HETEROCYCLES, Vol. 77, No. 2, 2009, pp. 1147 - 1161. © The Japan Institute of Heterocyclic Chemistry
Received, 4th August, 2008, Accepted, 18th September, 2008, Published online, 22nd September, 2008
DOI: 10.3987/COM-08-S(F)94

BENZIMIDAZOLINE-DIMETHOXYPYRENE. AN EFFECTIVE PROMOTER SYSTEM FOR PHOTOINDUCED ELECTRON TRANSFER PROMOTED REDUCTIVE TRANSFORMATIONS OF ORGANIC COMPOUNDS

Eietsu Hasegawa,* Harumi Hirose, Kosuke Sasaki, Shinya Takizawa, Takayuki Seida, and Naoki Chiba

Department of Chemistry, Faculty of Science, Niigata University, Ikarashi-2 8050, Niigata 950-2181, Japan

Abstract – 2-(*p*-Methoxyphenyl)-1,3-dimethylbenzimidazoline (ADMBI) and 2-(*o*-hydroxyphenyl)-1,3-dimethylbenzimidazoline (HPDMBI) are used as reducing reagents in 1,8-dimethoxypyrene (1,8-DMP) sensitized, photoinduced electron transfer (PET) reactions. This system was effectively used for PET induced, reductive transformations of various organic substrates, including α,β-epoxy ketones, the olefin tethered 2-bromomethyl-1-tetralone, and *o*-allyloxy-iodobenzene, as well as for the deprotection reactions of dodecyl-2-benzoylbenzoate and *N*-sulfonylindole. The results of studies show that 1,8-DMP is a more effective sensitizer than the previously used 9-methylcarbazole for deprotection of *N*-methyl-4-picolinium ester.

INTRODUCTION

About two decades ago, 1,3-dimethyl-2-phenylbenzimidazoline (DMPBI) was shown to be a hydride-transfer reagent for reductive transformations of organic compounds.[1] Subsequently, it was demonstrated that DMPBI promotes radical reactions, in which it acts as an effective hydrogen atom-donor.[2] These earlier observations suggested that DMPBI and its derivatives behave in a manner similar to biologically relevant dihydropyridines (*i.e.* NADH). This has been confirmed by the results of further later investigations in this area.[3]

In recent years, we have investigated photoinduced electron transfer (PET) reactions of carbonyl compounds and halides.[4-7] In this effort, a substance possessing both electron-donating and hydrogen

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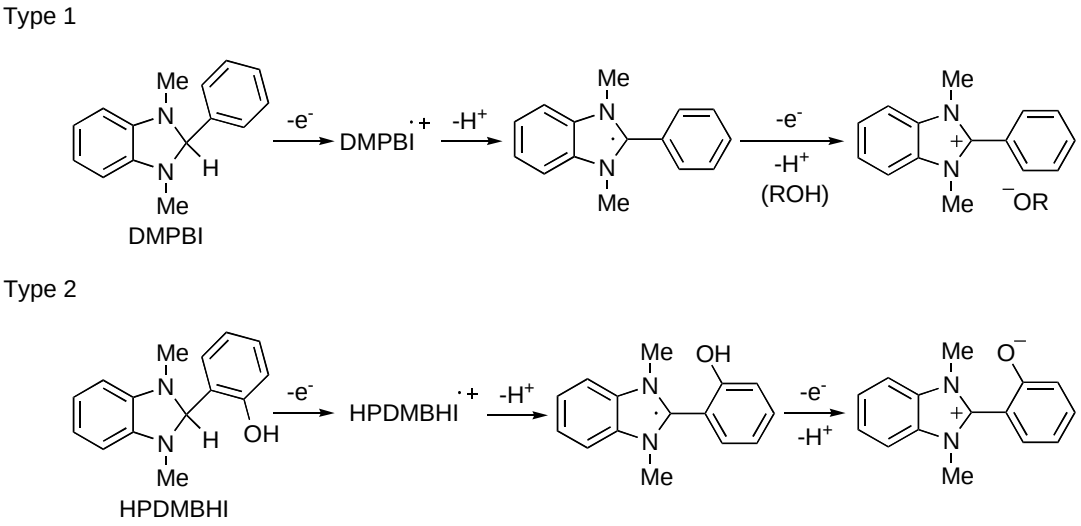
This paper is dedicated to Professor Emeritus Keiichiro Fukumoto on the occasion of his 75th birthday.

