



S0040-4039(96)00477-7

Photoinduced C₃-Unit Introduction to Electron-Deficient Molecules by Use of Cyclopropanone Silyl Acetals via Electron Transfer

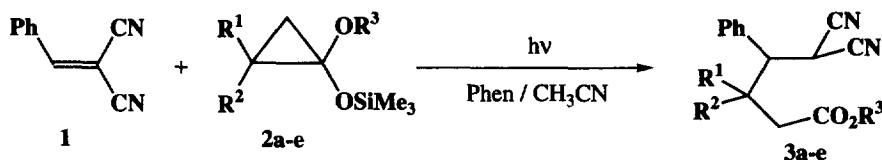
Kazuhiko Mizuno,* Toshinori Nishiyama, Naoki Takahashi, and Hiroo Inoue

Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, Sakai, Osaka 593, Japan

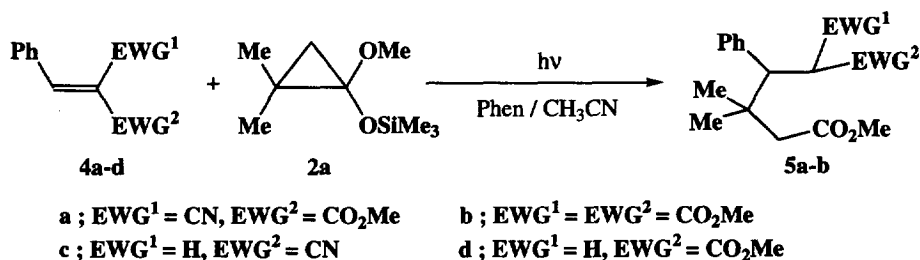
Abstract : Irradiation of an acetonitrile solution containing 1,1-dicyano-2-phenylethene or 1,2,4,5-tetracyanobenzene with 2,2-dimethylcyclopropanone silyl acetal in the presence of phenanthrene afforded regioselectively the addition or substitution product of C₃-unit bearing ester group. Copyright © 1996 Elsevier Science Ltd

Photoinduced electron transfer reactions of small ring compounds have been currently investigated from synthetic and mechanistic viewpoints.¹ Previously, we and others have reported the nucleophile-assisted ring opening reactions of cyclopropane derivatives via their radical cations generated by photoinduced electron transfer.²⁻⁴ However, little is known about the photochemical carbon-carbon bond forming reactions by use of the ring opening reaction of cyclopropane derivatives as synthetically useful C₃-unit. Very recently, Oku and Abe reported the photoreactions of cyclopropanone silyl acetals with arylmethyl methanesulfonates and carbonyl compounds to afford the C₃-unit introduction products.^{5,6} These results prompted us to report our independent work of the regioselective C₃-unit introduction to some electron-deficient arylalkenes and polycyanobenzenes by use of cyclopropanone silyl acetals via photoinduced electron transfer.^{7,8}

Photoreaction of 1,1-dicyano-2-phenylethene (**1**, 0.05 mmol) with 1-methoxy-2,2-dimethyl-1-trimethylsilyloxycyclopropane (**2a**, 0.15 mmol) in acetonitrile in the presence of phenanthrene (Phen, 0.01 mmol) with a high-pressure mercury lamp through Pyrex filter (> 280 nm light) afforded methyl 5,5-dicyano-3,3-dimethyl-4-phenylpentanoate (**3a**) in a 94 % yield. Similar photoreactions of 1-cyano-1-methoxycarbonyl-2-phenylethene (**4a**) with **2a** and **1** with 2,2-dialkyl-substituted cyclopropanone silyl acetals **2b-d** or 1-ethoxy-1-trimethylsilyloxycyclopropane (**2e**) in the presence of Phen gave the corresponding



a ; R¹=R²=R³=Me, b ; R¹=R²=Me, R³=Et, c ; R¹=R²=Me, R³=i-Pr,
d ; R¹=R²=(CH₂)₅, R³=Me, e ; R¹=R²=H, R³=Et



alkylated compounds (**5a**, **3b-e**) in high yields. However, the photoalkylation of less electron-deficient arylalkenes such as 1,1-dimethoxycarbonyl-2-phenylethene (**4b**), 1-cyano-2-phenylethene (**4c**), and 1-methoxycarbonyl-2-phenylethene (**4d**) using **2a** occurred inefficiently or did not occur, although a small amount of reduction products of **4b-d** were produced (< 3%). The results are summarized in Table 1.

