} < 7.6$), the photoadditions are concluded to be similarly singlet photoreactions.

Singlet and Triplet of 2-Pyridones and Factors of the Photoaddition Reactions.

Figure 2 and Figure 3 show frontier orbital energies and coefficients of the first-singlet and triplet excited states of 2-pyridone 1a by the PM3-CI-UHF method, and those of ground states of methyl acrylate 2 [4] and methyl 2,4-pentadienoate 3b by the PM3-CI-RHF method [13].

Formation of regioselective 3,4-endo-adduct in the photo-reaction of 2-pyridone singlet 1S with acrylate 2 (Scheme 4) can be explained from both effects of the 1S HSOMO-LUMO interaction in Figure 2 and of the electrostatic interaction in Figure 3. Formation of regioselective 5,6-exo-adduct in the case of 2-pyridone 1T with acrylate 2 is now interpreted from the good HSOMO (pyridone 1T)-LUMO (2) interaction between the 6-position of pyridone and the β -position of 2 because of the larger coefficient (0.64) at the 6-position in the pyridone 1T than that (0.58) in the 1S in Figure 2. The photocycloadditions of triplet 1 with acrylonitrile etc. gave 5,6-adducts regioselectively, and then it is similar to that of 2-pyrones as shown in Scheme 5 [8]. The reaction of triplet 1 with electron-donating ethylenes however gave no adducts [4]. It is in contrast to the reactivity of the triplet 2-pyrones. The different reactivity of 1 from 2-pyrones is inferred to come from more electron-donating

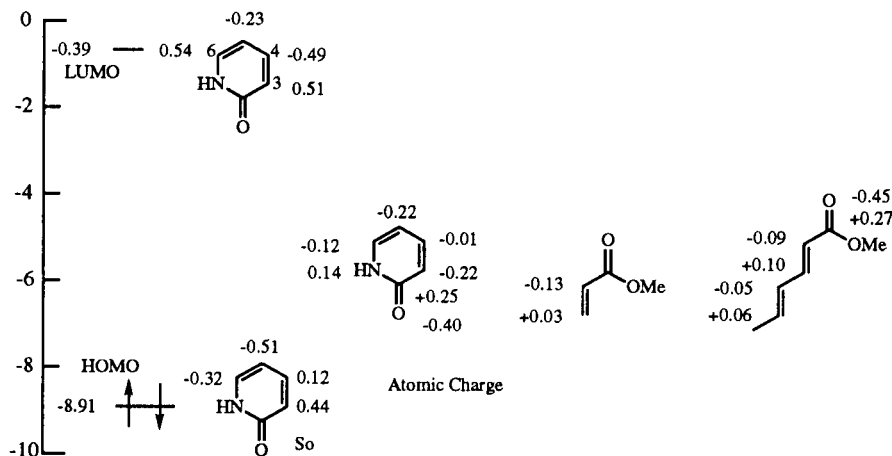
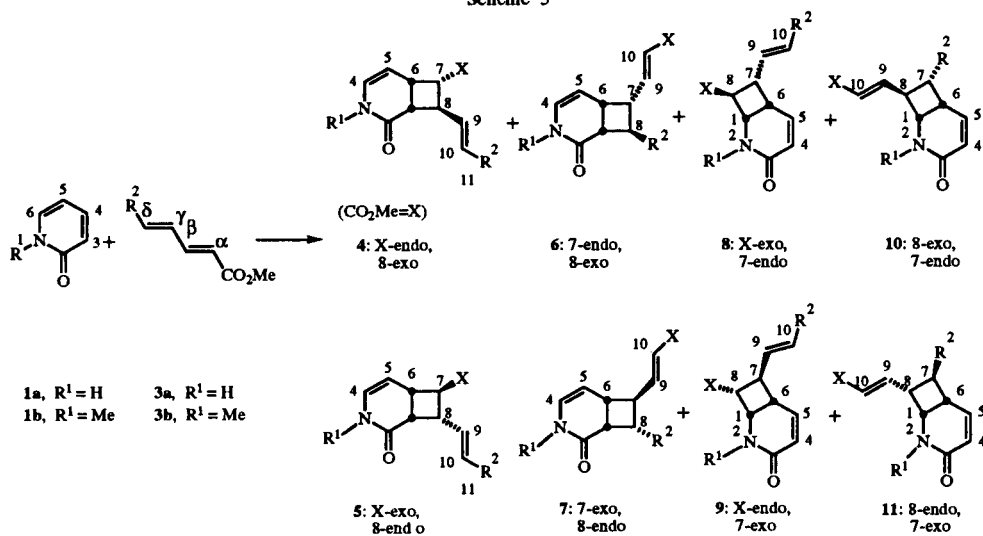
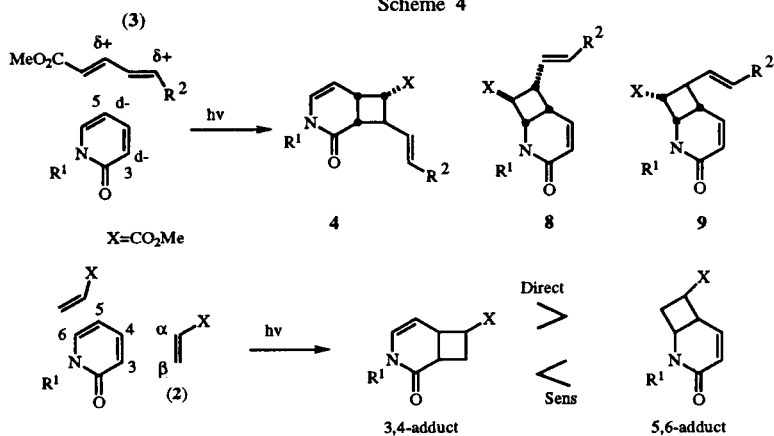