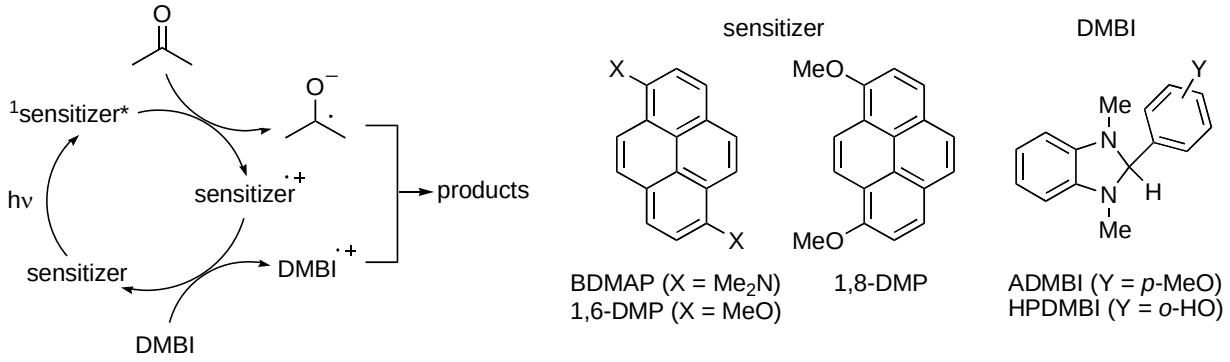
atom-donating abilities was required to serve as an effective reducing reagent. An evaluation of its properties suggested that DMPBI would meet these requirements. About ten years ago, we first applied DMPBI in PET promoted transformations of aromatic epoxy ketones to hydroxy ketones.[8] We found that the use of DMPBI led to processes that took place in much higher product yields than those that employed previously reported PET conditions.[4,9] In the reaction investigated, DMPBI serves as a two-electron- and one-proton-donor, therefore, addition of an appropriate proton-donor (ROH) is required to complete the reaction (Type 1 in Scheme 1). A second break-through occurred when 2-(*o*-hydroxyphenyl)-1,3-dimethylbenzimidazoline (HPDMBI) was employed in the above types of PET reactions. In this case, no additional proton-donor is required because HPDMBI acts as a two-electron- and two-proton-donor in which its phenolic group serves as a second proton source (Type 2 in Scheme 1).[10] Since the time of these early studies, we developed a variety of PET promoted reactions, in which several benzimidazolines (DMBI), including DMPBI and HPDMBI, were used to achieve reductive transformation of carbonyl compounds and halides.[11-16]



Scheme 1

For promoting PET reactions, photosensitization methods have been employed frequently owing to several advantageous features that do not exist with direct irradiation induced PET.[17] By using photosensitization, the photosensitizer is selectively excited by the light that is not absorbed by substrates. As a result, undesired photoreactions emanating from the excited states of the substrates do not take place. Dimethylamino- or methoxy-substituted arenes have been used as sensitizers for PET promoted reductive transformations of a variety of organic compounds.[18-20] Recently, we demonstrated that both 1,6-bis-dimethylaminopyrene (BDMAP) and 1,6-dimethoxypyrene (1,6-DMP) are effective sensitizers in cooperation with benzimidazolines (DMBIs) for PET reduction reactions of carbonyl compounds.[16] In the

photosensitization cycle followed in these processes (Scheme 2), the sensitizer first absorbs light to generate its singlet excited state, from which a single electron is transferred to a carbonyl substrate to generate the carbonyl radical anion (ketyl radical). The simultaneously formed radical cation of sensitizer is subsequently reduced by DMBI to regenerate its ground state. Finally, the formed radical cation of DMBI reacts with ketyl radicals to give reduction products.

