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Contrastive Photoreduction Pathways of Benzophenones Governed by Regiospecific Deprotonation of Imidazoline Radical Cations and Additive Effects

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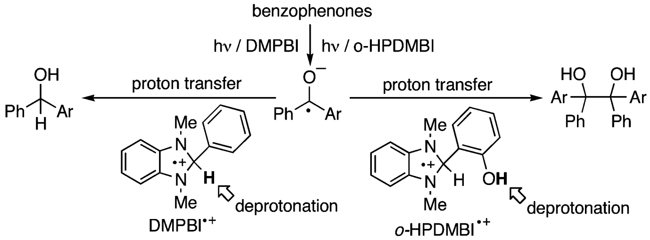

In the photoreaction of benzophenones with 1,3-dimethyl-2-phenylbenzimidazoline (DMPBI), benzhydrols were major products. Addition of H_2O accelerated the reaction with no change in the product distribution, while AcOH, PhOH, and metal salts such as $LiClO_4$ and $Mg(ClO_4)_2$ were effective additives to produce benzpinacols. In contrast, benzpinacols were exclusively formed regardless of the solvent and the additive in the reactions with 2-(*o*-hydroxyphenyl)-1,3-dimethylbenzimidazoline (*o*-HPDMBI). These observations are consistent with the hypothesis that DMPBI$^{\bullet+}$ donates a proton at the C_2 position to the benzophenone ketyl radicals while *o*-HPDMBI$^{\bullet+}$ donates a phenol proton.

Photoinduced electron-transfer (PET) processes provide useful methods to generate organic radical ions in solution, and the reaction pathways of radical ions are principally governed by not only their inherent property but also the surrounding medium including solvents and additives.[1] Because pairs of radical ions are uniquely generated with the PET methods in contrast to other nonphotochemical methods, specific interactions between the radical ion pairs are essentially important in the PET reaction systems.[1] Among the compounds that have been frequently subjected to PET reactions are amines[2] and ketones.[3] Previously, we reported[4,5] that 1,3-dimethyl-2-phenylbenzimidazoline (DMPBI)[6] and 2-hydroxyphenyl-1,3-dimethylbenzimidazolines (HPDMBI), shown in Chart 1, act as effective reagents to promote the photoinduced reduction of ketones. The synthetic utilities of these benzimidazolines are thus far recognized; however, their reaction behaviors in PET systems has been less explored. Therefore, we investigated photoreactions of benzophenone (**1a**), a simple but useful mechanistic probe substrate in various PET reactions,[7] and *m*-methylbenzophenone (**1b**) with DMPBI and 2-(*o*-hydroxyphenyl)-1,3-dimethylbenzimidazoline (*o*-HPDMBI). Here, we report contrastive photoreduction pathways of **1** governed by regiospecific deprotonation of the radical cations of DMPBI and *o*-HPDMBI and by properties of the proton donors and metal salts.

CHART 1

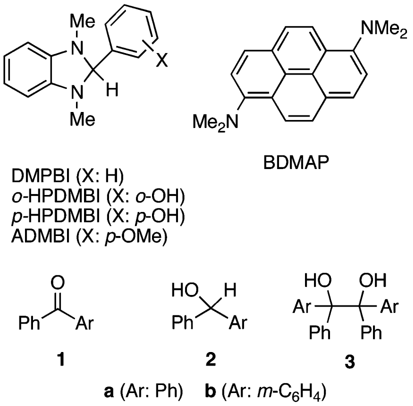

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TABLE 1. Photoreaction of 1b with DMPBI

