

Reductive Transformation of α , β -Epoxy Ketones and Other Compounds Promoted through Photoinduced Electron Transfer Processes with 1,3-Dimethyl-2-phenylbenzimidazoline (DMPBI)

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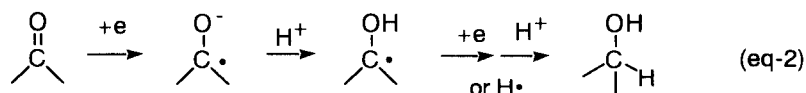
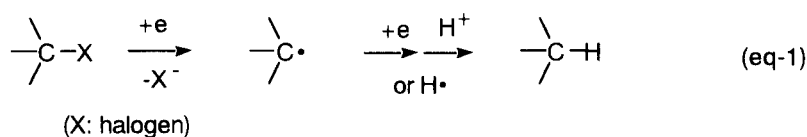
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Abstract: Photoreactions of epoxy ketones, aromatic ketones, haloketones, and aromatic halides with 1,3-dimethyl-2-phenylbenzimidazoline (DMPBI) were studied. Photoinduced single-electron transfer from DMPBI to such substrates initiates the reactions, followed by radical rearrangement and reduction to finally give several reduced products in modest to good yields. © 1999 Elsevier Science Ltd. All rights reserved.

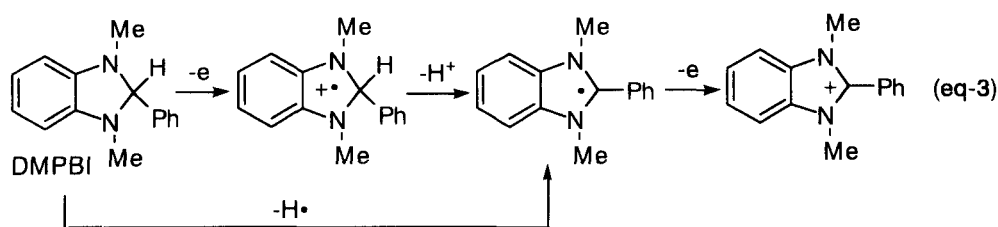
Introduction

Electron transfer reactions are chemically and biologically important processes for the conversion of organic molecules.¹ The reductive transformation of organic functional groups such as carbon-halogen bonds and carbonyls formally proceeds through sequential electron and proton transfers (eq-1 and eq-2).²



Photoinduced electron transfer (PET) is a useful way to achieve such chemical reactions.³ Because of the generation of higher energy molecules by photoexcitation, PET reactions are expected to be more efficient than

the corresponding thermal reactions. We have been investigating the PET reactions of various carbonyl compounds with amines.⁴ In these reaction systems, single-electron transfer from the ground states or the excited states of amines to the excited states or the ground states of carbonyl compounds initiates the reactions. Among the key properties required for amine donors to promote such reactions are good electron-donating ability as well as efficient fragmentation of their cation radicals. Chikashita and coworkers reported that 1,3-dimethyl-2-phenylbenzimidazoline (DMPBI) effectively reduced α -halo carbonyl compounds, acyl chlorides, and α,β -unsaturated carbonyl compounds in the presence or absence of proper Lewis acids.⁵ They proposed that hydride transfer from DMPBI to those substrates occurred. On the other hand, Tanner and coworkers later reported that a free-radical chain mechanism initiated by electron transfer operates in the reactions of carbonyl compounds with DMPBI.⁶ According to their mechanism, DMPBI is first oxidized to its cation radical, followed by deprotonation to give an α -amino radical which is converted to imidazolium (eq-3). Since



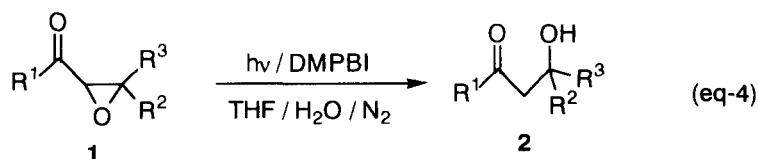
Tanner's observations suggest that DMPBI behaves like coenzyme NADH analogues, we anticipated that DMPBI would act as an effective reductant in PET reaction systems.⁷ This consideration was first tested by using DMPBI for the synthetically important conversion of α,β -epoxy ketones to β -hydroxy ketones.⁸ Irradiation of aromatic epoxy ketones with DMPBI produced the corresponding hydroxy ketones in good yields^{4c} which result was superior to that attained under the previously reported PET conditions.^{4a,8)} In this paper, we describe the synthetic generality and limitations of the PET reaction of several carbonyl compounds and halides with DMPBI.

