J. Org. Chem. **1997,** *62,* 3055−3061

Photochemical Reactions of Mesityl Azide with Tetracyanoethylene: Competitive Trapping of Singlet Nitrene and Didehydroazepine

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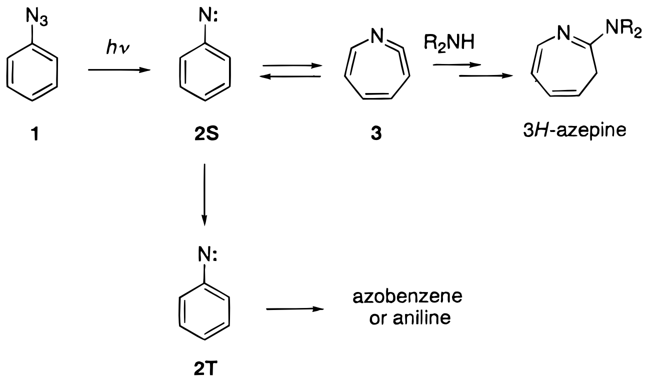
Received December 9, 1996⊗

Irradiation of the title azide **4** in the presence of TCNE gives a mixture of two stable adducts. One of them is identified as the azomethine ylide **5**, the structure of which is strictly determined by X-ray crystallography. The other is spectroscopically assigned to the spiroazepine **6**. The effect of wavelength of the light employed in the photolysis reveals that the TCNE−**4** charge-transfer complex (λ_{max} 454 and 550 nm in dichloromethane) does not participate in the adduct formation. The ratio of the adducts obtained in the photolysis is dependent linearly upon the initial concentration of TCNE, which strongly suggests that the adducts **5** and **6** are produced by competitive trapping of singlet mesitylnitrene (**8S**) and trimethyldidehydroazepine (**9**), respectively. The rate constant for the reaction of **8S** with TCNE is estimated to be on the order of 10^9 M^{-1} s^{-1} or greater. The PM3 calculation indicates that the azomethine ylide **5** is thermodynamically more stable than the aziridine **7**, which is thought to be initially formed by the reaction of **8S** with TCNE. Thus, we propose that these findings make the first example of competitive trapping of singlet arylnitrene and its ring-expanded isomer with an alkene, which definitely reveals the intervention of singlet nitrene in the photolysis of an aryl azide.

Studies of the photodecomposition processes of aryl azides have advanced in recent years.[1] Platz and his coworkers established the scheme of the photochemical decomposition of phenyl azide (**1**) by the use of spectroscopic techniques and quantitative product analyses, where singlet phenylnitrene (**2S**) was identified as the temperature-dependent branching point (Scheme 1).[2] At room temperature the ring expansion from **2S** to didehydroazepine (**3**) is favored over intersystem crossing to triplet phenylnitrene (**2T**), while at low temperature **2T** is responsible for the product formation since the rate of ring expansion decreases considerably.

Thus, singlet phenylnitrene (**2S**) is postulated to be a primary reactive intermediate formed upon the photolysis of phenyl azide (**1**). However, although triplet phenylnitrene (**2T**), as well as didehydroazepine (**3**), has been directly observed by means of IR and UV spectroscopy in matrices[3] and in solutions,[4] **2S** has not yet been detected by spectroscopy. Odum and Wolf reported that the singlet nitrene and the didehydroazepine formed photolytically from *p*-cyanophenyl azide were competitively trapped with dimethylamine to give the hydrazine and the 3*H*-azepine derivative, respectively.[5] It was also reported that highly electrophilic singlet nitrenes formed from aryl azides substituted with electron-withdrawing groups were captured by alkanes, alkenes, aromatics, and amines.[6] However, attempts to trap singlet phenylnitrene (**2S**), as well as arylnitrenes having no electron-withdrawing groups, with these external reagents have been unsuccessful. Very recently, it was reported that singlet nitrenes from the irradiation of phenyl, 4-biphenylyl, and 2-fluorenyl azide could be trapped by protonation in aqueous solutions to give nitrenium ions.[7]

Scheme 1



In the course of our studies on trapping of singlet arylnitrenes with electron-deficient alkenes, we found

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† Mie University.

⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1997.

(1) The photochemistry of aryl azides has reviewed; see, for example: (a) Iddon, B.; Meth-Cohn, O.; Scriven, E. F. V.; Suschitzky, H.; Gallagher, P. T. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 900. (b) Scriven, E. F. V. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1982. (c) *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic Press: New York, 1984. (d) Wentrup, C. *Reactive Molecules*; Wiley: New York, 1984; Chapter 4.

(2) Leyva, E.; Platz, M. S.; Persy, G.; Wirz, J. *J. Am. Chem. Soc.* **1986**, *108*, 3783.

(3) (a) Chapman, O. L.; Le Roux, J.-P. *J. Am. Chem. Soc.* **1978**, *100*, 282. (b) Donnelly, T.; Dunkin, I. R.; Norwood, D. S. D.; Prentice, A.; Shields, C. J.; Thompson, P. C. P. *J. Chem. Soc., Perkin Trans. 2* **1985**, 307. (c) Hayes, J. C.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 5879.

(4) (a) Shields, C. J.; Chrisope, D. R.; Schuster, G. B.; Dixon, A. J.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 4723. (b) Li, Y.-Z.; Kirby, J. P.; George, M. W.; Poliakoff, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 8092.

(5) Odum, R. A.; Wolf, G. *J. Chem. Soc., Chem. Commun.* **1973**, 360.

