Electron-Transfer Reactions of Aromatic α,β-Epoxy Ketones: Factors That Govern Selective Conversion to β-Diketones and β-Hydroxy Ketones

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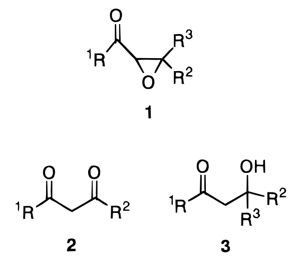
Photoreaction of *trans*-1-(4-cyanophenyl)-3-phenyl-2,3-epoxy-1-propanone (*trans*-4′-cyanochalcone epoxide) with various electron donors was studied. Irradiation of this epoxy ketone with amines produced 1-(4-cyanophenyl)-3-phenyl-1,3-propanedione and 1-(4-cyanophenyl)-3-hydroxy-3-phenyl-1-propanone in various ratios depending on the kinds of amine and solvent used. A reaction mechanism involving an amine cation radical-assisted rearrangement of the epoxy ketone anion radical was proposed to be most consistent with the marked change in the yield of β-diketone. On the other hand, the timing of proton transfer to the anionic intermediates is considered to be a key factor to yield the β-hydroxy ketone. Information obtained from the photochemical study was useful to find the reaction conditions for the conversion of several aromatic epoxy ketones to hydroxy ketones by the use of samarium diiodide. Addition of methanol significantly changed the product distribution. Proper choice of water or methanol as a proton source produced hydroxy ketones in moderate to good yields.

Introduction

Carbonyl compounds have been favorably subjected to thermally or photochemically induced electron-transfer reactions.[1] Although carbonyl anion radicals are common intermediates, the following chemical pathways differ depending on reaction conditions. In order to understand the reactivities of the anion radicals of certain carbonyl compounds, it is helpful to conduct their reactions under various electron transfer conditions. From this point of view, electron-transfer reactions of α,β-epoxy ketones should be informative. During our study focused on the reactivities of carbonyl anion radicals generated by photoinduced electron-transfer (PET) processes, we found that photoreactions of certain aromatic α,β-epoxy ketones with triethylamine produced β-diketones as major products instead of β-hydroxy ketones, which were also obtained as minor components.[2a] Photoreactions of ketones with amines usually give reduced products of ketones, such as alcohols and pinacols, through sequential electron-transfer and proton-transfer processes between them.[3] Therefore, it is quite rare for carbonyl compounds to undergo isomerization under the PET conditions with amines.[4] At that time, we tentatively proposed the unimolecular rearrangement of epoxy ketone anion radicals for this unexpected rearrangement.[2a] However, we have recently encountered several observations, some of which are certainly inconsistent with such a mechanism. Apparently, there is only limited information on the factors that govern selective conversion of aromatic epoxy ketones to diketones and hydroxy ketones.[2] About 10 years ago, Molander and co-worker reported that various aliphatic α,β-epoxy ketones were successfully converted to the corresponding hydroxy ketones by samarium diiodide.[5] In this case, protonation of the intermediate ketyls seems to be a key step in the reaction pathway to produce hydroxy ketones. Then, the question was raised in our minds whether hydroxy ketones are still major products in the samarium diiodide reductions of aromatic epoxy ketones that were subjected to photochemical study. The experimental results and the discussion focused on the mechanism of the photochemical formation of the diketones as well as hydroxy ketones will be described below. Samarium diiodide reductions of some aromatic epoxy ketones will follow.

Chart 1



	R^1	R^2	R^3
a	Ph	Ph	H
b	4-CNC$_6$H$_4$	Ph	H
c	Ph	Ph	Me
d	Ph	H	H
e	Ph	^{i}Pr	H
f	Me	Ph	H

Results and Discussion

Photoreactions of *trans*-4′-Cyanochalcone Epoxide with Various Electron Donors. When we irradiated *trans*-1,3-diphenyl-2,3-epoxy-1-propanone (*trans*-chalcone epoxide, **1a**) with an excess of triethylamine (TEA) in acetonitrile or methanol, dibenzoylmethane (**2a**) was the major product in both solvents (Chart 1).[2a] There

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[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1997.

(1) (a) Huffman, J. W. *Acc. Chem. Res.* **1983**, *16*, 399. (b) Pradhan, S. K. *Tetrahedron* **1986**, *42*, 6351. (c) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*: Springer-Verlag: Berlin, 1987. (d) *Photoinduced Electron Transfer, Part C*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988.