Results and Discussion

Photoreactions of epoxy ketones with DMPBI

As previously reported,^{4c} irradiation of 1,3-diphenyl-2,3-epoxy-1-propanone (**1a**, chalcone epoxide) with DMPBI produced 1,3-diphenyl-3-hydroxy-1-propanone (**2a**). The yields of **2a** in THF and benzene were greater than those in MeCN and MeOH. Addition of a proper amount of water was necessary to give **2a** in good yield: chalcone was a major product under dry conditions while the formation of a retro-aldol type product such as benzaldehyde was significant in the presence of large excess of water. Thus, the optimized condition to yield **2a** was determined as the irradiation of **1a** with DMPBI in ca 1% aqueous THF. On the other hand, we have found that heating of **1a** with DMPBI in THF also yielded **2a**. When **1a** (0.40 mmol) was heated at 55 °C for 12 h with DMPBI (1.6 equiv) in aqueous THF (THF / H₂O = 10 ml / 0.3 ml), 40% of **2a** was obtained with 4% of chalcone at the 71% conversion of **1a**. In the absence of water, both the conversion of **1a** (40%) and the yield of **2a** (25%) decreased while the yield of chalcone (12%) increased.

Notably, addition of azobisisobutyronitrile (AIBN, 0.1 equiv), a radical initiator, did not significantly affect the reaction: **2a** 50%, chalcone 6% at 77% conversion.⁹ The conversion of **1a** was not completed even though the reaction time was extended: 24 h, **2a** 54%, chalcone 7% at 84% conversion. On the other hand, raising the temperature decreased the yield of **2a**.



The above observations clearly suggest that the photochemical method is superior to the thermal method. Therefore, we employed the photochemical conditions for the conversion of other aromatic epoxy ketones (eq-4). Most of the epoxy ketones studied were converted to the corresponding hydroxy ketones in good to excellent yields (Table 1). These yields are as good as those obtained in the free-radical reactions using tributyltin hydride which we previously reported.^{8k}

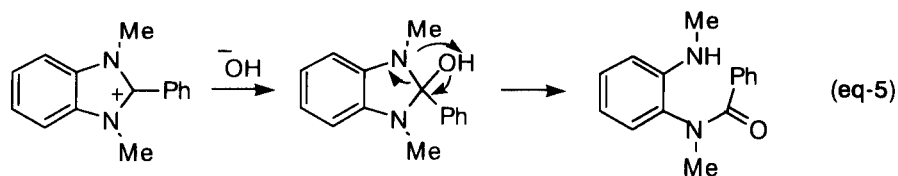
Table 1. Photoreactions of aryl substituted epoxy ketones **1** with DMPBI⁹

Entry	1	R ¹	R ²	R ³	Conv / %	Yield of 2 ^{b)} / %	Bu ₃ SnH ⁹⁾	
							hv	Δ
1	1a	Ph	Ph	H	100	88	93	83
2	1b	α-Naph	Ph	H	100	81	94	89
3	1c	<i>p</i> -MeOPh	Ph	H	100	95	-	-
4	1d	Ph	α-Naph	H	100	85	85	75
5	1e	Ph	<i>p</i> -MePh	H	100	80	85	84
6	1f	Ph	<i>p</i> -MeOPh	H	100	84	84	71
7	1g	Ph	<i>p</i> -ClPh	H	100	73	87	90
8	1h	Ph	Ph	Me	100	74	87	20
9	1i	Ph	H	H	100	67	84	89
10	1j	Ph	<i>i</i> -Pr	H	100	82	81	75
11	1k	Ph	COPh	H	100	37	75	53
12	1l	PhCH=CH	Ph	H	100	66	92	61