(6) (a) Banks, R. E.; Sparkes, G. R. *J. Chem. Soc., Perkin Trans.1* **1972**, 2964. (b) Banks, R. E.; Prakash, A. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1365. (c) Abramovitch, R. A.; Challand, S. R.; Yamada, Y. *J. Org. Chem.* **1975**, *40*, 1541. (d) Leyva, E.; Young, M. J. T.; Platz, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 8307. (e) Young, M. J. T.; Platz, M. S. *Tetrahedron Lett.* **1989**, *30*, 2199. (f) Keana, J. F. W.; Cai, S. X. *J. Org. Chem.* **1990**, *55*, 3640. (g) Poe, R.; Schnapp, K.; Young, M. J. T.; Grayzar, J.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 5054.

(7) (a) McClelland, R. A.; Davidse, P. A.; Hadzialilc, G. *J. Am. Chem. Soc.* **1995**, *117*, 4173. (b) McClelland, R. A.; Kahley, M. J.; Davidse, P. A.; Hadzialic, G. *J. Am. Chem. Soc.* **1996**, *118*, 4794.

S0022-3263(96)02290-6 CCC: $14.00

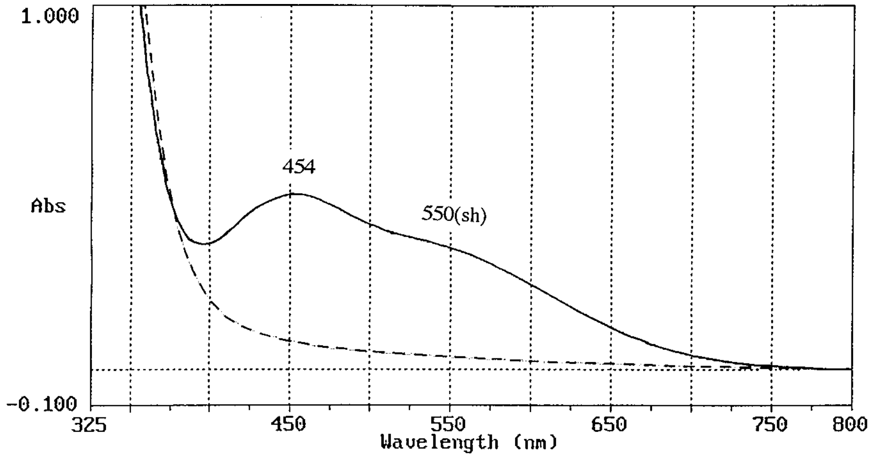

Figure 1. UV–vis spectrum of **4** in the absence (- - -) and in the presence (—) of TCNE in acetonitrile: [**4**] = 5.1×10^{-2} M, [TCNE] = 1.0×10^{-2} M.

that the singlet nitrene, as well as the didehydroazepine, derived photolytically from mesityl azide (**4**) was trapped with tetracyanoethylene (TCNE) to give a stable adduct in an appreciable yield. In this paper, we wish to report the first example of competitive trapping of singlet arylnitrene and didehydroazepine with an alkene, which reveals the intervention of singlet nitrene in the photolysis of an aryl azide having no electron-withdrawing groups.

Results

Absorption Spectra of Mesityl Azide (4) in the Presence of TCNE. Mesityl azide (**4**) is a light yellow liquid, the absorption spectrum of which shows an intense transition with maximum at 204 nm and a shoulder at around 240 nm (log ϵ = 4.45 and 3.82 in acetonitrile, respectively). The spectrum also exhibits a weak tailing to ca. 400 nm, so that the azide **4** can be photolyzed efficiently with the light of a high-pressure mercury lamp filtered by Pyrex or even by the optical glass filter cutting wavelength shorter than 350 nm (log ϵ = 2.05 and 1.06 at 313 and 366 nm in acetonitrile, respectively).

When TCNE was added to a solution of mesityl azide (**4**) in dichloromethane, the solution took on a dark red color. The UV–vis spectrum exhibited a transition with maximum at 454 nm and a shoulder at around 550 nm (Figure 1), both of which were not present in the spectrum of either **4** or TCNE. In acetonitrile, the new visible band appeared as shoulders around 415 and 510 nm. The colored species could be identified as a charge-transfer complex between mesityl azide (**4**) and TCNE on the basis of its similarity to well-known complexes between TCNE and a variety of other aromatics.[8] The two charge-transfer absorption bands observed in the complex between **4** and TCNE originate from the splitting of the degeneracy of highest occupied orbitals in benzene by ring substituents. The similar spectral splitting has been observed in the TCNE–*p*-xylene or –durene charge-transfer complex.[8]

In order to estimate the association constant for complex formation *K*, the concentration dependence of the absorption spectra of the TCNE–**4** charge-transfer complex was examined in dichloromethane and analyzed by the method of Merrifield and Phillips.[8] If the complex is assumed to be 1:1, the absorbance *A* for maximum absorption of the charge-transfer complex is correlated with the association constant *K* and the molar absorptivity ϵ by eq 1,

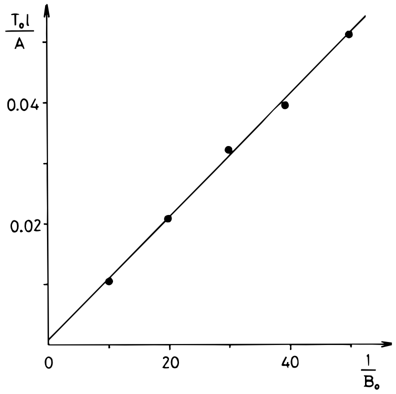

Figure 2. Concentration dependence of the absorbance for maximum absorption of the TCNE–**4** charge-transfer complex in dichloromethane.

