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PHOTOCHEMISTRY OF HETEROCYCLIC CAGE COMPOUND: PHOTOREACTION OF 2,7-DIHYDROAZEPINE TO GIVE 2,3-DIHYDROAZEPINE AND PHOTOREACTION OF THE 2,3-DIHYDROAZEPINE TO FORM 1,2-DIHYDROANILINE

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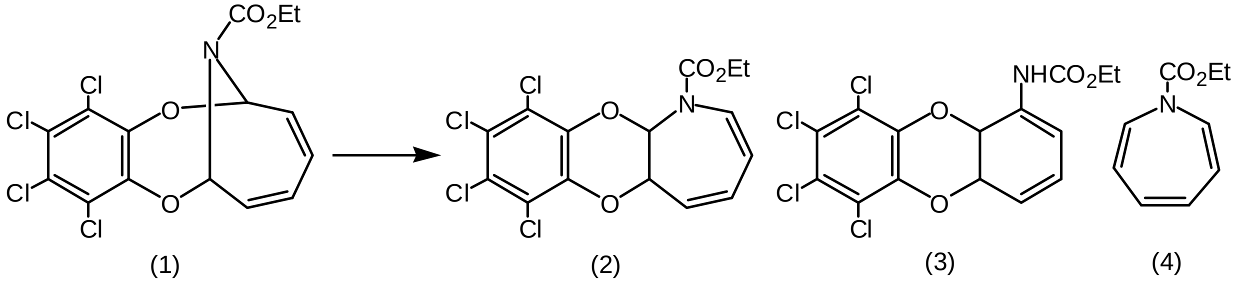
Abstract – Photoirradiation of a heterocyclic cage compound, 2,7-dihydroazepine derivative with a low pressure mercury lamp afforded a 2,3-dihydroazepine derivative. This reaction was influenced by the solvent used. On the other hand, the analogous photoirradiation of the 2,3-dihydroazepine derivative gave a 1,2-dihydroaniline derivative. An presence of triplet sensitizer promoted the reaction.

Much attention has been focussed on the photochemistries of heterocyclic systems from the view points of not only synthetic utility but also elucidation of the electronic behavior of the heterocyclic systems and mechanistic studies of the reactions. Photoreactions of azepine derivatives have been investigated energetically.[1] However, photochemistries of dihydroazepine derivatives, moreover, cage types of dihydroazepines is not investigated sufficiently.[2]

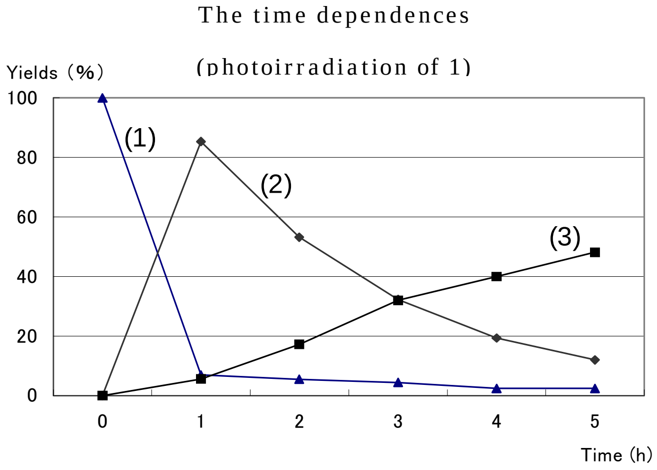
Previously, the authors have published on the synthesis of a new type of cage type heterocyclic system (**1**) by the reaction of azepine derivative with tetra -chloro-*o*-quinone.[3] Very recently, we documented on the photochemistries of cage type heterocyclic compounds.[4] As a series of our researches on the reactivities of heterocyclic compounds, we investigated photoreaction of **1**. Here the results are reported.