Figure 3. Estimated atomic charges of 2-pyridone (1a) methyl acrylate (2) and methyl 2,4-pentadienoate (3b)

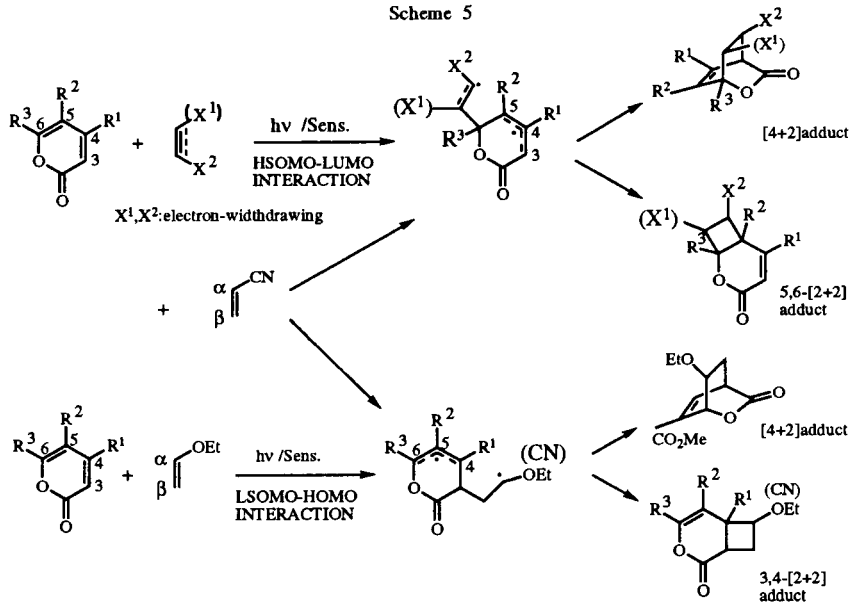
Scheme 3



Scheme 4



Scheme 5



property of **1**, and relatively smaller coefficients at the 3-position in the excited **1**.

The next purpose is such molecular orbital explanation about formations of photoadducts **4-11** between 1S of **1** and 2,4-pentadienoates **3**. The regioselective formations of adducts **4-7** are inferred to be brought by both effects of the 1S HSOMO-LUMO interaction in Figure 2 and of the electrostatic one in Figure 3. Their factors are similar to that for adducts, 3,4-endo-adducts between **1** and **2**. Formation of other regioselective adducts **8-11** can not be explained by the frontier orbital interactions, HSOMO-LUMO and LSOMO-HOMO. The electrostatic interactions between **1** and **3** in Figure 3 are inferred to be effective for formations of adducts **8-11** as the 5- β :6- α and 5- δ :6- γ interactions are favorable. We have reported that some electrostatic interaction between maleic anhydride and vinyl acetate are effective for the photochemical endo-[2+2] cycloadditions [14], and also photochemical dimerization of **1** preferentially gives a head-to-tail-[4+4]cycloadduct dimer from the electrostatic interaction [4,12,15].

The triplet **1** did not react with pentadienoates **3**. It is very in contrast to the triplet photoreactions with propenoates **2** [4]. The reason is inferred that the triplet energy of **1** was quenched by the dienoate **3** possessing a lower triplet level [16] and reacting as a triplet quencher. The energy profile of photocycloaddition reactions of **1** with **2** and **3** is shown in Figure 4. Namely, the photoreaction difference might come from following energy levels in those triplets: $2 > \text{sensitizer} > 1 > 3$.