(2) (a) Hasegawa, E.; Ishiyama, K.; Horaguchi, T.; Shimizu, T. *J. Org. Chem.* **1991**, *56*, 1631. (b) On the contrary, Cossy and co-workers reported that β-hydroxy ketone was a major isolable product in the photoreaction of chalcone epoxide **1a** with triethylamine: Cossy, J.; Bouzide, A.; Ibhi, S.; Aclinou, P. *Tetrahedron* **1991**, *47*, 7775.

(3) Yoon, U. C.; Mariano, P. S.; Givens, R. S.; Atwater, B. W., III. In *Advances in Electron Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press: Greenwich, 1994; Vol. 4; pp 117−205.

(4) (a) The observation made by Pandey might be another rare example in which the endo−exo isomerization of Diels−Alder adducts took place on irradiation with triethylamine, although the reaction mechanism was not fully understood.[4b] (b) Pandey, B.; Dalvi, P. V.; Athawale, A. A.; Pant, B. G.; Kewale, P. P. *J. Chem. Soc., Chem. Commun.* **1990**, 1505.

(5) Molander, G. A.; Hahn, G. *J. Org. Chem.* **1986**, *51*, 2596.

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Scheme 1

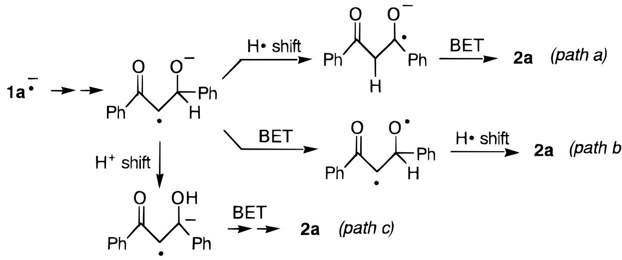

Chart 2

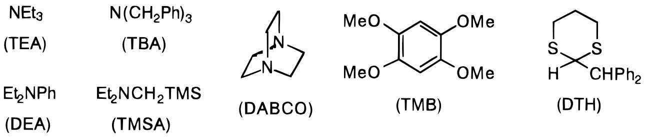

Table 1. Photoreactions of *trans*-Cyanochalcone Epoxide (1b) with Electron Donors in MeCN[a]

entry	donor	E_p^{ox}, V vs SCE	time, h	convn, %	yields,[b] % **2b**	yields,[b] % **3b**
1	TEA	0.89	3	51	40	7
2	TMB	0.77	3	7	0	0
3	DTH	1.22	5	17	0	0

[a] [**1b**] = 21 mM, [donor] = 42 mM; $\lambda > 340$ nm. [b] Isolated yields based on the conversion of **1b**.

Table 2. Photoreactions of *trans*-Cyanochalcone Epoxide (1b) with Amines in MeCN and Benzene[a]

entry	donor	E_p^{ox}, V vs SCE	solvent	time, h	convn, %	yields,[b] % **2b**	yields,[b] % **3b**
1	DABCO	0.71	MeCN	3	27	8	0
2	DABCO	0.71	benzene	3	34	71	0
3	TEA	0.89	MeCN	3	51	40	7
4	TEA	0.89	benzene	3	95	77	8
5	DEA	0.76	MeCN	5	21	0	5
6	DEA	0.76	benzene	5	57	7	42
7	TBA	1.17	MeCN	3	45	5	49
8	TBA	1.17	benzene	3	47	12	50
9	TMSA	0.57	MeCN	3	66	1	27
10	TMSA	0.57	benzene	3	83	30	27

[a] [**1b**] = 21 mM, [amine] = 42 mM; $\lambda > 340$ nm. [b] Isolated yields based on the conversion of **1b**.

are several possible pathways for the formation of **2a** as shown in Scheme 1. Among them is our previously proposed mechanism that involves a 1,2-hydrogen shift in the ring-opened anion radicals followed by a back-electron transfer (BET) to a triethylamine cation radical (path a).[2a] If any pathway shown in Scheme 1 is operable, **2a** should be always obtained as one of the major products as long as an initial electron transfer between the excited state of **1a** and the ground state of the electron donor is accomplished. To determine if either one of pathways a−c is responsible for the diketone formation, we chose *trans*-4′-cyanochalcone epoxide (**1b**) as a reactant since **1b** appears to be more versatile than **1a** for the reaction with a wide range of electron donors (Chart 2). Epoxide **1b** has greater quantum yield of the intersystem crossing and a longer triplet lifetime than **1a**.[6] In addition to this, the oxidizing ability of the excited **1b** should be stronger than that of **1a** in light of their reduction potentials.[7] Therefore, the excited triplet state of **1b** is expected to oxidize all of the electron donors shown in Chart 2.[8]

