PHOTOCHEMISTRIES OF OXADIAZABICYCLO[1.2.4]NONADIENE, OXADIAZABICYCLO[2.2.3]NONADIENE, AND OXATRIAZABICYCLO-[2.2.3]NONADIENE SYSTEMS: CYCLOREVERSION REACTIONS TO GENERATE AZEPINE OR DIAZEPINE DERIVATIVES AND ISOMERIZATION REACTION OF OXADIAZABICYCLO[2.2.3]NONADIENE SYSTEM TO OXADIAZABICYCLO[1.2.4]NONADIENE SYSTEM

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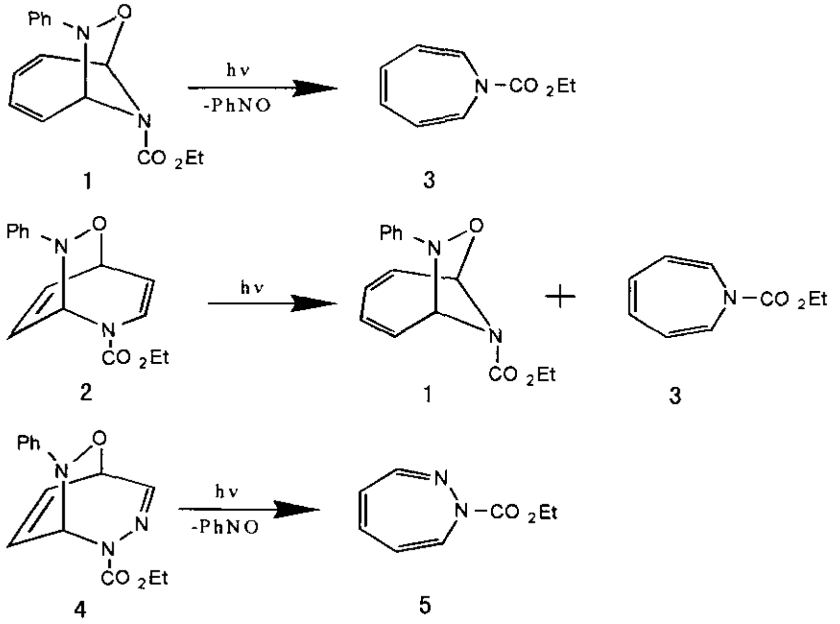
Abstract――――――An irradiation of an oxadiazabicyclo[1.2.4]nonadiene derivative in acetonitrile with a low pressure mercury lamp afforded an 1*H*-azepine derivative. An irradiation of an oxadiazabicyclo[2.2.3]nonadiene derivative gave an oxadiazabicyclo[1.2.4]nonadiene derivative and an 1*H*-azepine derivative. On the other hand, a photo-reaction of an oxatriaza-bicyclo [2.2.3]nonadiene derivative generated a 1*H*-1,2-diazepine derivative. All these reactions are considered to proceed through the same type of reaction intermediate.

Photochemistries of heterocyclic systems have attracted attentions of chemists from synthetic and theoretical view points. Photoreactions of typical monocyclic heterocycles have been progressed extensively and their reaction mechanisms have been made clear in detail.[1] However, photochemistries of cage type heterocycles do not seem to be investigated in detail.[2]

Previously, the authors reported on a photoreaction of 8-azatricyclo[3.2.1.0^{2,4}]octene derivatives to afford azabishomobenzene derivatives through a [$2\pi + 2\sigma$] type migration of a C-N bond.[3] We also reported that cage type heterocyclic compounds, oxadiazabicyclo[1.2.4]nonadiene (1) and oxadiazabicyclo[2.2.3]nonadiene derivatives (2), and oxadiazatricyclo[2.2.3]nonadiene derivatives (4) were afforded from thermal cycloaddition reactions of nitorosobenzene and an 1*H*-azepine derivative (3) and a 1*H*-1,2-diazepine derivative (5), respectively.[4] These facts prompted us to investigate photoreactions of the cage type heterocyclic systems (1), (2), and (4). In this report, the results are discussed.

