Photoinduced Electron Transfer Reactions of 3,3-Dialkylated 4,5-Diphenyl-3H-pyrazoles: A New Route to the Formation of the Solvent Adducts

Yao-Pin Yen* (顏耀平), Tseng-Min Huang (黃宗民), Yu-Ping Tseng (曾裕平), Hsuan-Yu Lin (林炫羽) and Ching-Cheng Lai (賴清正) Department of Applied Chemistry, Providence University, Sha-Lu, Taichung, Taiwan 433, R.O.C.

3,3-Dialkyl-4,5-diphenyl-3H-pyrazoles undergo readily photoinduced electron transfer (PET) reaction with 2,4,6-triphenylpyrylium tetrafluoroborate (TPP⁺) in acetonitrile to produce cyclopropenes and 2H-pyrroles. During prolonged irradiation, the new ring-closure products derived from 2H-pyrroles as the secondary photoproducts are also produced. However, the corresponding ester analog exhibits different behavior to obtain the cyclopropene as the primary photoproduct and a [2+2] dimer of the cyclopropene as the secondary photoproduct. A rationale for the different behavior is offered.

Keywords: Photoinduced electron transfer; 3H-pyrazoles; Cyclopropene.

INTRODUCTION

Photoinduced electron transfer (PET) reactions of cyclic azoalkanes have been the subject of considerable interest from a mechanistic viewpoint in recently years.¹ However, little is known about the photoinduced electron transfer reactions of 3H-pyrazoles which have an unsaturated carbon-carbon double bond with an azo chromophore in its skeleton. Kitamura² has synthesized some 3H-pyrazoles which have an electron-withdrawing substituent at C₅ and reported their PET reactions with TPP⁺. In addition to the primary photoproduct, cyclopropene, a new minor solvent adduct as a secondary photoproduct through cyclopropene derivative was also found in the reaction. It occurred to us that the relatively complex photochemical pathway of the solvent adduct could be simplified if the 3H-pyrazole has a phenyl group instead of an electron-withdrawing group at the C5 position. Additionally the solvent adduct could be diminished if the 3H-pyrazole has two electron-withdrawing groups at both C₄ and C₅ positions. In order to test the hypothesis of possibly simplifying the change of the secondary photoproduct to the primary photoproduct or possibly changing the reaction pathway, we synthesized 3,3-dialkyl 4,5-diphenyl-3H-pyrazoles and dimethyl-3,3-cyclopentyl-3H-pyrazole-4,5-dicarboxylate and investigated their PET reactions. In this paper we would like to describe results of their PET reactions with TPP^+ .

RESULTS AND DISCUSSION

Fluorescence Quenching of Singlet Excited Sensitizer by 3H-pyrazoles 1a-c

In order to examine the interaction between singlet excited sensitizer and 1a-c, fluorescence quenching experiments were performed. The fluorescence of the sensitizer, TPP^+ , was efficiently quenched by **1a-c** in acetonitrile, and the quenching rate constants, k_q , were calculated from the Stern-Volmer constants, $k_q \tau_s$, and the lifetime of the singlet excited sensitizer, τ_s . The lifetime of TPP⁺ was 2.7 ns.³ The quenching rate constants of **1a-c** were calculated to be $7.3 \times$ 10^9 , 2.1×10^{10} and 1.6×10^{10} M⁻¹s⁻¹, respectively. To explain these results, the Rehm-Weller correlation was examined between 1a-c and the excited singlet sensitizer. For oxidation potential, E^{ox}, during measurement of the **1a-c**, irreversible waves were obtained and the E^{ox} values of 1a, 1b, and 1c were determined to be 2.32, 1.89, and 1.65 V vs SCE, respectively. On the other hand, the reduction potential, E^{red} , of the excited sensitizer, $E^{red} + E_{o,o}$ (where $E_{o,o}$ indicates the singlet excitation energy obtained from the fluorescence o,o band), of TPP⁺ is 2.53 V vs SCE.⁴ The Δ G values of **1a-c** derived from Rehm-Weller's equation,⁵ E^{ox} - E^{red} - $E_{o,o} - e_0^2 / \epsilon a$ (a Coulomb term, $e_0^2/\epsilon a = 0.7$ Kcal mol⁻¹ in acetonitril⁶), were -5.2, -15.1 and -20.7 Kcal mol⁻¹, respectively. These results suggest that these reactions can proceed via an electron transfer.

