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# Intermediates in photolyses of 2,2'-diazidoazobenzene and 2-azidoazobenzene in low-temperature matrices

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#### Abstract

The photolyses of 2,2'-diazidoazobenzene (1) and 2-azidoazobenzene (4) were investigated in argon and 2-methyltetrahydrofuran (MTHF) matrices at cryogenic temperature. Nitrene and dinitrene were observed in the photolysis of 1 in an MTHF matrix by electron spin resonance (ESR). The dinitrene in an argon matrix was also observed by ultraviolet-visible (UV-vis) and Fourier transform infrared (FT-IR) spectroscopies. UV absorption bands at 430 and 460 nm and IR peak at 1263 cm<sup>-1</sup> were assigned to the dinitrene. Furthermore, mononitrene as an intermediate of the photolysis of 4 was confirmed by UV-vis and FT-IR spectroscopies in an argon matrix. An IR band at 1225 cm<sup>-1</sup> of mononitrene was observed. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Low-temperature matrix; Photolysis; Diazido compounds; Intermediates; Dinitrene

### 1. Introduction

Intermediates having two nitreno groups are a subject of interest in connection with the syntheses of high-spin organic compounds [1-3]. Many investigations of the intramolecular interaction of two nitreno groups have been reported on the basis of electron spin resonance (ESR) spectroscopy [4-8].

In the case of the photolysis of aromatic compounds substituted with two azido groups at p,p'position, a polymerization was observed in a solution [9,10]. It was suggested that the degree of polymerization of the polymers depended on the concentration of intermediates in the solution. The intermolecular reaction between intermediates, which were generated efficiently in pulsedlaser photolysis, led to a polymer in good yield. These intermediates in the photolysis of the diazides were identified as dinitrenes using matrix isolation technique [11].

In this paper, we report the identification of intermediates generated in the photolysis of 2,2'diazidoazobenzene (1) and 2-azidoazobenzene (4). Previously, thermal and photochemical decompositions of 1 in a solution were reported by Carboni and Castle [12], and Hall et al. [13]. They showed that decomposition of 1 proceeded stepwise by a loss of nitrogen to give 5,6H-dibenzo[b, f]-1,3a,4,6a-tetraazopentalene (3) via 2-(2-azidophenyl)-2H-benzotriazole (2) (Scheme

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1). They suggested that benzotriazole 2 was formed through a mononitrene generated in the first step of nitrogen loss from 1. However, a dinitrene as an intermediate was not observed in the solution. Therefore, we investigated the photolysis of the diazides using the matrix-isolation technique. The dinitrene was identified in lowtemperature matrices by ultraviolet-visible (UVvis), Fourier transform infrared (FT-IR), and ESR measurements. The mononitrene which generates at the first step of the photolysis of 1 was also confirmed by comparison with the spectroscopic data of the photolysis of 4 in cryogenic matrices.

### 2. Experimental section

#### 2.1. General data

2,2'-Diazidoazobenzene (1) was prepared from 2,2'-diaminoazobenzene through the reaction of its diazonium salt and sodium azide by a conventional procedure [14] and purified by recrystallization from a hexane-ether solution. 2-Azidoazobenzene (4) was prepared by coupling of 2-azidoaniline with aniline and purified by recrystallization from a hexane solution [15]. In IR, UV-vis, and nuclear magnetic resonance (Brucker AC200) spectra of 1 and 4, the impurity was not observed.

2-Methyltetrahydrofuran (MTHF, Tokyo Chemical Industry) was purified by distillation from sodium. Spectroscopic grade n-hexane (Kanto Chemical) was used without purification.

#### 2.2. ESR measurement at cryogenic temperature

The ESR spectra were measured with a JEOL JES-RE3X spectrometer equipped with an optical transmission cavity and Air products LDT-3 liquid helium transfer system. The experiment of ESR measurement was carried out in a similar manner to the reference [16].

Diazide 1 and azide 4 were dissolved in MTHF. The solution (ca.  $10^{-3}$  M) was placed in an ESR sample quartz tube (4 mm o.d.) and degassed by freeze-pump-thaw cycles. Photolysis of samples

was carried out at 20–77 K with monochromatic light at 365 nm (an USHIO 500 W high-pressure mercury lamp equipped with a JASCO CT-10 monochromator) in an ESR cavity. During the photolysis the ESR tube was rotated occasionally in order to make the photolysis homogeneous. All spectra were measured in the dark after the photolysis.

### 2.3. Photolyses of 1 in a solution

A hexane solution of 1 (ca.  $10^{-4}$  M) was irradiated at room temperature in a quartz cell (optical path length, 1 cm) with monochromatic light at 365 nm. The photolysis was followed by a UV-vis spectrophotometer (Shimadzu, UV-300).

