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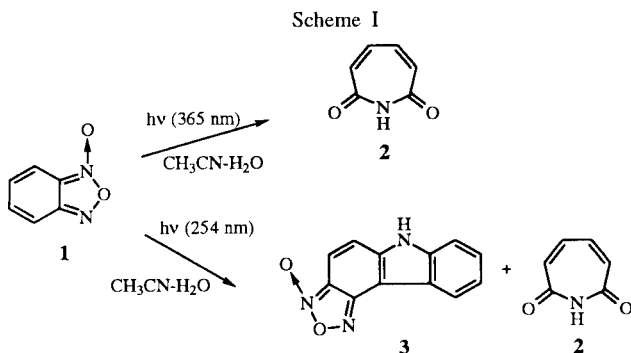
When pyrido[2,3-*c*]furoxan **4** was irradiated in acetonitrile containing a little water with a low pressure mercury lamp, 3-nitro-2-pyridone **5** was obtained. When compound **4** was irradiated in the presence of morpholine with a low pressure mercury lamp in an argon atmosphere, 6-morpholinopyridine 2,3-dioxime **6**, 6-morpholinopyrido[2,3-*c*]furan **7**, 3-amino-6-morpholino-2-nitropyridine **8**, and 3-amino-4,6-dimorpholino-2-nitropyridine **9** was produced. The results of photoreaction study indicated the only photo-product to be compound **6**. The main difference between these two reactions may be considered due to the behavior of nitrogen in the pyridine ring.

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The photoreactions of benzofuroxan **1** in acetonitrile containing a little water, under a high pressure mercury lamp, were found to give 1*H*-azepine-2,7-dione **2**, while under irradiation using a low pressure lamp, 6*H*-furanazo-[4,5-*c*]carbazole-3-oxide **3** and compound **2** was obtained. In the presence of an aromatic hydrocarbon, the formation

This reaction failed to occur in the presence of dry benzene or benzene containing a little water.

The participation of water in this reaction is suggested, and stabilization of an ionic intermediate in polar solvent may occur. The reaction mechanism may thus be considered to be as follows.



of compound **3** decreased and that of compound **2** increased. Mechanistic studies on the photoreaction suggest that the photosensitized formation of compound **2** with the aromatic hydrocarbon may be carried out by the reabsorption of the fluorescence of it near 365 nm and the presence of it may quench the formation of compound **3** [1].

In the determination of the photochemical reactivity of aromatic furoxans, pyrido[2,3-*c*]furoxan **4** was found to differ considerably in photoreactivity from compound **1**.

When compound **4** was irradiated in acetonitrile containing a little water with a low pressure mercury lamp in aerated atmosphere, 3-nitro-2-pyridone **5** was obtained.

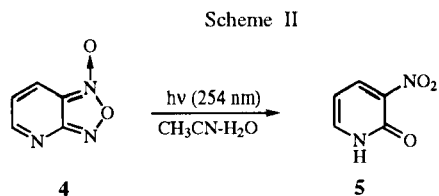


Table 1  
Yields of **5** on Photolysis of Compound **4** at 254 nm

solvent	reaction time (hours)	yield (%)
CH <sub>3</sub> CN-H <sub>2</sub> O (9:1)	5	7 (44) [a]
CH <sub>3</sub> CN-H <sub>2</sub> O (9:1)	30	18 (22) [a]
C <sub>6</sub> H <sub>6</sub>	5	0
C <sub>6</sub> H <sub>6</sub> -H <sub>2</sub> O (saturated)	5	0

