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Photoaddition of Ketene Silyl Acetals to Electron-deficient Arylalkenes via Single Electron Transfer

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

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

Abstract: Photoreaction of 1-cyano-2-phenylethene and 1,1-dicyano-2-phenylethene with β,β -dialkyl-substituted ketene silyl acetals in acetonitrile in the presence of aromatic hydrocarbon as a photosensitizer regioselectively afforded alkylated products in high yields.

Photoinduced electron transfer reactions of group 14 organometallic compounds have been extensively investigated in recent years.¹ We and others reported the photoalkylation, photoallylation, photoarylmethylation and photosilylation of electron accepting molecules such as cyanoaromatic compounds, electron-deficient alkenes, iminium salts, and carbonyl compounds by use of a variety of group 14 organometallic compounds.²⁻⁴ However, less electron-deficient alkenes such as 1-cyano-2-phenylethene did not react with these group 14 organometallic compounds. Very recently, Fukuzumi and Otera reported that the oxidation potentials of β,β -dialkyl-substituted ketene silyl acetals are extremely lower than those of group 14 organometallic compounds bearing allylic and arylmethyl groups.⁵ We now report a regioselective introduction of $R'O_2CR_2C$ groups to electron-deficient arylalkenes including 1-cyano-2-phenylethene and 1-methoxycarbonyl-2-phenylethene by use of β,β -dialkyl-substituted ketene silyl acetals via photoinduced electron transfer.^{6,7}

Irradiation of an acetonitrile solution containing 1,1-dicyano-2-phenylethene (**2a**, 0.05 mmol) and 1-methoxy-2-methyl-1-trimethylsiloxypropene (**1a**, 0.15 mmol) in the presence of phenanthrene (Phen, 0.01 mmol) with a high-pressure mercury lamp through Pyrex filter (> 280 nm light) gave 4,4-dicyano-2,2-dimethyl-3-phenylbutyric acid methyl ester (**3a**) in a 95 % yield.⁸ Similar photoreactions of 1-cyano-1-methoxycarbonyl-2-phenylethene (**2b**) and 2-(4-cyanophenyl)-1,1-dimethoxycarbonyl-2-phenylethene (**2c**) with **1a** gave the corresponding alkylated compounds **3b-c** accompanying the reduction products (**4b-c**). The photoreaction of **1a** with **2a** was also sensitized or co-sensitized by pyrene (Pyr) and biphenyl. Although this

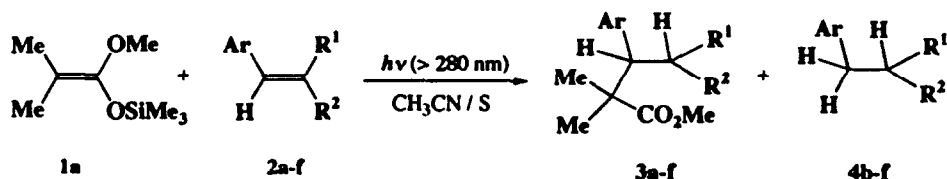


Table 1. Photoreaction of Electron-Deficient Alkenes **2** with **1a**.

	2				Sens ^b	Irradn Time / h	Yield / %			
	R ¹	R ²	Ar	E _{p2} ^{red} / V ^a			3	4		
2a	CN	CN	C ₆ H ₅	-1.45	Phen	0.5	3a 95	4a	0	
2a	CN	CN	C ₆ H ₅	-1.45	—	3	3a 88	4a	0	
2b	CN	CO ₂ Me	C ₆ H ₅	-1.61	Phen	6	3b 50	4b	trace	
2b	CN	CO ₂ Me	C ₆ H ₅	-1.61	—	72	3b 12	4b	trace	
2c	CO ₂ Me	CO ₂ Me	4-NC-C ₆ H ₄	-1.62	Phen	24	3c 19	4c	23	
2d	CO ₂ Me	CO ₂ Me	C ₆ H ₅	-1.85	Phen	48	3d 0	4d	11	
2d	CO ₂ Me	CO ₂ Me	C ₆ H ₅	-1.85	Pyr	24	3d 10	4d	43	
2e	H	CN	C ₆ H ₅	-2.62	Phen	48	3e trace	4e	5	
2e	H	CN	C ₆ H ₅	-2.62	Pyr	2	3e 90	4e	7	
2f	H	CO ₂ Me	C ₆ H ₅	-2.71	Phen	48	3f 0	4f	trace	
2f	H	CO ₂ Me	C ₆ H ₅	-2.71	Pyr	1	3f 65	4f	17	

^a Reduction potentials vs. Ag / Ag⁺ in acetonitrile. ^b Phen ; Phenanthrene , Pyr ; Pyrene

photoreaction slowly proceeded in the absence of a sensitizer, it occurred inefficiently in less polar solvents such as ethyl acetate and benzene.

The photoalkylation of less electron-deficient arylalkenes such as 1,1-dimethoxycarbonyl-2-phenylethene (**2d**), 1-cyano-2-phenylethene (**2e**) and 1-methoxycarbonyl-2-phenylethene (**2f**) by use of **1a** was sensitized by Pyr to give **3d**, **3e** and **3f**, respectively. The photoreaction of **2e** with **1a** was sensitized by a variety of aromatic hydrocarbons having low oxidation potentials. However, Phen and pentacene did not sensitize this photoalkylation and the absence of an aromatic hydrocarbon did not afford any product. The results are summarized in Table 2. It is notably here that the photoallylation and photoarylmethylation of **2e** and **2f** using allylic and arylmethyl group 14 organometallic compounds such as allyl- and benzyltrimethylsilanes did not occur even in the presence of a variety of photosensitizers.