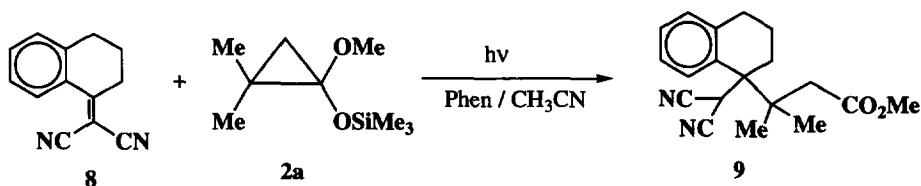
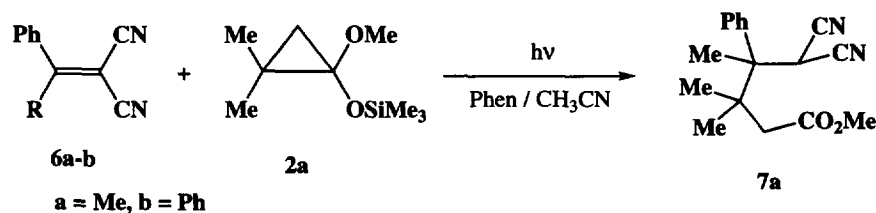
The tetra-substituted electron-deficient arylalkenes, 1,1-dicyano-2-phenylpropene (**6a**) and cyclic dicyanomethylene compound **8** with **2a** in the presence of Phen also gave the corresponding alkylated products **7a** and **9**, in 49 and 18% yields respectively. However, 1,1-dicyano-2,2-diphenylethene (**6b**) did not give the alkylated product. Notably here is that the quaternary carbon - quaternary carbon bond forming reaction proceeded regioselectively, although the yields were not high.

Table 1. Photoreaction of Electron-Deficient Alkenes with Cyclopropanone Silyl Acetals

Alkene ($E_{p/2}^{\text{red}} / V^{\text{a}}$)	Cyclopropane ($E_{p/2}^{\text{ox}} / V^{\text{b}}$)		Sens	Irradn time / h	Product					
	EWG ¹	EWG ²			R ¹	R ²	R ³	Yield ^c / %		
1 (-1.45)			2a (1.59)	Me	Me	Me	Phen	3	3a	94
1			2a				Pyrene	4	3a	92
1			2a				—	24		0
1			2b (1.76)	Me	Me	Et	Phen	4	3b	92
1			2c (1.67)	Me	Me	ⁱ Pr	Phen	3	3c	95
1			2d (1.80)	-(CH ₂) ₅ -		Me	Phen	8	3d	95
1			2e (2.20)	H	H	Et	Phen	15	3e	84
4a (-1.61)	CN	CO ₂ Me	2a				Phen	21	5a	87
4b (-1.85)	CO ₂ Me	CO ₂ Me	2a				Phen	24	5b	8
4c (-2.62)	H	CN	2a				Phen	48		0
4d (-2.71)	H	CO ₂ Me	2a				Phen	48		0