# 2.4. Photolysis of **1** and **4** in an MTHF matrix at 77 K

An MTHF solution of 1 (ca.  $10^{-4}$  M) was placed in a quartz cell (optical path length, 1 cm), and degassed by freez-pump-thaw cycles. The photolysis of the sample was carried out in liquid nitrogen with monochromatic light at 365 nm, and followed by a UV-vis spectrophotometer. The photolysis of 4 in an MTHF matrix was carried out in a similar manner to the photolysis of 1 in an MTHF matrix.

### 2.5. Photolyses of 1 and 4 in an argon matrix

Experiments in an argon matrix [17] were carried out at 18–20 K using a closed-cycle refrigera-





Fig. 1. ESR spectra obtained of the photolysis of 1 and 4 in an MTHF matrix upon 365 nm light irradiation: (a) the irradiation of 1 for 160 min at 77 K; (b) the irradiation of 4 for 40 min at 20 K.

tor system (Air Products, Displex CS-202). The photolyses were followed by UV-vis and FT-IR spectrophotometers (Shimadzu, FT-IR 8000). Sapphire and CsI plates were used for the UV-vis and FT-IR measurements, respectively.

Diazide 1 and azide 4 were sublimed at 338 and 300 K with argon gas, respectively, and deposited on cold plates. The isolated 1 in an argon matrix at 18–20 K was photolyzed with a high-pressure mercury lamp (USHIO 500 W) through a Toshiba UV-35 cut-off filter ( $\lambda > 350$  nm) and a water filter (path length 20 cm), and the isolated 4 in an argon matrix was irradiated with monochromatic light at 365 nm.

# 3. Results and discussion

# 3.1. The ESR measurement of intermediates from 1 and 4

The formation of intermediates from 1 and 4 in low-temperature matrices was confirmed by an ESR spectrometer (Fig. 1). Cryogenic ESR spectra were measured in an MTHF rigid matrix. At the initial stage (10 min) of photolysis of 1 at 77 K, the ESR spectrum showed a new resonance line at 665 mT. With subsequent irradiation (40 min), three new resonance lines appeared at 150,



Fig. 2. Intensity changes of ESR resonance of the photolysis of 1 in an MTHF matrix at 77 K.

275, and 370 mT as shown in Fig. 1(a). In addition, the measurement of ESR spectra in the photolysis of 4 at 20 K was also carried out in an MTHF rigid matrix. The irradiation of a matrix containing 4 showed a resonance at 665 mT as shown in Fig. 1(b).

A resonance line at around 330 mT has been assigned to doublet radicals which are often observed in the photolyses of azides in organic rigid matrices [18]. The resonance lines at 665 mT, which were observed in the photolysis of **1** and **4**, are triplet mononitrenes. It is known that the ESR resonance of triplet mononitrenes appeared around



Fig. 3. UV-vis spectra obtained by irradiation (365 nm) of 2-azidoazobenzene (**4**) in an argon matrix at 18 K: (a) before irradiation; (b) after irradiation for 16 min; and (c) after irradiation for 206 min.



Fig. 4. IR difference spectra of the photolysis of 4 in an argon matrix at 18 K between before (negative) and after 365 nm light irradiation: (a) after irradiation for 5 min; (b) after irradiation for 20 min; (c) after irradiation for 100 min. The peaks marked with  $\bullet$  and  $\blacksquare$  are assigned to the bands due to 8 and 5, respectively.

670 mT [19,20]. The intensity of resonance line at 665 mT observed in the photolysis of 1 was maximum at 120 min and decreased with further irradiation as shown in Fig. 2. And the resonance line at 150 mT appeared after the photolysis for 40 min. It is indicated that the photolysis of 1 in the cryogenic matrix proceeds in two steps. The resonance lines at 150, 275, and 370 mT in the photolysis of 1 come from a sole intermediate and are assigned to triplet dinitrene, 2,2'-dinitrenoazobenzene (7). According to the method by Wasserman et al. [21], the zero filed splitting parameters for triplet nitrene and dinitrene 7 were estimated to be D = 0.968 and 0.09 cm<sup>-1</sup>, respectively. Moreover, it was reported that the D value of 1,4-dinitrenobenzene (10) is 0.169 [22], and that of 4,4'-dinitrenoazobenzene (11) is 0.058 cm  $^{-1}$  [23]. Therefore the D value (0.09 cm<sup>-1</sup>) was consistent with the assignment of dinitrene 7, which has intramolecular interaction between two nitreno groups.