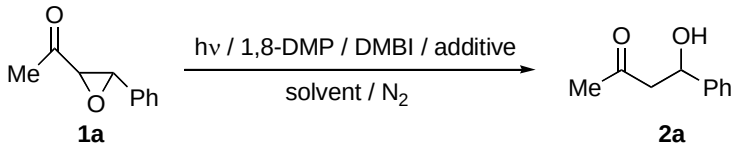


Scheme 2

RESULTS AND DISCUSSION

Below, we describe results arising from an investigation of PET sensitization reactions of organic substrates in which 1,8-dimethoxypyrene (1,8-DMP)[21] is used for the first time as an electron donor sensitizer together with 2-(*p*-methoxyphenyl)-1,3-dimethylbenzimidazoline (ADMBI) and 2-(*o*-hydroxyphenyl)-1,3-dimethylbenzimidazoline (HPDMBI). In earlier efforts, we have demonstrated that the conversion of epoxy-ketones to the corresponding hydroxy-ketones is a useful process to evaluate new electron transfer conditions.[4,5,7,8,10,12,13,16] Thus, the PET sensitization method that relies on the use of 1,8-DMP and DMBIs was first probed employing the ring opening reaction of epoxy-ketone **1a** (Table 1). As can be seen by viewing the data in Table 1, 1,8-DMP was found to be similarly effective to 1,6-DMP and BDMAP for reductive ring opening PET reactions of **1a** with ADMBI and HPDMBI in DMF (entries 1 and 2).[16] Notably, addition of $Mg(ClO_4)_2$ resulted in a higher conversion of **1a** and an increased yield of **2a** (compare entry 3 to entry 2). Solvent property is one of the key factors in governing PET reactions in solution.[17] As data in Table 1 show, reaction of **1a** takes place irregardless of the polarity of the solvent (entries 4~7).[22] It should be noted that the relatively less polar solvent benzotrifluoride (BTF) can also be used in this process. Although BTF is suggested to be a more environmentally benign solvent than benzene and methylene chloride,[23] it has not been previously used for PET reactions.[24] Another notable observation is that the pale yellow solution of 1,8-DMP in BTF and methylene chloride became brown on irradiation while a significant color change is not observed when **1a** and HPDMBI are present.

Table 1. 1,8- sensitized PET reaction of **1a** with DMBI in various solvents.[a]



1a **2a**

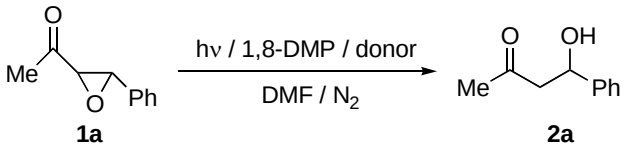
entry	DMBI	solvent	additive (equiv *vs* **1a**)	irrad time (min)	conv of **1a** (%)[b]	yield of **2a** (%)[b,c]
1	ADMBI	DMF	AcOH (7.0)	60	73	78
2	HPDMBI	DMF	-	60	45	70
3	HPDMBI	DMF	$Mg(ClO_4)_2$ (1.2)	30	83	89
4	HPDMBI	MeCN	-	60	25	72
5	HPDMBI	THF	-	60	58	83
6	HPDMBI	CH_2Cl_2	-	60	35	80
7	HPDMBI	BTF	-	60	75	83

[a]**1a** (0.20 mmol), 1,8-DMP (0.05 equiv *vs* **1a**), DMBI (1.2 equiv *vs* **1a**), solvent (2.0 mL), λ > 340 nm. [b]Determined by ^{1}H NMR. [c]Based on the conversion of **1a**.