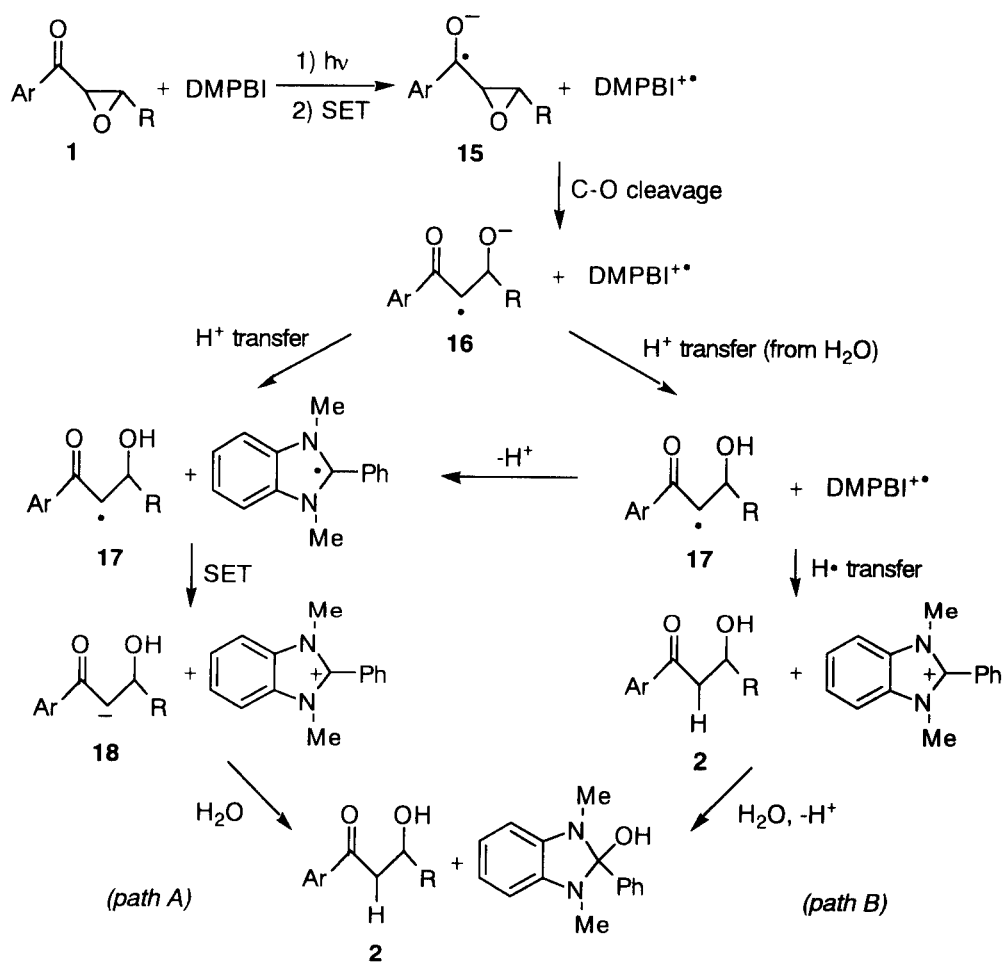
a) 500 W Xe-lamp, λ > 280 nm, **1** (0.40 mmol), DMPBI (1.2 equiv), THF (8 ml), H₂O (0.1 ml), 1 h.

b) Isolated yields. c) Cited from ref. 8k.

To gain more insight into the photoreaction mechanism, some additional experiments were conducted. First, when the reaction of **1b** with DMPBI was conducted in the presence of D₂O, deuterium incorporation at



the α -carbon of **2b** was observed. The percentage of deuterium incorporation was around 70% ($72 \pm 10\%$) which was independent of the reaction time. Therefore, the protonation from water to the anionic intermediate must be mainly responsible for the formation of **2b** and the proton exchange at the α -carbon of **2b** should be negligible during the photoreaction. Secondly, the experiment to search for the products derived from DMPBI



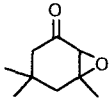
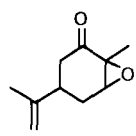
Scheme 1

revealed that *N*-benzoyl-*N*, *N*'-dimethyl-*o*-phenylenediamine was formed in the reaction of **1a** with DMPBI (98% based on the conversion of **1a**). This compound was probably produced from the rearrangement of initially formed 1,3-dimethyl-2-hydroxy-2-phenylbenzimidazoline which can be derived from nucleophilic attack of the hydroxide anion to benzimidazolium (eq-5).

On the basis of the above results as well as the previous observations obtained in the related photoreactions of epoxy ketones,^{4a,e,i} the reaction mechanism is proposed as shown in Scheme 1. Single-electron transfer from DMPBI to the excited state of epoxy ketone **1** produces its anion radical **15** and the cation radical of DMPBI.^{4e,10} Carbon-oxygen bond cleavage of **15** produces ring-opened anion radical **16**.^{4a,f} The alkoxy anion part of **16** abstracts a proton from the cation radical of DMPBI to become α -keto radical **17** and DMPBI radical. Since the DMPBI radical is considered to reduce **17** to its anion **18** which abstracts a proton to become **2**, the DMPBI cation is simultaneously produced and reacts through the sequence presented in eq-5 (*path A*). If **16** is first protonated by water, there might be two possible pathways followed. The generated hydroxide anion could abstract a proton from the cation radical of DMPBI to give the same pair of **17** and the DMPBI radical. If H₂O is replaced by D₂O in these cases, deuterium could be introduced at the α -carbon of **2** (*path A*). On the other hand, if **17** abstracts hydrogen-atom from either the cation radical of DMPBI or THF, no deuterium incorporation at the α -carbon of **2** is expected (*path B*).

While the above photochemical method seems to be generally effective for the conversion of aroyl possessing epoxy ketones, we have observed that acetyl substrates could not be converted to hydroxy ketones under similar conditions.^{4c} Since acetyl chromophore does not efficiently absorb Pyrex-filtered light ($\lambda > 280$ nm), we considered that the photosensitized condition might be useful in these cases. Then, we chose 1,6-bis(dimethylamino)pyrene (BDMAP)¹¹ as a sensitizer that absorbs the light above 340 nm. The excited singlet state of BDMAP could reduce alkyl carbonyls to produce their anion radicals.¹² As expected, epoxy ketones possessing alkyl carbonyls were converted to the corresponding hydroxy ketones by the photosensitization method (Table 2).¹³ Notably, while samarium diiodide, a well-known effective reductant for this type of

Table 2. Photosensitized reactions of alkyl carbonyl substituted epoxy ketones **1** with DMPBI^{a)}