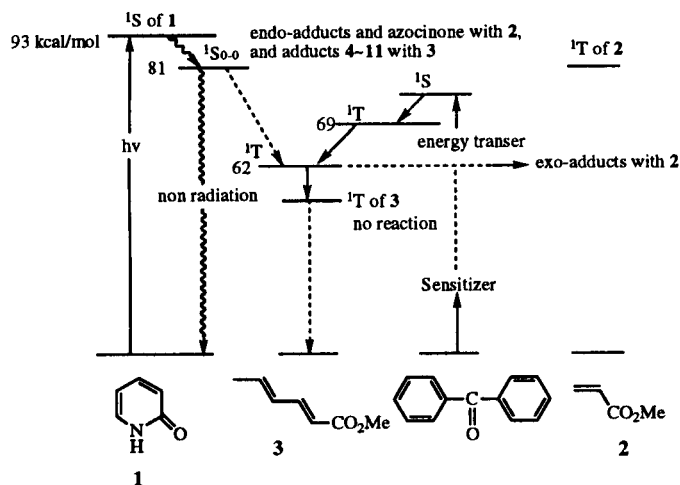


Figure 4. Energy profile of photochemical reactions of 2-pyridones **1** with propenoates **2** and 2,4-pentadienoates **3**.

EXPERIMENTAL

1H nmr spectra were determined with a JEOL JNM-GSX 400 (400 MHz) spectrometer (TMS as an internal standard), and ^{13}C nmr spectra were measured at 100.5 MHz on the JEOL JNM-GSX

400 instrument using deuteriochloroform as internal reference. The ir spectra were recorded with a JASCO A-3 spectrometer. Low-resolution mass spectral data were obtained with a JMS-OISG instrument at 70 eV. Photoirradiation was carried out in a Pyrex vessel by using a Riko 400 W high-pressure mercury lamp. Fluorescence spectra in methanol were recorded with a Hitachi F-3000 instrument.

Methyl 2-Oxo-[8-(*E*-1-propenyl)]-3-azabicyclo[4.2.0]oct-4-en-7-carboxylates **4ab**, **5ab**, Methyl [*E*-(8-Methyl-2-oxo-3-azabicyclo[4.2.0]oct-4-en-7-yl)]propenoates **6ab**, **7ab**, Methyl 3-Oxo-(*E*-1-propenyl)-2-azabicyclo[4.2.0]oct-4-en-8-carboxylates **8ab**, **9ab**, and Methyl [*E*-(7-Methyl-3-oxo-2-azabicyclo[4.2.0]oct-4-en-8-yl)]propenoates **10ab**, **11ab**.

A solution of 2-pyridone (**1a**) (0.95 g, 10 mmoles) and methyl sorbate (**3b**) (6.30 g, 50 mmoles) in acetonitrile (100 ml) was irradiated under nitrogen with 400 W high-pressure mercury lamp through a Pyrex jacket for 12 hours at room temperature. The solvent was removed under reduced pressure and filtered to give a photo [4+4]cycloadduct [17] of **1a** in 6% yield and as a thick white syrup. The syrup was chromatographed using silica gel column and ethyl acetate-hexane eluent and the fractions were monitored by tlc of silicagel plate to give eight types of photoadducts, **4ab** (124 mg, 6%), **5ab** (64 mg, 3%), **6ab** (34 mg, 2%), **7ab** (28 mg, 1%), **8ab** (82 mg, 4%), **9ab** (37 mg, 2%), **10ab** (89 mg, 4%), and **11ab** (114 mg, 5%). The characterization of **4ab-11ab** are as follows.

endo-7-exo-8 Adduct **4ab** was obtained as a colorless oil; ir (neat): 3414, 1762, 1686 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.66 (d, 3H, $J = 6.4$ Hz, Me), 2.96 (m, 1H, 1-H), 3.29 (m, 1H, 7-H), 3.42 (m, 1H, 6-H), 3.65 (m, 1H, 8-H), 3.75 (m, 3H, Me), 4.83 (dd, 1H, $J = 8.0, 4.4$ Hz, 5-H), 5.52 (dd, 1H, $J = 6.4, 1.52$ Hz, 9-H), 5.65 (m, 1H, 10-H), 6.09 (dd, 1H, $J = 8.0, 2.0$ Hz, 4-H), 8.04 (s, 1H, NH); ms: m/z 221 (M^+).