A solution of an oxadiazabicyclo[1.2.4]nonadiene derivative (1)(UV(n-hexane): 238nm, log ε =3.50) in anhydrous acetonitrile was irradiated with a low pressure mercury lamp. After evaporation of the solvent at 0°C,[5] the reaction mixture was thin layer chromatographed on silica gel to give 1-ethoxycarbonyl-1*H*-azepine (3)(UV(n-hexane): 238nm, log ε =3.79). The time dependence of the yields of the recovery of 1 and the product (3) measured by HPLC is shown in Figure 1.

The photoreaction of an oxadiazabicyclo[2.2.3]nonadiene derivative (2) under the same reaction conditions as above afforded the oxadiazabicyclo[1.2.4]nonadiene derivative (1) and 3. An oxatriazabicyclo[2.2.3]nonadiene derivative (4) was irradiated under the same reaction conditions as above to give 1-ethoxycarbonyl-1*H*-1,2-diazepine (5).[6] The time dependences of the product yields of the reactions of 2 and 4 measured by HPLC are given in Figures 2 and 3, respectively.



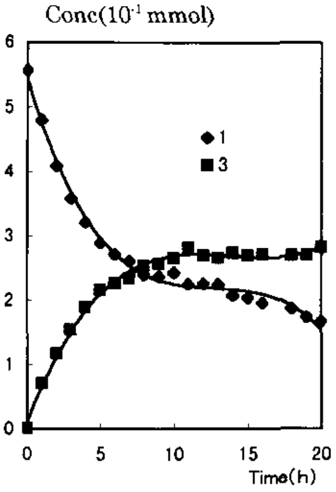


Figure 1 Photoreaction of 1

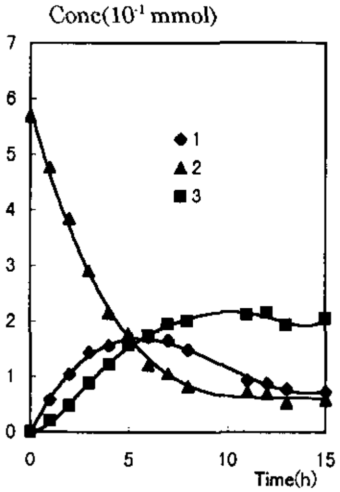


Figure 2 Photoreaction of 2

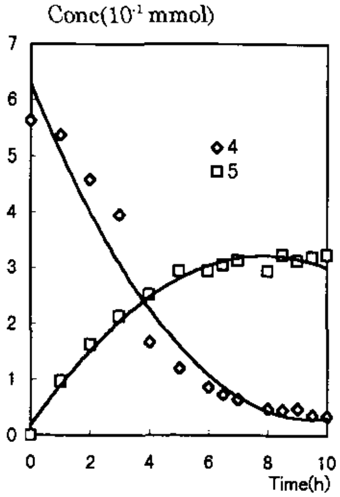
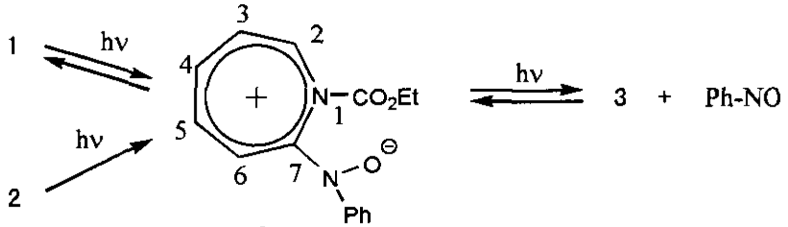


Figure 3 Photoreaction of 4

The Figure 1 shows that the concentrations of 1 and 3 remain almost unchanged after about 11 hours from the start of the reaction, suggesting that 1 and 3 reach at an equilibrium at this stage. In the Fgure 2, the concentration of 1 diminishes after about 7 hours, whereas the concentration of 3 stays constant after about 8 hours. Considering the existence of an equilibrium between 1 and 3 under the reaction conditions, Fgure 2 is thought to show that two independent routes exist for the formation of 3 from 2, *i.e.*, the direct formation from 2 and the secondary formation from the primary product (1). Figure 3 demonstrates that 4 decomposes to form 5 as time passes.