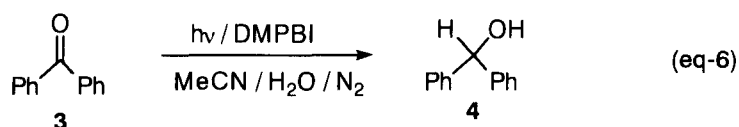
Entry	1	R ¹	R ²	R ³	Conv / %	Yield of 2 ^{b)} / %	Bu ₃ SnH ^{c)}	
							h ν	Δ
1	1m	Me	Ph	H	85	42	24	91
2	1n	Me	<i>n</i> -Pen	H	89	42	40	80
3	1o				99	74	44	23
4	1p				80	29	-	-

a) 500 W Xe-lamp, $\lambda > 340$ nm, **1** (0.40 mmol), DMPBI (2.5 equiv), BDMAP (0.05 equiv), DMF (8 ml), H₂O (0.2 ml), Entries 1, 4: 10 h, Entries 2, 3: 20 h. b) Isolated yields. c) Cited from ref. 8k.

conversion, was reported to be ineffective for the reduction of **1p**.^{8c} our photochemical method was able to convert **1p** to **2p** although optimization of the reaction conditions has not been completed yet. The yields of hydroxy ketones in the above examples were modest; however, this photosensitization method is interesting since reduction of other aliphatic substrates by using low-energy visible light would be also possible.

Photoreactions of Miscellaneous Compounds with DMPBI

As previously described,^{4a,b,f} anion radicals of epoxy ketones are quite reactive which must be due to their combined properties of relief of ring strain and liberation of an anionic leaving group. Therefore, photoinduced reduction of a simple aromatic ketone such as benzophenone **3** by DMPBI must be interesting to evaluate the ability of DMPBI in PET reactions (eq-6). Usually, photoreaction of **3** in the presence of amines



produced radical-radical coupling products such as pinacol and ketone-amine adducts.¹⁴ In principle, reduction of ketone to alcohol requires two electrons as well as two protons (see eq-2). Therefore, we considered that an additional proton source should be added to the reaction solution. Thus, irradiation of **3** with DMPBI (1.2 equiv) in aqueous MeCN (MeCN / H₂O = 8 ml / 0.2 ml) for 2 h, 79% of benzhydrol **4** was isolated at 81% conversion of **3**.¹⁵ The formation of N-benzoyl-N, N'-dimethyl-o-phenylenediamine was also observed in the photoreaction of **3** with DMPBI in aqueous MeCN.

We have observed that irradiation of ethyl 2-bromomethyl-1-indanone-2-carboxylate with DMPBI

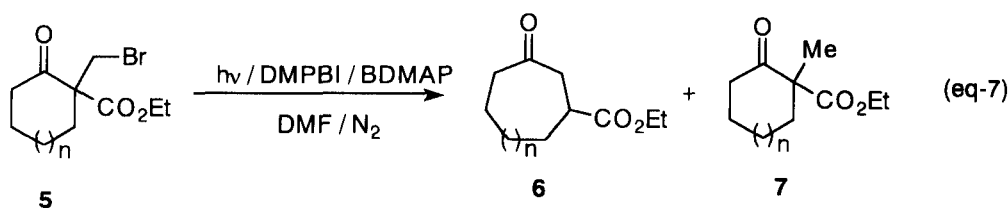


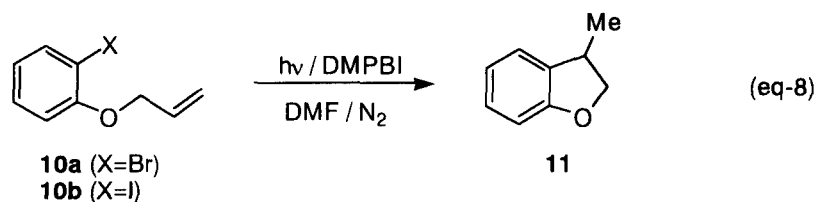
Table 3. Photosensitized reactions of bromomethylated cyclic keto esters **5** with DMPBI^a

Entry	5	n	Conv / %	Yields ^{b)} / %	
				6	7
1	5a	0	100	56	0
2	5b	1	82	29	26 ^{c)}
3	5c	2	100	84	4 ^{c)}

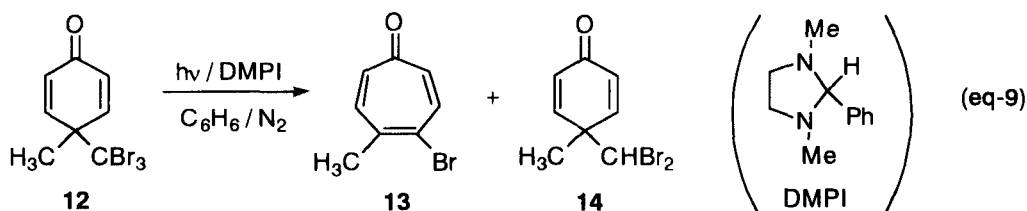
a) 500 W Xe-lamp, $\lambda > 340$ nm, **5** (0.40 mmol), DMPBI (1.2 equiv), BDMAP (0.05 equiv), DMF (8 ml), 4 h. b) Isolated yields. c) Determined by ¹H-NMR of the mixture of **5** and **7**.