The expected reaction pathway followed in these reactions is outlined in Scheme 2. Irradiation selectively generates the excited state of 1,8-DMP (1,8-DMP*) whose reducing ability is similar to those of 1,6-DMP and BDMAP.[25] Single electron transfer (SET) from 1,8-DMP* to **1a** occurs to produce the radical cation of 1,8-DMP (1,8-DMP$^{\bullet+}$) and the radical anion of **1a** (**1a**$^{\bullet-}$). $Mg(ClO_4)_2$ could suppress the back electron transfer from **1a**$^{\bullet-}$ to 1,8-DMP$^{\bullet+}$ through an ion-pair exchange effect, and therefore the quantum efficiency of the reaction increases.[26] 1,8-DMP$^{\bullet+}$ returns to its ground state by SET from DMBI. If SET with **1a** is absent, 1,8-DMP* undergoes energy wasting decay and, in some cases decomposition occurs as is observed in BTF and methylene chloride solutions lacking **1a**.

We next examined reactions of **1a** in which the DMBIs are replaced by other electron donors, including ascorbic acid (AA)[19,27] and 3,5-bis(ethoxycarbonyl)-2,6-dimethylpyridine (Hantzch dihydropyridine, HDHP)[10,28] which have been previously used for PET reactions. As the results presented in Table 2 demonstrate, by using AA, Et_3N and HDHP reaction does not take place and **1a** is recovered almost quantitatively (entries 1-3). On the other hand, Me_2NPh promotes reaction of **1a** to some extent (entry 4) and, as already described, both HPDMBI and ADMBI are effective. These observations can be understood by considering the thermodynamic/kinetic feasibility of SET from these donors to 1,8-DMP$^{\bullet+}$. Looking at the calculated free energy changes (ΔG) given in Table 2, it is seen that endoergonic SET is expected for AA, Et_3N and HDHP whose oxidation potentials are greater than that of 1,8-DMP. In contrast SET between 1,8-DMP$^{\bullet+}$ and Me_2NPh, HPDMBI or ADMBI, whose oxidation potentials are lower than that of 1,8-DMP, should be exoergonic.

Table 2. 1,8-DMP sensitized PET reaction of **1a** with various donors.[a]

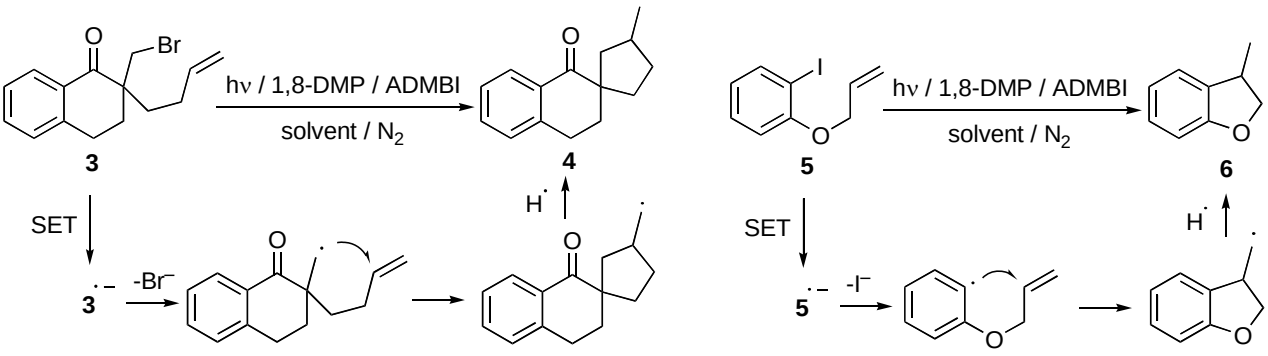


1a **2a**

entry	donor	$E^{ox}_{1/2}$ (V *vs* SCE)	ΔG [b] (kcal/mol)	conv of **1a** (%)[c]	yield of **2a** (%)[c,d]
1	AA	1.08	5.8	- [f]	
2[e]	Et_3N	0.98	3.5	- [f]	
3	HDHP	0.93	2.3	- [f]	
4[e]	Me_2NPh	0.78	-1.2	34	32
5	HPDMBI	0.30[g]	-12.2	45	70
6[e]	ADMBI	0.28[g]	-12.7	73	78