#### 3.2. The photolysis of 4 in an argon matrix

UV-vis spectral changes of the photolysis of **4** in an argon matrix are shown in Fig. 3. Upon irradiation, new absorption maxima at ca. 370, 385 and 415 nm appeared in a longer wavelength region than those of azide **4**. Upon further irradiation, the absorption maxima at 297, 304, 312, 319, and 328 nm of 2-phenyl-2H-benzotriazole (**5**) [24] were observed, while absorption maxima appearing at 370, 385 and 415 nm decreased with the same behavior. These spectral changes were



Scheme 2.



Fig. 5. UV-vis spectra obtained by irradiation ( $\lambda > 350$  nm) of 2,2'-diazidoazobenzene (1) in an argon matrix at 18 K: (a) before irradiation; (b) after irradiation for 10 s; (c) after irradiation for 1 min; (d) after irradiation for 2 min; (e) after irradiation for 10 min; and (f) after irradiation for 30 min.

also observed in the photolysis of **4** in an MTHF matrix. These results indicated that the same intermediate was formed in the argon and MTHF matrices. Therefore the absorption maxima at 370, 385 and 415 nm corresponds with 2-nitrenoa-zobenzene (**8**), which showed the resonance line at 665 mT in cryogenic ESR spectrum.

The FT-IR spectral changes of the photolysis of **4** in an argon matrix showed two steps as shown in Fig. 4. The peaks at 683, 770, and 1225 cm<sup>-1</sup> appeared upon irradiation, and then these peak intensities decreased in the same behavior upon further irradiation. Finally, the peaks at 1502, 1345, 1293, 964, 815, 759, 747, and 688 cm<sup>-1</sup> appeared. These eight peaks were ascribed to 2-phenyl-2H-benzotriazole (**5**). Therefore, the peaks at 683, 770, and 1225 cm<sup>-1</sup> correspond with nitrene **8**. The peak position of 1225 cm<sup>-1</sup> would be ascribed to C–N stretching mode [25]. Hayes and Sheridan reported the IR bands of

triplet phenylnitrene in an argon and a nitrogen matrix [26]. They showed major IR bands at 1552, 1524, 1287, 1286, 1148, 1079, 746 and 654 cm<sup>-1</sup> of phenylnitrene without the assignment of these bands. The bands at 1287 and 1286 cm<sup>-1</sup> may correspond to the band at 1225 cm<sup>-1</sup> observed in the photolysis of **4** though the wavenumber shift of ca. 60 cm<sup>-1</sup> was observed. Moreover, Dunkin and Thomson reported the IR peak at 1284 cm<sup>-1</sup> of pentafluorophenyl nitrene [27]. Therefore, the photolysis of **4** in low-temperature matrix is summarized in Scheme 2.

# 3.3. The photolysis of 1 in an argon matrix

The photochemical changes of **1** irradiated in an argon matrix were followed by UV-vis spectroscopy, as shown in Fig. 5. The similar spectral changes were observed in UV-vis spectra in the MTHF and the argon matrices. In the first step of the photolysis, UV-vis spectra showed the decrease of **1** and the appearance of new absorption maximum at 440 nm after 10 s (Fig. 5b). In the next step, maxima at 430 and 460 nm appeared confining 440 nm band (Fig. 5c, d). Subsequently,



Fig. 6. UV-vis spectra of 2,2'-diazidoazobenzene (1) in a hexane solution at room temperature: (a) before irradiation; (b) after irradiation for 2 min; and (c) after irradiation for 20 min.



Fig. 7. IR spectra of the photolysis of 1 in an argon matrix at 18 K upon the irradiation ( $\lambda > 350$  nm): (a) before irradiation; (b) after irradiation for 1 min; (c) after irradiation for 2 min; (d) after irradiation for 4 min; (e) after irradiation for 9 min; (f) after irradiation for 19 min; (g) after irradiation for 59 min; (h) after irradiation for 89 min. The peaks marked with  $\Delta$ ,  $\bigcirc$  and  $\Box$ , are assigned to the bands due to 6, 7 and 3, respectively.

new absorption maxima appeared at 252, 381, and 402 nm, while the maxima at 430 and 460 nm decreased (Fig. 5e, f). The maxima at 252, 381, and 402 nm were the band of 3 [28], which also formed in the photolysis of 1 in the solution (Fig. 6). On the contrary, the maxima at 440, 430, and 460 nm were not observed in the photolysis of 1 in solution at room temperature. The photolysis of 1 in a solution proceeded via 2, and then 3 was formed. However, the formation of 2 was not observed in the photolysis of 1 in cryogenic matrices. The UV-vis absorption bands observed in the photolysis of 1 in cryogenic matrices were compared with the results of ESR experiments. In the case of ESR measurement, it should be noted that the generation rates of 6 and 7 were very slow because of low intensity of light leading to the ESR tube (Figs. 1 and 2). Therefore, the absorption maximum at 440 nm was assigned to mononitrene 6, and the maxima at 430 and 460 nm were ascribed to dinitrene 7.

