# New Findings in Photochemistry of *p*-Nitrophenyl Azide in the Presence of an Amine: Generation and Trapping of Enamines

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(Received March 19, 1999; CL-990186)

4, 5-Dihydro-5-diethylamino-1-(*p*-nitrophenyl)-1, 2, 3-triazole (**3**) was obtained in the photolysis of *p*-nitrophenyl azide (**1**) in triethylamine (TEA), for which the structure was determined by X-ray crystallographic analysis. The formation of the triazoline **3** is reasonably explained in terms of trapping of *N,N*-diethylvinylamine (**5**) generated *in situ* with the starting azide **1**. The reaction sequence involving a single electron transfer from TEA to the electronically excited azide is proposed for the formation of the enamine **5**.

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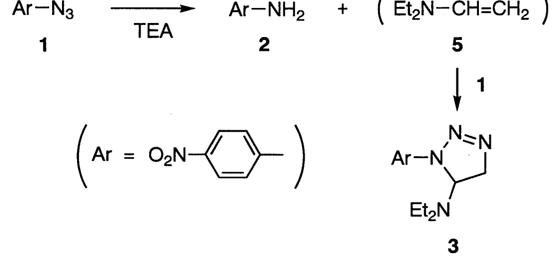
The photochemistry of nitro-substituted aryl azides has been the subject of great interest because of their application in biochemical photoaffinity labeling.[1,2] A characteristic photoreactivity of *p*-nitrophenyl azide (**1**) has been demonstrated in the irradiation in diethylamine,[3] where *p*-nitroaniline (**2**) is exclusively obtained with no trace of the 3*H*-azepine which is established as the usual photoproduct of aryl azides.[4] In 1986, Schuster and his co-workers reported detailed studies of the photochemistry of **1**.[5] In their papers, the formation of the aniline **2** in the irradiation of **1** in the presence of a tertiary amine, i.e., *N,N*-dimethyl-*tert*-butylamine, was explained by the mechanism involving a single electron transfer from the amine to the triplet nitrene, followed by a hydrogen transfer from the amine radical cation to the nitrene radical anion. In the course of our studies on photochemistry of aryl azides,[6] we found that the photolysis of **1** in a tertiary amine having *β*-hydrogens, such as triethylamine (TEA) and tri-*n*-propylamine, yielded not only the aniline **2**, but an additional photoproduct which showed characteristic multiples at $\delta$ 4-5 in its $^1$H NMR spectrum. In this paper, we report the structure of the product obtained in the irradiation of **1** in TEA, the formation of which leads us to propose the reaction sequence for photolysis of **1** different from that presented by Schuster and his co-workers.[5]

A degassed solution of the azide **1** (25 mg, 0.15 mmol) in TEA (25 mL) was irradiated with the Pyrex-filtered light of a high-pressure mercury lamp. After separation by the use of gel permeation liquid chromatography, two reaction products were isolated, one of which was readily identified as the aniline **2** (57%). The structure of the second photoproduct obtained in 24% yield as light-yellow needles, which exhibited a set of signals characteristic of the partial structure -CH$_A$H$_B$-CH$_X$- at $\delta$ 4.1-5.1 in its $^1$H NMR spectrum,[7] was determined as 4,5-dihydro-5-diethylamino-1-(*p*-nitrophenyl)-1,2,3-triazole (**3**) by X-ray crystallographic analysis.[8] The ORTEP diagram is given in Figure 1. The triazoline **3** was obtained in organic solvents in the presence of TEA, together with the aniline **2** and *p,p'*-dinitroazobenzene (**4**) which is known to be produced through the dimerization of the triplet nitrene.[5] As shown in Table 1, the product distribution was very dependent on the solvent used in the photolysis, as well as on the TEA concentration.