[a]**1a** (0.20 mmol), 1,8-DMP (0.05 equiv *vs* **1a**), donor (1.2 equiv *vs* **1a**), DMF (2.0 mL), $\lambda > 340$ nm, 60 min. [b]$\Delta G = 23.06$ [$E^{ox}_{1/2}$ (donor) - E^{o} (1,8-DMP)]. [c]Determined by ^{1}H NMR. [d]Based on the conversion of **1a**. [e]AcOH (7.0 equiv *vs* **1a**) was added. [f]**1a** was recovered. [g]Reference 16.

On the basis of above observations, photosensitization system consisting of 1,8-DMP and DMBIs is expected to be ideally suited for PET reduction reactions of a variety of substances. To probe the viability of this proposal, we examined two representative dehalogenation reactions of the olefin tethered 2-bromomethyl-1-tetralone **3**[14] and *o*-allyloxy iodobenzene **5**[12] which produce the corresponding products **4** and **6** through an 5-*exo* radical cyclization pathway[29] (Scheme 3 and Table 3).



Scheme 3

PET spirocyclization reaction of **3** to give **4**, sensitized by 1,8-DMP and ADMBI proceeds both in DMF and BTF in yields that are comparable to those promoted by using 1,6-DMP and BDMAP (entries 1 and 2).[16] In the case of BTF, precipitation of imidazolium bromide interfered with light absorption by 1,8-DMP. Addition of water to the BTF solution solved this problem to some extent, and the conversion of **3** and the yield of **4** increased slightly (entry 3). The 1,8-DMP and ADMBI based photosensitization

method was also effective in inducing the dehalogenation/cyclization reaction of olefin tethered aromatic iodide **5** in DMF and BTF although the yields of **6** were relatively low (entries 4 and 5). Notably, when ADMBI is replaced by the hydrogen atom donor 1,4-cyclohexadiene (CHD, 53 equiv), only a trace amount of **6** is detected.

Table 3. 1,8-DMP sensitized PET reactions of **3** and **5** with ADMBI.[a]

entry	halide	solvent	irrad time (h)	conv of halide (%)[b]	product	yield of product (%)[b,c]
1	**3**	DMF	5	95	**4**	62
2	**3**	BTF	5	76	**4**	71
3	**3**	BTF[d]	5	83	**4**	81
4	**5**	DMF	8	85	**6**	36
5	**5**	BTF	8	73	**6**	28

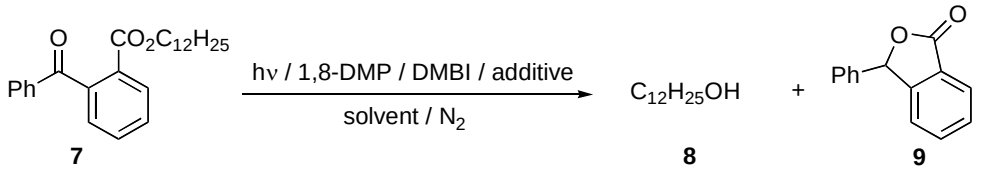
[a]**3** (0.50 mmol); **5** (0.20 mmol), 1,8-DMP (0.05 equiv *vs* halide), ADMBI (1.2 equiv *vs* halide), solvent (5.0 mL for **3**, 4.0 mL for **5**), $\lambda > 360$ nm for **3**; $\lambda > 340$ nm for **5**. [b]Determined by ^{1}H NMR. [c]Based on the conversion of halide. [d]H_2O (1 mL) was added as a co-solvent.