$$\frac{T_0 l}{A} = \frac{1}{B_0}\left[\frac{T_0}{\epsilon} + \frac{1}{\epsilon K}\right] + \frac{1}{\epsilon} \tag{1}$$

where T_0 and B_0 are the initial concentrations of TCNE and mesityl azide (**4**), respectively, and *l* is the cell length (1 cm). Figure 2 displays the plot of $T_0 l/A$ against $1/B_0$, which gives a straight line (correlation coefficient 0.999). By the least-squares analysis of the plot, we obtain *K* and ϵ as 0.917 and 1090, respectively. The association constant *K* for the formation of the TCNE–**4** charge-transfer complex is ca. 20 times smaller than that for the TCNE–mesitylene complex reported under the same conditions.[8] This observation is possibly explained in terms of steric and electronic repulsion between TCNE and an azide moiety of **4**, which prevents the close approach between two components and, therefore, the formation of a stable complex.[9]

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[8] Merrifield, R. E.; Phillips, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 2778.

[9] The electronic influence of the azido group on an aromatic ring should be also considered. At the present time, however, little is known about the electronic character of the azido group because of its high reactivity. Smith and his co-workers reported that the azido group strengthened the acidity of benzoic acid, while electrophilic aromatic substitution was markedly activated by the azido substitution: Smith, P. A. S.; Hall, J. H.; Kan, R. O. *J. Am. Chem. Soc.* **1962**, *84*, 485.

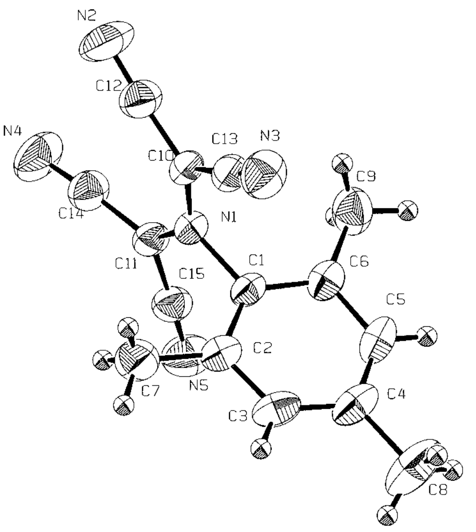
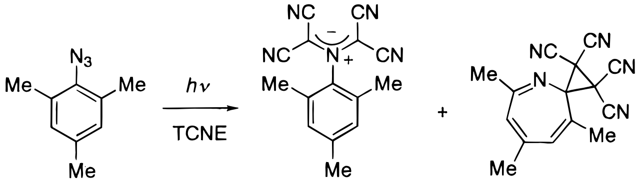
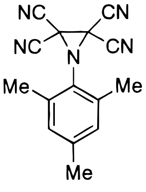


Figure 3. ORTEP diagram of **5**. Carbon and nitrogen atoms are shown as 50% probability surfaces, and hydrogen atoms are displayed as arbitrary spheres.

Photoproducts of Mesityl Azide (4) in the Presence of TCNE. A solution of **4** (10 mM) containing 2 equiv of TCNE in acetonitrile was irradiated with the Pyrex-filtered light of a high-pressure mercury lamp. After separation by the use of gel permeation liquid chromatography, two adducts **5** and **6** were isolated. The first adduct was obtained in 22% yield as yellow granules. In its ^{1}H NMR spectrum, the methyl signals appeared at δ 2.35 and 2.39 with an intensity ratio of 2:1, and the aromatic protons appeared at δ 7.13 as a singlet. The ^{13}C NMR spectrum of the adduct showed two signals assigned to the cyano carbons at δ 108.6 and 109.8. These spectroscopic data indicated the presence of a plane of symmetry in this adduct, which was not inconsistent with the aziridine structure **7**. There were no precedents, however, for the isolation of aziridines in the reaction of an arylnitrene having no electron-withdrawing group with an alkene, though pentafluorophenylnitrene was reported to add to tetramethylethylene to give an aziridine derivative.[6c,g] In order to get the unambiguous molecular structure of the adduct, X-ray crystallographic study was carried out. To our surprise, the adduct is not the aziridine **7**, but the azomethine ylide **5**, where the original carbon−carbon double bond of TCNE is cleaved. The ORTEP diagram is given in Figure 3. The azomethine ylide unit N[C(CN)$_2$]$_2$ in **5** is almost planar, where deviations of atoms from the mean plane defined by these 11 atoms are within 0.24 Å. Moreover, the mean plane of the azomethine ylide unit is completely perpendicular to the plane defined by carbon atoms comprising the mesitylene unit, so that **5** has a molecular framework of C_{2v} symmetry.



4 **5** **6**



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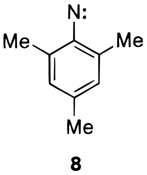
The second adduct obtained in 73% yield was identified as the spiroazepine **6**. This adduct is the analogue of the TCNE adduct of 2-nitrenobiphenyl, for which the structure has been determined by X-ray crystallographic analysis.[10] In the ^{1}H NMR spectrum of **6**, the protons on the azepine ring appeared in a higher field (δ 6.48 and 6.74) compared with the corresponding protons of the aromatic adduct **5** (δ 7.13). The ^{13}C NMR spectrum showed a signal assigned to the imino carbon in a considerably low field (δ 175.2). Three signals assigned to the carbons of cyclopropane ring and four cyano carbons appeared at δ 24.8, 29.7, and 66.1 and δ 106.6, 107.8, 108.7, and 108.8, respectively. An inequivalence of the two dicyanomethylene groups is attributed to the slow inversion of the spiroazepine ring in solution. All of these spectroscopic features are in agreement with those of the TCNE adduct of 2-nitrenobiphenyl.