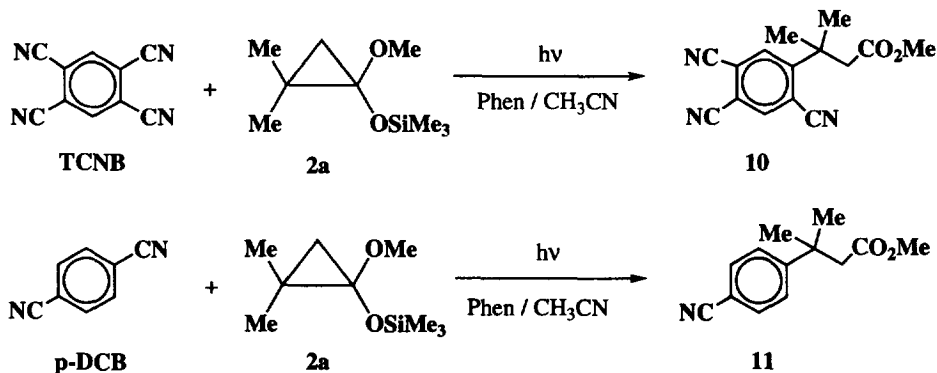
^a Reduction potentials vs. Ag / Ag⁺ in acetonitrile. ^b Oxidation potentials vs. Ag / Ag⁺ in acetonitrile.

^c Isolated yields based on the electron-deficient alkenes used. The photoproducts were isolated by column chromatography on silica gel. Their structures were determined by their spectroscopic properties and elemental analyses.



The photoreaction of **1** with **2a** proceeded efficiently in the presence of aromatic hydrocarbons such as Phen and pyrene as photosensitizers. The rate for the formation of **3a** decreased with decreasing the solvent polarity, and the starting materials were almost recovered in benzene. A small amount of water, which is contained in acetonitrile, is indispensable for this photoreaction. The addition of D₂O to the **1**+**2a** reaction system afforded a mono-deuterated compound **3a-d₁**.

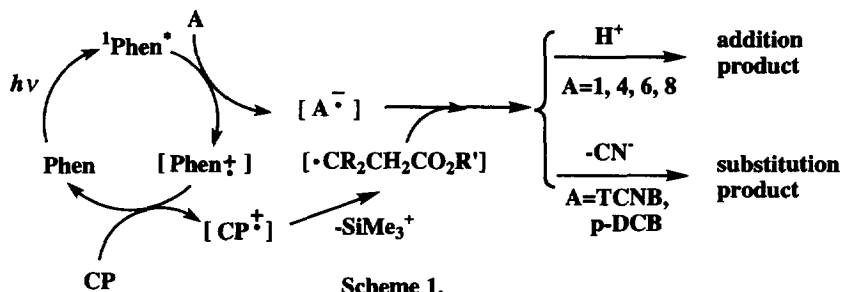
Irradiation of an acetonitrile solution containing **2a** and 1,2,4,5-tetracyanobenzene (TCNB) in the presence of Phen afforded methyl 3-methyl-3-(2,4,5-tricyanophenyl)butanoate (**10**) in a 78% yield. Similar irradiation of **2a** with 1,4-dicyanobenzene (p-DCB) in the presence of Phen gave methyl 3-(4-cyanophenyl)-3-methylbutanoate (**11**) in a 73% yield.



The fluorescence of Phen in acetonitrile was efficiently quenched by **1**, TCNB, and p-DCB, but it was not quenched by **2a**. The free energy changes (ΔG) for a single electron transfer process from the excited singlet Phen ($^1\text{Phen}^*$) to **1**, TCNB, and p-DCB were estimated to be negative (-103, -154, and -79 kJ/mol), but the value from **2a** to $^1\text{Phen}^*$ was positive (72 kJ/mol).⁹

From these results, the photoalkylation of electron-deficient arylalkenes and polycyanobenzenes by use of cyclopropanone silyl acetals can be explained by the redox-type electron transfer mechanism as shown in Scheme 1.^{1,10} The radical cation ($\text{CP}^{+\bullet}$) of cyclopropanone silyl acetal (CP) is generated by a secondary electron transfer from CP to $\text{Phen}^{+\bullet}$, which is produced by a primary electron transfer from $^1\text{Phen}^*$ to the electron accepting molecule (A). The key process of this mechanism is a coupling of $\text{A}^{\bullet-}$

with $\cdot\text{CR}_2\text{CH}_2\text{CO}_2\text{R}'$, which is generated by the O-Si cleavage of $\text{CP}^{\ddagger+}$, followed by protonation or decyanation to give an addition or substitution product.