produced ethyl 1-tetralone-3-carboxylate.¹⁸ Therefore, it must be reasonable to consider that a photosensitization method using BDMAP and DMPBI would also promote the radical cyclization and ring expansion reaction of 2-bromomethyl-1-cycloalkanone-2-carboxylates **5**. Similar free-radical reactions using tributyltin hydride were previously studied by Dowd and Beckwith.¹⁶ As expected, ring expansion products **6** were mainly obtained while simply reduced product **7b** was another major product in the reaction of **5b** (eq-7, Table 3). The tendency of the product distribution depending on the ring size is quite similar to that of the related free-radical reactions,¹⁶ which would suggest that alkyl radical intermediates are also generated and undergo cyclization and ring expansion in these photoreactions.

The photochemical method using DMPBI was found to be also useful for the reduction of aromatic halides. Irradiation of 1-bromonaphthalene **8** with DMPBI (1.2 equiv) in DMF (8 ml) for 2 h, 47% of naphthalene **9** was isolated at 89% conversion of **8**. This observation would suggest that the carbon-bromine bond was cleaved to produce an aryl radical. Therefore, we became interested in photoreaction of 1-allyloxy-2-bromobenzene **10a** with DMPBI since aryl radical cyclization to give 3-methyl benzofuran **11** was expected (eq-8).¹⁷ Although the expected reaction did not occur in this case, replacement of bromine by iodine resulted in the formation of **11** in 61% yield at the 95% conversion of 1-allyloxy-2-iodobenzene **10b**. These observations must be rationalized by the difference in the electron-accepting property of the halobenzene moiety.¹⁸



As described above, photoreaction with DMPBI is useful for reduction of various substrates. However, there is some limitation to the use of DMPBI which we unexpectedly encountered when 4-tribromomethyl-4-methyl-2,5-cyclohexadienone **12** was treated with DMPBI. In this case, the mixing of **12** and DMPBI without irradiation caused some reaction of **12** to give a complex mixture. After some attempts to search for proper alternatives to DMPBI, it was eventually found that irradiation of **12** (0.40 mmol) with 1,3-dimethyl-2-phenylimidazolidine (DMPI, 2.5 equiv) in benzene (8ml) produced the expected ring-expansion product, 4-bromo-5-methyltropone **13**^{4c} in 49% yield along with a small amount of monobrominated dienone **14** (5%) at the 81% conversion of **12** (eq-9).



Conclusion

We have found that 1,3-dimethyl-2-phenylbenzimidazoline (DMPBI) is an effective reductant for the photochemical conversion of certain compounds, such as epoxy ketones, aromatic ketones, aromatic halides, and haloketones. Although the available mechanistic information is limited at present, single-electron transfer between DMPBI and such substrates is considered to be an initial step. The generation of radical intermediates which are reduced to an anionic species before or after rearrangement is a common feature of these photochemical reactions. Since DMPBI is easily prepared and its wide modifications are possible, photoinduced electron transfer reactions using DMPBI and its derivatives will be further investigated in this laboratory, hopefully to discover new characteristics which are different from the well-known metal-based radical reactions.

Experimental Section

General Procedures.

Reaction substrates were prepared according to literature procedures: **1a-o**,^{4a,8k,19} **1p**,^{8f} **5**,^{16b,20} **10**,¹⁷ **12**.^{4c,h} All photoproducts are known: **2a-o**,^{4a,8k,19} **2p**,^{8f} **6**,^{16b,20} **7**,^{16b,20} **11**,¹⁷ **13**,^{4c,h} **14**.^{4c,h} Benzophenone **3**, benzhydrol **4**, 1-bromonaphthalene **8**, and naphthalene **9** are commercially available. 1,3-Dimethyl-2-phenylbenzimidazoline (DMPBI),^{5a} 1,3-dimethyl-2-phenylimidazolidine (DMPI),²¹ and 1,6-Bis(dimethyl-amino)pyrene (BDMAP)²² were prepared by reported procedures. Tetrahydrofuran was distilled from sodium-benzophenone under N₂. DMF was dried with molecular sieves 4A and distilled with KOH under N₂. Benzene was treated with H₂SO₄, 5% NaOH, CaCl₂, and then distilled with CaH₂. Water for the reaction was obtained through an ion-exchange column. Other reagents and solvents were purchased and used without further purification.

