Photoinduced Electron Transfer Reaction of 3,3-Dimethyl-3*H*-pyrazoles: The Formation of Solvent Adducts through Cyclopropene Derivatives

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3,3-Dimethyl-3*H*-pyrazoles were photolyzed, and in the presence of 2,4,6-triphenylpyrylium tetrafluoroborate (TPP^+) as a sensitizer in acetonitrile; in addition to cyclopropenes, 2*H*-pyrroles were obtained as solvent adducts to 1,3-radical cation intermediate.

Biradicals and radical-cations, which are generated by photolysis[1] and the photoinduced electron transfer (PET) reaction[2] of cyclic azoalkanes, give cyclization products and/or rearrangement products. On the other hand, 3*H*-pyrazoles, which have an unsaturated carbon-carbon double bond with an azo chromophore in its skeleton, have been as a vinyl carbene precursor and the mechanism of carbene generation has been studied.[3] In the present paper, we report the photochemistry of 3,3-dimethyl-3*H*-pyrazoles **1** in the presence of 2,4,6-triphenylpyrylium tetrafluoroborate (TPP^+) as an electron accepting sensitizer, and the comparison of the two radical-cations (**6** and **9**) generated in the reaction.

3*H*-pyrazoles **1a-d** were prepared by the cycloaddition of 2-diazopropane to the corresponding alkynes.[2g] The structure of **1a** was identified by an X-ray crystallographic analysis.[4]

In order to examine the interaction between singlet excited sensitizers and **1**, fluorescence quenching experiments were performed. Fluorescences of TPP^+ and 9,10-dicyanoanthracene (DCA) were efficiently quenched by **1a** with the quenching rate constants (k_q) of 1.1×10^{10} and 1.3×10^{9} $l\ mol^{-1}\ s^{-1}$, respectively. For other pyrazoles, the k_qs were close to the diffusion-controlled limit. The differences in free energy (ΔG) for single electron transfer (SET) are exergonic or slightly endergonic (ΔG is calculated as -11.8 and 1.15 kcal mol^{-1} for **1a** and TPP or DCA, respectively) as calculated from the oxidation potentials of the pyrazoles (for example E_{ox} of **1a** is 2.02 V vs. SCE) using the Rehm-Weller equation.[5] These results suggest that these reactions proceed via an electron transfer.

3*H*-pyrazoles **1** in the presence of TPP^+ were irradiated in acetonitrile using a 405 nm light under deaerated conditions. The pyrazoles **1** lost nitrogen to give the corresponding cyclopropenes **2**, which were the same products obtained in the direct photolysis of **1**, and the product **3** having acetonitrile unit. The product distributions are summerized in Table 1. In the photo-reaction of **1** in the presence of DCA, only **2** was obtained. The electron transfer reaction of cyclopropene derivatives sensitized by DCA is known to cause their dimerization,[6,7] but the corresponding dimers were not obtained in each reactions.

Table 1. Conversion yields of **2** and **3** for photolysis of **1** with TPP^+ [a]

		Yield (%)[b]	
Pyrazole	Decomposition (%)	**2**	**3**
1a	10	85	trace
	51	35	15
1b	9	49	28
1c	30	20	22
1d[c]	25	82	trace[d]

[a] 3*H*-pyrazole **1** (5-8 mM) with TPP^+ (ca. 1.5 mM) in acetonitrile was irradiated using a 405 nm light (1 kW Hg lamp) under deaerated conditions. [b] Conversion yields based on the decomposition obtained by GC analysis. [c] The concentration of **1d** was 1 mM. When the concentration was 6 mM, only precipitation was obtained. [d] These yields were estimated by GC and GC-MS analysis. *See* ref. 8.