Acknowledgment : We are indebted to Professor Oku and Dr. Abe (Kyoto Institute of Technology) for helpful discussion. This work is partially supported by the Grant-in-Aid for Scientific Research on Priority Area-Research on "New Development of Organic Electrochemistry" from the Ministry of Education, Science, Sports, and Culture of Japan and Shorai Foundation for Science and Technology. We thank Shin-Etsu Chemical Co. Ltd., for gift of chlorotrimethylsilane.

References and Notes

- Reviews: Mizuno, K.; Otsuji, Y. in *Topics in Current Chemistry, Vol. 169, Electron Transfer I*, ed by Mattay, J., Springer-Verlag, Berlin (1994), pp. 301-346; Chanon, M.; Ebersson, L. in *Photoinduced Electron Transfer, Part A*, ed by Fox, M. A.; Chanon, M. Elsevier, Amsterdam (1988) pp. 409-597; Muller, F.; Mattay, J. *Chem. Rev.*, **1993**, *93*, 99-117, and references cited therein.
- Mizuno, K.; Ogawa, J.; Otsuji, Y. *Chem. Lett.*, **1981**, 741-744; Mizuno, K.; Yoshioka, K.; Otsuji, Y. *Chem. Lett.*, **1983**, 941-944.
- Rao, V. R.; Hixson, S. S. *J. Am. Chem. Soc.*, **1978**, *100*, 535-541.
- Dinnocenzo, J. P.; Schmittel, M. *J. Am. Chem. Soc.*, **1987**, *109*, 1561-1562; Dinnocenzo, J. P.; Lieberman, D. R.; Simpson, T. R. *J. Am. Chem. Soc.*, **1993**, *115*, 366-367.
- Abe, M.; Oku, A. *J. Chem. Soc. Chem. Commun.*, **1994**, 1673-1674; Abe, M.; Oku, A. *J. Org. Chem.*, **1995**, *60*, 3065-3073.
- Lewis-acid catalyzed or thermal ring opening of cyclopropanone silyl acetals: Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.*, **1977**, *99*, 7360-7362; Abe, M.; Oku, A. *Tetrahedron Lett.*, **1994**, *35*, 3551-3554; Oku, A.; Abe, M.; Iwamoto, M. *J. Org. Chem.*, **1994**, *59*, 7445-7452.
- Mizuno, K.; Takahashi, N.; Yuuki, H. 41st Symposium on Organometallic Chemistry (Japan), Sakai, October 1994, Abstr. p. 412; Mizuno, K. 68th Annual Meeting of the Chemical Society of Japan, Kyoto, March 1995, Abstr., No. 1H925.
- The photoalkylation of electron-deficient molecules via electron transfer: Ohashi, M.; Miyake, K.; Tsujimoto, K. *Bull. Chem. Soc. Jpn.*, **1980**, *53*, 1683-1688; Lan, J.; Schuster, G. B. *J. Am. Chem. Soc.*, **1985**, *107*, 6710-6711; Nakadaira, Y.; Kyushin, S.; Ohashi, M. *J. Synth. Org. Chem.*, **1990**, *48*, 331-342; Mizuno, K.; Takahashi, N.; Nishiyama, T.; Inoue, H. *Tetrahedron Lett.*, **1995**, *36*, 7463-7366, and references cited therein.
- Rehm, D.; Weller, A. *Isr. J. Chem.*, **1970**, *8*, 259-271.
- Majima, T.; Pac, C.; Sakurai, H. *J. Am. Chem. Soc.*, **1981**, *103*, 4499-4508.

(Received in Japan 5 January 1996; revised 4 March 1996; accepted 7 March 1996)