No other products were detected in the ^{1}H NMR spectrum of the photoreaction mixture. The ratio of the adducts formed during the early stages of the photoreaction remained constant. However, continued irradiation of the solution containing both adducts with a Pyrex-filtered light resulted in an increase in the product ratio [**5**]:[**6**], which was due to the photochemical decomposition of the spiroazepine **6**. Both adducts **5** and **6** were obtained in dichloromethane and benzene in the analogous ratios, though the yields were slightly lower compared with in acetonitrile. Finally, we confirmed that neither **5** nor **6** was formed in the dark.

Both adducts were fairly stable at room temperature, but they decomposed gradually on heating in benzene at 130 °C to give a complex mixture from which nothing could be identified. Neither photochemical nor thermal interconversion between **5** and **6** could be observed.

Thus, two adducts **5** and **6** are isolated in the photolysis of mesityl azide (**4**) in the presence of TCNE, the structures of which formally correspond to the TCNE adducts of mesitylnitrene (**8**) and trimethyldidehydroazepine (**9**), respectively. The mechanism for the formation of both adducts is discussed in the following sections.



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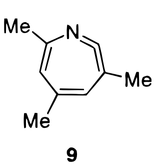

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Wavelength Effect on the Photolysis. The effect of wavelength on the photolysis of **4** in the presence of TCNE was examined to elucidate whether the charge-transfer complex between **4** and TCNE was responsible for the formation of the adducts **5** and **6**. However, on irradiation of the charge-transfer absorption band in acetonitrile with a xenon arc lamp through the glass filter cutting wavelength shorter than 520 nm for 20 h, neither **5** nor **6** was obtained, and more than 90% of the starting

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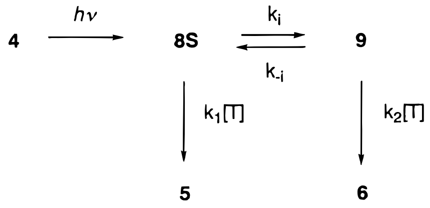
[10] Murata, S.; Sugawara, T.; Iwamura, H. *J. Chem. Soc., Chem. Commun.* **1984**, 1198.

Scheme 2



materials was recovered. It was reported that irradiation of the charge-transfer absorption bands of TCNE−toluene systems gave 3-phenylpropane−1,1,2,2-tetracarbonitrile.[11] We could not detect this type of addition product in the excitation of the charge-transfer absorption bands of the TCNE−**4** complex, either, which is probably due to the instability of the complex as indicated by the small association constant *K*. On the other hand, irradiation of **4** in the presence of TCNE (2 equiv) with the light filtered by a 30 nm band-pass filter centered at 360 nm for 6 h resulted in the formation of the adducts **5** and **6** in 18% and 71% yields, respectively, in which the conversion of the starting azide **4** was 60%. Note that the ratio of the adducts **5** and **6** obtained in the photolysis with the light through the band-pass filter (360 ± 15 nm), where the charge-transfer absorption bands were not excited, was nearly identical to that obtained with the Pyrex-filtered light (>300 nm). The same wavelength effect on the photolysis of **4** in the presence of TCNE was observed in dichloromethane.

These observations strongly suggest that both adducts **5** and **6** are produced by trapping of reactive intermediates formed from free rather than complexed azide and that the TCNE−**4** charge-transfer complex does not participate in the adduct formation. Moreover, the mechanism involving the radical cation of the azide **4** and the TCNE radical anion, which would be formed through a single electron transfer from the excited azide to TCNE, can be ruled out for the adduct formation because both adducts **5** and **6** were obtained in analogous yields in irradiation of the azide **4** and TCNE in the oxygen-saturated solution.[12]

Thus, we propose that both adducts **5** and **6** originate primarily from the reaction of the nitrene generated through the direct excitation of the azide **4** with TCNE.

Dependence of Product Ratio upon TCNE Concentration. We found that the ratio of the two adducts **5** and **6** obtained in the photolysis of the azide **4** in the presence of TCNE was dependent upon the initial concentration of TCNE; the yield of the azomethine ylide **5** increased with increasing TCNE concentration, and the spiro-azepine **6** decreased. If the two adducts **5** and **6** are produced by trapping of singlet mesitylnitrene (**8S**) and trimethyldidehydroazepine (**9**) with TCNE, respectively, and these two reactive intermediates are related as shown in Scheme 2, then the ratio of the adducts [**5**]:[**6**] is given by eq 2,

$$\frac{[\mathbf{5}]}{[\mathbf{6}]} = \frac{k_1 k_{-i}}{k_2 k_i} + \frac{k_1}{k_i}[\mathrm{T}] \tag{2}$$

where [T] is the concentration of TCNE, which is assumed to remain constant throughout the reaction, and the rate constants *k*'s are defined as shown in Scheme 2. We examined the dependence of the product ratio [**5**]:[**6**] on the TCNE concentration under the defined conditions ([**4**] = 5.0 mM, [T] = 10−60 mM, in acetonitrile, λ > 300 nm, 1 h), where the conversion of the azide **4** was 20−30%. Under these conditions, the photodecomposition of the adducts could be neglected, and the concentration of TCNE could be considered unchanged during the photoreaction. Figure 4 illustrates a plot of [**5**]/[**6**] versus [T], which gives a straight line (correlation coefficient 0.999). Thus, the dependence of the product ratio [**5**]:[**6**] upon the TCNE concentration [T] is found to obey eq 2, which appears to justify the mechanism for the adduct formation shown in Scheme 2.