Anal. Calcd. for $C_{16}H_{23}NO_5$: C, 60.18; H, 7.21; N, 4.38. Found: C, 59.88; H, 7.13; N, 4.52.

exo-7-endo-8 Adduct **5ab** was obtained as a colorless oil; ir (neat) 3454, 1728, 1670 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.66 (d, 3H, $J = 6.6$ Hz, Me), 3.02 (m, 1H, 1-H), 3.29 (m, 1H, 7-H), 3.37 (m, 1H, 6-H), 3.70 (m, 1H, 8-H), 3.72 (s, 3H, Me), 5.02 (dd, 1H, $J = 8.0, 3.7$ Hz, 5-H), 5.50 (dd, 1H, $J = 6.8, 15.2$ Hz, 9H), 5.60 (m, 1H, 10-H), 6.01 (dd, 1H, $J = 8.0, 2.0$ Hz, 4-H), 7.80 (s, 1H, NH); ms: m/z 221 (M^+).

Anal. Calcd. for $C_{16}H_{23}NO_5$: C, 60.18; H, 7.21; N, 4.38. Found: C, 59.97; H, 7.01; N, 4.37.

endo-7-exo-8 Adduct **6ab** was obtained as a colorless oil; ir (neat): 3430, 1728, 1683 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.24 (d, H, $J = 5.6$ Hz, Me), 2.80 (m, 2H, 1-H, 6-H), 3.00 (m, 1H, 7-H), 3.30 (m, 1H, 8-H), 3.72 (s, 3H, Me), 4.85 (dd, 1H, $J = 8.0, 5.2$ Hz, 5-H), 5.85 (d, 1H, $J = 15.6$ Hz, 10-H), 6.00 (d, 1H, $J = 8.0$ Hz, 4-H), 6.97 (dd, 1H, $J = 15.6, 8.0$ Hz, 9-H), 7.50 (s, 1H, NH); ms: m/z 221 (M^+).

Anal. Calcd. for $C_{16}H_{23}NO_5$: C, 60.18; H, 7.21; N, 4.38. Found: C, 59.89; H, 7.11; N, 4.02.

exo-7-endo-8 Adduct **7ab** was obtained as a colorless oil; ir (neat): 3434, 1726, 1680 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.24 (d, 3H, $J = 5.6$ Hz, Me), 2.82 (m, 1H, 1-H), 3.00 (m, 2H, 6-H, 7-H), 3.30 (m, 1H, 8-H), 3.71 (s, 3H, Me), 5.20 (dd, 1H, $J = 8.0, 5.2$ Hz, 5-H), 5.85 (d, 1H, $J = 15.4$ Hz, 10-H), 6.10 (dd, 1H, $J = 8.0, 2.0$ Hz, 4-H), 6.97 (dd, 1H, $J = 15.4, 8.0$ Hz, 9-H), 7.60 (s, 1H, NH); ms: m/z 221 (M^+).

Anal. Calcd. for $C_{16}H_{23}NO_5$: C, 60.18; H, 7.21; N, 4.38. Found: C, 60.02; H, 7.17; N, 4.33.

endo-7-exo-8 Adduct **8ab** was obtained as a colorless oil; ir (neat): 3445, 1720, 1672 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.70 (d, 3H, $J = 4.0$ Hz, Me), 2.89 (m, 1H, 6-H), 3.15 (m, 1H, 7-H), 3.45 (m, 1H, 8-H), 3.74 (s, 3H, Me), 4.38 (t, 1H, $J = 8.8$ Hz, 1-H), 5.58 (m, 2H, 9-H, 10-H), 5.80 (d, 1H, $J = 10.0$ Hz, 4-H), 6.50 (dd, 1H, $J = 10.0, 4.4$ Hz, 5-H), 6.10 (bs, 1H, NH); ms: m/z 221 (M^+).

Anal. Calcd. for $C_{16}H_{23}NO_5$: C, 60.18; H, 7.21; N, 4.38. Found: C, 59.92; H, 7.20; N, 4.16.

exo-7-endo-8 Adduct **9ab** was obtained as a colorless oil; ir (neat): 3440, 1726, 1674 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.70 (d, 3H, $J = 6.4$ Hz, Me), 3.20 (m, 1H, 7-H), 3.35 (m, 2H, 6-H, 8-H), 3.72 (s, 3H, Me), 4.18 (t, 1H, $J = 8.0$ Hz, 1-H), 5.45 (m, 1H, 9-H), 5.60 (m, 1H, 10-H), 5.99 (d, 1H, $J = 10.0$ Hz, 4-H), 6.50 (dd, 1H, $J = 10.0, 4.0$ Hz, 5-H), 6.30 (bs, 1H, NH); ms: m/z 221.