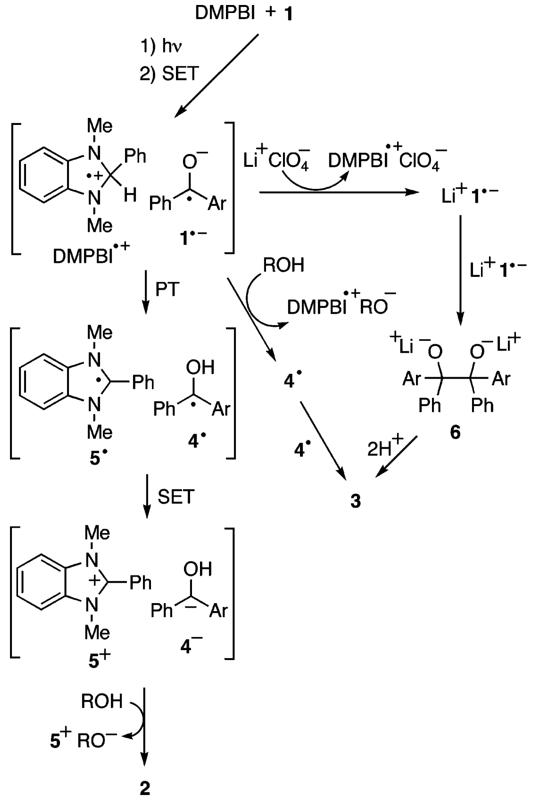
entry	solvent	additive (equiv vs **1b**)	conv of **1b**[c] (%)	yields[c,d] (%) **2b**	yields[c,d] (%) **3b**
1[a]	MeCN	–	37	88	0
2[a]	MeCN	H_2O (13.9)	88	88	0
3[a]	MeCN	PhOH (6.0)	100	8	92
4[a]	MeCN	AcOH (2.4)	100	0	100
5[a]	MeCN	$LiClO_4$ (1.2)	100	8	86
6[a]	MeCN	$Mg(ClO_4)_2$ (1.2)	89	7	91
7[b]	DMF	–	4	0	0
8[b]	DMF	H_2O (13.9)	14	100	0
9[b]	DMF	AcOH (6.6)	56	6	86

[a] **1b** (0.20 mmol), MeCN (4 mL), $\lambda > 280$ nm for 2 h for entries 1−6. [b] **1b** (0.20 mmol), BDMAP (0.010 mmol), DMF (2 mL), $\lambda > 360$ nm for 4 h for entries 7−9. [c] Determined with ^{1}H NMR. [d] Based on the conversion of **1b**.

We first conducted a preparative photoreaction ($\lambda > 280$ nm) of **1a** and DMPBI (1.2 equiv versus **1a**) in THF and found low conversion of **1a** (21%) and predominant formation of benzhydrol (**2a**) (78% yield).[8,9] Although addition of H_2O (13.9 equiv versus **1a**) increased the conversion of **1a** to 48%, **2a** was still the sole product (85%). When H_2O was replaced with AcOH (6.6 equiv versus **1a**), however, a significant amount of benzpinacol (**3a**, 47%) was obtained along with **2a** (53%) at 65% conversion of **1a**. To investigate in detail the photoreaction of benzophenone−DMPBI systems, we then conducted photoreactions of **1b** and DMPBI under various conditions, as shown in Table 1, in which the quantities of **1b**, **2b**, and **3b** in the reaction mixtures were easily determined with ^{1}H NMR based on the signals of the methyl protons of **1b**, **2b**, and **3b**. In the reactions with the proton donors, the conversion of **1b** was significantly increased in the presence or absence of 1,6-bis(*N*,*N*′-dimethylamino)pyrene (BDMAP)[4b−e,5,10] as a sensitizer (entries 2−4 or 8 and 9).[11] Addition of the proton donors also changed the yields of **2b** and **3b** in varying extent, apparently depending on the acidity of proton donors (pK_a[12] in water: H_2O 15.75; PhOH 10.0; AcOH 4.75) (entries 2−4 and 8 and 9). Note that addition of metal salts such as $LiClO_4$ and $Mg(ClO_4)_2$ markedly changed the product distribution (entries 5 and 6).[13] Interestingly, photoreactions of **1b** with triethylamine, *N*,*N*-diethylaniline, *N*,*N*-dimethylaniline, or tribenzylamine in aqueous MeCN predominantly produced **3b** (59−95%) along with a small amount of **2b** (2−11%).