^{*} Corresponding author. E-mail: ypyen@pu.edu.tw

PET Decomposition of 3H-pyrazoles 1a-c

During some PET decompositions of **1a-b** by TPP⁺ in acetonitrile, cyclopropenes 2a-b and products 3a-b were produced as the primary photoproducts. If irradiation is prolonged, some additional secondary photoproducts 4a-b also appeared. However, in contrast, decomposition of 1c by TPP^+ , only gave the corresponding cyclopropene 2c. In prolonged irradiation, a dimer 5 instead of 3c was produced. The product distributions are summarized in Table 1. The structures of 2a-c, 3a-b and 4a-b were determined by their spectral data (¹H and ¹³C NMR, MS, IR) and their NOE measurements (see the supporting information). Products **3a-b** were adducts of the nitrogen-eliminated intermediate from the corresponding 1a-b to acetonitrile. Products 4a-b were the subsequent cyclization and dehydrogenation product from the corresponding **3a-b**. The structure of **5** was characterized by its spectral data and by its X-Ray crystal structure (Fig. 1).

The course of PET decomposition of these compounds is shown separately in Fig. 2.

The curves show the general trend that while the amount of product 2 increased with irradiation time, the amount of products 3-5 either remained constant (4a-b, 5) or increased a little with time (3a-b). The product yield of 2 plateaus after 4 or 5 h of irradiation, and the yields of 3a-b increased with an induction time. This suggested that product 2 likely underwent secondary PET decomposition but at varying efficiencies. Indeed, the irradiation of cyclopropenes 2a-c in the presence of TPP⁺ under the same conditions showed the rapid decomposition of 2a-c and the production of 3a-b and 5, respectively.

Fluorescence Quenching of Single Excited Sensitizer by Cyclopropenes 2a-c

The fluorescence of TPP⁺ was quenched by cyclopro-

Table 1. Product Yields of Photoinduced Electron Transfer Reactions of 3H-Pyrazoles **1a-c** in Acetonitrile

Compound	Decomposition (%)	Yield ^a			
		2	3	4	5
1a	20	27	14	_	_
	27	38	16	1	_
1b	18	36	13	_	_
	26	41	13	1	_
1c	12	71	_	_	_
	21	58	-	_	3

^a Conversion yields based on the reactant consumed and obtained by GC analysis.



Fig. 1. ORTEP plots of dimer 5.



Fig. 2. Progress of PET decomposition of 3H-pyrazoles 1a, 1b, 1c (●) was monitored by GLC and appearance of products 2a, 2b, 2c (▲), 3a, 3b (★), 4a, 4b (■) and 5 (♦); left (1a), middle (1b) and right (1c).

	$k_q (M^{-1}s^{-1})$	$E^{ox} (ev)^a$	ΔG^{b} (Kcal mol ⁻¹)
2a	$2.0 imes 10^{10}$	1.44	-25.6
2b	2.1×10^{10}	1.42	-25.7
2c	$1.3 imes 10^{10}$	2.14	-9.4

Table 2. Quenching Rate Constants, Oxidation Potentials and
Free Energy Changes of Cyclopropenes 2a-c

^a VS SCE. Measured by cyclic voltametry in dry acetonitrile. ^b Derived from Rehm-Weller's equation, $\Delta G = E^{ox} - E^{red} - E_{o,o} - E^{red} - E_{o,o} - E^{red} - E^{re$

 $e_o^2/\epsilon a.$

penes **2a-c**. The quenching rate constants, oxidation potentials and the free energy changes, ΔG , between sensitizer and cyclopropenes are summarized in Table 2. These results suggest that **2a-c** can undergo PET reactions with TPP⁺.