An anhydrous acetonitrile solution (1.25×10^{-2} M) of 2,7-dihydroazepine derivative (**1**) (UV (in methanol) 216 nm, log ε = 4.84) was photoirradiated with a low pressure mercury lamp for 5 h at room temperature. After evaporation of the solvent at 0℃, the reaction mixture was thin layer chromatographed on silica gel to give a 1,2-dihydroazepine derivative (**2**)[3] and a 1,2-dihydroaniline derivative (**3**)[3] in 11 and 43% yields, respectively.



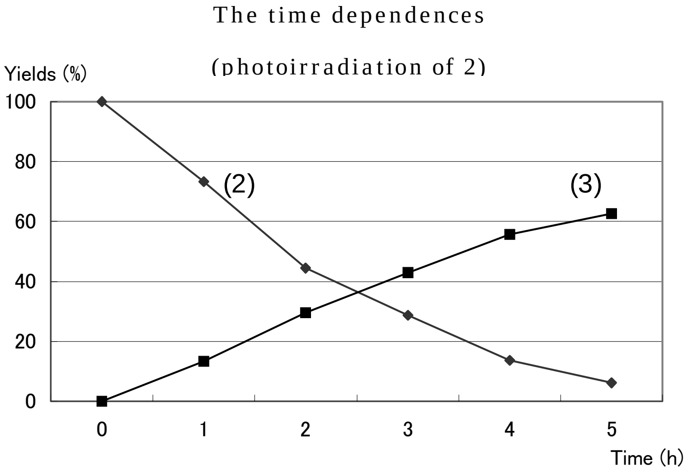
Scheme 1

Because it is known that **1** thermally rearranges to **2**,[3] the time dependences of the product yields of the reaction was monitored with an HPLC (column: YAMAMURA A-303 (S-5 120A ODS), solvent: methanol : H_2O = 4 : 1) as shown in Figure 1, which demonstrated that **2** was a product of the photoreaction of **1**.


The time dependences

(photoirradiation of 1)

Figure 1


The time dependences

(photoirradiation of 2)

Figure 2

The short time irradiation of **1** under the same reaction conditions as above but for 30 min afforded mainly **2** in 42 % yield accompanied by a small amount of **3**. The solvents used influenced this reaction. When acetone was used for the solvent, the yield of **2** was reduced to 28%. On the other hand, in THF, a new product, an azepine derivative (**4**) was formed in 14 % yield accompanied by 14% yield of **2**. The results of the short time irradiation of **1** are summarized in Table 1 together with the dielectric constants of the solvents.[5] In all cases, recovery of **1** was not detected.

Table 1

Solvents		Acetonitrile	Acetone	THF
Dielectric constants		1.22	1.06	0.84
Yields (%)	2	42	28	14
	3	trace	0	0
	4	0	0	14

As suggested in Figure 1, photoirradiation of an anhydrous acetonitrile solution of **2** (1.25×10^{-2} M) (UV (in methanol) 215 nm, log ε = 4.91) with a low pressure mercury lamp for 5 h at room temperature afforded **3**. The time dependences of the yields of **2** and **3** monitored with a similar technique as the case of Figure 1 are shown in Figure 2.

The results of the photoirradiation of **2** in several kinds of solvents are summarized in Table 2, showing that except acetone, the solvents used do not to influence on the product yields. In all cases, recovery of **2** was not detected.