Anal. Calcd. for $C_{16}H_{23}NO_5$: C, 60.18; H, 7.21; N, 4.38. Found: C, 60.02; H, 7.17; N, 4.23.

endo-7-exo-8 Adduct **10ab** was obtained as a colorless oil; ir (neat): 3434, 1714, 1672 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.07 (d, 3H, $J = 6.6$ Hz, Me), 2.7 (m, 2H, 7-H, 8-H), 3.40 (m, 1H, 6-H), 3.72 (s, 3H, Me), 4.16 (m, 1H, 1-H), 5.83 (d, 1H, $J = 16.4$ Hz, 10-H), 5.95 (d, 1H, $J = 10.0$ Hz, 4-H), 6.58 (dd, 1H, $J = 10.0, 8.8$ Hz, 5-H), 7.05 (dd, 1H, $J = 16.4, 8.0$ Hz, 9-H), 7.20 (bs, 1H, NH); ms: m/z 221 (M^+).

Anal. Calcd. for $C_{16}H_{23}NO_5$: C, 60.18; H, 7.21; N, 4.38. Found: C, 60.10; H, 7.11; N, 4.15.

exo-7-endo-8 Adduct **11ab** was obtained as a colorless oil; ir (neat): 3430, 1714, 1670 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.07 (d, 3H, $J = 6.8$ Hz, Me), 2.70 (m, 2H, 7-H, 8-H), 3.40 (m, 1H, 6-H), 3.72 (s, 3H, Me), 4.35 (m, 1H, 1-H), 5.85 (d, 1H, $J = 15.6$ Hz, 10-H), 5.95 (d, 1H, $J = 10.8$ Hz, 4-H), 6.48 (dd, 1H, $J = 10.8, 2.0$ Hz, 5-H), 6.80 (bs, 1H, NH), 6.93 (dd, 1H, $J = 15.6, 8.0$ Hz, 9-H); ms: m/z 221 (M^+).

Anal. Calcd. for $C_{16}H_{23}NO_5$: C, 60.18; H, 7.21; N, 4.38. Found: C, 60.07; H, 6.99; N, 4.16.

Methyl 8-Ethenyl-3-methyl-2-oxo-3-azabicyclo[4.2.0]oct-5-ene-7-carboxylates **4ba**, **5ba**, Methyl [E-(3-Methyl-2-oxo-3-azabicyclo[4.2.0]oct-4-en-endo-7-yl)]propenoates **6ba**, Methyl 7-Ethenyl-2-methyl-3-oxo-2-azabicyclo[4.2.0]oct-4-ene-8-carboxylates **8ba**, **9ba**.

A solution of 1-methyl-2-pyridone (**1b**) (0.22 g, 2.0 mmoles) and methyl 2,4-pentadienoate (**3a**) (1.12 g, 10.0 mmoles) in acetonitrile (20 ml) was irradiated for 12 hours at room temperature. The solvent was removed *in vacuo* and the resulting residue was chromatographed over silica gel using ethyl acetate-hexane eluent to give seven types of photoadducts, **4ba** + **5ba** (33 mg, 2:1 mixture, 8%), **6ba** (26 mg, 6%), **8ba** (97 mg, 22%), **9ba** (142 mg, 32%). The characterization of **4ba-9ba** are as follows.

A mixture of endo-7-exo-8 adduct **4ba** and exo-7-endo-8 adduct **5ba** was obtained as a colorless oil; ir (neat): 1726, 1660 cm^{-1} ; **4ba**, 1H nmr (deuteriochloroform): δ 3.00 (m, 1H, 1-H), 3.05, 3.70 (s, each 3H, Me), 3.27 (m, 1H, 7-H), 3.45 (m, 1H, 6-H), 3.58 (m, 1H, 8-H), 4.82 (dd, 1H, $J = 8.2, 4.0$ Hz, 5-H), 5.12 (m, 2H= CH_2), 5.86 (m, 1H, 9-H), 6.05 (d, 1H, $J = 8.2$ Hz, 4-H); **5ba**, 1H nmr (deuteriochloroform): δ 3.02, 3.68 (each s, H, Me), 3.4 (m, 2H, 7-H, 8-H), 3.6 (m, 2H, 1-H, 6-H), 5.04 (dd, 1H, $J = 8.0, 5.5$ Hz, 5-H), 5.12 (m, 2H= CH_2), 5.95 (d, 1H, $J = 8.0$ Hz, 4-H), 5.97 (m, 1H, 9-H); ms: m/z 221 (M^+).