The FT-IR spectral changes on the photolysis of **1** measured in an argon matrix were similar to those obtained in the UV-vis spectra. The FT-IR spectra are shown in Fig. 7. The photolysis of **1** proceeded in three steps as follows; (1) bands at 680, 744, 759, and 1225 cm<sup>-1</sup> appeared upon irradiation (Fig. 7b, c); (2) these peak intensities decreased and the intensities at 739, 1096, and 1263 cm<sup>-1</sup> increased upon further irradiation; and (3) the bands (1389, 1155, 1103, 812, 748, and 733 cm<sup>-1</sup>) ascribed to **3** were observed with decrease of intensities of other peaks (Fig. 7e–h). The bands (1501, 1312, 1292, 1276, 1217, 963, 761, and 745 cm<sup>-1</sup>) ascribed to **2** were not observed during the photolysis of **1** in an argon matrix. Therefore the reaction path from **6** to **2** would be suppressed in a cryogenic matrix (Scheme 3).

The intermediate observed in the first step on the IR spectra can be assigned 2-azido-2'-nitrenoazobenzene (6), and the intermediate observed in the second step can be assigned 2,2'-dinitrenoazobenzene (7) on the basis of the UV-vis spectroscopic analysis. As mentioned above, it is indicated that the C-N stretching band of nitrene 8 appeared at 1225 cm<sup>-1</sup>. Therefore the IR peak at 1225 cm<sup>-1</sup> of nitrene 6 would

be assigned to the C-N stretching band in the same manner. On the other hand, the IR peaks at 739, 1096 and 1263 cm<sup>-1</sup> were assigned to the dinitrene 7. The IR peaks at 1263 cm<sup>-1</sup> would be assigned to C-N or C=N stretching band of dinitrene 7. Previously, we reported that the IR peaks at 1759 and 1779 cm<sup>-1</sup> were ascribed to the C=N stretching band of 1,4-dinitrenobenzene (10) in an argon matrix [11]. These peaks appeared at higher wavenumber positions compared with the corresponding band of 7 (1263 cm<sup>-1</sup>). The reason for the shift of IR peaks could be explained in terms of the double bond character of nitrene. Because of strong interaction of two nitreno groups in dinitrene 10, a quinonoid structure of dinitrene 10 was confirmed. Therefore, it is considered that the double bond character in dinitrene 7 is relatively week than dinitrene 10. These assignments are consistent with ESR observation. We have reported on the relationship between singlet-triplet energy gaps and the D values for some quinonoidal dinitrenes [29]. The D values are related to the magnitude of polarized  $\pi$  spin.



Scheme 3.

Thus, a small D value indicates that the interaction of two nitreno groups was relatively small. As mentioned above, in the case of dinitrene 7, the D value is smaller than that of dinitrene 10. It is indicated that the double bond character of C-N bond of 10 would be stronger than that of 7.

The conversion of 7 into 3 proceeded photochemically. As mentioned above, 3 was observed in the matrix with further irradiation of 7. However, in the photolysis of 1 in the MTHF matrix, 3 was not observed when the matrix containing 7 was melted to room temperature. In conclusion, the photolysis of 1 in low-temperature matrices can be summarized in Scheme 3.

#### 4. Conclusion

The photolyses of 2,2'-diazidoazobenzene 1 and 2-azidoazobenzene 4 were investigated in lowtemperature matrices. In the photolysis of 4 in low-temperature matrices, mononitrene 8 as an intermediate was observed in ESR, IR and UV-vis spectra. The IR band at 1225 cm<sup>-1</sup> of C-N stretching mode of 8 was assigned. In the case of the photolysis of 1, the generated intermediates of mononitrene 6 and dinitrene 7 were confirmed. The photolyses of **1** in low-temperature matrices proceeded by stepwise loss of nitrogen to give 6 and 7. The IR bands at 1225 and 1265 cm<sup>-1</sup> were ascribed to the C-N stretching band of 6 and 7, respectively. The peak position of the C-N stretching mode of 7 and the D value estimated by ESR spectrum suggested that the interaction of two nitreno groups of 7 was relatively small compared with 1,4-dinitrenobenzene 10.

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