A Novel (3+2) Photocycloaddition of (2',2'-Diarylvinylidene)cyclopropanes with Organic Carbonitriles via Photoinduced Electron Transfer

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Abstract: The 9,10-Dicyanoanthracene-sensitized photoreaction of (2',2'-diaryl-vinylidene)cyclopropanes with organic carbonitriles gave 2-substituted 3-(2',2'-diarylvinylidene)-1-pyrrolines via photoinduced electron transfer.

Recently, much attention has been focused on the photocycloaddition via photoinduced electron transfer.^{1,2} However, little is known about the (3+2) photocycloaddition via this process with the exception of photo-initiated 1,3-dipolar cycloaddition.² We now report a novel (3+2) photocycloaddition of (2',2'-diarylvinylidene)cyclopropanes with organic carbonitriles via photoinduced electron transfer.

Irradiation of an acetonitrile solution containing 3-[2',2'-bis(4-methoxyphenyl)vinylidene]-1,1,2,2-tetramethylcyclopropane (**1a** $, <math>1x10^{-2}$ mol/dm³), Mg(ClO4)2 ($1x10^{-2}$ mol/dm³) and a catalytic amount of 9,10-dicyano-anthracene (DCA) ($5x10^{-4}$ mol/dm³) through aqueous CuSO4-NH3 filter solution



Vinylidene- cyclopropane	Organic Carbonitrile	(3+2)Photo- cycloadduct	Yield / % ^a
1a	MeCN	2a	86
1a	EtCN	2 b	88
1a	PhCN	2 c	90
3	MeCN	4	89
1b	MeCN		0
5	MeCN		0
6	MeCN		0

 Table 1. (3+2)Photocycloaddition of Vinylidenecyclopropanes with Organic Carbonitrile via Photoinduced Electron Transfer

^a Isolated yields based on vinylidenecyclopropanes used.



Me

Me



(> 400 nm) under argon atmosphere afforded 3-[2',2'-bis(4-methoxy-phenyl)vinylidene]-2,4,4,5,5-pentamethyl-1-pyrroline (2a) in 86% yield. In the absence of Mg(ClO4)2, the (3+2) photocycloaddition hardly occurred and most of the starting materials were recovered. Under oxygen atmosphere, the photooxygenation of 1a occurred to give 4,4'-dimethoxybenzophenone as a major product along with a small amount of 2a.

Similar irradiation of 1a in propionitrile and benzonitrile in the presence of DCA and Mg(ClO4)2 gave the (3+2) cycloadducts 2b-c in high yields. The DCA-sensitized photoreaction of 3 in acetonitrile gave the (3+2) photocycloadduct 4, but the photoreaction of 1b, 5 and 6 did not give the corresponding cyclo-adducts. In the case of 5, the cis-trans photoisomerization of the methyl groups attached to the 1- and 2-positions of the cyclopropane ring was observed.

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The cycloadducts **2a-c** and **4** were isolated by column chromatography on silica gel. Their structures were established by the analyses of ¹H NMR, ¹³C NMR, H-H COSY, H-H NOESY, IR, UV and Mass spectra, and also by chemical conversions.³

The reduction of **2a** with NaBH4 in methanol quantitatively gave **7**, which was converted to **8** by acetylation with acetic anhydride.³ The IR spectrum of **2a** showed the stretching vibration of the allenyl group at 1937 cm⁻¹ and that of the imino group at 1607 cm⁻¹. The ¹³C signal of the central carbon of the allenic group of **2a** appeared at δ 200.9. In the H-H NOESY spectrum of **7**, the NOE was observed between the aromatic protons and the methyl protons that was derived from acetonitrile.