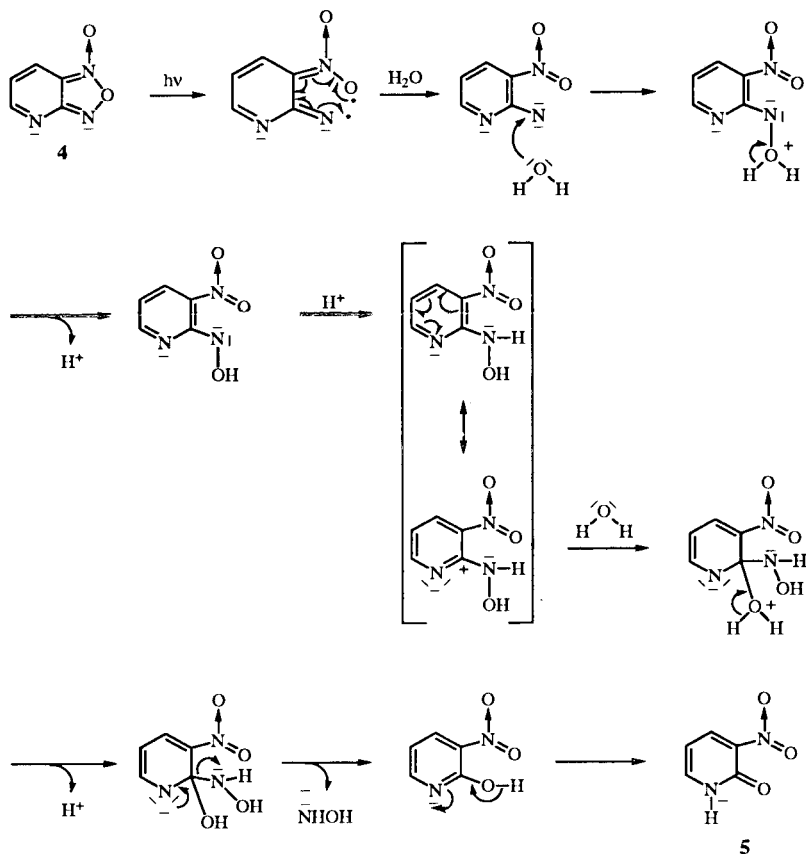
[a] Yield based on consumed pyrido[2,3-*c*]furoxan.

The photolysis of **4** using a low pressure mercury lamp in the presence of morpholine in an atmosphere of prepurified argon gave 6-morpholinopyridine 2,3-dioxime **6**, 6-morpholinopyrido[2,3-*c*]furan **7**, 3-amino-6-morpholino-2-nitropyridine **8**, and 3-amino-4,6-dimorpholino-2-nitropyridine **9**.

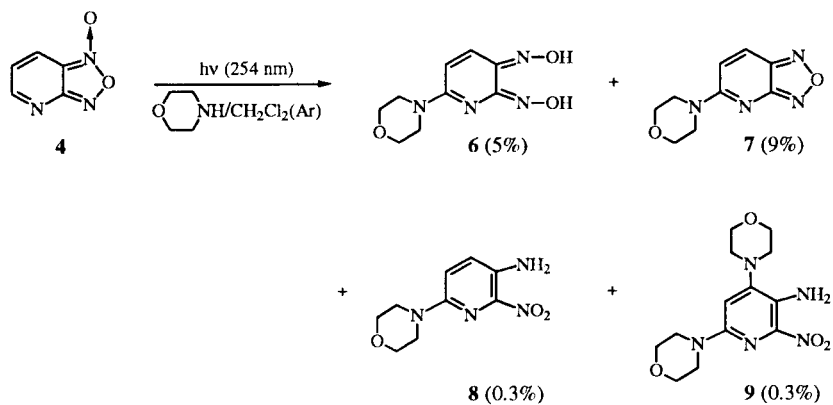
Compound **8** can be obtained by the above reaction in the dark [2]. To determine the formation mechanism of **6** and **7**, product yields were measured with hplc at regular time intervals during the photoreaction. The only photo-product was found to be compound **6** in the photolysis. Product **7** may possibly be produced by the dehydration with silica gel used for a chromatogram on post-treatment following termination of the reaction. When compound **6**, adsorbed on silica gel for tlc plate for 12 hours, was developed by being dipped in a solvent, compound **7** was obtained in 14% yield.

Compound **4**, irradiation using a low pressure mercury lamp with morpholine in aerated atmosphere, showed very little reaction. The effects of oxygen suggest the formation of **6** in photolysis to possibly occur in an excited triplet state of the molecules of this compound.