Anal. Calcd. for $C_{12}H_{15}NO_3$: C, 65.15; H, 6.78; N, 6.33. Found: C, 65.50; H, 6.91; N, 6.25.

endo-7 Adduct **6ba** was obtained as a colorless oil; ir (neat): 1724, 1660 cm^{-1} ; 1H nmr (deuteriochloroform): δ 2.6 (m, 2H, 8- CH_2), 3.02, 3.73 (each s, 3H, Me), 3.2 (m, 1H, 1-H), 3.4 (m, 2H, 6-H, 7-H), 4.80 (dd, 1H, $J = 8.5, 1.6$ Hz, 5-H), 5.80 (d, 1H, $J = 15.6$ Hz, 10-H), 6.03 (d, 1H, $J = 8.0$ Hz, 4-H), 7.00 (dd, 1H, $J = 15.6, 7.0$ Hz, 9-H); ms: m/z 221 (M^+).

Anal. Calcd. for $C_{12}H_{15}NO_3 \cdot 1/2H_2O$: C, 62.61; H, 6.95; N, 6.08. Found: C, 62.70; H, 6.57; N, 6.01.

endo-7-exo-8 Adduct **8ba** was obtained as a colorless oil; ir (neat): 1725, 1662 cm^{-1} ; 1H nmr (deuteriochloroform): δ 2.95, 3.72 (each s, 3H, Me), 3.24 (q, 1H, $J = 8.8$ Hz, 7-H), 3.4 (m, 2H, 6-H, 8-H), 4.12 (t, 1H, $J = 8.8$ Hz, 1-H), 5.20 (d, 1H, $J = 11.6$ Hz, =CH), 5.21 (d, 1H, $J = 15.6$ Hz, =CH), 5.81 (m, 1H, 9-H), 5.97 (d, 1H, $J = 9.2$ Hz, 4-H), 6.35 (dd, 1H, $J = 9.2, 4.0$ Hz, 5-H); ms: m/z 221 (M^+).

Anal. Calcd. for $C_{12}H_{15}NO_3$: C, 65.15; H, 6.78; N, 6.33. Found: C, 65.41; H, 6.94; N, 6.27.

exo-7-endo-8 Adduct **9ba** was obtained as a colorless oil; ir (neat): 1723, 1661 cm^{-1} ; 1H nmr (deuteriochloroform): δ 2.84, 3.91 (each s, 3H, Me), 3.14 (m, 1H, 8-H), 3.30 (m, 1H, 6-H), 3.42 (m, 1H, 7-H), 4.40 (t, 1H, $J = 9.2$ Hz, 1-H), 5.15 (d, 1H, $J = 8.8$ Hz, =CH), 5.17 (d, 1H, $J = 18.4$ Hz, =CH), 5.82 (d, 1H, $J = 9.6$ Hz, 4-H), 5.96 (m, 1H, 9-H), 6.43 (dd, 1H, $J = 9.6, 4.0$ Hz, 5-H); ms: m/z 221 (M^+).

Anal. Calcd. for $C_{12}H_{15}NO_3$: C, 65.15; H, 6.78; N, 6.33. Found: C, 64.91; H, 6.67; N, 6.22.

Methyl 2-Oxo-[8-(E-1-propenyl)]-3-methyl-3-azabicyclo[4.2.0]oct-5-ene-7-carboxylates (**4bb**, **5bb**), Methyl [E-(3,8-Dimethyl-2-oxo-3-azabicyclo[4.2.0]oct-4-en-7-yl)]propenoate (**6bb**, **7bb**), Methyl 2-[Methyl-7-(E-1-propenyl)]-3-oxo-2-azabicyclo[4.2.0]oct-4-ene-8-carboxylates (**8bb**, **9bb**), and Methyl [E-(2, endo-7-Dimethyl-3-oxo-2-azabicyclo[4.2.0]oct-4-en-exo-8-yl)]propenoate (**10bb**).