PET Decomposition of Cyclopropenes 2a-c

PET decompositions of cyclopropenes **2a-b** gave initially two similar products **3a-b**, in 54% and 50% yield, respectively. After prolonged irradiation of **2a-b**, two new additional products **4a-b** were also isolated (31 and 28%, respectively) (Table 3). Their structures were characterized by their spectral data. The nature of the secondary reactions was determined in the following additional experiments. Irradiation of a solution of an isolated sample of **3a** was found to give **4a** in 75% yield. Similarly, irradiation of **3b** gave **4b** in 51% yield. Thus, the complete sequences of reaction during irradiation of **1a-b** can be summarized in the following manner:

$$1a-b \xrightarrow{hv / TPP^{+}} \lambda > 400 \text{ nm} \qquad 2a-b + 3a-b + 4a-b$$

$$\downarrow hv / TPP^{+} \lambda > 400 \text{ nm} \qquad 3a-b + 4a-b$$

$$\downarrow hv / TPP^{+} \lambda > 400 \text{ nm} \qquad 4a-b$$

In contrast, PET decomposition of **2c** only yielded a dimer product, **5**, in 44% yield, and the complete sequence of irradiation of **1c** can also be summarized as follows:

$$\frac{1c}{\lambda > 400 \text{ nm}} \xrightarrow{\text{lc} + 5} 2c + 5$$

$$\frac{1}{\lambda > 400 \text{ nm}} 5$$

To explain the above PET results, we propose the mechanism displayed in Scheme I. The formation of the primary products **2a-c** likely followed the reaction pathway proposed by Kitamura.² The PET reaction of **1a-c** with TPP^+ has been sug-

Table 3.	Product Yields of Photoinduced Electron Transfer
	Reactions of Cyclopropenes 2a-c in Acetonitrile

Compound	Decomposition (%)	Yield ^a			
		3	4	5	
2a	14	54	-	_	
	31	38	31	-	
2b	15	50	-	_	
	30	41	28	_	
2c	30	_	_	44	

^a Conversion yields based on the reactant consumed and obtained by GC analysis.

gested to involve a single electron transfer from the 1a-c to an excited sensitizer TPP⁺ resulting in the formation of an initial radical cation 6^{+} and the neutral radical TPP. 6^{+} immediately loses a nitrogen to form the radical cation 7 and redistributes to a more stable configuration $\mathbf{8}^2$. At this stage there are two possible pathways for the interpretation of intermediate 8 leading to cyclopropene 2. The first pathway is the back electron transfer (BET) from the TPP• to 8 to form a diradical or vinylcarbene intermediate and then it undergoes 1,3-cyclization to produce cyclopropene 2 (path A). Alternatively, 8 can undergo intramolecular cyclization to form the cyclopropene radical cation and subsequently follows the BET from TPP• to yield cyclopropene 2 (path B). Besides the cyclopropene, the formation of the primary photoproducts **3a-b** is proposed to proceed via the following reaction pathway: addition of acetonitrile with 8a-b results in the formation of intermediates 9a-b. The back electron transfer from TPP• to **9a-b** would produce **3a-b** (path C).

The presence of such primary photoproducts **3a-b** could be due to the phenyl group (R_3) with high resonance stability that would stabilize the intermediate **8** and favor addition with acetonitrile. Hence, it appears that the presence of phenyl groups indeed accomplished the stated goal to change the complex pathway to a simple pathway.

Since the products **3a-b** are also produced in the PET reactions of **2a-b**, the formation of **3a-b** is proposed to undergo the following pathways. The cyclopropenes **2a-b** react with TPP⁺ to form the radical cation 2^{+•}. The C-C bond of **2^{+•}** is then cleaved to form **8a-b**. The addition of acetonitrile with **8a-b** results in the formation of the intermediate **9a-b**. The back electron transfer from TPP• to **9a-b** would produce the solvent-adducts, **3a-b**. Since all the wavelengths of the UV absorption spectra of **3a-b** are shorter than 400 nm, the formation of the final products **4a-b** can be explained by the PET reaction of **3a-b** through cyclization and dehydrogenation.

