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Generation and reactions of 3-alkylidene-1-pyrazoline radical cations by photoinduced electron transfer

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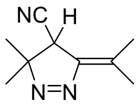
Abstract—The behavior of the 3-alkylidene-1-pyrazoline radical cations generated by photoinduced electron transfer reactions was examined. The nitrogen-retained radical cations have been detected using laser flash photolysis. The photochemical products indicate that *E*/*Z* isomerization, intramolecular cyclization, and solvent addition (acetonitrile) occurred.

Radical cations generated from cyclic azoalkanes by photoinduced electron transfer (PET) have recently been investigated and rearrangement and solvent addition reactions are reported,[1–5] and in our previous studies using 1-pyrazolines, the PET reaction was found involving the radical cation intermediates.[4] In the one electron oxidation of cyclic diazo compound typically gives nitrogen eliminated products and nitrogen-retained products have not been obtained. In this paper, we report the first example of the obtaining of nitrogen-retained products and the successful detection of the nitrogen-retained radical cations in the PET reactions of cyclic azoalkanes, 3-alkylidene-1-pyrazolines (**1**, **2a**, and **2b**).



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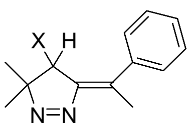

2a: X = CO_2Me
2b: X = CN

In order to investigate the interaction between the singlet excited sensitizers and the pyrazolines, fluorescence quenching experiments were performed in acetonitrile (Table 1). The fluorescence quenching rate constants (k_q) of 2,4,6-triphenylpyrylium tetrafluoroborate (TPP^+) and *N*-methylquinolinium tetrafluoroborate (NMQ^+) as well-known electron accepting sensitizers by **1**, **2a**, and **2b** estimated from the Stern–Vomer plots indicate that the single electron transfer from the pyrazolines to the singlet excited TPP^+ molecule is diffusion-controlled. However, the quenching rate constant of 9,10-dicyanoanthracene (DCA) by **2a** was 10 times lower than those of TPP^+ and NMQ^+. TPP^+ and NMQ^+ are favorable sensitizers in a PET reaction because they lead to a better charge separation than DCA. The free energy change (ΔG) in acetonitrile were estimated using the Rehm–Weller equation, $\Delta G = 23.06(E_{ox} - E^*_{red}) - e_o^2/\varepsilon_a$.[6] The oxidation potentials of the pyrazolines were determined from the half-peak potentials of cyclic voltammetry as the obtained peaks were irreversible. The singlet excited reduction potentials of TPP^+, NMQ^+, and DCA are 2.53, 2.70, and 1.97 V, respectively. ΔG values are negative in all cases and it was confirmed that the processes of the PET efficiently proceed during the electron transfer from the molecules of the pyrazolines to the singlet excited sensitizer molecule (Table 1). TPP^+ and DCA, which had absorption bands at 405 nm, were used as sensitizers of photoproducts studies, and NMQ^+, which did not have an absorption band at longer than 350 nm, was used as a sensitizer of laser flash photolysis (LFP) studies.

Keywords: Photoinduced electron transfer; Pyrazoline; Radical cation; Laser flash photolysis.

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Table 1. Redox potentials of 3-alkylidene-1-pyrazolines, their quenching rate constants (k_q) by TPP$^+$ and DCA, and their free energy change (ΔG) relationship

Pyrazoline	E_{ox}/V vs SCE	ΔG/kcal mol^{-1}			k_q/L mol^{-1} s^{-1}		
		TPP$^+$	DCA	NMQ$^+$	Tpp$^+$	DCA	NMQ$^+$
1	+2.15	−9.5	—	—	7.4×10^{10}	—	—
2a	+1.85	−16.4	−3.5	−20.3	3.5×10^{10}	2.1×10^{9}	5.4×10^{10}
2b	+1.99	−13.0	—	−17.1	2.3×10^{10}	—	3.9×10^{10}

TPP$^+$ sensitization of **1** by the irradiation of 405 nm light in deaerated acetonitrile for 180 h was performed. Surprisingly, in the TPP$^+$-sensitized reaction, a reduction product **3** and a solvent (acetonitrile) adduct **4**, both of which retained the azo moieties, were obtained. The product yield was determined by GC analysis (Table 2). For the reaction in deaerated benzene, **3** was obtained by irradiation for 18 h in the presence of TPP$^+$. Because of the presence of an exocyclic double bond, the alternative reactions proceed without any denitrogenation.