In some cases, above the DMBIs act as effective reducing reagents for PET reactions carried out in the absence of 1,8-DMP. This technique serves as a practical alternative particularly for reactions of substrates which absorb Pyrex™-glass filtered light of which ordinary photoreaction vessels are made. For example, irradiation ($\lambda > 280$ nm) of 1,3-diphenyl-2-propene-1-one oxide **1b** (chalcone epoxide, 0.40 mmol) with HPDMBI (1.2 equiv) in THF or BTF (4.0 mL) for 1 h leads to production of the desired hydroxy-ketone **2b** (81% yield at 84% conv of **1b** in THF; 91% yield at 81% conv of **1b** in BTF). Similarly, when **3** (0.50 mmol) was irradiated with ADMBI (1.2 equiv) in MeCN or BTF (5.0 mL) for 4 h, **4** was obtained in moderate to good yields (60% in MeCN; 74% at 98% conv of **3** in BTF). Also, irradiation of **5** (0.20 mmol) with ADMBI (1.2 equiv) in BTF (4.0 mL) for 4 h gave **6** in a 35% yield at 73% conversion of **5**.

Photodeprotection reaction is recognized as a useful technique in photolithography as well as chemical biology.[30] As described above, BTF was found to be a tolerable solvent for PET reactions. Then, we decided to apply 1,8-DMP sensitized PET method in various solvents including BTF to three representative deprotection reactions.

Nitrobenzyl and phenacyl groups have been used previously for photoremovable protecting groups for alcohols and amines, especially in peptide synthesis.[31] About ten years ago, Porter, *et al.* reported that benzoylesters of alcohols are removed efficiently by using photochemical methods. For example, irradiation ($\lambda > 280$ nm) of dodecyl 2-benzoyl benzoate **7** with cyclohexyl amine (10 equiv) in 1:1 benzene and MeCN leads to generation of dodecanol **8** and the lactone **9** (95% each).[32] When 1,8-DMP

Table 4. 1,8-DMP sensitized PET reaction of **7** with DMBI.[a]

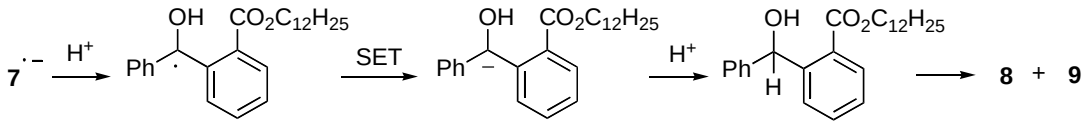


7 **8** **9**

entry	DMBI	solvent	additive (equiv *vs* **7**)	conv of **7** (%)[b]	yields (%)[b,c] **8**	**9**
1	HPDMBI	DMF	-	52	~100	79
2	ADMBI	DMF	AcOH (7.0)	~100	95	84
3	ADMBI	BTF	AcOH (7.0)	99	93	-[d]

[a]**7** (0.20 mmol), 1,8-DMP (0.05 equiv *vs* **7**), DMBI (1.2 equiv *vs* **7**), solvent (2.0 mL), $\lambda > 360$ nm, 6 h. [b]Determined by ^{1}H NMR. [c]Based on the conversion of **7**. [d]Small amount of **9** (~3%) was detected.

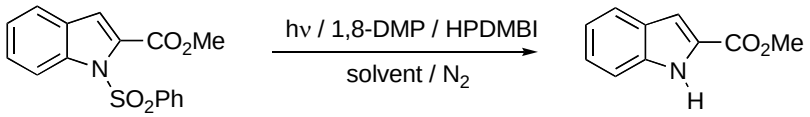
sensitized method using DMBI was applied to the deprotection reaction of **7**, the desired dodecanol **8** is obtained in excellent yields (> 90%) (Table 4). While **9** is also obtained in reasonable yields in DMF, only small amount of this substance is detected when BTF is used as solvent. This finding is difficult to explain. A plausible mechanism for the deprotection reaction is shown in Scheme 4. Ketyl radical ($7^{\bullet-}$) accepts two protons and a single electron from $DMBI^{\bullet+}$ and AcOH to produce an intermediate diarylcarbinol which then undergoes lactonization to produce **8** and **9**.