Similar irradiations of **2a** with **1b** and **6** with **1a** afforded the corresponding alkylated compounds **5** and **7** in 95 and 40% yields, respectively.

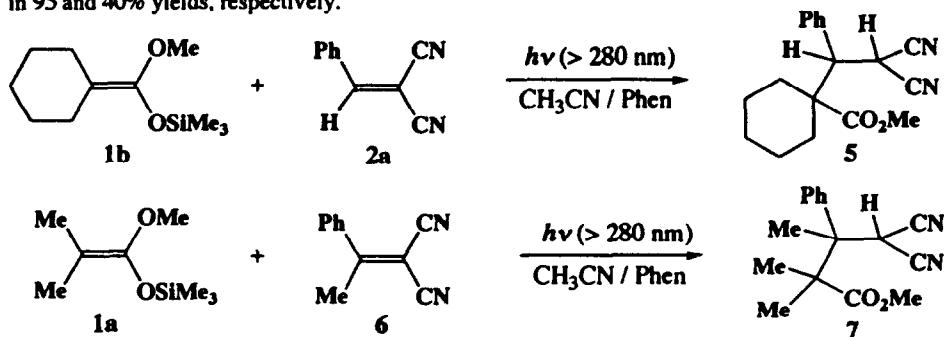


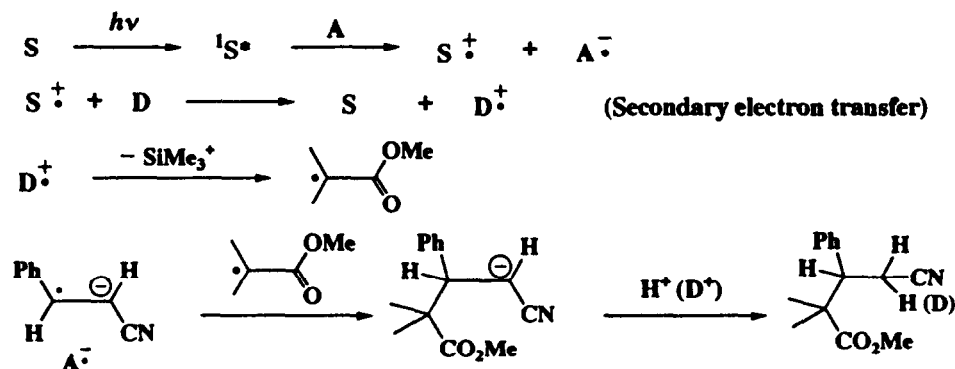
Table 2. Effect of Sensitizers on Photoalkylation of **2e** with **1a**.^a

Sensitizer	$E_{1/2}^{\text{ox}}$ ^b $E_{1/2}^{\text{red}}$ ^b		Irradn Time / h	Yield / %		Φ_{rel} ^c
	$E_{1/2}^{\text{ox}}$ ^b	$E_{1/2}^{\text{red}}$ ^b		3e	4e	
Triphenylene	1.17	-2.08	30	24	51	<0.01
Phenanthrene (Phen)	1.12	-2.06	40	trace	10	<0.001
Chrysene	0.97	-1.87	8	90	9	0.56
Benz[a]anthracene	0.80		8	88	11	0.55
Pyrene (Pyr)	0.78	-1.71	2	90	7	1.00
Anthracene	0.71	-1.57	10	87	12	0.77
Perylene	0.47	-1.29	12	45	50	0.20
Tetracene	0.39	-1.20	20	30	9	0.05
Pentacene		-1.03	8	0	70	0

^a $E_{1/2} = 0.57$ V (vs. Ag/Ag⁺) for **1a** in acetonitrile. ^b Oxidation and reduction potentials vs. Ag/Ag⁺ estimated from the SCE values in acetonitrile. ^c Relative quantum yields for the formation of **3e** after 5 min irradiation.

The fluorescence of Pyr in acetonitrile was quenched by **2e** in a diffusion controlled rate ($k_q > 10^{10}$ mol⁻¹ dm³ s⁻¹), but it was also quenched by **1a** ($k_q = 8.1 \times 10^9$ mol⁻¹ dm³ s⁻¹). The free energy changes (ΔG) for a single electron transfer process from the excited singlet Pyr (¹Pyr*) to **2a-d** were estimated to be negative, and the values from ¹Pyr* to **2e-f** and from **1a** to ¹Pyr* were slightly positive or almost null.

From these results, the photoalkylation of electron-deficient arylalkenes (**A**) by use of ketene silyl acetals (**D**) can be explained by the redox-type radical cation transfer mechanism as shown in Scheme 1.¹⁰

Scheme 1.

In the cases of **2a-c**, the rates for the formation of **3a-c** were accelerated by the addition of Phen (Table 1). However, the formation of **3d-f** was not sensitized by Phen, but sensitized by Pyr and some selected aromatic hydrocarbons (Table 2). Therefore, the most important process of this mechanism is a secondary electron transfer from D to the radical cation of aromatic hydrocarbon such as Pyr ($S^{+\bullet}$) to generate $D^{+\bullet}$. The photoreaction occurs efficiently, when the difference of the oxidation potentials between S and D is smaller than 0.5 V. The coupling of $A^{+\bullet}$ with $\bullet CR_2CO_2R'$, which is generated by the O-Si cleavage of $D^{+\bullet}$, followed by protonation gives alkylated products. This process was supported by the deuterium incorporation experiment by an addition of a small amount of D_2O to the reaction system.

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