Based on the results of these experiments, we proposed the reaction mechanism for the TPP$^+$-sensitized reaction of **1** as shown in Scheme 1. A single electron transfer from **1** to the singlet excited TPP$^+$ affords an initial radical cation intermediate **1**$^{\cdot+}$ and a 2,4,6-triphenylpyranyl radical (TPP$^{\cdot}$). The radical cation **1**$^{\cdot+}$ may produce a radical cation **5**$^{\cdot+}$ by two hydrogen abstractions from the solvent, and the resulting radical cation **5**$^{\cdot+}$ gives **3** via a back electron transfer (BET) from TPP$^{\cdot}$. A competitive route involving the formation of **4** is present. The radical cation **1**$^{\cdot+}$ is added to acetonitrile by nucleophilic addition,[5,7–9] to give a radial cation species **6**$^{\cdot+}$. This radical cation **7**$^{\cdot+}$ is then immediately generated by a 1,4-hydrogen shift from **6**$^{\cdot+}$, subsequently producing **4** via a BET.

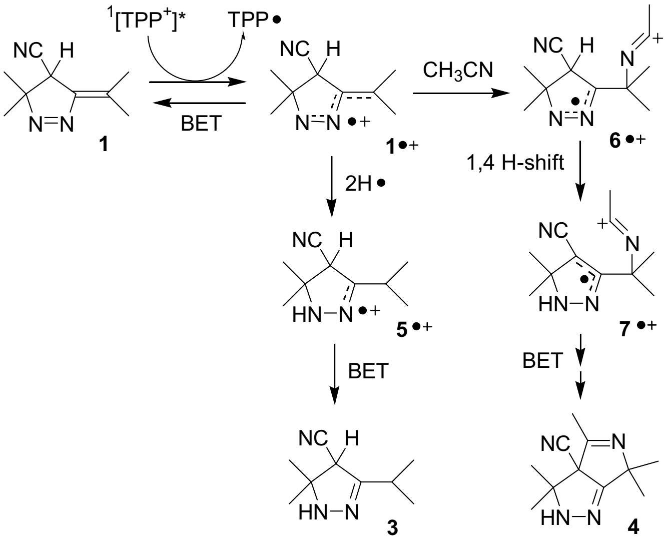
The radical cation species of the pyrazolines having a phenyl group on the vinylidene carbon, **2a**$^{\cdot+}$ and **2b**$^{\cdot+}$, are expected to be more stable in comparison with **1**$^{\cdot+}$ due to the effect of the phenyl group. The TPP$^+$-sensitized photoreactions of these pyrazolines proceeded in a non-nitrogen-extrusion manner to give not only the geometric isomers **8** but also the cyclized indene derivatives **9** in acetonitrile and benzene (Table 2). No formation of the Ritter-type solvent adduct were observed in the PET of **2**, and it is explained by the steric hindrance of the substituted phenyl moiety and by the delocalization of the cationic charge on the phenyl ring. The DCA-sensitized photoreaction of **2a** gave the same products in acetonitrile, however, in the case of benzene, **9a** was not obtained.

These results imply that the TPP$^+$-sensitized photoreactions caused the *E*/*Z* isomerization and the intramolecular cyclization via the nitrogen-retained radical cation intermediates derived from these pyrazolines. The geometric isomerization predominantly proceeded at the beginning, and the indene derivative **9b** was gradually produced during the rapid conversion between **2b** and **8b** (Fig. 1). Furthermore, these PET reactions in acetonitrile apparently occurred much faster than that in benzene.

Based on these results, we proposed the reaction mechanisms of the TPP$^+$ and the DCA-sensitized photoreaction of **2a** and **2b** as shown in Scheme 2. A single electron transfer occurred from **2** to the singlet excited TPP$^+$ or DCA and then radical cation intermediates **10**$^{\cdot+}$ were formed. The BET from the radical cations[10] produced **10**$^{\cdot\cdot}$, which regenerated pyrazoline **2** and **8**. The processes of the *E*/*Z* isomerizations are similar to that of the radical cation intermediates derived from the olefin or the styrene derivatives.[11] Another reaction path is present. Intermediate **10**$^{\cdot+}$ undergoes a 1,4-hydrogen shift to produce the 1,3-radical cation species **11**$^{\cdot+}$. The intramolecular cyclization subsequently occurred via BET that produced intermediates **12**, which afforded **9** by the aromatization via the 1,4-hydrogen shift. From the results of Figure 3, it is clear that the *E*/*Z* isomerization was reversible and much faster than the cyclization by the 1,3-hydrogen shift in **10**$^{\cdot+}$. This mechanism was supported by the reaction of **8**, which