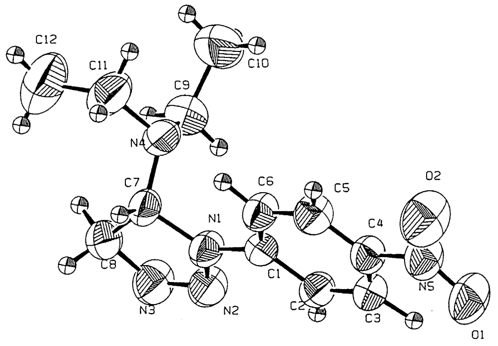


**Figure 1.** ORTEP diagram of **3**.

**Table 1.** Dependence of the photoproducts on solvent and TEA concentration in the photolysis of the azide **1**[a]

| Solvent | [TEA]/M | Yield/%[b] | | |
|---|---|---|---|---|
| | | **2** | **3** | **4**[c] |
| Benzene | 0 | <1 | - | 64 |
| Benzene | 0.07 | 26 | 3 | 38 |
| Benzene | 0.36 | 50 | 17 | 13 |
| Benzene | 0.72 | 56 | 24 | 6 |
| Dichloromethane | 0.72 | 60 | 24 | 4 |
| Acetonitrile | 0.72 | 45 | 3 | 5 |
| Methanol | 0.72 | 31 | <1 | 33 |

[a] [**1**] = 6 mM. [b] Yield based on photolytically-reacted azide.
[c] Containing a small amount of *p,p'*-dinitroazoxybenzene.

The formation of the triazoline **3** is reasonably interpreted in terms of trapping of *N,N*-diethylvinylamine (**5**) generated in the course of the photoreaction with the starting azide **1**. It is well-known that nitro-substituted phenyl azides react thermally with electron-rich alkenes, such as enamines,[9] enamides,[10] and enol ethers,[11] to give [3 + 2]cycloaddition products. Though a regiochemistry of the cycloaddition was determined by the derivation

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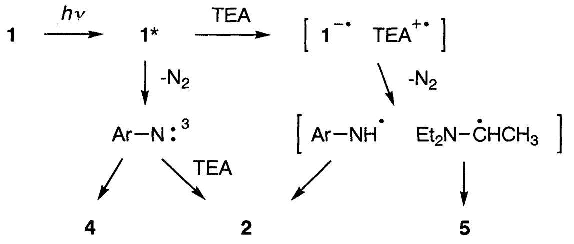
of the cycloadducts to the known triazoles[12] and was explained in terms of electronic control in the transition state,[9b,10] we believe that the molecular structure of **3** presents the first unambiguous evidence for the orientation in azide cycloaddition reactions.[13]

Moreover, to our knowledge, the triazoline **3** provides the first example of trapping of *N,N*-diethylvinylamine (**5**), which is estimated to be an extremely unstable enamine,[14] with a 1,3-dipole. The enamine **5** is known to be produced in the photoreaction of an electron-accepting sensitizer with TEA.[15] Further, it has been established by CIDNP studies that the enamine **5** is formed from the α-aminoethyl radical, $Et_2NCH^{\cdot}CH_3$, produced through the proton transfer from TEA radical cation to the sensitizer radical anion.[15a,d] It is reasonable to assume that in the photoreaction of **1** with TEA, the enamine **5** is generated by the analogous mechanism involving a sequential electron and proton transfer. Thus, the isolation of the triazoline **3**, which implies the generation of the enamine **5**, provides a direct indication that a single electron transfer participates in photolysis of **1**. Though these results are not inconsistent with those reported by Schuster and his co-workers,[5] it appears to be necessary to modify their reaction scheme, since the generation of the α-aminoethyl radical cannot be explained by their mechanism.

It is probable that the enamine **5** is produced through a hydrogen transfer from the α-aminoethyl radical to the *p*-nitrophenylaminyl radical within the solvent cage. This expectation is supported by the observation that the use of a polar solvent, where the initially-formed radical ion pair tends to dissociate into free radical ions, is unfavorable for the formation of **5**, that is, of the triazoline **3** (Table 1). Though it is reasonable to think that the formation of **3** is accompanied by that of the aniline **2**, the ratio of **2** to **3** varies significantly with the TEA concentration, as shown in Table 1. This observation suggests the presence of another pathway to the formation of **2**.

