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Photoinduced Electron Transfer Reactions of Cyclopropanone Acetal with Conjugated Enones in the Presence of a Redox-Type Photosensitizer

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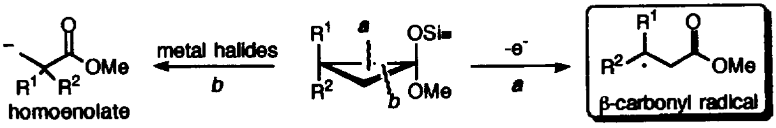
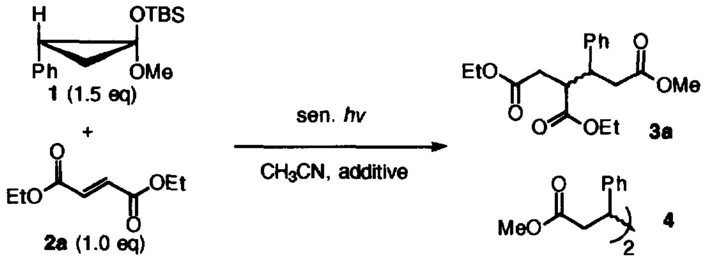
Abstract: Photoreactions of the cyclopropanone acetal **1** with conjugated enones **2** in the presence of phenanthrene or pyrene as a redox-type photosensitizer gave the corresponding cross-coupling product **3** or mixtures of **3** with **5** in good yields together with the β-carbonyl radical-dimer **4**.

Photoinduced electron transfer (PET) reactions have, over the past 15-20 years, attracted a variety of mechanistic[1] and synthetic[2] studies. From the synthetic view point, we have been interested in the oxidative ring-opening reaction of cyclopropanone acetals.[3] As shown in eq 1, the oxidative bond-cleavage of cyclopropane rings in an electron transfer reaction was found to occur predominantly at the more substituted carbon-carbon bond (site *a*) to give a β-carbonyl radical, in marked contrast to the bond-cleaving site in the generation of homoenolate intermediates[4] (site *b*). The site-reversion in the ring-cleavage process and the subsequent C-C coupling reaction are synthetically useful because bond formation occurs preferentially at the sterically hindered site. In the extension of synthetic utility of the present reaction, we now report here the PET reactions of cyclopropanone acetal with conjugated enones sensitized by redox-type photosensitizers[5], such as phenanthrene or pyrene.[6]



(1)

First of all, the photoreaction of 2-phenylcyclopropanone acetal **1** with a symmetrically substituted unsaturated diester, i.e. diethyl fumarate **2a**, in the presence of phenanthrene (1.0 eq) was performed in a degassed acetonitrile solution using a high-pressure Hg-lamp through a Pyrex filter (> 280 nm) at 0 °C (Table 1, entry 1). Adduct **3a** was not observed as a component of the product mixture. Also, direct irradiation in the presence of $Mg(ClO_4)_2$ led to only partial *cis-trans* isomerization of **2a**. When the same reaction was repeated in the presence of both $Mg(ClO_4)_2$ (1.0 eq) and phenanthrene (1.0 eq), however, the desired product **3a** was obtained in good yield together with the dimer **4** of β-carbonyl radical (entry 2 and eq 2). Thus, it is evident that the presence of both phenanthrene and $Mg(ClO_4)_2$ was necessary for the formation of adduct **3a**. The role of $Mg(ClO_4)_2$ can be explained in terms of its stabilization effect on the radical anion derived from **2a** suppressing the back electron transfer process.[7] In the presence of catalytic quantities of phenanthrene (0.1 eq), the yield of **3a** was found to decrease, whereas when pyrene was used (Uranium filter, *hν* > 320 nm), the yield of **3a** increased slightly even with catalytic quantities of pyrene (compare entries 3-5).



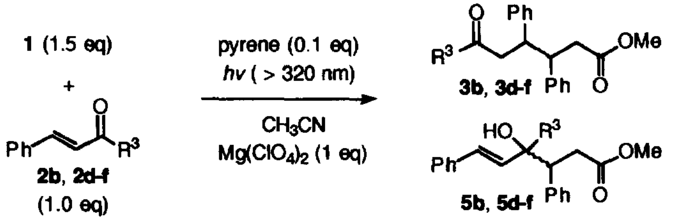
(2)

Table 1. Photoreaction of **1** with Diethyl Fumarate **2a**.

entry	time (h)	sen. (eq)	additive[a]	products and yields (%)[b]	
1	3.5	phen. (1.0 eq)	none	-	
2	3.5	phen. (1.0 eq)	$Mg(ClO_4)_2$ (1.0 eq)	**3a** (43)	**4** (20)
3	3.5	pyrene (1.0eq)	$Mg(ClO_4)_2$ (1.0 eq)	**3a** (50)	**4** (17)
4	5.0	pyrene (0.5eq)	$Mg(ClO_4)_2$ (1.0 eq)	**3a** (46)	**4** (16)
5	5.0	pyrene (0.1eq)	$Mg(ClO_4)_2$ (1.0 eq)	**3a** (48)	**4** (16)

[a] $Mg(ClO_4)_2$ contains 17wt% of water. [b] Isolated yields based on **2a**.