Table 2. Product yield of photoinduced electron transfer reaction of **1**, **2a**, and **2b** irradiating by a 1 kW high pressure mercury lamp equipped with >405 nm solution filter

Pyrazoline	Sensitizer	Solvent	Irrad. time/h	Conv./%	Conversion yield/%			
					3	**4**	**9**	**10**
1	TPP$^+$	CH_3CN	180	62	8	22		
		PhH	18	71	45	—		
2a	TPP$^+$	CH_3CN	1	68			56	25
		PhH	1	64			41	56
2b	TPP$^+$	CH_3CN	1	73			45	27
		PhH	1	57			47	22
2a	DCA	CH_3CN	12	21			44	19
		PhH	24	36			38	0



Scheme 1.

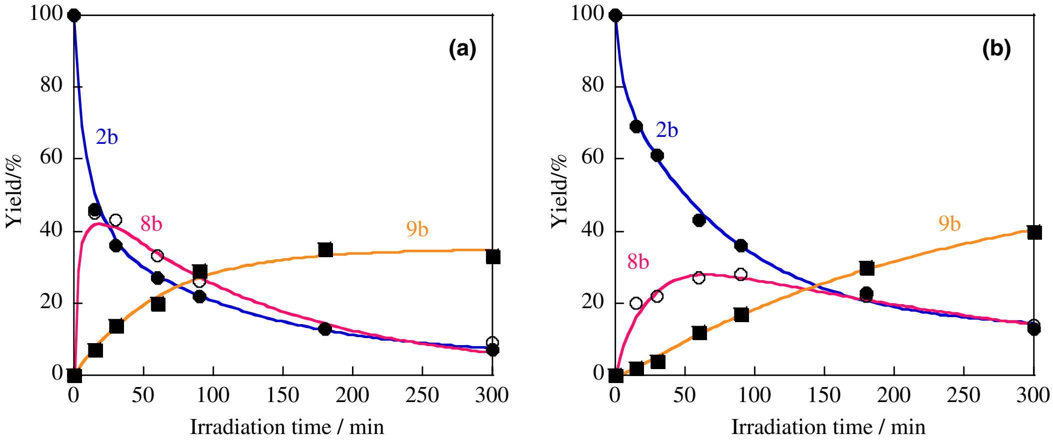


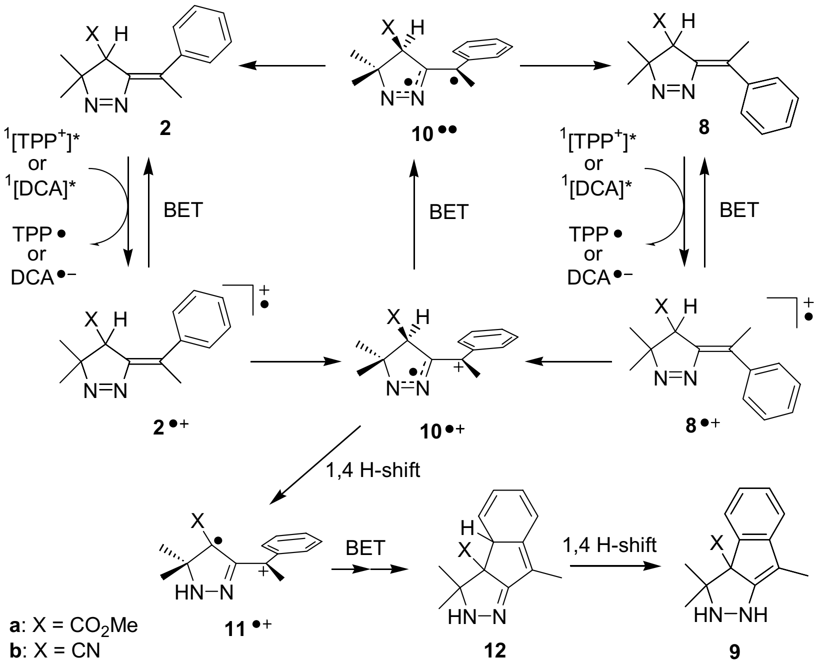
Figure 1. Formation of **8b** and **9b** for TPP^+ sensitization of **2b**: (a) in acetonitrile, (b) in benzene.