A plausible reaction mechanism for the reaction of **1** with DMPBI is proposed in Scheme 1. Light-induced single electron transfer (SET) produces a radical ion pair [DMPBI$^{\bullet+}$ **1**$^{\bullet-}$].[14] Subsequent proton transfer (PT) produces a radical pair [**5**$^{\bullet}$ and **4**$^{\bullet}$] that successively undergoes SET to give a DMPBI-derived cation (**5**$^{+}$) and a carbanion (**4**$^{-}$).[15] Protonation to **4**$^{-}$ gives **2** in the presence of H_2O. Feasibility of the SET process between **5**$^{\bullet}$ and **4**$^{\bullet}$ could be consistent with the fact that the formation of **2** was predominant in the case of DMPBI and not in the cases of simple tertiary amines.[16] In the presence of AcOH and PhOH, these proton donors intercept **1**$^{\bullet-}$ with protonation to give **4**$^{\bullet}$.[18] Because the potential reducing agent **5**$^{\bullet}$ is not generated in this case, **4**$^{\bullet}$ survives to undergo dimerization with another **4**$^{\bullet}$ to **3**. Ion pair exchange[7i] between [DMPBI$^{\bullet+}$ **1**$^{\bullet-}$] and the metal salt, represented by $LiClO_4$ in Scheme 1, also prevents PT from DMPBI$^{\bullet+}$ to **1**$^{\bullet-}$ to give the metal-coordinated ketyl radical (Li^+**1**$^{\bullet-}$) that dimerizes to **6**, which finally converts to **3**.

SCHEME 1



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[8] A preliminary observation that the irradiation of **1a** with DMPBI predominantly produced **2a** in aqueous MeCN was reported.[4c]

[9] Yields of the products reported in this Note represent those based on the conversion of the corresponding starting materials unless otherwise stated.

[10] Okada, K.; Okamoto, K.; Oda, M. *J. Am. Chem. Soc.* **1988**, *110*, 8736.

[11] Similar marked change of the product distribution depending on the proton donors was also observed in the BDMAP-sensitized photoreaction of cyclohexylphenyl ketone with DMPBI in DMF (alcohol/pinacol = 100:0 for H_2O and 10:90 for AcOH).

[12] Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

[13] Although the influence of alkali metal salts on the PET processes of **1a** and amines has been thoroughly investigated,[7i] surprisingly, the influence of the salts on the product formation has not been explored well.

[14] Feasibility of electron transfers between **1** and amines was confirmed by discussion using their redox potential data. For details, see the Supporting Information.

[15] One reviewer suggested another possible pathway in which the ion radical pair [DMPBI$^{\bullet+}$ **1**$^{\bullet-}$] is converted to an ion pair [**5**$^{+}$ PhArCH-O^{-}] by a hydrogen atom transfer. This pathway must be a minor one, even if it exists, because a hydrogen atom transfer from DMPBI$^{\bullet+}$ to the sterically more crowded ketyl carbon of **1**$^{\bullet-}$ should be less likely than a proton transfer to the oxy anion part of **1**$^{\bullet-}$.

[16] Electron-donating ability of **5**$^{\bullet}$ is considered to be greater than those of α-amino radicals derived from simple tertiary amines on the basis of the oxidation potentials of the benzthiazolyl radical that possesses a structure similar to that of **5**$^{\bullet}$ (−1.3 V versus SCE)[17a] and those of simple α-amino radicals (ca. −1.0 V versus SCE).[17b]

[17] (a) Shukla, D.; Liu, G.; Dinnocenzo, J. P.; Farid, S. *Can. J. Chem.* **2003**, *81*, 744. (b) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.

[18] Because the pK_a value of the protonated ketyl radical of **1a** in water has been reported to be 9.3,[19] the protonation to **1**$^{\bullet-}$ by AcOH or PhOH must be a reasonably efficient process.

TABLE 2. Photoreaction of 1b with *o*-HPDMBI

entry	solvent	additive (equiv vs **1b**)	conv of **1b**^{c} (%)	yields^{c,d} (%)	
				2b	**3b**
1^a	MeCN	–	52	0	100
2^a	MeCN	H_2O (13.9)	47	0	100
3^a	MeCN	AcOH (6.6)	100	0	100
4^a	MeCN	$LiClO_4$ (1.2)	100	0	100
5^a	MeCN	$Mg(ClO_4)_2$ (1.2)	100	0	100
6^a	THF	–	86	0	100
7^a	THF	AcOH (6.6)	85	0	96
8^a	DMF	–	54	8	91
9^b	DMF	–	34	0	100
10^b	DMF	AcOH (6.6)	79	0	93