The fluorescence of DCA in acetonitrile was quenched by 1a at nearly diffusion controlled rate. The free energy change (Δ G) for a single electron transfer process from 1a to the excited singlet DCA (1 DCA^{*}) was estimated to be negative.⁴

All the above results can be explained in terms of the mechanism shown in Scheme 1. The first step is a single electron transfer from 1a to $^{1}DCA^{*}$ to form the radical ion pair [DCA^{-•}···1a^{+•}]. The dissociation of the radical ion pair to the free radical ions competes with back-electron

Scheme 1. DCA hv $^{1}DCA^{*}$ $^{1}DCA^{*} + 1a \longrightarrow [DCA^{*} \cdots 1a^{+}]$ $[DCA^{*} \cdots 1a^{+}] \longrightarrow DCA + 1a$ $[DCA^{*} \cdots 1a^{+}] \longrightarrow DCA^{*} + 1a^{+}$ $1a^{+} \longrightarrow [Ar \longrightarrow Me \longrightarrow Me] \longrightarrow Ar \longrightarrow Ar \longrightarrow Ne \longrightarrow Me \longrightarrow Me$ transfer from DCA^{-•} to $1a^{+•}$. The free radical cation $1a^{+•}$ reacts with organic carbonitriles to give 2a via a Ritter-type addition and the subsequent cyclization.^{5,6} The role of Mg(ClO4)₂ is probably to suppress a back-electron transfer from DCA^{-•} to $1a^{+•}$ and able to stabilize the ring-opened radical cation of 1a.⁷

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References

- Photoinduced Electron Transfer, Part A-D, ed by Fox, M. A.; Chanon, M., Elsevier,; Amsterdam, 1988; Photoinduced Electron Transfer I-III:Topics in Current Chemistry 156, 158, 159, ed by Mattay, J., Springer-Verlag,; Berlin, 1990-1991.
- 2. Muller, F.; Mattay, J. Chem. Rev. 1993, 93, 99.
- 3. Physical properties for **2a** and **8**: **2a**: oil; ¹H NMR (270 MHz, CDCl3) δ 1.12 (s, 6H), 1.17 (s, 6H), 2.10 (s, 3H), 3.82 (s, 6H), 7.08 (ABq, 8H, $\Delta v = 105.6$ Hz, J=8.5 Hz); ¹³C NMR (67 MHz, CDCl3) 17.9, 24.7, 24.8. 49.4, 55.3, 74.5, 114.0, 115.2, 121.9, 128.9, 129.3, 159.2, 165.9, 200.9; IR (neat) 1937, 1607 cm⁻¹. **8**: mp 144-145 °C; ¹H NMR (270 MHz, CDCl3) δ 1.05 (s, 3H), 1.15 (s, 3H), 1.29 (s, 3H), 1.47 (s, 3H), 1.49 (d, 3H, J =6.5 Hz), 2.10 (s, 3H), 3.82 (s, 3H), 3.83 (s, 3H), 4.62 (q, 1H, J=6.5 Hz), 6.86-6.90 (m, 4H), 7.25-7.31 (m, 4H); ¹³C NMR (67 MHz, CDCl3) δ 20.6, 22.0, 23.0, 24.1, 25.5, 48.6, 55.3, 55.4, 67.7, 113.9, 118.2, 129.0, 129.5, 129.7, 159.0, 159.1, 170.1, 196.3; IR (KBr) 2026, 1638 cm⁻¹; Anal. Calcd for C₂₇H₃₃O₃N: C, 77.29; H, 7.93; O, 11.44; N, 3.34. Found: C, 77.15; H, 8.00; N, 2.96.
- 4. The ΔG value(-121.5 kJ/mol) was calculated according to the Rehm-Weller equation: Oxidation potential of **1a** (0.36 V vs Ag/Ag⁺), the excited singlet energy of DCA (2.89 eV), the reduction potential of DCA (-1.33 V vs Ag/Ag⁺): Rehm, W.; Weller, A. Isr. J. Chem. **1970**, *8*, 259.
- 5. Krimen, L. I.; Cota, D. J. Org. React. 1969, 17, 213.
- 6. Evans, T. R.; Wake, R. W.; Jaenicke, O. The Exciplexes, ed by Gordon, M.; Ware, W. R., Academic Press Inc., New York, 1975, p. 345; Mattes, S. L.; Farid, S. J. Chem. Soc., Chem. Commun. 1980, 126.
- 7. Mizuno, K.; Ichinose, N.; Otsuji, Y. J. Org. Chem. 1992, 57, 1855 and references cited therein.

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