Scheme I



On the other hand, the PET reaction of 2c will undergo a different pathway to form the [2 + 2] dimer **5** as the secondary photoproduct. It may be due to 2c having two electronwithdrawing substituents (R₃) that would destabilize the formation of 8c, making this pathway not competitive against the dimerization of 2c. Hence, it appears that the presence of electron-withdrawing groups indeed accomplished the stated goal for blocking the formation of the solvent-adduct. A facile process can be proposed for the formation of **5** from 2c. The excited TPP⁺ reacts with 2c at a diffusion-controlled rate leading to the formation of the radical ion $2^{+\bullet}$ and TPP•. Recombination of this radical ion pair partially gives ${}^{3}[2]^{*}$, which reacts with **2c** to give the dimer **5**.⁷

EXPERIMENTAL SECTION

General Information

Melting points were determined on a Yamaco micro melting points apparatus and are uncorrected. IR spectra

were obtained on a Perkin Elmer 2000 spectrophotometer in KBr. ¹H NMR spectra were determined on a Bruker AC-250 spectrometer in CDCl₃ with TMS as an internal standard. Gas chromatography (GC) analyses were performed on an HP 5890 chromatograph. Mass spectra were recorded using an HP 5890 and 5890 MSD. Fluorescence spectra were measured on a Perkin-Elmer LB-50 spectrofluorimeter.

Materials

3,3-Dimethyl-4,5-diphenyl-3H-pyrazole (**1a**), 3,3-cyclopentyl-4,5-diphenyl-3H-pyrazole (**1b**) and dimethyl-3,3cyclopentyl-3H-pyrazole-4,5-dicarboxylate (**1c**) were prepared according to published procedures.⁸ The UV absorption spectra of all these compounds exhibit a shoulder absorption band around 290-380 nm. (The extinction coefficients for **1a-c** were 4.9×10^3 , 6.6×10^3 and 2.5×10^3 M⁻¹cm⁻¹, respectively.)

Oxidation Potentials of the 3H-Pyrazoles

Oxidation potentials of 3H-pyrazoles **1a-c** were measured by cyclic voltammetry (CHI 600A) at a platinum electrode in argon-saturated dry acetonitrile with 0.10 M tetraethylammonium perchlorate as the supporting electrolyte. The scan speed was 200 mVs⁻¹, and the reference electrode was the SCE. Obtained peaks were irreversible in all cases, and the oxidation potentials were determined from the halfpeak potentials.

PET Photolyses

Degassed acetonitrile solutions of **1a** or **1b** or **1c** (10 mM) and TPP⁺ (1.0 mM) were irradiated with a Hanovia medium-pressure 450 W mercury lamp through a filter solution (CuSO₄ + NaNO₂ + NH₄OH) (λ = 400-500 nm).⁹ The reaction was monitored by GC/MS, and the yield of the product was determined by quantitative GLC and based on the number of moles of reactant consumed.

Isolation of the Decomposition Products of 1a-c

The primary photoproducts, cyclopropenes **2a-c** and solvent-adducts **3a-b** as well as the secondary photoproducts, **4a-b** and a new dimmer product **5** were isolated from the TPP-sensitized decomposition of **1a-c**. **1a** or **1b** or **1c** (0.73 mmol) and TPP⁺ (0.07 mmol) were dissolved in 300 mL of acetonitrile and irradiated with a Hanovia medium-pressure Hg lamp through a filter solution (CuSO₄ + NaNO₂ + NH₄OH) for 4-6 h after nitrogen purging. After concentration of the solution, products were separated by flash chromatography (Al₂O₃, n-hexane:ether = 20:1). **2a** (17% yield). mp 34-36 °C (mp 43.5-44 °C¹⁰); ¹H NMR (250 MHz, CDCl₃) δ : 7.61-7.65 (m, 4H), 7.41-7.47 (m, 4H), 7.31-7.34 (m, 2H). 1.49 (s, 6H); IR (neat): 3060, 3025, 2943, 2857, 1807, 1596, 1491, 1445, 1271, 754, 689 cm⁻¹; MS *m*/*z* (%): 220 (M⁺, 28), 205 (100), 189 (13), 178 (15), 166 (12), 128 (14), 115 (13), 77 (18).