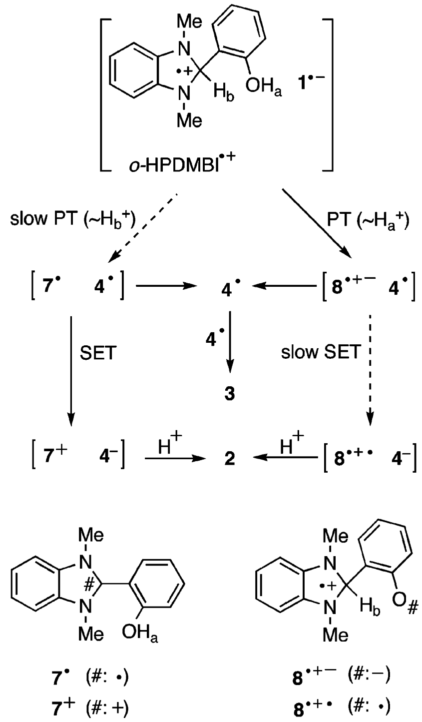
^{a} **1b** (0.20 mmol), solvent (4 mL), $\lambda > 280$ nm for 2 h for entries 1–8. ^{b} **1b** (0.20 mmol), BDMAP (0.010 mmol), DMF (2 mL), $\lambda > 360$ nm for 4 h for entries 9 and 10. ^{c} Determined with ^{1}H NMR. ^{d} Based on the conversion of **1b**.

We next conducted photoreactions of **1b** with *o*-HPDMBI and found a marked change in product distributions from those with DMPBI. As shown in Table 2, **3b** was exclusively produced in high yield regardless of the reaction conditions. Particularly, the exclusive formation of **3b** was contrastive to the predominant formation of **2b** with DMPBI in the presence of H_2O. Significant conversion of **1b**, even in the absence of proton donors, was also notable (entries 1, 6, and 8). Interestingly, addition of AcOH significantly increased the conversion of **1b** in MeCN and DMF (compare entries 1 and 9 with 3 and 10, respectively); however, the conversion of **1b** did not change very much with or without AcOH in THF (entries 6 and 7). Again, both $LiClO_4$ and $Mg(ClO_4)_2$ increased the conversion of **1b** and led to the exclusive formation of **3b**.

To gain further insight into the effects of the hydroxy substituent on the phenyl group at the C_2 position of DMPBI, we conducted photoreactions of **1b** with *p*-HPDMBI or 2-(*p*-methoxyphenyl)-1,3-dimethylbenzimidazoline (ADMBI) in MeCN. The reaction with *p*-HPDMBI produced **3b** (94%) at 52% conversion of **1b**, whereas the reaction with ADMBI in the presence of H_2O (13.9 equiv versus **1b**) produced **2b** (98%) at 100% conversion of **1b**. The fact that *p*-HPDMBI behaves similarly to *o*-HPDMBI rather than ADMBI suggests that electron-donating properties of the hydroxy substituents of *o*- and *p*-HPDMBIs are not crucial factors, but their proton-donating abilities are responsible for the exclusive formation of **3b**.

On the basis of these observations, we propose a plausible mechanism for the reaction of *o*-HPDMBI and **1**, as shown in Scheme 2. The initially generated *o*-HPDMBI$^{\bullet+}$ releases either a phenol proton (H_a) or a proton at the C_2 position (H_b). If H_b^+ is transferred to **1**$^{\bullet-}$, the resulting radical **7**$^{\bullet}$ would reduce **4**$^{\bullet}$ to **4**$^-$, which finally becomes **2** similarly to the reaction with DMPBI (see Scheme 1). However, this was not witnessed. Instead, *o*-HPDMBI$^{\bullet+}$ donates H_a^+ to **1**$^{\bullet-}$, and the phenoxide part[20] of the resulting zwitter ion radical **8**$^{\bullet+-}$ does not reduce **4**$^{\bullet}$ to **4**$^-$ so that **4**$^{\bullet}$ has an opportunity to undergo dimerization to **3**. When a proper proton donor is added to the reaction system, protonations to **1**$^{\bullet-}$ from the proton donor and from *o*-HPDMBI$^{\bullet+}$ are competitive. This situation should be more plausible in polar solvents than in nonpolar solvents because a dissociation of [*o*-HPDMBI$^{\bullet+}$ **1**$^{\bullet-}$] is most likely to occur in the former solvents. Note that the addition of AcOH significantly increased the conversion of **1b** in both MeCN and DMF, but not in THF (compare entries 1, 9, and 6 to 3, 10, and 7, respectively, in Table 2). The above hypothesis of the deprotonation regioselectivity of *o*-HPDMBI$^{\bullet+}$ is particularly noteworthy because the proton at the C_2 position of *o*-HPDMBI$^{\bullet+}$ (H_b) is considered to be more acidic than the phenol proton (H_a) judging from their expected acidities.[22] Therefore, it must be assumed that the order of their kinetic acidities[25] is reverse to that of the corresponding thermodynamic acidities in these reaction systems.