We first conducted the photoreaction of **1b** with triethylamine (TEA), 1,2,4,5-tetramethoxybenzene (TMB), and 2-(diphenylmethyl)-1,3-dithiane (DTH) as electron donors in acetonitrile (Table 1). Immediately, we noticed that the reaction progressed quite slowly, and dibenzoylmethane (**2b**) was not formed in the reactions with TMB and DTH while it was obtained as the major product in the reaction with TEA. Particularly noteworthy is that the stronger electron donor TMB was much less efficient for the reaction than TEA. This seems to be inconsistent with any of the mechanisms shown in Scheme 1. These results would suggest that the electron-donating ability of the donor is not a sufficient factor to promote the reaction. Subsequently, we made another interesting observation, viz., that the yield of **2b** significantly increased in the photoreaction with TEA in a nonpolar solvent, such as benzene (see below).

The above observations encouraged us to study the photoreactions of **1b** with various amines in both acetonitrile and benzene (Table 2). Unexpectedly, the yields of **2b** were higher in benzene than in acetonitrile.[9] This would suggest that the rearrangement of **1b** to **2b** does not occur after the diffusion of the initially formed ion radical pair into free ion radicals but occurs within the ion radical pair accompanied by an amine cation radical. The most noteworthy observation presented in Table 2 is that the ratio (**2b**/**3b**) was significantly influenced by the amine structure. For example, **3b** was the major product in the reaction with tribenzylamine (TBA). This could be explained by the efficient proton transfer from the cation radical of TBA to the anionic intermediates derived from the anion radical of **1b**.[10] In the opposite sense, the nonformation of **3b** in the reaction with 1,4-diazabicyclo[2.2.2]octane (DABCO) could be also understood because the cation radical of DABCO is known to be exceptionally stable and a poor proton donor, unlike other aliphatic amine cation radicals.[11]

On the basis of the observations described above, a new mechanism for the formation of **2b** has to be considered,

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[6] (a) Quantum yield of the intersystem crossing: 0.88 for **1a** and 0.98 for **1b**; triplet lifetime: 3.3 ns for **1a** and 85 ns for **1b**.[6b] (b) Kumar, C. V.; Ramaiah, D.; Das, P. K.; George, M. V. *J. Org. Chem.* **1985**, *50*, 2818:

[7] (a) Reduction potentials of epoxy ketones studied here have been reported.[2a,7b] For example, these are −1.70 V and −1.39 V vs SCE for **1a** and for **1b**, respectively.[7b] (b) Hasegawa, E.; Ishiyama, K.; Horaguchi, T.; Shimizu, T. *Tetrahedron Lett.* **1991**, *32*, 2029.

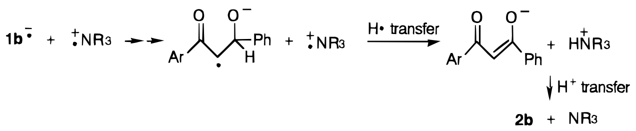
[8] (a) Electron transfer from the ground states of all donors studied to the triplet excited state of **1b** (^{3}**1b***) must be exothermic since the oxidation potentials of the donors[8b] are smaller than the reduction potential of ^{3}**1b*** that is calculated to be 1.65 V from the reduction potential[7a] and the triplet energy of **1b**. Since the triplet energy of **1b** is not known, it is assumed to be about 70 kcal/mol from the known triplet energy of *p*-cyanoacetophenone.[8c] (b) Oxidation potentials (V vs SCE; scan rate, 100 mV/s or 200 mV/s) were measured in MeCN containing 0.1 M Et_4NClO_4. (c) Wagner, P. J.; Truman, R. J.; Puchalski, A. E.; Wake, R. *J. Am. Chem. Soc.* **1986**, *108*, 7727.