Table 2

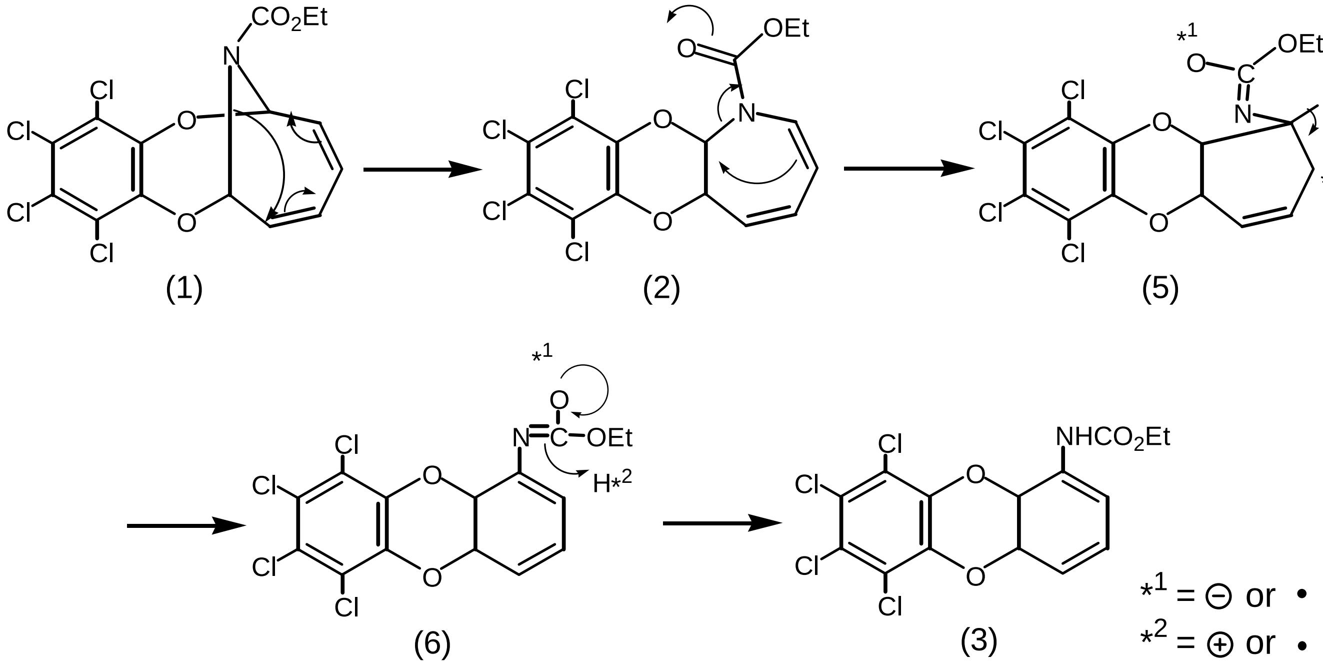
Solvents	Yields of **3** (%)
Acetonitrile	56
Ethanol	56
Acetone	73
THF	58

Table 3

Sensitizers	Yields of **3** (%)
Acetophenone	74
Benzonitrile	88
9-Cyanoanthracene	56
Acetone	73
None*	56

* Reaction with no sensitizer

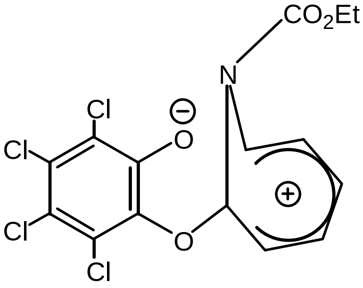
The improvement of the yield of **3** in acetone solvent suggested a possibility of a sensitization reaction. Table 3 shows the yield of **3** in the reaction of **2** in acetonitrile under the presence of several kinds of sensitizers. Triplet sensitizers, acetone, acetophenone, and especially benzonitrile, promoted the yields of **3**, but electron transfer type sensitizer, 9-cyanoanthracene had no effect on the yield.



Scheme 2

The reaction is considered to proceed as follows. The azepine derivative (**4**) is considered to be formed through a [6π+4σ] type cycloreversion reaction of **1**. Formally, a [4π+2σ] type rearrangement of **1** can generate **2.** However, considering that the yield of **2** is better in the polar solvents as shown in Table 1, there is a good possibility of the formation of **2** to proceed *via* a stepwise mechanism through an ionic intermediate such as **7**.

An ionic or radical type ring contraction process in **2** can afford an intermediate (**5**), which then gave the final product (**3**) *via* a proton (hydrogen) transfer process illustrated in Scheme 2.



(7)

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