Photoreactions were conducted in a Pyrex tube (2.5 cm diameter) immersed in a water bath with a 500 W Xe-lamp as a light source. Separation of photoreaction mixtures was performed by column chromatography with Wakogel C-200 silica gel and preparative TLC on 20 cm x 20 cm plates coated with Wakogel B-5F silica gel. Identification of photoproducts was mainly accomplished by their IR and NMR data: NMR spectra were measured in CDCl₃ with Me₄Si as the internal standard at 90, 200 MHz for ¹H NMR; 22.49, 49 MHz for ¹³C NMR respectively.

Photoreactions of **1**, **3**, **8**, **10** with DMPBI.

A solution of reactant (0.40 mmol) and DMPBI (0.48 mmol) in an appropriate solvent (THF, MeCN, or DMF, 8 ml) in the presence or absence of H₂O (0.1 ml for **1**, 0.2 ml for **3**) was purged with dry N₂ for 5 min followed by irradiation for an appropriate time (1 h for **1**, 2 h for **3** and **8**, 4 h for **10**). Each work-up procedure is as follows. In the reaction of **1**, column chromatography (CH₂Cl₂) of the crude product mixture obtained by concentration of photolysate gave **2**. In the reaction of **3**, to the photolysate was added CH₂Cl₂ followed by anhydrous MgSO₄. Column chromatography (EtOAc / C₆H₁₄ = 1 / 5, 1 / 3, 1 / 1 sequentially) of the crude product mixture obtained by concentration of the solution gave **4** with unreacted **3**. In the case of **8**,

a half-scale of the above reactions was conducted. Conversion of **8** and yield of **9** were determined by GC analysis using triphenylmethane as an internal standard. In the reaction of **10**, extraction of the reaction solution with ethyl acetate was performed. Column chromatography (C_6H_6 / C_6H_{14}) of the crude product mixture gave unreacted **10**. Since chromatography caused decomposition of **11**, the yield of **11** was determined by 1H -NMR of the product mixture using the peak of co-existing **10** as a reference.

Deuterium labeling experiment.

A THF solution (8 ml) of **1b** (0.40 mmol), DMPBI (0.48 mmol) and D_2O (0.1 ml) was purged with dry N_2 for 5 min followed by irradiation for 1 h. Column chromatography (CH_2Cl_2) of the crude product mixture obtained by concentration of photolysate gave **2b** (0.25 mmol, 61%). 1H -NMR analysis of **2b** revealed that 71% deuteration (71%-D) was observed at the α -carbon to carbonyl of **2b**. Similarly, photoreactions for shorter time were performed: 10 min, conv of **1b** 96%, **2b** (0.26 mmol, 65%, 83%-D); 1 min, conv of **1b** 40%, **2b** (0.088 mmol, 22%, 62%-D).

Identification of the products derived by DMPBI.

Irradiation of **1a** (0.40 mmol) and DMPBI (0.48 mmol) in aqueous solvents was performed by the procedures described above. The crude product mixture was directly analyzed by 1H -NMR using triphenylmethane as a standard to determine the formation of **2a** (0.35 mmol, 88%) and *N*-benzoyl-*N*, *N'*-dimethyl-*o*-phenylenediamine (0.39 mmol, 98%). In the reaction of **3**, *N*-benzoyl-*N*, *N'*-dimethyl-*o*-phenylenediamine, while not quantified, was also detected as a major component in the crude product mixture by 1H -NMR.

N-benzoyl-*N*, *N'*-dimethyl-*o*-phenylenediamine was independently prepared by the reaction of 1,3-dimethyl-2-phenylbenzimidazolium iodide with KOH at room temperature in MeOH.

BDMAP Photosensitized reactions of **1**, **5** with DMPBI.

A solution of reactant (0.40 mmol) and DMPBI (1.00 mmol for **1**, 0.48 mmol for **5**), and BDMAP (0.02 mmol) in DMF (8 ml) in the presence or absence of H_2O (0.2 ml for **1**) was purged with dry N_2 for 5 min followed by irradiation through Toshiba UV-37 filtered light for an appropriate time (10 h for **1m** and **1p**, 20 h for **1n** and **1o**, 4 h for **5**). To the photolysate was added water, followed by extraction with ethyl acetate. The extract was treated with water, saturated aqueous NaCl, and dried over anhydrous $MgSO_4$. Each separation procedure is described as follows. In the reaction of **1**, column chromatography (CH_2Cl_2 / C_6H_6 = 3 / 1) of the crude product mixture gave **2** and unreacted **1**. In the reaction of **5**, column chromatography (EtOAc / *n*- C_6H_{14} = 1 / 3) of the crude product mixture gave **6** along with unreacted **5** and **7**.

Photoreaction of **12** with DMPI.

A benzene solution (8 ml) of **12** (0.40 mmol) and DMPI (1.00 mmol) was purged with dry N_2 for 5 min followed by irradiation for 1 h. Column chromatography (EtOAc / C_6H_{14} = 1 / 1) of the crude product mixture obtained by concentration of photolysate gave **13** and a mixture of unreacted **12** and **14** whose yields were determined by 1H -NMR.

Thermal reactions of 1 with DMPBI.