[9] In most of the cases studied, ^{1}H NMR analyses of the reaction mixtures suggested that the peaks for **2b** and **3b** observed for the reactions in acetonitrile were significantly smaller than those in benzene. The isolated yields of **2b** and **3b** were indeed low in such cases (compare entries 1 and 5 with 2 and 6 in Table 2, respectively). Therefore, the relatively low yields in Table 2 would not be mainly due to the isolation technique although it was, of course, difficult to isolate the low-yielding products, particularly at the low conversion of **1b** in acetonitrile. The formation of benzaldehyde was sometimes observed in the crude reaction mixture; however, its yield (not determined) appeared to be low. Eventually, we were unable to isolate and identify the other products from the photoreaction mixture.

[10] (a) Acidity of the cation radical of TBA is considered to be higher than that of TEA since deprotonation from the former produces the α-amino radical possessing a relatively stable benzilic structure.[10b] (b) Zhang, X.; Yeh, S. R.; Hong, S.; Freccero, M.; Albini, A.; Falvey, D. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1994**, *116*, 4211.

[11] Chow, Y. L.; Danen, W. C.; Nelsen, S. F.; Rosenblatt, D. H. *Chem. Rev.* **1978**, *78*, 243.

Scheme 2



in which **2b** is formed through a pathway that is promoted by DABCO (E_p^{ox} = 0.71) but not by TMB (E_p^{ox} = 0.77). We would like to propose the reaction mechanism shown in Scheme 2. In this mechanism, an amine cation radical abstracts a β-hydrogen from the ring-opened epoxy ketone anion radical to give the ammonium and the enolate of **2b**. Although such a process is quite novel within a pair of the photogenerated carbonyl anion radicals and amine cation radicals, hydrogen abstraction by an amine cation radical has been well documented (see Hofmann–Löffler–Freytag reaction).[12] Thus, hydrogen abstraction from an anion radical by an amine cation radical could be operable when anion radical intermediates possess relatively weak carbon–hydrogen bonds as in the case of **1b**. This process should be more favorable in a less polar solvent because this shifts the equilibrium of free ion radicals to ion radical pairs. The striking contrast in the ratio (**2b**/**3b**) observed in the reaction with TEA compared to that with diethylaniline (DEA) should be also addressed. Although the proton-donating ability of the cation radical of DEA is considered to be lower than that of TEA,[13] the yield of the reduced product **3b** for DEA was higher than that for TEA. On the other hand, the yield of **2b** for TEA was higher than that for DEA. This could be consistent with the mechanism in Scheme 2 since the efficiency of the hydrogen abstraction by the amine cation radical must be qualitatively correlated with the N–H bond strength of the corresponding ammonium salt.[14] For the effective formation of **2b**, the fragmentation of the amine cation radical is undesirable. It is known that α-silylamine cation radicals undergo efficient fragmentation.[10b] Thus, the yield of **2b** significantly decreased for the reaction with TMSA compared to the reaction with TEA.

Other notable observations were provided by conducting the photoreaction of **1b** with TEA in the presence of salts. Irradiation of an acetonitrile solution of **1b** with TEA on addition of $LiClO_4$ (2 equiv vs **1b**) significantly decreased the yield of **3b** (ca. 1%), while the yield of **2b** was increased (69%) at 52% conversion of **1b**.[15] On the other hand, n-Bu_4NClO_4 had little influence on both the conversion of **1b** and the product yields. These results would suggest that the complexation of the lithium cation to the anionic intermediates inhibits proton transfer from the amine cation radicals. This interaction would not interfere with the hydrogen abstraction process between the ion radical pairs but probably enable the amine cation radical to survive to participate in such a process and eventually increase the yield of **2b**, which was actually observed.

Consequently, the above solvent effects would be most consistent with the postulate that both **2b** and **3b** are produced through ion radical pairs rather than in free ion radicals. If the interaction within the ion radical pairs is responsible for the formation of the desired products, the choice of less polar solvents for the preparative photoreactions would sometimes be favorable even though the initial electron transfer appears to be less efficient.[1d,3]

Since hydroxy ketones are reduced products from epoxy ketones, the timing of the protonation to the anionic intermediates generated from epoxy ketones is considered to be a key factor for the effective formation of these compounds.[16] In other words, inefficient protonation of anionic intermediates would decrease the yield of hydroxy ketones. This was exemplified by the observations in the photoreaction of **1b** with DABCO (entries 1 and 2 in Table 2) and the photoreaction with TEA in the presence of $LiClO_4$. From a synthetic viewpoint, transformation of epoxy ketones to hydroxy ketones is much more important than that to diketones.[5,17] Therefore, it would be interesting to ascertain if the formation of diketones is a problem, particularly, when certain aromatic epoxy ketones, such as chalcone epoxides, are subjected to other electron-transfer conditions. Thus, we conducted the reactions of aromatic epoxy ketones with samarium diiodide, which will be discussed in the following section.