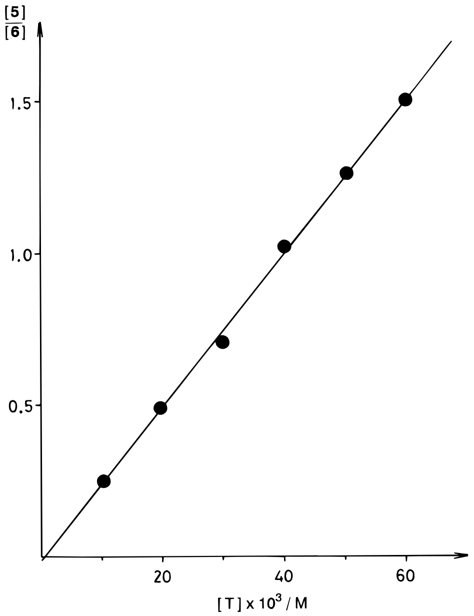


Figure 4. Dependence of the product ratio upon the TCNE concentration in the photolysis of **4**.

Comments on Photochemical Reactions of Aryl Azides with Electron-Deficient Alkenes. Finally, we have to refer to the photochemical reaction of aryl azides other than mesityl azide (**4**) with electron-deficient alkenes. As reported previously, irradiation of 2-azidobiphenyl in the presence of TCNE gives a stable spiroazepine-type adduct, the structure of which has been unambiguously determined by X-ray crystallographic analysis.[10] When phenyl, 2-methylphenyl, or 2,4-dimethylphenyl azide is irradiated in acetonitrile containing TCNE, the ^{1}H NMR spectrum of the photoreaction mixture indicates the formation of TCNE adducts of the corresponding nitrene. However, all attempts to isolate the adducts from the reaction mixture have been unsuccessful because of their instability. One of the adducts is characterized by a proton signal at δ 8.2−8.5. This signal gives reliable evidence of the formation of a spiroazepine-type adduct because the isolated adduct of 2-nitrenobiphenyl shows a doublet assigned to the imino proton at δ 8.25 in its ^{1}H NMR spectrum.[10] Thus, the didehydroazepine formed photolytically from phenyl, 2-methylphenyl, or 2,4-dimethylphenyl azide is undoubtedly trapped with TCNE to give the corresponding spiroazepine-type adduct. On the other hand, we have no evidence for the formation of an azomethine ylide-type TCNE adduct in the photolysis of aryl azides other than

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[11] Ohashi, M.; Suwa, S.; Osawa, Y.; Tsujimoto, K. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2219.

[12] It has been reported that the radical anion intermediates are effectively quenched by O_2: (a) Spada, L. T.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 391. (b) Akaba, R.; Kamata, M.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1992**, *33*, 8105. (c) Murata, S.; Nakatsuji, R.; Tomioka, H. *J. Chem. Soc., Perkin Trans. 2* **1995**, 793.

4 owing to the lack of characteristic ^{1}H NMR signals in this type of adduct. Thus, at the present stage we cannot determine whether an azomethine ylide-type adduct is also produced but decomposes in the course of isolation or the formation of the azomethine ylide **5** is due to a higher nucleophilicity of singlet mesitylnitrene (**8S**) compared with the nitrenes generated by photolysis of phenyl, 2-methylphenyl, or 2,4-dimethylphenyl azide. In any event, it is thought that the success in competitive trapping of singlet nitrene and didehydroazepine with TCNE in the photolysis of mesityl azide (**4**) is primarily attributed to the high stability of the both adducts **5** and **6**, which arises from steric and electronic effects of three methyl groups.

We also examined the photochemical reaction of mesityl azide (**4**) with electron-deficient alkenes other than TCNE. However, when **4** was irradiated in the presence of maleic anhydride, dimethyl fumarate, or fumaronitrile, no corresponding adducts could be detected in the photoreaction mixture, but azomesitylene and 2,4,6-trimethylaniline were isolated as photoproducts. Azobenzenes and anilines are known to be produced through the dimerization and the hydrogen abstraction of triplet arylnitrenes, respectively.[1] Thus, it is found that in the case of alkene having a lower electrophilicity compared with TCNE, the rate of reaction of **8S** and **9** with the alkene is considerably reduced, so that intersystem crossing from **8S** to **8T** becomes a predominant pathway.

Discussion

On the basis of our observations, we propose that singlet mesitylnitrene (**8S**) and trimethyldidehydroazepine (**9**) are responsible for the formation of the azomethine ylide **5** and the spiroazepine **6**, respectively, as shown in Scheme 2. In this section, the reactivities of these intermediates with TCNE, as well as other possible mechanisms for the formation of the adducts, are discussed.