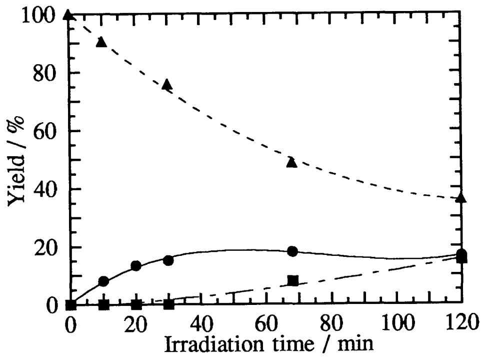
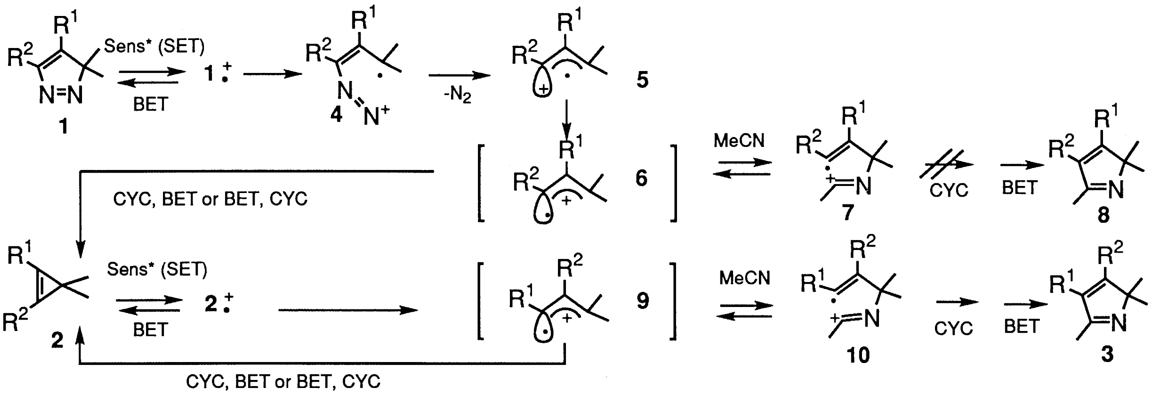


Figure 1. Decomposition of 3*H*-pyrazole **1a** and formation of products. 5.26 mM of **1a** with TPP^+ (1.4 mM) in MeCN was irradiated using 405 nm light (1 kW Hg lamp) under degassed conditions. **1a** (- - -▲- - -); **2a** (—●—); **3a** (– – -■- – -).

The structure of **3** was determined by ^1H NMR and its NOE measurement.[8] The ^1H NMR spectrum was simple[9] and the NOE signal was only observed between the aromatic proton and the methyl proton originated from the acetonitrile. **3** is not the adduct of the nitrogen-eliminated intermediate from **1** to acetonitrile. It is impossible to explain the formation of **3** with the simple PET mechanism, because the structure of the solvent adducts was not **8** which forms from nitrogen eliminated intermediate of **6** (Scheme 1). We investigated the time correlation of product yields. Figure 1 shows the decrease of **1a**, and the yields of **2a** and the solvent adduct **3a**. The product yield of **2a** plateaus after an hour of irradiation, and the yield of **3a** increased with an induction time. The irradiation of isolated **2a** in the presence of TPP^+ under the same conditions showed the rapid decomposition of **2a** and the production of **3a** at 30% conversion yield. Furthermore, the TPP^+ fluorescence was quenched by cyclopropene **2a** with k_q value of 1.7×10^{10}, and the calculated ΔG between **2a** and TPP^+ is -11.8 kcal mol^{-1} (E_{ox}=2.02 V for **2a**). From these results, it is apparent that the formation of **3a** from the TPP^+ sensitized decomposition of **1a**



compound (R^1, R^2): **a**(Ph, CO_2Me), **b**(p-ClC_6H_4, CO_2Me), **c**(p-MeC_6H_4, CO_2Me), **d**(H, CO_2Me)

Scheme 1. Reaction mechanism for photolysis of 3*H*-pyrazole **1** in the presence of TPP^+ as a sensitizer.

proceeds *via* **2a**. Moreover, the structures of **3** support this mechanism. The addition of acetonitrile to radical cation intermediates is rarely reported,[2b,f,10] and none reported the addition of acetonitrile to cyclopropenes to form 2*H*-pyrrole derivatives.