SCHEME 2



In conclusion, we have found that the photoproduct distributions from **1** markedly changed depending on DMPBI or *o*-HPDMBI and also were influenced by the property of the additives. The contrastive observations between DMPBI and *o*-HPDMBI are consistent with the hypothesis that DMPBI$^{\bullet+}$ donates a proton at the C_2

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[19] Lilie, J.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 170.

[20] Reducing abilities of the phenoxide ions should be much lower than those of α-amino radicals,[16] judging form their oxidation potentials. The oxidation potential of the phenoxide ion was reported to be ca. 0 V versus SCE.[21]

[21] Yousefzadeh, P.; Man, C. K. *J. Org. Chem.* **1968**, *33*, 2716.

[22] Acidities of some amine radical cations were reported.[23] For example, the pK_a of the radical cation of *N*,*N*-dimethylaniline was estimated to be 9 in MeCN.[23a] The pK_a value of phenol in MeCN was estimated to be 27.[12,24]

[23] (a) Nelsen, S. F. *J. Am. Chem. Soc.* **1988**, *108*, 4879. (b) Dinnocenzo, J. P.; Banach, T. E. *J. Am. Chem. Soc.* **1989**, *111*, 8646. (c) Parker, V. D.; Tilset, M. *J. Am. Chem. Soc.* **1991**, *113*, 8778.

[24] Liu, W. Z.; Bordwell, F. G. *J. Org. Chem.* **1996**, *61*, 4778.

[25] The concept of kinetic acidity has been often applied to rationalize the reaction of radical ion pairs generated by PET processes.[26] Then it was suggested that the kinetic acidity of a certain radical cation is influenced by the nature of a radical anion generated simultaneously.

position to $1^{\bullet-}$, whereas *o*-HPDMBI$^{\bullet+}$ donates a phenol proton to $1^{\bullet-}$ rather than a proton at the C_2 position. Investigation of the factors to control the regioselectivity of deprotonation of *o*-HPDMBI$^{\bullet+}$ is the next subject to be undertaken.

Experimental Section

General Procedure for Photoreaction of 1b with Amines. A solution of **1b** (0.20 mmol) and amine (0.24 mmol) with or without BDMAP (0.010 mmol) in a solvent (MeCN, THF, and DMF 4 mL; DMF 2 mL for the BDMAP sensitized reactions) in the presence or absence of H_2O, PhOH, AcOH, $LiClO_4$, or $Mg(ClO_4)_2$ was purged with N_2 for 5 min prior to irradiation. The irradiation and workup procedures were essentially the same as those of the reactions of **1a** described in the Supporting Information. The photolyzates containing PhOH, $LiClO_4$, and $Mg(ClO_4)_2$ were worked up in the same manner to that containing AcOH. Each photoproduct mixture was analyzed with ^1H NMR (200 MHz) using triphenylmethane as an internal standard. Benzhydrol **2b**[27] and benzpinacol **3b**[28] were identified by comparison of their spectral data with those of the products obtained by the $NaBH_4$ and SmI_2 reductions of **1b**, respectively. Quantities of **1b**, **2b**, and **3b** were determined on the basis of integrations of the methyl peaks of these compounds (2.42 ppm for **1b**, 2.34 ppm for **2b**, 2.19 and 2.20 ppm for the two diastereomers of **3b**) and the methine peak of triphenylmethane (5.56 ppm).

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Supporting Information Available: General experimental procedures, preparations of *o*-HPDMBI, *p*-HPDMBI, and ADMBI, their IR and NMR spectra and cyclic voltammogram, photoreaction procedure for **1a**, and additional discussion. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) Guijarro, D.; Yus, M. *Tetrahedron* **2000**, *56*, 1135.

(28) Yamamoto, J.; Matsuo, A.; Okamoto, Y. *Nippon Kagaku Kaishi* **1988**, 1709.