Samarium Diiodide-Promoted Transformation of Aromatic α,*β*-Epoxy Ketones. In connection with our interest in the reactivities of epoxy ketone anion radicals, we noticed Molander's report that various epoxy ketones were converted to the corresponding hydroxy ketones in good to excellent yields.[5] Interestingly, there were no aryl-substituted epoxy ketones among their substrates. Therefore, we decided to explore the reactivities of representative aromatic epoxy ketones **1a,c–f** shown in Chart 1 under electron-transfer conditions using samarium diiodide. Since samarium diiodide is a well-known single electron reductant,[18] a hypothetical mechanism is proposed for the formation of hydroxy ketones in Scheme 3. Accordingly, efficient proton transfer and electron transfer to the involved intermediates must be essential to increase the yield of hydroxy ketones. Protonation of the anion radicals of epoxy ketones produces the oxiranylmethyl radicals, which undergo selective Cα–O bond cleavage to give the alkoxy radicals,[17h] and,

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(12) (a) See ref 11. (b) Stella, L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 337.

(13) The order of efficiency for proton transfer from amine cation radicals to carbonyl anion radicals is known to be as follows: TEA > DEA > DABCO.[13b] (b) Devadoss, C.; Fessenden, R. W. *J. Phys. Chem.* **1990**, *94*, 4540; **1991**, *95*, 7253.

(14) (a) Bordwell has recently reported the bond dissociation enthalpies (BDE) of the conjugate acids of various amines in acetonitrile: 95.5 kcal/mol for TEA; 82.0 kcal/mol for dimethylaniline; 91.3 kcal/mol for DABCO. Therefore, the corresponding BDE for DEA is assumed to be smaller than that for TEA.[14b] (b) Liu, W. Z.; Bordwell, F. G. *J. Org. Chem.* **1996**, *61*, 4778.

(15) (a) A similar observation has been already made in our previous study.[2a] Effects of $LiClO_4$ on the PET reaction pathways have been reported in several cases.[15b,c,d] (b) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 4875. (c) Hasegawa, E.; Xu, W.; Mariano, P. S.; Yoon, U. C.; Kim, J. U. *J. Am. Chem. Soc.* **1988**, *110*, 8099. (d) Salt effects on organic reactions in general: Loupy, A.; Tchoubar, B.; Astruc, D. *Chem. Rev.* **1992**, *92*, 1141.

(16) (a) On the basis of this concept, we have recently discovered an effective photochemical method for the conversion of epoxy ketones to hydroxy ketones by the use of 1,3-dimethyl-2-phenylbenzimidazoline as a reductant in aqueous solutions.[16b] (b) Hasegawa, E.; Kato, T.; Kitazume, T.; Yanagi, K.; Hasegawa, K.; Horaguchi, T. *Tetrahedron Lett.* **1996**, *48*, 7079.

(17) (a) Robinson, C. H.; Henderson, R. *J. Org. Chem.* **1972**, *37*, 565. (b) Weile, G. R.; McMorris, T. C. *J. Org. Chem.* **1978**, *43*, 3942. (c) Shapiro, E. L.; Gentles, M. J.; Kabasakalian, P.; Magatti, A. *J. Org. Chem.* **1981**, *46*, 5017. (d) Osuka, A.; Takaoka, K.; Suzuki, H. *Chem. Lett.* **1984**, 271. (e) McChesney, J. D.; Thompson, T. N. *J. Org. Chem.* **1985**, *50*, 3473. (f) Miyashita, M.; Suzuki, T.; Yoshikoshi, A. *Tetrahedron Lett.* **1987**, *28*, 4293. (g) Inokuchi, T.; Kusumoto, M.; Torii, S. *J. Org. Chem.* **1990**, *55*, 1548. (h) Hasegawa, E.; Ishiyama, K.; Kato, T.; Horaguchi, T.; Shimizu, T.; Tanaka, S.; Yamashita, Y. *J. Org. Chem.* **1992**, *57*, 5352. (i) Engman, L.; Stern, D. *J. Org. Chem.* **1994**, *59*, 5179.

