

Tohru Takabatake and Minoru Hasegawa*

College of Pharmacy, Nihon University,
7-7-1 Narashinodai, Funabashi-shi,
Chiba 274, Japan
Received July 21, 1993

1*H*-Azepine-2,7-dione **2** afforded photodimer **8** by irradiation using a high or low pressure mercury lamp. Photodimer **8** had a unique structure which must have formed with the prototropy in one of the two molecules of compound **2**. Measurement of the fluorescence spectra of **2** indicated a spectrum of the excimer during the dimerization of **2**. Irradiation of the dimer of **2** at its wave-length of maximal absorption failed to cause it to change into a monomer of **2**.

J. Heterocyclic Chem., **31**, 215 (1994).

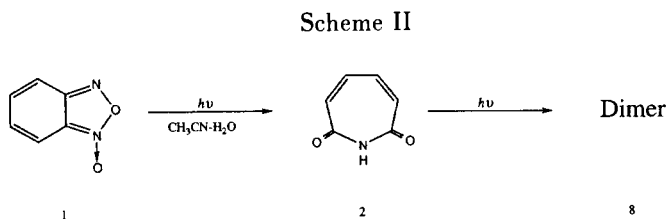
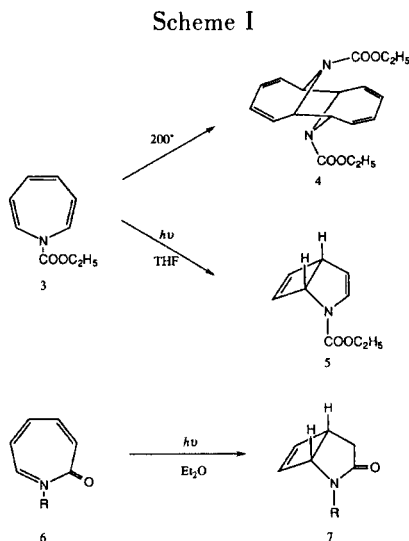
The previous paper [1] indicated benzofuroxan **1** on irradiation at 365 nm in acetonitrile containing a little water to give 1*H*-azepine-2,7-dione **2**.

In this study, examination was made of the photolysis of product **2**.

Azepine **3** when heated at 200° gives a dimer **4** [2]. The photolysis of compound **3** yields a cyclized compound **5** [3]. The photoreaction of 1-alkylazepine 2-oxide **6** yields cyclized compound **7**, as also observed for azepine **3** [4].

Compound **2** by irradiation with a high pressure or low pressure mercury lamp was found to give photodimer **8** of **2**.

did not affect any protons. On the other hand, the irradiation of 5-H and 6-H affected both 4-H and 7-H. Furthermore a NOE was observed between 4-H and 12-H. Here we propose the structure of the photodimer **8**, as shown in Figure 1.



Stereochemical assignment of photodimer **8** was made based on its nmr spectra using homonuclear decoupling and a NOE experiment. The irradiation of 11-H and 12-H

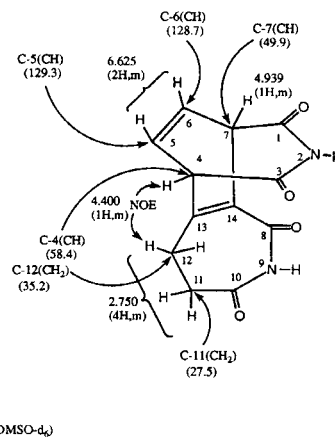


Figure 1. Structure of Photodimer **8**.

The photodimerization of **2** was conducted using a high or low pressure mercury lamp. The photolysis of **2** in the presence of acetonitrile containing water proceeded more rapidly to produce photodimer **8** in good yield. Water molecule would thus appear essential for prototropy in one of the two molecules of compound **2**.

Table 1
Yields of Photodimer **8** on Photolysis of **2**

Solvent	Photolysis at 365 nm		Photolysis at 254 nm	
	Time (h)	Yield (%)	Time (h)	Yield (%)
CH ₃ CN-H ₂ O (9:1) dry CH ₃ CN	2	65	1	24
	2	15	1	16
	10	37		
CH ₂ Cl ₂	2	trace	1	8
	10	16	4	16