A solution of **1b** (1.1 g, 10 mmoles) and **3b** (6.3 g, 50 mmoles) in acetonitrile (100 ml) was irradiated for 8 hours. After removing the solvent *in vacuo*, the resulting residue was chromatographed over silica gel using ethyl acetate-hexane eluent to give seven types of photoadducts, **4bb** (250 mg, 11%), **5bb** (60 mg, 3%), **6bb** (80 mg, 3%), **7bb** (110 mg, 5%), **8bb** (350 mg, 15%), **9bb** (350 mg, 15%), and **10bb** (270 mg, 12%). The characterization of **4bb-10bb** are as follows.

endo-7-exo-8 Adduct **4bb** was obtained as a colorless oil; ir (neat): 1732, 1664 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.66 (d, 3H, $J = 6.4$ Hz, Me), 3.00 (m, 1H, 1-H), 3.05, 3.71 (each s, 3H, Me), 3.23 (m, 1H, 7-H), 3.39 (m, 1H, 6-H), 3.62 (m, 1H, 8-H), 4.83 (dd, 1H, $J = 8.0, 4.4$ Hz, 5-H), 5.6 (m, 2H, 9-H, 10-H), 6.02 (dd, 1H, $J = 8.0, 2.0$ Hz, 4-H); ms: m/z 235 (M^+).

Anal. Calcd. for $C_{12}H_{15}NO_3 \cdot 1/2H_2O$: C, 63.93; H, 7.38; N, 4.48. Found: C, 63.82; H, 7.19; N, 4.85.

exo-7-endo-8 Adduct **5bb** was obtained as a colorless oil; ir (neat): 1728, 1662 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.66 (d, 3H, $J = 6.6$ Hz, Me), 3.01, 3.68 (each s, H, Me), 3.45 (m, 2H, 7-H, 8-H), 3.7 (m, H, 1-H, 6-H), 5.23 (dd, 1H, $J = 8.1, 3.7$ Hz, 5-H), 5.5 (m, 1H, 10-H), 5.8 (dd, 1H, $J = 15.0, 9.5$ Hz, 9-H), 5.95 (d, 1H, $J = 8.1$ Hz, 4-H); ms: m/z 235 (M^+).

Anal. Calcd. for $C_{13}H_{17}NO_3 \cdot 1/2H_2O$: C, 63.93; H, 7.38; N, 4.84. Found: C, 64.30; H, 7.13; N, 5.15.

endo-7-exo-8 Adduct **6bb** was obtained as a colorless oil; ir (neat): 1726, 1664 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.19 (d,

3H, $J = 5.6$ Hz, Me), 2.75 (m, 1H, 7-H), 3.05, 3.65 (each s, 3H, Me), 3.1 (m, 2H, 1-H, 6-H), 3.3 (m, 1H, 8-H), 4.83 (dd, 1H, $J = 8.0, 5.5$ Hz, 5-H), 5.83 (d, 1H, $J = 15.6$ Hz, 10-H), 6.03 (d, 1H, $J = 8.0$ Hz, 4-H), 6.97 (dd, 1H, $J = 15.6, 8.2$ Hz, 9-H); ms: m/z 235 (M^+).

Anal. Calcd. for $C_{13}H_{17}NO_3 \cdot 1/2H_2O$: C, 63.93; H, 7.38; N, 4.84. Found: C, 63.69; H, 7.01; N, 5.10.

exo-7-endo-8 Adduct **7bb** was obtained as a colorless oil; ir (neat): 1728, 1662 cm^{-1} ; 1H nmr (deuteriochloroform): δ 0.97 (d, 3H, $J = 5.6$ Hz, Me), 3.03, 3.66 (each s, 3H, Me), 5.30 (d, 1H, $J = 8.8$ Hz, 5-H), 5.70 (d, 1H, $J = 16.8$ Hz, 10-H), 5.90 (d, 1H, $J = 8.8$ Hz, 4-H), 7.10 (dd, 1H, $J = 16.8, 12.0$ Hz, 9-H); ms: m/z 235 (M^+).

Anal. Calcd. for $C_{13}H_{17}NO_3 \cdot 1/2H_2O$: C, 63.93; H, 7.38; N, 4.84. Found: C, 64.15; H, 7.21; N, 4.99.

endo-7-exo-8 Adduct **8bb** was obtained as a colorless oil; ir (neat): 1724, 1660 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.69 (d, 3H, $J = 6.4$ Hz, Me), 2.94, 3.71 (each s, 3H, Me), 3.20 (m, 1H, 7-H), 3.30 (m, 2H, 6-H, 8-H), 4.08 (m, 1H, 1-H), 5.46 (m, 1H, 9-H), 5.60 (m, 1H, 10-H), 5.97 (d, 1H, $J = 10.0$ Hz, 4-H), 6.38 (dd, 1H, $J = 10.0, 8.8$ Hz, 5-H); ms: m/z 235 (M^+).