(18) (a) Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *96*, 307 and references cited therein. (b) Curran, D. P.; Fevig, T. L.; Jasperse, C. P.; Totleben, M. J. *Synlett* **1992**, 943.

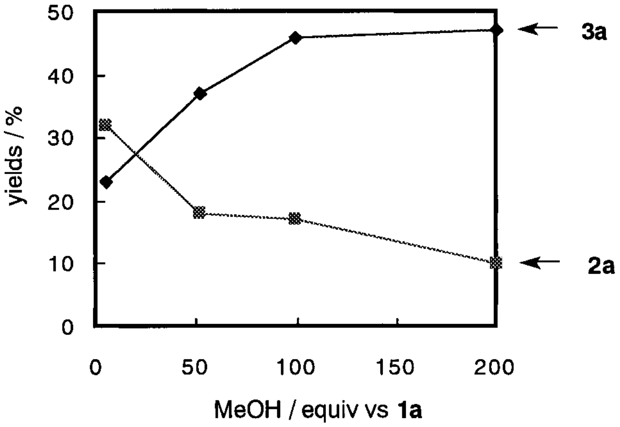
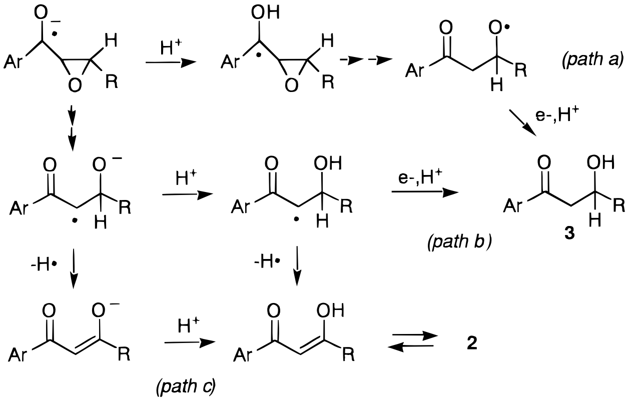


Figure 1. Effect of MeOH quantity on the yields of diketone **2a** and hydroxy ketone **3a** in the reaction of chalcone epoxide (**1a**) with samarium diiodide (2.2 equiv vs **1a**) in tetrahydrofuran at −78 °C (the vertical axis represents isolated yields based on the conversion of **1a**).

Scheme 3



finally, the hydroxy ketones (path a). On the other hand, if protonation to the anion radicals of epoxy ketones does not occur, diketone formation is expected to become a competitive pathway (path c), particularly for the reaction of the substrates possessing both a β-aryl group and a β-hydrogen atom (path b). Thus, we decided to explore first the reactivity of **1a** with samarium diiodide.

When **1a** was treated with 2.2 equiv of samarium diiodide at room temperature, no formation of **3a** was observed while small amounts of **2a** (10%) and chalcone (3%) were obtained. Addition of 100 equiv of methanol did not much affect the yield of **2a** (11%). Eventually, lowering the reaction temperature to −78 °C was found to be essential for the formation of **3a**. As seen in Figure 1, increasing the quantity of methanol to the reaction solution increased the yield of **3a** and decreased the yield of **2a**, as is expected from the mechanism in Scheme 3. The maximum yield of **3a** was 47% and the minimum yield of **2a** was 10% in these experiments (the conversion of **1a** = 93−96%). While 1,3-diphenyl-2-propen-1-one (chalcone) was also isolated (6−20%), its yield was not a function of the quantity of methanol added. Finally, we found that addition of water (100 equiv vs **1a**) significantly decreased the yield of **2a** (ca. 3%) while the yield of **3a** (ca. 60%) was better than that on addition of methanol.

Next, several aryl-substituted epoxy ketones were treated with samarium diiodide on addition of methanol or water (Table 3). In these experiments, an excess of samarium diiodide (2.7−2.9 equiv vs **1**) was used to achieve better conversion of **1**. As mentioned above, in the case of chalcone epoxide **1a**, aqueous conditions were better than methanolic conditions for the formation of **3a**. In the cases of epoxy ketones **1d**−**f**, the yields of hydroxy ketones **3d**−**f** on addition of methanol were better than those achieved on addition of water. The yields of hydroxy ketone **3c** were similar for the reactions of **1c** in both aqueous and methanolic solutions.