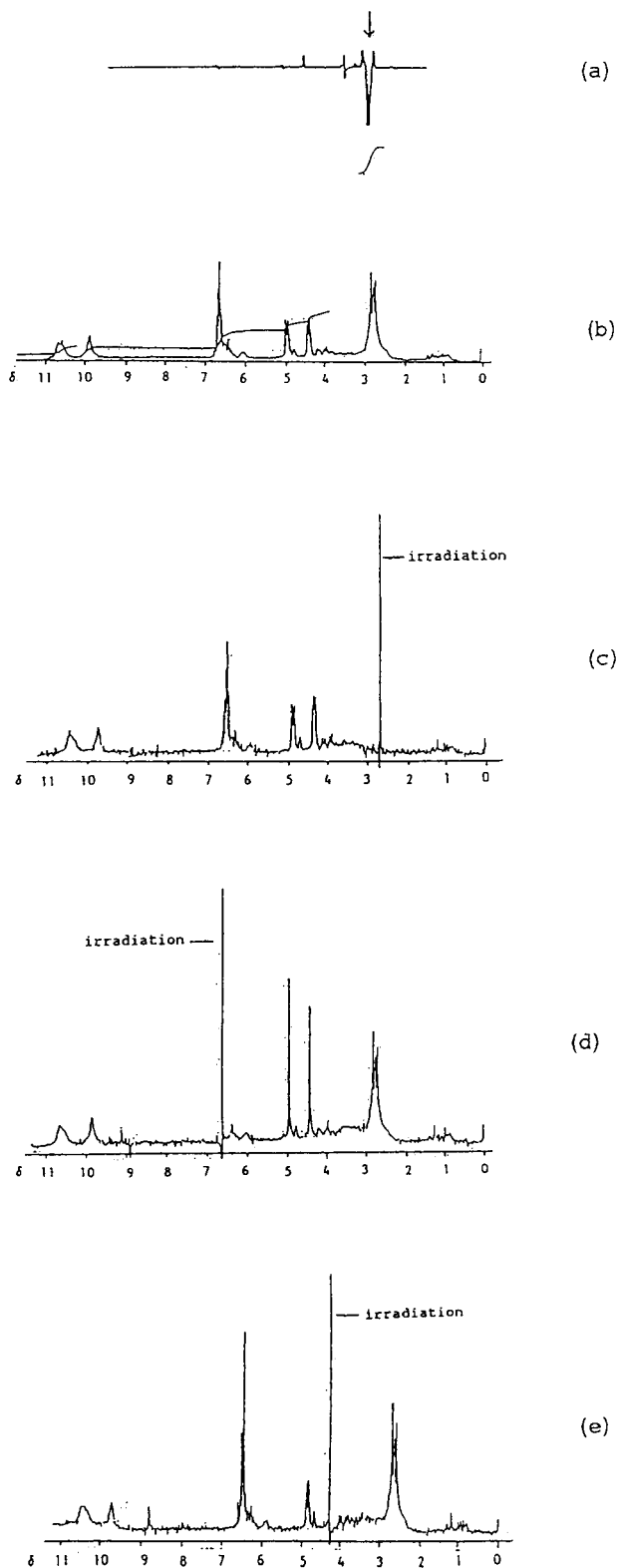
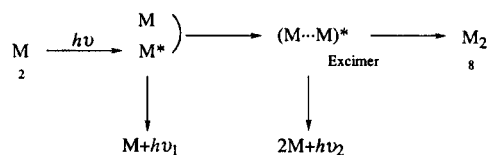


Figure 2. Nmr Spectra of Photodimer **8** (a) NOE spectrum; (b) nmr spectrum of **8**; (c) ~ (e) homonuclear decoupling.

For clarification of the photodimerization mechanism of **2**, its fluorescence spectrum was obtained at various concentrations. Compound **2** fluoresced at 416 nm in very dilute solution. At 416 nm, the spectrum was quenched, and another fluorescence appeared at 405 and 505 nm, the intensity of which gradually increased with concentration. The initial fluorescence spectrum would thus appear to be due to the monomer of **2**. The spectrum appearing subsequently may have resulted from an excimer during dimerization. The spectral behavior of **2** suggest dimerization to proceed through the excimer state as shown in Scheme III.

Scheme III



Photodimer **8** showed an absorption maximum at 210 nm. The effects of irradiation of the dimer at that wavelength were thus examined, but the dimer was not converted to the monomer of **2**.

EXPERIMENTAL

Compound **2** was prepared as previously described [1]. The photoreactions were carried out with Nikko Sekiei Works photochemical reactor. Melting points were determined with a Yanagimoto micromelting point apparatus and are uncorrected. The ir spectra were recorded on a Jasco IR-810 spectrometer. The ^1H and ^{13}C nmr spectra were recorded on a JNM-EX 90 FT NMR instrument with TMS as the internal standard. The mass spectra were recorded on a Hitachi M-2000 spectrometer with an electron beam energy of 70 eV. Microanalyses were performed at the microanalytical laboratory of the Center for Instrumental Analysis in College of Science and Technology, Nihon University.

Photolysis of 1*H*-Azepine-2,7-dione (**2**) at 365 nm.

A solution of 50 mg (2.0×10^{-1} mole) of compound **2** dissolved in 5 ml of acetonitrile:water (9:1, v/v) was irradiated using a 400-W high pressure mercury lamp with a Pyrex filter at room temperature. After irradiation for 2 hours, an aliquot was taken, and product **8** was determined with an hplc apparatus using the calibration curve.

Photodimer **8**.