Formation of the Azomethine Ylide 5. The azomethine ylide **5** seems to be produced by trapping of singlet mesitylnitrene (**8S**) with TCNE. This provides the first example of the capture of a singlet arylnitrene having no electron-withdrawing groups with an alkene. The least-squares analysis of the plot shown in Figure 4 gives us kinetic information on the reactivity of **8S**. From the slope of the plot, the ratio of the rate constant for the reaction of **8S** with TCNE to that for the ring expansion of **8S** to **9**, k_1/k_i, is obtained as 25.2 M^{-1}. Platz and his co-workers reported the absorption spectrum of didehydroazepine (**3**) by laser flash photolysis of phenyl azide (**1**),[2] and more recently, Schuster and his co-workers directly observed **3** and its derivatives by the use of time-resolved IR spectroscopy.[4] Both groups detected **3** immediately after the photolysis of **1** with the 20 ns laser pulse, which leads to a value of $>5 \times 10^7$ s^{-1} for the rate constant for the ring expansion of **2S** to **3**. If we assume $k_i > 5 \times 10^7$ s^{-1}, the rate constant for the reaction of **8S** with TCNE, k_1, is calculated to be $>1.3 \times 10^9$ M^{-1} s^{-1}. However, if we assume that the reaction of **8S** with TCNE is diffusion controlled (in acetonitrile, $k_1 = 1.9 \times 10^{10}$ s^{-1}),[13] a maximum rate for k_i is calculated to be 7.5×10^8 s^{-1}, which is not consistent with the value of $10^{11\pm1}$ s^{-1} estimated for **2S** by Platz and his co-workers.[2,14] The reason for this discrepancy is not elucidated yet, though it would be possible that three methyl groups on the benzene ring retard the isomerization from the singlet nitrene to the didehydroazepine or that Platz and his co-workers underestimated the activation energy for the ring expansion process from **2S** to **3**. In any event, it should be emphasized that the rate constant for the reaction of singlet mesitylnitrene (**8S**) with TCNE is predicted to be on the order of 10^9 M^{-1} s^{-1} or greater.

An alternative candidate for the reactive intermediate participating in the formation of the azomethine ylide **5** is triplet mesitylnitrene (**8T**). In analogy with the carbene chemistry,[15] the spin state of the nitrene involved in an addition reaction to alkenes would be determined by whether the stereochemistry of the alkenes is retained or not. Unfortunately, these stereochemical studies could be inapplicable to the formation of **5** because of the cleavage of the initial carbon−carbon bond of the alkene. Thus, though we cannot strictly exclude the mechanism involving **8T**, we should point out that the triplet mechanism is incompatible with our observations as follows. It has been established that the ring expansion from singlet phenylnitrene (**2S**) is favored over intersystem crossing to its triplet state **2T** at room temperature and that this is also the case for singlet 2,6-dimethylphenylnitrene.[2] Thus, it is reasonable to think that the rate of isomerization of the singlet nitrene **8S** to the didehydroazepine **9** is much greater than that of intersystem crossing to **8T** under our photoreaction conditions. If **5** is produced by trapping of **8T** with TCNE, then **9** is the bifurcation point for the formation of the azomethine ylide **5** and the spiroazepine **6** because **8T** is formed through intersystem crossing of **8S**, which is regenerated by **9**. Consequently, an increase in the initial concentration of TCNE should result in the acceleration of trapping of **9** with TCNE, which would lead to a decrease in the product ratio [**5**]:[**6**]. It is not the case as demonstrated in Figure 4.

We wish to give a discussion on the pathway to the azomethine ylide **5** from singlet mesitylnitrene (**8S**) and TCNE. Taking into account the reactions of a singlet carbene with alkenes,[15] it seems reasonable to think that **8S** reacts concertedly with TCNE to give the aziridine **7**. However, we could not detect **7** in the photoreaction mixture. In order to gain further information about the TCNE-adducts derived from **8S**, theoretical calculations using the PM3 method were carried out. We optimized the geometries of the azomethine ylide **5** and the aziridine **7** and calculated their heat of formation. Some selected bond lengths and angles of the optimized structures, as well as the calculated heat of formation, are given in Table 1. The PM3-optimized geometry of **5** is in fair agreement with the molecular structure determined by X-ray crystallography. As shown in Table 1, the heat of formation of **7** is much greater than that of **5**, which is probably due to a steric strain in **7**, so that it is revealed that the cleavage of the $C(CN)_2-C(CN)_2$ bond of **7** to give **5** is a thermodynamically favored process. Thus, we propose that the aziridine **7** would be initially

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[13] Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

[14] McClelland and his co-workers estimated the rate constant for the ring expansion of **2S** as $(2-4) \times 10^{10}$ s^{-1}, which was based on the assumption that the rate constant for the protonation of **2S** was equal to that of alkylamines: ref 7b.

[15] For reviews on carbene chemistry, see, for example: (a) *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1973, 1975; Vols. 1 and 2. (b) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1971. See also ref 1d.

Table 1. Selected Bond Lengths (Å), Bond Angles (Deg), Torsion Angles (Deg), and Calculated Heat of Formation (kcal mol^{-1}) of 5 and 7[a]

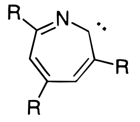
	5		7
	PM3	X-ray	PM3
N1−C1	1.470	1.479(7)	1.439
N1−C10	1.363	1.347(4)	1.495
C10−C11	2.435[b]	2.429(5)[b]	1.531
C10−N1−C11	126.6	128.8(4)	61.6
C10−C12−N2	175.0	173.5(5)	177.7
C10−C13−N3	177.9	177.4(4)	180.0
C12−C10−C13	114.9	117.1(3)	111.4
C2−C1−N1−C10	89.8	88.7(2)	53.2
heat of formation	188.855		200.233

[a] Atom numbers of **7** correspond to those of **5**, which are designated in Figure 3. [b] Interatomic distances.