2b (25% yield). ¹H NMR (250 MHz, CDCl₃) δ : 7.65-7.75 (m, 4H), 7.41-7.51 (m, 4H), 7.30-7.40 (m, 2H), 1.89-1.99 (m, 4H), 1.74-1.83 (m, 4H); ¹³C NMR (CDCl₃) δ : 129.8, 128.5, 128.4, 128.3, 128.0, 126.2, 32.3, 30.4, 26.3, 25.4; IR (neat): 3062, 3019, 2949, 2851, 2401, 1808, 1493, 1446, 1216, 759 cm⁻¹; MS *m/z* (%): 246.2 (M⁺, 100), 231.2 (8), 217.1 (100), 178.1 (29), 166.1 (10), 139.1 (18), 111.1 (28); HRMS calcd for C₁₉H₁₈: 246.1409; Found 246.1406.

2c (35% yield); ¹H NMR (250 MHz, CDCl₃) δ : 3.86 (s, 6H), 1.63-1.78 (m, 8H); ¹³C NMR (CDCl₃) δ : 160.3, 127.6, 52.6, 40.4, 34.5, 26.3; IR (neat): 2955, 2869, 1835, 1721, 1436, 1252, 1062 cm⁻¹; MS *m*/*z* (%): 210 (M⁺, 4), 167 (10), 150 (25), 119 (38), 118 (28), 91 (100), 67 (39), 59 (61); HRMS calcd for C₁₁H₁₄O₄: 210.0892; Found: 210.0900.

3a (9% yield); ¹H NMR (250 MHz, CDCl₃) δ : 7.22-7.30 (m, 6H), 7.07-7.14 (m, 4H), 2.24 (s, 3H), 1.41 (s, 6H); ¹³C NMR (CDCl₃) δ : 170.0, 167.7, 136.8, 135.2, 133.8, 129.2, 128.3, 128.2, 127.4, 127.1, 78.4, 23.4, 18.2; IR (neat): 3059, 2974, 2928, 1444, 1379, 1292, 761, 701 cm⁻¹; MS *m/z* (%): 261 (M⁺, 100), 246 (11), 205 (46), 178 (11), 83 (31); HRMS calcd for C₁₉H₁₉N: 261.1518; Found: 261.1515.

3b (2% yield); ¹H NMR (250 MHz, CDCl₃) δ : 7.15-7.33 (m, 6H), 7.03-7.11 (m, 4H), 2.30 (s, 3H), 2.20-2.29 (m, 2H), 2.11-2.20 (m, 2H), 1.77-1.91 (m, 4H); ¹³C NMR (CDCl₃) δ : 164.8, 137.7, 135.4, 134.0, 129.3, 128.7, 128.2, 127.4, 127.1, 89.8, 37.2, 34.4, 26.0, 18.2; IR (neat): 3062, 2919, 2847, 1440, 1373, 1101, 763, 687 cm⁻¹; MS *m/z* (%): 287 (M⁺, 100), 272 (13), 259 (51), 246 (25), 216 (18), 202 (29); HRMS calcd for C₂₁H₂₁N: 287.1674; Found: 287.1670.

4a (3% yield); ¹H NMR (250 MHz, CDCl₃) δ : 8.79-8.86 (m, 2H), 8.55-8.61 (m, 1H), 8.18-8.24 (m, 1H), 7.65-7.79 (m, 4H), 2.95 (s, 3H), 1.72 (s, 6H); ¹³C NMR (CDCl₃) δ : 167.3, 157.7, 131.2, 131.1, 131.0, 127.5, 127.2, 126.9, 126.6, 126.2, 125.6, 123.8, 123.7, 123.6, 74.3, 25.2, 22.6; IR (neat): 3083, 2971, 2926, 2855, 1436, 1378, 759 cm⁻¹; MS *m/z* (%): 259 (M⁺, 100), 244 (50), 215 (10), 203 (56), 101 (9); HRMS calcd for C₁₉H₁₇N: 259.1362; Found: 259.1353.

4b (3% yield); ¹H NMR (250 MHz, CDCl₃) δ: 8.76-8.88 (m, 2H), 8.51-8.63 (m, 1H), 8.01-8.22 (m, 1H), 7.65-7.78 (m, 4H), 2.91-3.03 (s, 3H), 2.39-2.40 (m, 4H), 2.18-2.31 (m, 2H), 1.85-1.96 (m, 2H); ¹³C NMR (CDCl₃) δ: 155.3, 131.6, 131.2, 127.6, 127.3, 127.0, 126.4, 126.3, 125.2, 124.0, 123.7, 123.6, 84.4, 37.3, 27.3, 22.0; IR (KBr): 3078, 2952, 2866, 1600, 1445, 1377, 756, 726 cm⁻¹; MS m/z (%): 285 (M⁺, 66), 270 (19), 256 (21), 244 (100), 214 (35), 201 (42); HRMS calcd for C₂₁H₁₉N: 285.1517; Found 285.1513.