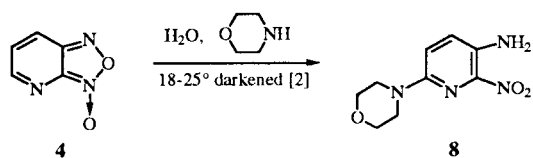
Scheme III



Scheme IV



Scheme V



The irradiation of compound **4** with morpholine may be concluded to possibly afford 6-morpholino derivative **10**, fol-

lowing which the N-O bond in frazan ring is cleaved, and hydrogenated to produce the dioxime derivative **6**, as follows.

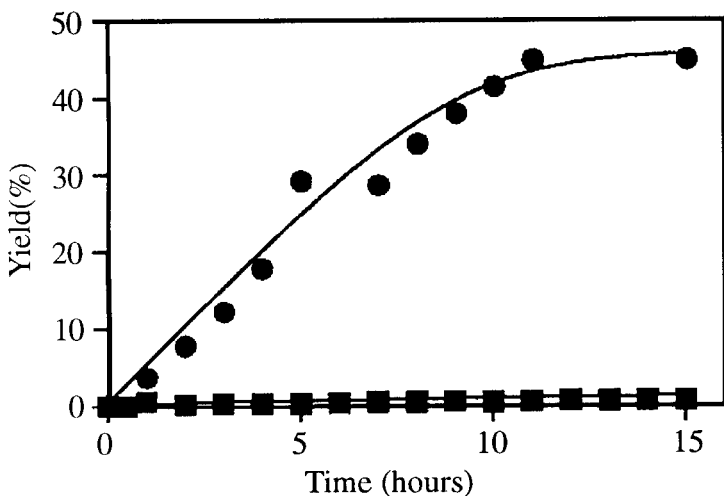
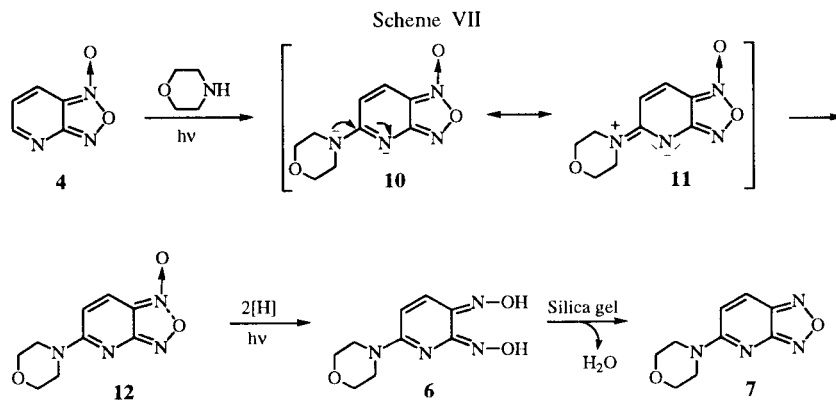
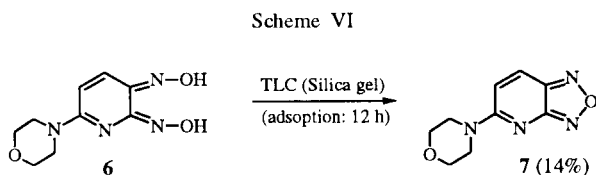


Figure 1. Time-course of the yield of products during photolysis of 4 with morpholine by hplc:

- 6-Morpholinopyridine 2,3-Dioxime 6.
- 6-Morpholinopyrido[2,3-*c*]furan 7.



## EXPERIMENTAL

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  $^1\text{H}$  nmr spectra were recorded on a JNM-EX 90 FT NMR instrument and JNM-GSX 400 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. The hplc was carried out with a Shimadzu LC-5A chromato-

graph. Microanalyses were performed at the microanalytical laboratory of the Center for Instrumental Analysis in College of Science & Technology, Nihon University.