An aqueous THF (THF / H₂O = 10 ml / 0.3 ml) or dry THF (10 ml) solution of **1** (0.40 mmol) and DMPBI (0.64 mmol) in the presence or absence of AIBN (0.04 mmol) was heated at 55 °C under N₂ for 12 h. Column chromatography (CH₂Cl₂) of the crude product mixture obtained by concentration of the reaction solution gave **2** along with unreacted **1** and chalcone.

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References and Notes

1. (a) Ebersson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987. (b) *Advances in Electron Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press: Greenwich, 1991-1995, Vol 1-5.
2. (a) Savéant, J. M. In *Advances in Electron Transfer Chemistry*; Mariano, P. S. Ed.; JAI Press: Greenwich, 1994; Vol. 4; pp 53-116. (b) Berger, D. J.; Tanko, J. M. In *The Chemistry of Double-Bonded Functional Groups*; Patai, S. Ed.; Wiley, New York, 1997; pp 1281-1354.
3. *Photoinduced Electron Transfer, Part C*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988.
4. (a) Hasegawa, E., Ishiyama, K., Horaguchi, T., Shimizu, T. *J. Org. Chem.* **1991**, *56*, 1631. (b) Hasegawa, E., Ishiyama, K., Horaguchi, T., Shimizu, T. *Tetrahedron Lett.* **1991**, *32*, 2029. (c) Hasegawa, E., Tamura, Y., Horaguchi, T., Isogai, K., Suzuki, T. *Tetrahedron Lett.* **1994**, *35*, 8643. (d) Hasegawa, E., Katagi, H., Nakagawa, D., Horaguchi, T., Tanaka, S., Yamashita, Y. *Tetrahedron Lett.* **1995**, *36*, 6915. (e) Hasegawa, E., Kato, T., Kitazume, T., Yanagi, K., Hasegawa, K., Horaguchi, T. *Tetrahedron Lett.* **1996**, *37*, 7079. (f) Hasegawa, E., Ishiyama, K., Fujita, T., Kato, T., Abe, T. *J. Org. Chem.* **1997**, *62*, 2396. (g) Hasegawa, E., Tamura, Y., Tosaka, E., *J. Chem. Soc., Chem. Commun.* **1997**, 1895. (h) Hasegawa, E., Tamura, Y., Suzuki, K., Yoneoka, A., Suzuki, T. *J. Org. Chem.* in press.
5. (a) Chikashita, H., Itoh, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1747. (b) Chikashita, H., Ide, H., Itoh, H. *J. Org. Chem.* **1986**, *51*, 5400.
6. (a) Chen, J., Tanner, D. D. *J. Org. Chem.* **1988**, *53*, 3898. (b) Chen, J., Tanner, D. D. *J. Org. Chem.* **1989**, *54*, 3842. (c) Tanner, D. D., Chen, J., Chen, L., Luelo, C. *J. Am. Chem. Soc.* **1991**, *113*, 8074. (d) Tanner, D. D., Chen, J. *J. Org. Chem.* **1992**, *57*, 662. (e) Tanner, D. D., Chen, J., Luelo, Peters, P. M. *J. Am. Chem. Soc.* **1992**, *114*, 713.
7. (a) Review: Fukuzumi, S. *Advances in Electron Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press: Greenwich, 1992; Vol. 2; pp67-175. (b) Applications of NADH analogues to PET reactions: Pac, C., Miyauchi, Y., Ishitani, O., Ihama, M., Yasuda, M., Sakurai, H. *J. Org. Chem.* **1984**, *49*, 26;