In the reaction of **1** with unsaturated monoesters, e.g. ethyl cinnamate **2b** and coumarine **2c**, the expected cross-coupled products **3b** and **3c**, which were formed by the alkylation at the benzylic position of the unsaturated ester, were obtained (eq 3 and entries 1-2, Table 2). With unsaturated enones **2d-f** (entries 3-5, Table 2), both 1,4-addition products **3d-f** and 1,2-addition products **5d-f** were obtained in good yields together with the radical dimer **4**. The formation of products **3** and **5** suggests the intermediacy of allylic radical species derived from the conjugated enone. As expected, the yield of 1,2-adduct **5** was found to decrease with the increasing bulkiness of R^3 group (compare entries 3-5).



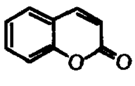
(3)

Table 2. Photoreaction of **1** with enones **2b-f** in the presense of pyrene.

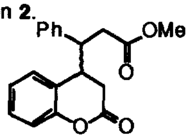
entry	enone 2	time (h)	products and yields (%)[a]		
1	**2b** (R^3 = OEt)	2	**3b** (60)	**5b** (0)	**4** (7)
2[b]	**2c**	2.5	**3c** (56)	**5c** (0)	**4** (9)
3	**2d** (R^3 = H)	6	**3d** (33)	**5d** (22)	**4** (5)
4	**2e** (R^3 = CH_3)	8	**3e** (38)	**5e** (25)	**4** (4)
5	**2f** (R^3 = Ph)	8	**3f** (52)	**5f** (2)	**4** (7)

[a] Isolated yieds based on **2**.

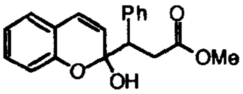
[b]



2c



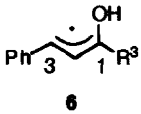
3c



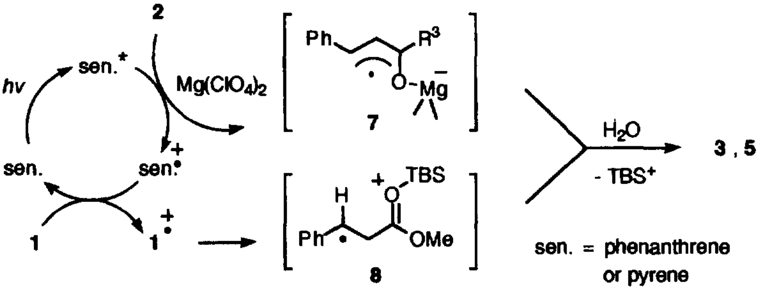
5c

In addition to the steric effect, the regioselectivity of the coupling reaction may also be influenced by the relative spin density in the allylic radical intermediate **7** (Scheme 1). To confirm this, the spin density was calculated by the PM3-UHF method on the model allylic radical **6** (Table 3).[8] In allylic radical **6b** derived from unsaturated ester **2b**, the spin density at C3 position was larger than at C1, whereas, in **6d-f**, the spin densities were almost the same at both positions. It is concluded, therefore, that the regioselectivity of the coupling reaction of such allyl radicals is regulated by both the electronic and steric effects.[9]

Table 3. Calculated Spin Density of Allyl Radical **6** by PM3-UHF Method.

		spin density	
		C1	C3
 **6**	**6b** (R^3 = OEt)	0.51	0.61
	6d (R^3 = H)	0.59	0.61
	6e (R^3 = CH_3)	0.60	0.60
	6f (R^3 = Ph)	0.56	0.56

In order to investigate the mechanism of the present photochemical reaction, the fluorescence quenching experiments (excitation at 350nm, detection at 372 and 391nm) for the singlet excited-state pyrene by diethyl fumarate **2a** and cyclopropanone acetal **1**, respectively, were performed in acetonitrile at 25 °C. An efficient quenching by **2a** was observed, whereas acetal **1** did not quench at all. From these observations, the mechanism shown in Scheme 1 is proposed. The electron transfer between **1** and **2** is mediated by a photosensitizer to give the radical ion pair **7** and **8**,[10] followed by their coupling to give product **3** or a mixture of **3** and **5**, depending on the substituent R^3.



Scheme 1

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References and Notes

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4. Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1977**, *99*, 7360.
5. a) Majima, T.; Pac, C.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 4499. b) Mizuno, K.; Takahashi, N.; Nishiyama, T.; Inoue, H. *Tetrahedron. Lett.* **1995**, *36*, 7463.
6. Conjugated enones in excited states are intermolecularly unreactive as a consequence of rapid *cis-trans* photoisomerization in solution.[11] In fact, the PET reactions between **1** and **2a** did not take place under direct irradiation. Therefore, a redox-type photosensitizer is required to facilitate the PET reaction.
7. For the stabilization of radical ions by metal salts, see: Mizuno, K.; Hiromoto, Z.; Ohnishi, K.; Otsuji, Y. *Chem. Lett.* **1983**, 1059, and references cited theirin.
8. Stewart, J. J. P. *J. Comp. Chem.* **1989**, *10*, 209.
9. See also: Past, D. J.; L'Hermine, G. *Tetrahedron* **1993**, *49*, 3259.
10. The intervention of both metal stabilized-radical anion **7** and ring-opened radical cation **8** possessing a silyl group was suggested in the photoreaction with carbonyl compounds.[3d]
11. Egerton, P. L.; Hyde, E. M.; Trigg, J.; Payne, A.; Beynon, P.; Mijovice, M. V.; Reiser, A. *J. Am. Chem. Soc.* **1981**, *103*, 3859

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