This compound was obtained as colorless needles (ethanol:water, 95:5, v/v), mp 269-271°; ir (potassium bromide): ν 3220 (NH), 2860 (CH), 1710, 1685, 1665 (C=O) cm^{-1} ; uv (acetonitrile): λ max nm (log ϵ) 210 (1.67); ^1H nmr (DMSO- d_6): δ 2.750 (m, 4H), 4.400 (m, 1H), 4.939 (m, 1H), 6.625 (m, 2H), 9.922 (s, 1H), 10.701 (s, 1H); ^{13}C nmr (DMSO- d_6): δ 172.4 (C-8), 169.3 (C-10), 168.4 (C-3), 167.6 (C-1), 163.5 (C-13), 152.8 (C-14), 129.3 (C-5, CH),

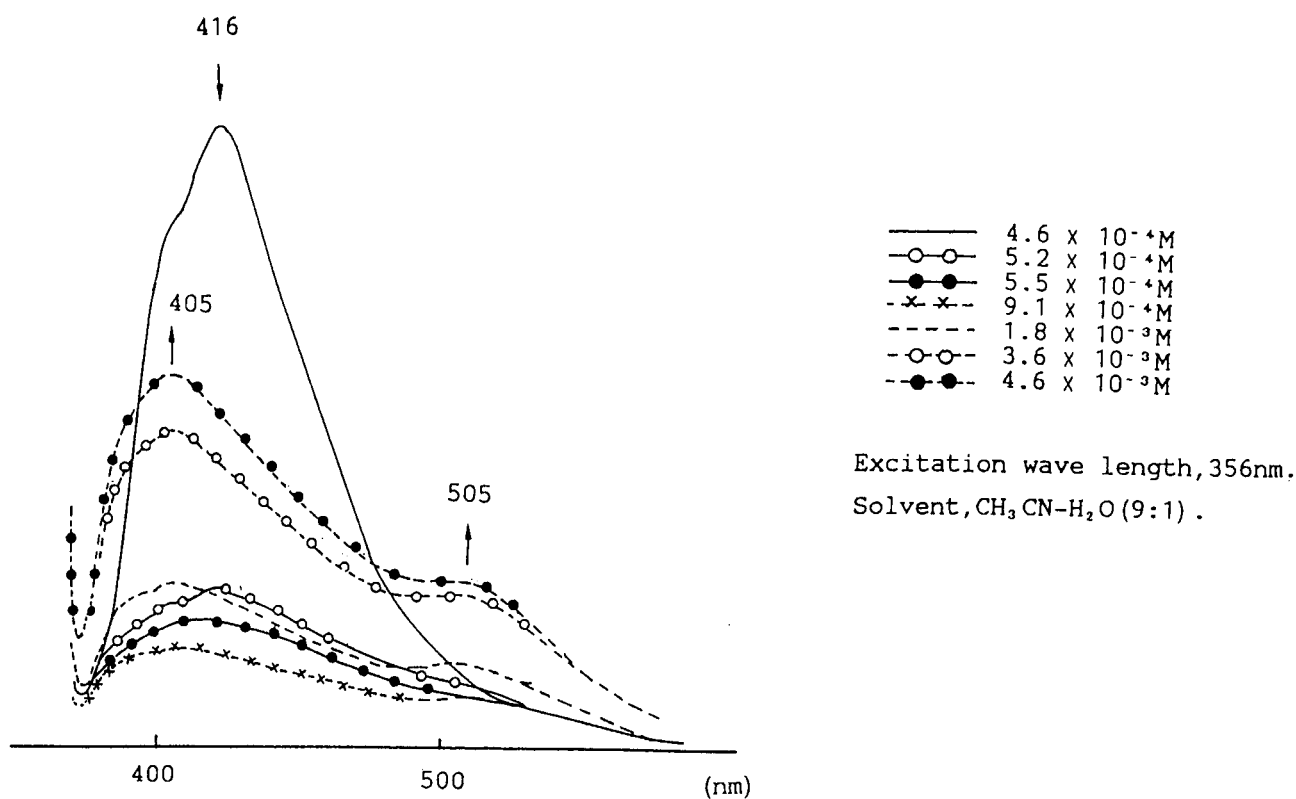


Figure 3. Concentration Dependence of Fluorescence of 2.

128.7 (C-6, CH), 58.4 (C-4, CH), 49.9 (C-7, CH), 35.2 (C-12, CH₂), 27.5 (C-11, CH₂); hrms: (m/z) 246.0614. Calcd. for C₁₂H₁₀N₂O₄; M, 246.06165.

Anal. Calcd. for C₁₂H₁₀N₂O₄: C, 58.53; H, 4.09; N, 11.38. Found: C, 58.25; H, 4.06; N, 11.11.

REFERENCES AND NOTES

* Author to whom correspondence should be addressed.

- [1] M. Hasegawa and T. Takabatake, *J. Heterocyclic Chem.*, **28**, 1079 (1991).
- [2] A. L. Johnson and H. E. Simmons, *J. Am. Chem. Soc.*, **88**, 2591 (1966).
- [3] L. A. Paquette and J. H. Barrett, *J. Am. Chem. Soc.*, **88**, 1718 (1966).
- [4] E. Vogel, R. Erb, G. Lenz and A. A. Bothner, *Liebigs Ann. Chem.*, **682**, 1 (1965).