had produced **2** and **9**, and the presence of the intermediate $\mathbf{10}^{\cdot+}$ is confirmed that the same transient absorption spectra were observed by the LFP of **2** and **8** described below. Furthermore, for the DCA-sensitized photoreaction of **2a** in benzene solution, because of the fast BET process between $\mathbf{10}^{\cdot+}$ and the DCA radical anion, the cyclization by the 1,4-hydrogen shift in $\mathbf{10}^{\cdot+}$ did not occur. This cyclization process is similar to the one for the direct irradiation of diazene[12] and another of aryl substituted [3]dendralene.[13]

In order to spectroscopically observe the radical cation species, nanosecond LFP studies were carried out by the irradiation at 308 nm wavelength (XeCl excimer laser) for **1**, **2a**, and **2b**. NMQ^+ as an electron accepting sensitizer and toluene as a cosensitizer were used in oxygen-saturated acetonitrile.[14–17]

For the pyrazoline **1**, a strong absorption maximum at 370 nm with a broader and weaker band at 530 nm were observed at 0.20 and 1 μs after the laser pulses (Fig. 2), and these absorption bands decayed with the same first-order kinetics and a lifetime of ~1 μs indicating that both bands come from one species. This species is assigned to the nitrogen-retained radical cation produced by the PET reaction of **1** by comparison with the reported conjugated 1,3-diene radical cations (e.g., 2,5-dimethyl-2,4-hexadiene has absorptions at 365 and 470 nm),[18] and by the results of the products distribution of the sensitized photolysis of **1**. The similar results were also appeared in the LFP of **2a** and **2b**.

The LFP of **2a** and **2b** under similar conditions exhibited characteristic transient absorption bands with absorption maxima at ca. 400 and 510 nm as shown in Figure 3. In these cases, both bands decayed single exponentially with lifetimes of 20 and 13 μs for $\mathbf{2a}^{\cdot+}$ and $\mathbf{2b}^{\cdot+}$, respectively. The shapes of these spectra have similarity with that of the spectra of **1** but their lifetimes are different. Styrene type radical cations have been generated by



Scheme 2.

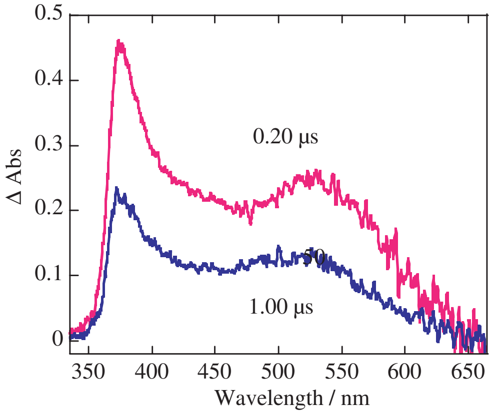


Figure 2. Transient absorption spectra in the NMQ$^+$–toluene cosensitization of **1** in acetonitrile under oxygen.

the two-photon ionization of the parent olefin or PET sensitization in polar solvents, and their transients have shown one strong band at wavelengths from 350 to 380 nm and another one near 590–670 nm.[19] In addition to that described above, the radical cation of the 1,3-diene showed an absorption in a similar region. Furthermore, from the products of sensitized photolysis of **2a** and **2b** these absorption spectra are assigned to the radical cations of **2a** and **2b**.

In summary, in the sensitized photolysis the nitrogen-retained products were obtained and the characteristic transient absorptions of the radical cations derived from the 3-alkylidene-1-pyrazolines were observed from the LFP studies. This is the first example of cyclic diazo compounds PET reactions, which do not eliminate nitrogen.