Anal. Calcd. for $C_{13}H_{17}NO_3 \cdot 1/2H_2O$: C, 63.93; H, 7.38; N, 4.48. Found: C, 64.07; H, 7.19; N, 4.80.

exo-7-endo-8 Adduct **9bb** was obtained as a colorless oil; ir (neat): 1726, 1662 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.70 (d, 3H, $J = 4.0$ Hz, Me), 2.87, 3.68 (each s, 3H, Me), 3.05 (m, 1H, 6-H), 3.25 (m, 1H, 7-H), 3.35 (m, 1H, 8-H), 4.40 (t, 1H, $J = 8.8$ Hz, 1-H), 5.5 (m, H, 9-H, 10-H), 5.80 (d, 1H, $J = 10.0$ Hz, 4-H), 6.43 (dd, 1H, $J = 10.0, 3.0$ Hz, 5-H); ms: m/z 235 (M^+).

Anal. Calcd. for $C_{13}H_{17}NO_3 \cdot 1/2H_2O$: C, 63.93; H, 7.38; N, 4.48. Found: C, 64.04; H, 7.21; N, 4.78.

endo-7-exo-8 Adduct **10bb** was obtained as a colorless oil; ir (neat): 1722, 1664 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.15 (d, 3H, $J = 6.8$ Hz, Me), 2.60 (m, 1H, 7-H), 2.70 (m, 1H, 8-H), 2.97, 3.75 (each s, 3H, Me), 3.40 (m, 1H, 1-H), 3.50 (m, 1H, 6-H), 5.85 (d, 1H, $J = 16.4$ Hz, 10-H), 5.98 (d, 1H, $J = 10.8$ Hz, 4-H), 6.33 (dd, 1H, $J = 10.8, 2.0$ Hz, 5-H), 6.90 (dd, 1H, $J = 16.4, 8.0$ Hz, 9-H); ms: m/z 235 (M^+).

Anal. Calcd. for $C_{13}H_{17}NO_3 \cdot 1/2H_2O$: C, 63.93; H, 7.38; N, 4.48. Found: C, 63.77; H, 7.23; N, 4.74.

REFERENCES AND NOTES

- [1a] M. Demuth and G. Mikhail, *Synthesis*, 145 (1989); [b] D. D. Keukeleire, and Shu-L. He, *Chem. Rev.*, **93**, 145 (1993).
- [2] D. I. Schuster, *Chem. Rev.*, **93**, 3 (1993).
- [3a] I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, Chapter 4, John Wiley and Sons, New York, NY, 1976; [b] J. W. Storer, L. Reimondi, and K. N. Houk, *J. Am. Chem. Soc.*, **116**, 9675, (1994) and references therein.
- [4] K. Somekawa, R. Izumi, K. Taniguchi, T. Suishu, and S. Tokita, *Nippon Kagaku Kaishi*, 271 (1990); *Chem. Abstr.*, **113**, 96904y (1990).
- [5] K. Somekawa, H. Okuhira, M. Sendayama, T. Suishu, and T. Shimo, *J. Org. Chem.*, **57**, 5708 (1992).
- [6] T. Naito, and C. Kaneko, *J. Synth. Org. Chem. Japan*, **42**, 51 (1984) and many references cited therein.
- [7] E. Sato, Y. Ikeda, and Y. Kanaoka, *Ann. Chem.*, 781 (1989).
- [8] K. Somekawa, T. Shimo, and T. Suishu, *Bull. Chem. Soc. Japan*, **65**, 354 (1992).
- [9] J. L. Broeker, L. E. Eksterowicz, A. Belk, and K. N. Houk, *J. Am. Chem. Soc.*, **117**, 1847 (1995).
- [10] D. Andrew, D. J. Hastings, and A. C. Weedon, *J. Am. Chem. Soc.*, **116**, 10870 (1994) and references cited therein.
- [11] T. Suishu, T. Shimo, and K. Somekawa, *Tetrahedron*, **53**, 3545 (1997).
- [12] L. J. Sharp IV, and G. S. Hammond, *Mol. Photochem.*, **2**, 225 (1970).
- [13] J. J. P. Stewart, *J. Comput. Chem.*, **10**, 209 (1989).
- [14] K. Somekawa, R. Hara, K. Kinnami, F. Muraoka, T. Suishu, and T. Shimo, *Chem. Letters*, 407 (1995).
- [15] I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, Chapter 6, John Wiley and Sons, New York, NY, 1976.
- [16] S. L. Murov, *Handbook of Photochemistry*, Marcel Dekker Inc., New York, NY, 1993, 4.
- [17] W. L. Dilling, N. B. Teffertiller, and A. B. Michell, *Mol. Photochem.*, **5**, 371 (1973).