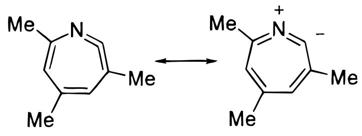
produced by the concerted reaction of **8S** with TCNE and then isomerize immediately to the azomethine ylide **5**. To validate this assumption, however, estimation of the activation energy for the isomerization of **7** to **5** is required.

Formation of the Spiroazepine 6. Kinetic information on the reactivity of trimethyldidehydroazepine (**9**) with TCNE can be obtained from the intercept of the plot of [**5**]/[**6**] against [T], which corresponds to k_1k_{-i}/k_2k_i. Unfortunately, as shown in Figure 4, the intercept of the plot is zero within the experimental error. Assuming $k_ik_{-i}/k_2k_i < 0.01$, we obtain the ratio of the rate constant for the regeneration of **8S** from **9** to that for the reaction of **8S** with TCNE, k_{-i}/k_2, as $<4 \times 10^{-4}$ M. Thus, it is found that the isomerization of **8S** to **9** is practically irreversible in the presence of TCNE (10−60 mM). The intrinsic lifetime for didehydroazepine (**3**) has been estimated to be 4.8 ms in heptane by the extrapolation of the plot of the decay rate constant of **3** against the phenyl azide concentration to zero.[4b] If we employ this value to estimate k_{-i}, the rate constant for the reaction of **9** with TCNE, k_2, is calculated to be $>5.2 \times 10^5$ M^{-1} s^{-1}.

The spiroazepine **6** could be considered to be obtained by trapping of 2-aza-3,5,7-trimethylcycloheptatrienylidene (**10**) with TCNE. However, at the present stage we cannot insist that **10** is the reactive intermediate responsible for the formation of **6** for the following three reasons. First, though didehydroazepine (**3**) is established as a reactive intermediate in the photochemistry of phenyl azide (**1**),[1] the intermediacy of 2-azacycloheptatrienylidene (**11**) is controversial at present. There have been no reports for a direct observation of **11** or an isolation of the products derived from **11**. In 1974, Wentrup estimated that **11** was 25 kcal mol^{-1} thermochemically less stable than phenylnitrene (**2**).[16] The semiempirical calculations carried out by Shillady and Trindle also suggested that **11** was less stable than **2**, but the energy gap was much dependent on the method.[17] However, recent MNDO calculations of Schuster and his co-workers showed that **11** in a triplet state was an accessible species, the energy of which was only 3 kcal mol^{-1} above that of didehydroazepine (**3**).[4b] Second, in the analysis of the plot of [**5**]/[**6**] against the TCNE concentration, the intermediacy of **10** in the formation of **6** is not necessarily required, since trapping with TCNE of **10** equilibrated with trimethyldidehydroazepine (**9**) cannot be kinetically distinguished from trapping of **9** with TCNE. Finally, the formation of **6** can be interpreted by an electrophilic reaction of TCNE with **9**, which has a canonical structure **9a**.[3a]



10: R = Me, **11**: R = H



9 **9a**

Thus, in this paper, we assign the reactive intermediate involved in the formation of **6** tentatively as trimethyldidehydroazepine (**9**). In order to validate the intermediacy of the carbene **10**, further experimental, as well as theoretical, studies are required.

Conclusions

Irradiation of mesityl azide (**4**) in the presence of TCNE gave a mixture of two stable adducts, which were identified as the azomethine ylide **5** and the spiroazepine **6**. On the basis of the effects of wavelength of the light employed in the photolysis and the TCNE concentration on the product ratio, it is proposed that the adducts **5** and **6** are produced by trapping of singlet mesitylnitrene (**8S**) and trimethyldidehydroazepine (**9**) with TCNE, respectively. To our knowledge, this provides the first example of competitive trapping of singlet arylnitrene and its ring-expanded isomer with an alkene. Moreover, the intermediacy of singlet nitrene in the photochemistry of an aryl azide having no electron-withdrawing groups is established for the first time by these findings.

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded at 270 and 67.8 MHz, respectively. Gel permeation liquid chromatography (GPC) was performed on a JASCO HLC-01 high-pressure liquid chromatograph equipped with a Shodex GPC H-2001 column. Column chromatography was done on Fuji Davison silica gel BW-127ZH. TCNE was synthesized according the literature[18] and purified by sublimation.

Mesityl Azide (4). To a solution of 910 mg (0.73 mmol) of 2,4,6-trimethylaniline (Tokyo Kasei Kogyo Co., Ltd.) in 12 mL of THF was added a mixture of concentrated hydrochloric acid (3 mL) and water (24 mL). The reaction mixture was stirred for 15 min at 0 °C, and a solution of 925 mg (13.4 mmol) of $NaNO_2$ in 10 mL of water was added dropwise to the solution, keeping the temperature of the reaction mixture below 5 °C. The reaction mixture was stirred for 15 min at 0 °C, and excess nitrous acid was removed by addition of urea. To the cooled reaction mixture was added dropwise a solution of 1.09 g (16.7 mmol) of NaN_3 in 11 mL of water. After the addition, the reaction mixture was stirred for 1 h at room temperature. The organic material was extracted with ether, and the extract was washed with dilute hydrochloric acid (0.1 M) and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was developed on a silica gel column with hexane to give 748 mg (69%) of **4** as a light yellow liquid. The identity and purity of **4** were established by ^{1}H NMR and IR spectra: ^{1}H NMR ($CDCl_3$) δ 2.16 (3H, s), 2.23 (6H, s), 6.73 (2H, s); IR (NaCl) 2080, 1480, 1270, 850 cm^{-1}; UV (acetonitrile) λ_{max} (log ϵ) 204 (4.45), 242sh (3.82) nm.