Table 3. Reactions of Epoxy Ketones 1 with Samarium Diiodide in the Presence of Methanol or Water in Tetrahydrofuran[a]

				yields,[b] %		
entry	epoxide	ROH	convn, %	**2a**	**3a**	enone
1	**1a**	MeOH	100	11	38	4
2	**1a**	H_2O	96	4	60	29
3	**1c**	MeOH	94	0	82	0
4	**1c**	H_2O	100	0	79	0
5	**1d**	MeOH	100	0	72	0
6	**1d**	H_2O	97	0	48	0
7	**1e**	MeOH	100	0	66	5
8	**1e**	H_2O	100	0	40	36
9	**1f**	MeOH	100	0	65	0
10	**1f**	H_2O	100	0	53	18

[a] **1**, 0.67 mmol; THF, 20 mL; SmI_2, 2.7−2.9 equiv; ROH, 100 equiv; −78 °C; 30 min. [b] Isolated yields based on the conversion of **1**.

As seen in Table 3, lower yields of hydroxy ketones in aqueous solutions are apparently due to the significant formation of enones. To suppress the formation of enone remains a problem to be solved to attain the better yield of the hydroxy ketones. Although the reason for the significant formation of enones under the aqueous conditions is unclear, one possibility is that dehydration of hydroxy ketones is caused in the presence of Lewis acidic Sm(III) generated from the decomposition of samarium diiodide by water.[19,20] Notably, when 2.2 equiv of samarium diiodide was used for the aqueous reaction (not much excess against **1a**), the yield of enone was low (5%) while 17% of **1a** was recovered along with 73% of **3a** based on the conversion of **1a**. This would suggest that a substantial amount of samarium diiodide indeed decomposed to become inefficient as an electron-transfer reductant.

Conclusion

We have found that irradiation of *trans*-4′-cyanochalcone epoxide with amines produced both β-diketone and β-hydroxy ketone. Characteristic effects of the electron-donor structure and solvent on the ratio of those products let us propose a novel but plausible mechanism in which β-diketone is formed via the processes involving the amine cation radical-assisted β-hydrogen abstraction from the ring-opened form of the epoxy ketone anion radical. On the other hand, the effective formation of β-hydroxy ketone requires better proton-donating ability of the amine cation radical. This would suggest that the timing of proton transfer to the anionic intermediates is a key factor to yield the β-hydroxy ketone. On the basis of the information obtained from the photochemical study, we were able to determine the proper reaction

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(19) (a) Samarium diiodide is considered to be less stable against water than methanol in tetrahydrofuran.[19b] (b) Hasegawa, E.; Curran, D. P. *J. Org. Chem.* **1993**, *58*, 5008.

(20) Addition of triethylamine (5 equiv) indeed reduced the yield of enone to less than 10%, which seems to be consistent with this consideration. However, the fact that the yield of **3a** became low (about 20%) was also witnessed, a result that is not easy to rationalize.

conditions for the conversion of some aromatic epoxy ketones to β-hydroxy ketones in moderate to good yields by the use of a combination of samarium diiodide and proton donors.

Experimental Section

General Procedures. Triethylamine (Wako) and diethylaniline (Wako) were distilled with CaH$_2$. Tribenzylamine (Tokyo Kasei) and diazabicyclooctane (Tokyo Kasei) were purified by sublimation. *N*,*N*-Diethyl(trimethylsilyl)methylamine was prepared according to the literature procedure.[21] 1,2,4,5-Tetramethoxybenzene was prepared and recrystallized from methanol.[22] Preparation of 2-(diphenylmethyl)-1,3-dithiane was accomplished by the literature procedure.[23] Lithium perchlorate (Wako) and tetra-*n*-butylammonium perchlorate (Tokyo Kasei) were used as received. Acetonitrile (Wako) was distilled over P$_2$O$_5$ and subsequently with CaH$_2$. Benzene (Wako) was treated with H$_2$SO$_4$, 5% NaOH, and CaCl$_2$ and then distilled with CaH$_2$. Methanol (Wako) was distilled and dried with molecular sieves 3A. Tetrahydrofuran was distilled from sodium−benzophenone under N$_2$. Water for the reaction was obtained through an ion-exchange column. Samarium diiodide was prepared from Sm (Aldrich) and iodine (Wako) in tetrahydrofuran.[24] Epoxy ketones were known compounds, and their preparations were reported: **1a,c,d,e,**[2a] **1b**,[17h] **1f**.[17g] Products obtained for the reactions were identified by direct comparison of their ^{1}H-NMR spectra with those of authentic samples.