In the reactions in which the yields of **2** are low, their mass balances are also low (Table 1). This tendency can be explained by the following reasons. Some of **2** were thermally unstable and polymerized,[3a,11] thus the yields of **3** from PET reactions of **2** were low. In fact, precipitates regarded as a polymer were observed in some reactions.[11]

We postulate that this reaction mechanism using TPP^+ is as follows (Scheme 1). SET occurs between the 3*H*-pyrazole **1** and an excited sensitizer to form the initial radical cation $\mathbf{1}^{\bullet+}$ and the neutral radical of the sensitizer ($TPP^{\bullet}$). $\mathbf{1}^{\bullet+}$ immediately loses a nitrogen to form the radical cation **6**. At this step, C-N bond cleavage between the olefin and azo group is unfavorable since conjugation between olefin and azo group is interrupted. After elimination of nitrogen, cation site must be at σ-orbital, however, MOPAC calculation shows that the stable configuration of the cation radical is **6** (π-type cation), therefore electron in **5** might be redistributed to more stable configuration **6** quickly. The back electron transfer (BET) from the $TPP^{\bullet}$ to **6** and cyclization (CYC) or CYC and BET produce cyclopropene **2**. If **2** is unstable, its polymerization could occur. Here, if **2** can undergo PET to an excited sensitizer, the radical cation $\mathbf{2}^{\bullet+}$ is formed. The C-C bond of $\mathbf{2}^{\bullet+}$ is then cleaved to form **9**, and acetonitrile, which is a weak nucleophile, adds to **9**, and resulting in the formation of 2*H*-Pyrrole **3**. The reason why only **9** gives **3** but **6** does not give **8** might be explained as follows. Acetonitrile adds to the cation radical **6** to give **7** or **9** to give **10**. However, spin density of R_2 substituted carbon of **7** must be low by a substitution of electron-withdrawing ester group and it prevents further cyclization (CYC) to **8**, thus **7** might return to **6**. To examine the possibility of generation of **6** by SET of **2** in the presence of TPP^+, a trapping experiment by alcohol was performed, but it was unsuccessful at this moment.

In the case of DCA, the acetonitrile adduct was not formed because BET from $DCA^{\bullet-}$ to **6** or **9** can occur more efficiently than that from $TPP^{\bullet}$.[12]

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4 Colorless crystals of **1a** are prismatic, the space group is $P2_1/a$ (#14) with a = 8.523(1) Å, b = 18.485(23) Å, c = 8.544(1) Å, V = 1262.6(3) $Å^3$, Z = 4, and Dc = 1.211 $g{\cdot}cm^{-3}$. The final R value was 0.078 for 1371 reflections with I > 3.50s(I).

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8 **3d** was only detected on GC and GC-MS, because of its low yield.

9 For example, **1a**: 270 MHz, $CDCl_3$; d 7.24-7.38 (m, 2H,Ar), 7.25-7.19 (m, 3H, Ar), 3.61 (s, 3H, CO_2Me), 2.12 (s, 3H, MeC=N), 1.45 (s, 6H, Me).

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11 **2a-d** are not stable. Especially **2d** was polymerized in a few hours at rt; *cf.* ref 3(a).

12 The $\mathbf{2}^{\bullet+}/TPP^{\bullet}$ or $\mathbf{10}/TPP^{\bullet}$ pair may make solvent separated pairs more efficiently than the $\mathbf{2}^{\bullet+}/DCA^{\bullet-}$ or $\mathbf{10}/DCA^{\bullet-}$ pair. *cf.* T. Karatsu, H. Kobayashi, E. Shinkai, and A. Kitamura, *Chem. Lett.*, 2131(1992).