Concentration Dependence of the Absorption Spectra of the TCNE−4 Charge-Transfer Complex. Five solutions ranging in concentration from 2.00×10^{-2} to 9.99×10^{-2} M of **4** in dichloromethane containing TCNE (1.01×10^{-2} M) were

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[16] Wentrup, C. *Tetrahedron* **1974**, *30*, 1301.
[17] Shillady, D. D.; Trindle, C. *Theor. Chim. Acta* **1976**, *43*, 137.
[18] Carboni, R. A. *Organic Synsesis*; Wiley: New York, 1963; Collect. Vol. IV, p 877.

prepared, and the absorbance for maximum absorption (454 nm) of the TCNE−**4** charge-transfer complex formed in the solutions was measured by means of a UV−vis spectrophotometer. The results are analyzed according to eq 1 and are shown in Figure 2.

Irradiation of 4 for Preparative Experiments. The azide **4** (32 mg, 0.20 mmol) was dissolved in 20 mL of acetonitrile containing TCNE (51 mg, 0.40 mmol). The solution was placed in a Pyrex tube, purged with N_2 for 10 min, and irradiated for 8 h with a 300-W high-pressure mercury lamp at room temperature. After evaporation of the solvent under reduced pressure, the residue was separated by GPC with chloroform eluent to give two TCNE−mesitylnitrene adducts **5** and **6**. The identity and purity of the new adducts were established by ^{1}H and ^{13}C NMR spectra. Moreover, the structure of **5** was strictly determined by X-ray crystallography. The yield of the adducts mentioned in the text was determined by the integration of ^{1}H NMR in the crude reaction mixture on the basis of the reacted material. [*N*-Mesityl-*N*-(dicyanomethyl)imino]dicyanomethanide (**5**): yellow granules; mp 213 °C dec; ^{1}H NMR ($CDCl_3$) δ 2.35 (6H, s), 2.39 (3H, s), 7.13 (2H, s); ^{13}C NMR ($CDCl_3$) δ 16.4, 21.4, 29.7, 108.6, 109.8, 131.3, 132.3, 136.1, 144.6. 4-Aza-1,1,2,2-tetracyano-5,7,9-trimethylspiro[2.6]nona-4,6,8-triene (**6**): yellow granules; mp 155 °C dec; ^{1}H NMR ($CDCl_3$) δ 2.22 (3H, s), 2.30 (3H, s), 2.36 (3H, s), 6.48 (1H, s), 6.74 (1H, s); ^{13}C NMR ($CDCl_3$) δ 18.9, 24.7 (overlapping of two carbons), 24.8, 29.7, 66.1, 106.7, 107.8, 108.7, 108.8, 126.7, 130.7, 134.1, 149.7, 175.2.

Irradiation of 4 for Analytical Experiments. In a typical run, a solution (5 mL) of **4** (4.1 mg, 0.025 mmol) and TCNE (6.4 mg, 0.05 mmol) in acetonitrile was placed in a Pyrex tube, purged with N_2 for 10 min, and irradiated for 1 h at room temperature. The consumption of the material (20−30%) and the yield of the adducts based on the reacted material were determined by the integration of ^{1}H NMR in the crude reaction mixture. In the experiment for the effect of wavelength employed in the photolysis, irradiation was carried out with a 300-W high-pressure mercury lamp through band-pass filter (360 ± 15 nm) or with a 500-W xenon arc lamp through cutoff glass filter (>520 nm). In the experiment for the TCNE-concentration dependence of the product ratio, six solutions ranging in TCNE concentration from 1.02×10^{-2} to 6.02×10^{-2} M were irradiated with a 300-W high-pressure mercury lamp. The results are analyzed according to eq 2 and are shown in Figure 4.

X-ray Crystallography of 5. Crystal data: $C_{15}H_{11}N_5$, FW = 261.29, orthorhombic, space group $Fdd2$, $a = 13.4088(6)$ Å, $b = 17.6432(9)$ Å, $c = 11.8141(8)$ Å, $V = 2794.9(3)$ Å^3, $Z = 8$, $D_c = 1.242$ g cm^{-3}, $\mu = 6.01$ cm^{-1}. A crystal suitable for the crystallography was grown from dichloromethane−hexane. A yellow crystal (0.8 × 0.8 × 0.5 mm) was mounted on a Rigaku AFC-5R automated four-circle diffractometer, and the intensity data were collected using Cu Kα radiation ($\lambda = 1.541\ 78$ Å). The $\omega - 2\theta$ scan technique was employed at a scan rate of 16.0° min^{-1} in ω, and the scan range was calculated by $1.37° + 0.30° \tan \theta$. A total of 598 independent reflections with in the range $2\theta < 120.2°$ were measured, and 541 reflections with $I > 3.0\sigma I$ were used for the structure determination and refinement. The structure was solved by direct methods (MITHRIL) and refined by a full-matrix least-squares technique with anisotropic thermal parameters for non-hydrogen atoms. All of the hydrogen atoms were located on a difference map, except two hydrogens of the methyl group at the 4-position, the positional parameters of which were obtained by calculation. The positional and isotropic thermal parameters of hydrogens were not refined but were included in the calculation of structure factors. The weighting scheme $w = 4F_o^2/\sigma^2(F_o^2)$ was employed. The final R and R_w values were 0.056 and 0.061, respectively. All calculations were carried out using the TEXSAN crystallographic software package of Molecular Structure Corporation.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of new compounds **4**−**6** (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9622901