### Photolysis of Pyrido[2,3-*c*]furoxan (4) in Acetonitrile-water.

A solution of 0.51 g (3.7 mmol) of compound 4 dissolved in 250 ml of acetonitrile:water (9:1, v/v) was irradiated using a 160 W low pressure mercury lamp at room temperature. After irradiation for 30 hours, an aliquot was taken, and unreacted 4 or product 5 were determined with an hplc apparatus using the calibration curves.

### Photolysis of Pyrido[2,3-*c*]furoxan (4) with Morpholine in Dichloromethane.

A solution of 1.00 g (7.3 mmol) of compound 4 and 1.58 g (18.1 mmol) of morpholine dissolved in 250 ml of methylene chloride was irradiated using a 160 W low pressure mercury lamp in an argon atmosphere at room temperature. After irradiation for 15 hours, unreacted 4, product 6 (83 mg, 5%), 7 (140 mg, 9%), 8 (5 mg, 0.3%) and 9 (8 mg, 0.3%) were separated by column chromatograph and determined.

### 6-Morpholinopyridine 2,3-Dioxime (6).

This compound was obtained as colorless crystals (hexane: ethylacetate (8:2, v/v)), mp 154–157°; ir (potassium bromide):  $\nu$  3450, 3350 (–OH), 1620, 1570, 1520, 1440 (C=N, C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  14.31 (s, 1H), 9.53 (s, 1H), 7.25 (d, 1H), 6.59 (d, 1H), 3.81 (s, 8H); ms: (m/z) 224 ( $\text{M}^+$ ), 206 ( $\text{M}^+ - \text{H}_2\text{O}$ ).

*Anal.* Calcd. for  $\text{C}_9\text{H}_{12}\text{N}_4\text{O}_3$ : C, 48.21; H, 5.40; N, 24.99. Found: C, 48.37; H, 5.29; N, 24.73.

### 6-Morpholinopyrido[2,3-*c*]furan (7).

This compound was obtained as yellow needles (ethanol), mp 170–175°; ir (potassium bromide):  $\nu$  1620, 1580, 1480, 1430 (C=N, C=C)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  7.92 (d, 1H), 7.16 (d, 1H), 3.85 (s, 8H); ms: (m/z) 206 ( $\text{M}^+$ ), 176 ( $\text{M}^+ - \text{NO}$ ).

*Anal.* Calcd. for  $\text{C}_9\text{H}_{10}\text{N}_4\text{O}_2$ : C, 52.42; H, 4.89; N, 27.17. Found: C, 52.25; H, 4.88; N, 27.11.

### 3-Amino-6-morpholino-2-nitropyridine (8).

This compound was characterized by comparison of the melting point, ir and  $^1\text{H}$ -nmr spectra with those of authentic sample

prepared according to ref [2].

3-Amino-4,6-dimorpholino-2-nitropyridine (**9**).

This compound was obtained as red needles (hexane), mp 200~203°; ir (potassium bromide):  $\nu$  3456, 3340, 1564, (NH<sub>2</sub>), 1627, 1517, 1434 (C=N, C=C) cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  6.63 (s, 1H), 5.89 (s, 2H), 3.90 (t, 4H), 3.83 (t, 4H), 3.45 (t, 4H), 3.00 (t, 4H); ms: (m/z) 309 (M<sup>+</sup>), 292 (M<sup>+</sup>-NH<sub>2</sub>).

Dehydration of Compound **6**.

A solution of 9.2 mg of compound **6** dissolved in methylene chloride was adsorbed on a tlc plate (Merck silica gel plate 60

F<sub>254</sub> Art.5717). After 12 hours, the tlc plate was developed by being dipped in ethyl acetate, and compound **7** separated in 14% yield.

#### REFERENCES AND NOTES

\* Author to whom correspondence should be addressed.

[1] M. Hasegawa and T. Takabatake, *J. Heterocyclic Chem.*, **28**, 1079 (1991).

[2] S. K. Kotovskaya, G. A. Mokrushina, I. Ya. Postovskii, and M. V. Polyakova, *Chem. Heterocyclic Comp.*, **5**, 654 (1981).