^{1}H-NMR and ^{13}C-NMR spectra were recorded in CDCl$_3$ with Me$_4$Si as the internal standard at 90 and 22.49 MHz, respectively. Photoreactions were conducted in a Pyrex tube (2.5 cm diameter) immersed in a water bath with a 500 W Xe−Hg lamp as a light source through a glass cut-off filter (Toshiba UV-37, $\lambda > 340$ nm). Column chromatography was performed with Wakogel C-200 silica gel. Preparative TLC was performed on 20 cm × 20 cm plates coated with Wakogel B-5F silica gel.

Photoreactions of *trans*-4′-Cyanochalcone Epoxide (1b) with Electron Donors. Epoxide **1b** (0.60 mmol) and donor (1.22 mmol) were dissolved in an appropriate solvent (29 mL). This solution was purged with dry N$_2$ for 10 min and then irradiated for an appropriate time. Concentration of the photolysate at ambient temperature gave a residue that was subsequently separated by column chromatography or TLC for the reactions with triethylamine, 1,2,4,5-tetramethoxybenzene, and 2-(diphenylmethyl)-1,3-dithiane. For the reactions with less volatile amines, such as diethylaniline, tribenzylamine, diazabicyclooctane, and *N*,*N*-diethyl(trimethylsilyl)methylamine, the residue was extracted with chloroform or benzene followed by treatment with 2 N HCl, aqueous NaHCO$_3$, aqueous NaCl, and anhydrous Na$_2$SO$_4$. When the salts were added to the photoreaction solutions, the residue was extracted with methylene chloride followed by treatment with water and anhydrous Na$_2$SO$_4$. Isolated diketone **2b** and hydroxy ketone **3b**[17h] were identified by their spectral data.

Physical and spectral data of diketone **2b**: mp 152−154 °C (EtOH) (uncorrected); ^{1}H-NMR (CDCl$_3$) δ 6.85 (s, 1H), 7.42−7.62 (m, 3H), 7.70−7.80 (m, 2H), 7.94−8.11 (m, 4H), 16.7 (broad s, 1H, enolic OH); ^{13}C NMR (CDCl$_3$) δ 93.9 (d), 15.6 (s), 118.1 (s), 127.4 (d), 127.5 (d), 128.8 (d), 132.4 (d), 133.1 (d), 135.2 (s), 139.4 (s), 182.2 (s), 187.5 (s); IR (KBr) 2224, 1596, 1554, 1294, 764 cm^{-1}. Anal. Calcd for C$_{16}$H$_{11}$NO$_2$: C, 77.10; H, 4.45; N, 5.62. Found: C, 77.17; H, 4.72; N, 5.67.

Reactions of Epoxy Ketones 1 with Samarium Diiodide. To a 0.1 M tetrahydrofuran solution of SmI$_2$ (18 mL, 1.8 mmol, in the case of 2.7 equiv vs **1**) placed in a dry ice−acetone bath (−78 °C) was added a proton donor. Subsequently, 2 mL of a tetrahydrofuran solution of epoxide **1** (0.67 mmol) was added within 2−3 min. After the resulting mixture was stirred for 30 min, the reaction was quenched by saturated NaHCO$_3$ or saturated NH$_4$Cl. This was extracted with ether, and the extract was washed with saturated Na$_2$S$_2$O$_3$, saturated NaHCO$_3$, and saturated NaCl and dried with MgSO$_4$. The residue obtained by concentration of the dried etheral solution was separated by column chromatography or TLC. Isolated diketone **2**, hydroxy ketone **3**, and enone were identified by their spectral data.

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(21) Hasegawa, E.; Brumfield, M. A.; Mariano, P. S.; Yoon, U. C. *J. Org. Chem.* **1988**, *53*, 5435.

(22) Benington, F.; Morin, R. D.; Clark, L. C. *J. Org. Chem.* **1955**, *20*, 102.

(23) Kamata, M.; Murakami, Y.; Tamagawa, Y.; Kato, M.; Hasegawa, E. *Tetrahedron* **1994**, *50*, 12821.

(24) Imamoto, T.; Ono, M. *Chem. Lett.* **1987**, 501.