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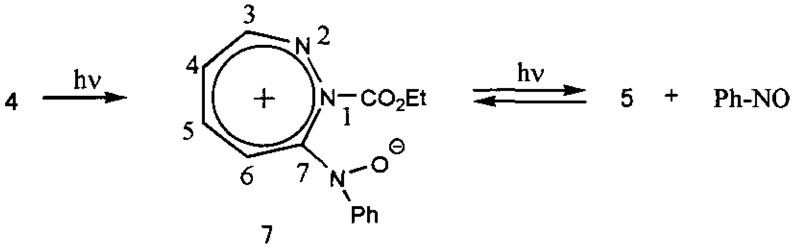

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The reaction mechanisms of the reactions of 1 and 2 can be considered to be as follows. Irradiations of 1 and 2 result in the C-O bond fission to form the same ionic reaction intermediate (6). A bond formation between the oxygen atom and the 2 position carbon of 6 can (re)form 1, on the other hand, a removal of nitorosobenzene from 6 affords 3.[7] The existence of an equilibrium between 1 and 3 as shown in Fgure 1 suggests that the reaction paths to form 1 and 3 from 6 are reversible. The reason why only 1 is reformed from 6 and 2 is not maybe attributed to the bigger stability of 1 compared to 2. Thus, the heat of formations was calculated by MINDO 3 method for 1 and 2 to be -54.38 and -34.33 KJ, respectively, demonstrating that 1 is more stable than 2.

The reaction of 4 is considered to proceed through an analogous path as that of 2. Thus, irradiation of 4 forms an ionic intermediate (7), which then decomposes to 5 and nitorosobenzene.

EXPERIMENTAL

National GL-15 ultra violet lamps were used for irradiation. The time dependence of the yields of the reaction products were measured by HPLC (HITACHI L-6000 pump and HITACHI L-4000 UV Detector) using a YAMAMURA A-303 (S-5 120A ODS) column. Wakogel B5-F was used for thin layer chromatography. Acetonitrile was distilled from calcium hidride and used immediately.

Photoreaction of 1. A solution of 1 (152 mg, 0.56 mmol) in anhydrous acetonitrile (15 mL) was irradiated under a nitrogen atmosphere. After irradiation of 20 h, the solvent was evaporated on a rotary evaporator at 0°C and the resulted residue was thin layer chromatographed on silica gel using hexane-ethyl acetate (7:3) as a developing solvent to give 3 (45 mg, 49 %, R_f=0.65).

Photoreaction of 2. A solution of 2 (155 mg, 0.57 mmol) in anhydrous acetonitrile (15 mL) was irradiated for 20 h to give 1 (19.6 mg, 13 %, R_f=0.52 (hexane-ethyl acetate7:3))and 3 (33.7 mg, 36 %, R_f=0.65(hexane-ethyl acetate7:3)).

Photoreaction of 4. A solution of 4 (154 mg, 0.56 mmol) in anhydrous acetonitrile (15 mL) was irradiated for 20 h to give 5 (20 mg, 22 %, R_f=0.50(hexane-ethyl acetate13:7)).

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5. A solvent evaporation at a temperature higher than room temperature caused a cycloaddition reaction between 3 and nitorosobenzene to reproduce 1 and 2.[4]
6. The structures of all the products were deduced on the basis of their spectral properties and confirmed by the coincidences of these properties to those of the authentic samples.
7. 6 has been proposed as an intermediate in the cycloaddition reaction between 3 and nitorosobenzene to form 1 and 2.[4] The present result can be considered to support the reaction mechanism of the cycloaddition reaction between 3 and nitorosobenzene.

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