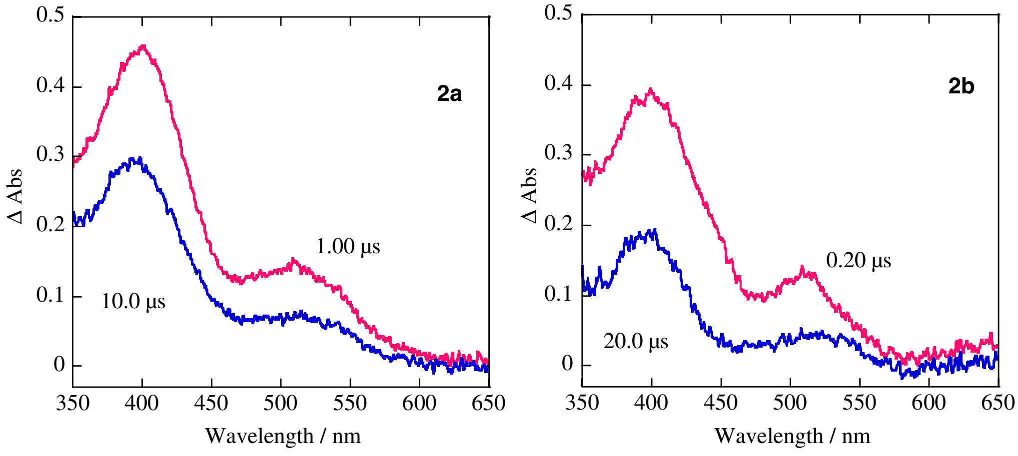


Figure 3. Transient absorption spectra in the NMQ$^+$–toluene cosensitization of **2a** and **2b** in acetonitrile under oxygen.

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References and notes

1. (a) Adam, W.; Sahin, C.; Sendelbach, J.; Walter, H.; Chen, G.-F.; Williams, F. *J. Am. Chem. Soc.* **1994**, *116*, 2576–2584; (b) Adam, W.; Kammel, T.; Toubartz, M.; Steenken, S. *J. Am. Chem. Soc.* **1997**, *119*, 10673–10676.
2. Ikeda, H.; Minegishi, T.; Miyashi, T. *Tetrahedron Lett.* **1996**, *37*, 4377–4380.
3. Engel, P. S.; Keys, D. E.; Kitamura, A. *J. Am. Chem. Soc.* **1985**, *107*, 4964–4975.
4. (a) Karatsu, T.; Hotta, H.; Kitamura, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1451–1452; (b) Karatsu, T.; Itoh, H.; Kinugawa, T.; Ebashi, Y.; Hotta, H.; Kitamura, A. *J. Org. Chem.* **1995**, *60*, 8270–8277.
5. (a) Miyagawa, N.; Karatsu, T.; Kitamura, A. *Chem. Lett.* **1997**, *38*, 1005–1006; (b) Karatsu, T.; Shiochi, N.; Aono, T.; Miyagawa, N.; Kitamura, A. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1227–1231.
6. Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259–271.
7. (a) Zona, T. A.; Goodman, J. L. *Tetrahedron Lett.* **1992**, *33*, 6093–6096; (b) Zona, T. A.; Goodman, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 4925–4926.
8. Mizuno, K.; Nire, K.; Sugita, H.; Otsuji, Y. *Tetrahedron Lett.* **1993**, *34*, 6563–6566.
9. (a) de Lijser, H. J. P.; Arnold, D. R. *J. Org. Chem.* **1997**, *62*, 8432–8438; (b) de Lijser, H. J. P.; Arnold, D. R. *J. Phys. Chem. A* **1998**, *102*, 5592–5598.
10. (a) Ikeda, H.; Takasaki, T.; Takahashi, Y.; Konno, A.; Matsumoto, M.; Hoshi, Y.; Aoki, T.; Suzuki, T.; Goodman, J. L.; Miyashi, T. *J. Org. Chem.* **1999**, *64*, 1640–1649; (b) Ikeda, H.; Akiyama, K.; Takahashi, Y.; Nakamura, T.; Ishizaki, S.; Shiratori, Y.; Ohaku, H.; Goodman, J. L.; Houmam, A.; Wayner, D. D. M.; Tero-Kubota, S.; Miyashi, T. *J. Am. Chem. Soc.* **2003**, *125*, 9147–9157.
11. Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1980**, *102*, 4303–4310.
12. Van Hijfte, L.; Little, R. D. *J. Org. Chem.* **1985**, *50*, 3940–3942.
13. Okada, K.; Maehara, K.; Oda, M. *Tetrahedron Lett.* **1994**, *35*, 5251–5252.
14. Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 4669–4683.
15. Dockery, K. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P. *J. Am. Chem. Soc.* **1997**, *119*, 1876–1883.
16. Ikeda, H.; Minegishi, T.; Abe, H.; Konno, A.; Goodman, J. L.; Miyashi, T. *J. Am. Chem. Soc.* **1998**, *120*, 87–95.
17. Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290–4301.
18. Lew, C. S. Q.; Brisson, J. R.; Johnston, L. J. *J. Org. Chem.* **1997**, *62*, 4047–4056.
19. (a) Schepp, N. P.; Johnston, L. J. *J. Am. Chem. Soc.* **1994**, *116*, 6895–6903; (b) Shukla, D.; Lu, C.; Schepp, N. P.; Bentrude, W. G.; Johnston, L. J. *J. Org. Chem.* **2000**, *65*, 6167–6172.