The reaction sequence, which we tentatively propose to explain our findings, is shown in Scheme 1. In a high TEA concentration, the electron transfer from TEA to the electronically excited azide to give a pair of $TEA^{+\cdot}$ and the azide radical anion $\mathbf{1}^{-\cdot}$ could compete with a loss of $N_2$ to give the triplet nitrene which is a precursor of both **2** and **4**.[16] A loss of $N_2$ from $\mathbf{1}^{-\cdot}$, followed by the proton transfer from $TEA^{+\cdot}$, could lead to the formation of **2** accompanied by the generation of **5**. The azide radical anion $\mathbf{1}^{-\cdot}$ has been postulated previously as a transient intermediate in the electrochemical reduction of **1**.[17]



**Scheme 1.** (Ar = $p$-$O_2NC_6H_4$-)

In conclusion, the isolation of the triazoline **3** in the irradiation of **1** in TEA gives the opportunity to reinvestigate the reaction scheme for photolysis of **1**. Further work to elucidate the photoreactivity of nitro-substituted aryl azides is ongoing in our laboratory.[18]

This work was supported by grants from the Ministry of Education, Science, Sports and Culture, Japan (No. 09440214) and from the Core Research for Evolutional Science and Technology (CREST).

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7 Spectroscopic data for **3**: mp 95-96 °C dec; $^1H$ NMR ($CDCl_3$) $\delta$ 0.98 (6H, t, $J$ = 7.2 Hz), 2.33-2.40 (2H, m), 2.43-2.50 (2H, m), 4.12 (1H, dd, $J$ = 18.0, 10.4 Hz), 4.48 (1H, dd, $J$ = 18.0, 3.7 Hz), 5.12 (1H, dd, $J$ = 10.4, 3.7 Hz), 7.57 (2H, d, $J$ = 9.2 Hz), 8.23 (2H, d, $J$ = 9.2 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 13.1, 41.6, 66.1, 71.2, 114.8, 125.4, 142.3, 145.2.

8 Crystal data for **3**: triclinic, $P\bar{1}$ (No. 2), $a$ = 9.9983(6) Å, $b$ = 11.2046(6) Å, $c$ = 6.1873(4) Å, $\alpha$ = 99.472(5)°, $\beta$ = 90.453(5)°, $\gamma$ = 79.314(5)°, $V$ = 671.66(7) Å$^3$, Z = 2, $D_{calcd}$ = 1..302 g cm$^{-3}$, $R$ = 0.071, $R_w$ = 0.085 ($w = 4F_0^2/\sigma^2(F_0^2)$) for 1675 refs with $I > 3\sigma(I)$. Structure was solved and refined with the TEXSAN crystallographic software package.

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13 While we assume that the triazoline **3** is formed by the reaction of the azide **1** in its ground state with the enamine **5**, the possibility that the excited azide $\mathbf{1}^*$ participates in the cycloaddition cannot be ruled out.

14 The lifetime of the enamine **5** is estimated to be several seconds in solutions: a) M. Goez, J. Rozwadowski, and B. Marciniak, *J. Am. Chem. Soc.*, **118**, 2882 (1996). b) M. Goez, V. Zubarev, and G. Eckert, *J. Am. Chem. Soc.*, **120**, 5347 (1998).

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16 At the present stage, we cannot draw a definitive conclusion concerning the spin state of the electronically excited state responsible for the electron transfer. We feel that the triplet excited azide $\mathbf{1}^{*3}$ could participate in the electron transfer, because the nitro substituent would reduce the lifetime of the singlet excited state owing to an acceleration of intersystem crossing. Moreover, since the electron transfer from TEA ($E_{ox}$ 1.15 V *vs.* SCE) to triplet excited nitrobenzene ($E_{red}$ -1.08 V *vs.* SCE, $E_T$ 58 kcal mol$^{-1}$) is evaluated to be an exothermic process ($\Delta G_{et}$ = ca. -7 kcal mol$^{-1}$), the rate of electron transfer from TEA to $\mathbf{1}^{*3}$ is expected to be ≥ $10^9$ s$^{-1}$ in a high TEA concentration (≥ 1 M).

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18 While the photochemical formation of **3** was strictly confirmed, we found that **3** was detected even in a solution of **1** in TEA standing in the dark. The mechanism of the reaction is now under examination.