5 (4% yield). mp 196-197 °C; ¹H NMR (250 MHz, CDCl₃) δ : 1.48-1.60 (m, 8H), 1.65-1.75 (m, 8H), 3.72 (s, 12H); IR (neat): 2950, 2848, 1737, 1460, 1358, 1276, 1102, 958 cm⁻¹; MS *m/z* (%): 421 (M+1, 23), 329 (15), 307 (36), 301 (19), 289 (25), 269 (17), 154 (100), 89 (62), 77 (65); HR-MS (FAB) calcd for C₂₂H₂₉O₈ (M+H⁺): 421.1863; Found: 421.1859.

ACKNOWLEDGEMENT

We thank the National Science Council of the Republic of China for financial support (contract NSC-89-2113-M-126-001).

Received August 20, 2003.

REFERENCES

 (a) Karatsu, T.; Hotta, H.; Kitamura, A. J. Chem. Soc. Chem. Commun. 1991, 1451. (b) Zona, T. A.; Goodman, J. L. J. Am. Chem. Soc. 1993, 115, 4925. (c) Adam, W.; Sendelbach, J. J. Org. Chem. 1993, 58, 5310 and 5316. (d) Adam, W.; Sahin, C.; Sendelbach, J.; Walter, H.; Chen, G.-F.; Williams, F. J. Am. Chem. Soc. 1994, 116, 2576. (e) Ikeda, H.; Minegishi,
T.; Miyashi, T. J. Chem, Soc. Chem. Commun. 1994, 297. (f)
Zona, T. A.; Goodman, J. L. J. Am. Chem. Soc. 1995, 117,
5879. (g) Karatsu, T.; Itoh, H.; Kikunaga, T.; Ebashi, Y.;
Hotta, H.; Kitamura, A. J. Org. Chem. 1995, 60, 8270. (h)
Ikeda, H.; Minegishi, T.; Takahashi, Y.; Miyashi, T. Tetrahedron lett. 1996, 39, 4377.

- Miyagawa, N.; Karatsu, T.; Kitamura, A. Chem. Lett. 1997, 1005.
- Akaba, R.; Niimura, Y.; Fukushima, T.; Kawai, Y.; Tajima, T.; Kuragami, T.; Negishi, A.; Kamata, M.; Sakuragi, H.; Tokumaru, K. J. Am. Chem. Soc. 1992, 114, 4460.
- Chanon, M.; Ebersen, L. In *Photoinduced Electron Transfer*; Fox, M. A.; Chanon, M. Eds.; Elsevier: New York, 1988; Part A, p. 470.
- 5. Rehm, D.; Weller, A. Ber. Bunsenges. Physik. Chem. 1969, 73, 834.
- Kavarnos, G. J. In *Photoinduced Electron Transfer 1, Topics* in *Current Chemistry 156*; Springer-Verlag: New York, 1990, p 31.
- Brown-Wensley, K. A.; Mattes, S. L.; Faird, S. J. Am. Chem. Soc. 1978, 100, 4162.
- (a) Williams, W. M.; Dobier, W. R. J. Am. Chem. Soc. 1972, 84, 3955. (b) Leigh, W. J.; Arnold, D. R. Can. J. Chem. 1979, 57, 1186. (c) Yen, Y. P.; Chen, S. F.; Heng, Z. C.; Huang, J. C.; Kao, L. C.; Lai, C. C.; Liu, R. S. H. Heterocycles. 2001, 55, 1859.
- 9. Eriksen, J.; Foots, C. S. J. Am. Chem. Soc. 1980, 102, 6083.
- Baumstark, A. L.; McCloskey, C. J.; Witt, K. E. J. Org. Chem. 1978, 43, 3609.