- Ishitani, O., Yanagida, S., Takamuku, S., Pac, C. *J. Org. Chem.* **1987**, *52*, 2790; Okada, K., Okubo, K., Morita, N., Oda, M. *Chem. Lett.* **1993**, 2021.
8. (a) Fieser, L. F. *J. Am. Chem. Soc.* **1953**, *75*, 4395. (b) Robinson, C. H., Henderson, R. *J. Org. Chem.* **1972**, *37*, 565. (c) Weile, G. R., McMorris, T. C. *J. Org. Chem.* **1978**, *43*, 3942. (d) Shapiro, E. L., Gentles, M., Kabasakalian, P., Magatti, A. *J. Org. Chem.* **1981**, *46*, 5017. (e) Osuka, A., Takaoka, K., Suzuki, H. *Chem. Lett.* **1984**, 271. (f) McChesney, J. D., Thompson, T. N. *J. Org. Chem.* **1985**, *50*, 3473. (g) Molander, G. A., Hahn, G. *J. Org. Chem.* **1986**, *51*, 2596. (h) Miyashita, M., Suzuki, T., Yoshikoshi, A. *Tetrahedron Lett.* **1987**, *28*, 4293. (i) Inokuchi, T., Kusumoto, M., Torii, S. *J. Org. Chem.* **1990**, *55*, 1548. (j) Cossy, J., Bouzide, A., Ibhi, S., Aclinou, P. *Tetrahedron* **1991**, *47*, 7775. (k) Hasegawa, E., Ishiyama, K., Kato, T., Horaguchi, T., Shimizu, T. *J. Org. Chem.* **1992**, *57*, 5352. (l) Engman, L., Stern, D. *J. Org. Chem.* **1994**, *59*, 5179.
9. This observation is highly in contrast to those in the reactions reported by Tanner: addition of AIBN significantly increased the yields of reduced products, which was rationalized by the electron transfer induced radical chain mechanism.⁹
10. On addition of much excess water, significant retro-aldol fragmentation was observed.^{4e} To rationalize this observation, we proposed an initial proton transfer from water to **15**, followed by carbon-oxygen bond cleavage of oxiranyl methyl radical to give β -keto alkoxy radical.^{8k}
11. Okada, K., Okamoto, K., Oda, M. *J. Am. Chem. Soc.* **1988**, *110*, 8736.
12. Oxidation potential of the singlet excited state of BDMAP was estimated to be about -2.4 V (vs. SCE).^{4a,11}
13. The reaction did not smoothly proceed without DMPBI. For example, irradiation of BDMAP with **1o** in the absence of DMPBI did not produce **2o** at all. Apparently, decomposition of BDMAP was much more significant in this case than in the case using DMPBI. Therefore, DMPBI is necessary for the effective photosensitization reaction in which DMPBI may act as a reductant for the conversion of the cation radical of BDMAP to its neutral form.
14. (a) Cohen, S. G., Baumgarten, R. J. *J. Am. Chem. Soc.* **1965**, *87*, 2996; **1967**, *89*, 3471. (b) Davidson, R. S. *J. Chem. Soc., Chem. Commun.* **1966**, 575. (c) Pac, C., Sakurai, H., Tosa, T. *J. Chem. Soc., Chem. Commun.* **1970**, 1311. (d) Cohen, S. G., Stein, N. M. *J. Am. Chem. Soc.* **1971**, *93*, 6542. (e) Recent example of the related reaction: Jones, P. B., Pollastri, M. P., Porter, N. A. *J. Org. Chem.* **1996**, *61*, 9445 and references cited therein.
15. Aqueous THF as well as wet benzene were not effective solvent systems. On the other hand, the yield of **4** which was produced in non-aqueous MeCN was less than that in aqueous MeCN. Therefore, irradiation in aqueous polar solvents should be recommended for the reduction of simple aromatic ketones by DMPBI.
16. (a) Dowd, P., Choi, S. C. *J. Am. Chem. Soc.* **1987**, *109*, 3493; **1987**, *109*, 6548. (b) Dowd, P., Choi, S. C. *Tetrahedron* **1989**, *45*, 77. (c) Beckwith, A. L. J., O'Shea, D. M., Gerba, S., Westwood, S. W. *J. Chem. Soc., Chem. Commun.* **1987**, 666. (d) Beckwith, A. L. J., O'Shea, S., Westwood, S. W. *J. Am. Chem. Soc.* **1988**, *110*, 2565.
17. Free radical reactions of 1-allyloxy-2-halobenzenes: (a) Beckwith, A. L. J., Gara, W. B. *J. Chem. Soc., Perkin Trans 2* **1975**, 795. (b) Beckwith, A. L. J., Goh, S. W. *J. Chem. Soc., Chem. Commun.*

- 1983**, 905. (c) Abeywickrema, A. N., Beckwith, A. L. J. *Tetrahedron Lett.* **1986**, 27, 109. (d) Bhandal, H., Patel, V. F., Pattenden, G., Russel, J. J. *J. Chem. Soc., Perkin Trans 1* **1990**, 2691-2701. (e) Chatgililoglu, C., Dickhaut, J., Giese, B. *J. Org. Chem.* **1991**, 56, 6399.
18. (a) Reduction potentials of halobenzenes (vs. SCE): bromobenzene, -2.32 V; iodobenzene, -1.62 V.^{18b}
(b) Mann, C. K., Barns, K. K. *Electrochemical Reactions in Nonaqueous Systems*: Marcel Dekker: New York, 1970.
19. Spectral and elemental analysis data of epoxy ketones **1b**, **1d**, **1k**, **1l** and hydroxy ketones **2b**, **2d**, **2k**, **2l** were reported as Supplementary Material of reference 8k.
20. Shono, T., Kise, N., Uematsu, N., Morimoto, S., Okazaki, E. *J. Org. Chem.* **1990**, 55, 5037.
21. DMPI was prepared by Mangeney's procedure: Mangeney, P., Gosmini, R., Raussou, S., Commercon, M., Alexakis, A. *J. Org. Chem.* **1994**, 59, 1877. General procedure of protection of aldehydes by N, N'-dimethyl-1,2-ethylenediamine: Greene, T. W., Wuts, P. G. M. *Protective Groups in Organic Synthesis*: Wiley, New York, 1991: pp 218-219.
22. Zweig, A., Maurer, A. H., Roberts, B. G. *J. Org. Chem.* **1967**, 32, 1322.