Scheme 4

Desulfonylation reactions of *N*-sulfonamides generally take place under relatively vigorous conditions.[33] Recently, Padwa, *et al.* reported a PET based mild desulfonylation method using Et_3N and nBu$_3$SnH. This method was applied to the desulfonylation reaction of *N*-sulfonylindole **10**, which produces the deprotected product **11** (96%).[34] Accordingly, sulfonyl substitution at the benzene-ring occurs in the absence of nBu$_3$SnH. We believed that this methodology, using an environmentally undesired organotin reagent and high energy short wavelength light (254 nm), could be advantageously modified by substituting the PET conditions we have developed (Table 5). Indeed, desulfonylation of the *N*-sulfonylindole **10** takes place smoothly and in excellent yield by employing PET reaction with 1,8-DMP and HPDMBI in MeCN (entry 1). Although a longer irradiation time is required when reaction is carried out in BTF, the yield of **11** remains high. The expected pathway followed in this process is shown in Scheme 5. Radical anion $\mathbf{10}^{\bullet-}$, formed by SET between 1,8-DMP* and **10** ($E^{red}_{1/2}$ = -0.95 V *vs*

Table 5. 1,8-DMP sensitized PET reaction of **10** with HPDMBI. [a]

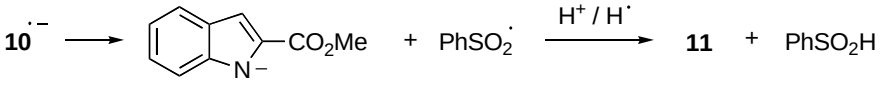


10 **11**

entry	solvent	irrad time (min)	conv of **10** (%)	yield of **11** (%)[b,c]
1	MeCN	30	100	93
2	BTF	120	97	84

[a]**10** (0.40 mmol), 1,8-DMP (0.05 equiv *vs* **10**), HPDMBI (1.2 equiv *vs* **10**), solvent (4.0 mL), $\lambda > 360$ nm. [b]Isolated yield. [c]Based on the conversion of **10**.

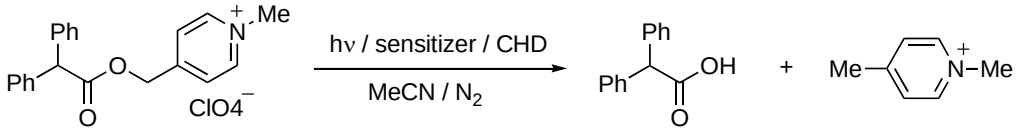
SCE), undergoes desulfonylation to give indole anion and sulfonyl radical which accept a respective proton and hydrogen atom from HPDMBI$^{\bullet+}$ to produce **11** and $PhSO_2H$.



Scheme 5

The final process we have explored is the deprotection of *N*-methylpicolinium carboxylate **12** that was first reported by Falvey and co-workers.[35] In Falvey's work, a stoichiometric amount of 9-methylcarbazol (9-MC) was used as a sensitizer and an excess amount of CHD was employed as a hydrogen atom and proton donor. We reexamined this process using both 1,8-DMP and 9-MC with CHD in MeCN (Table 6). Using stoichiometric amounts of these sensitizers, no significant differences in conversion and product

Table 6. 1,8-DMP sensitized PET reaction of **12** with CHD.[a]



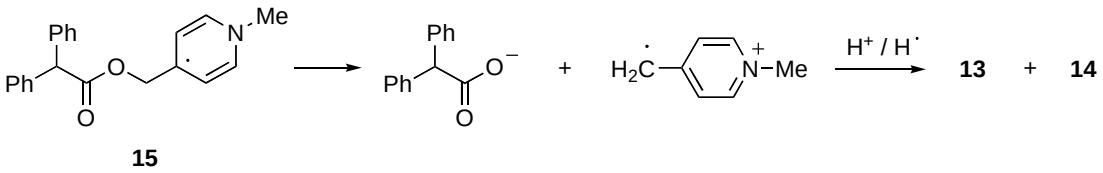
12 **13** **14**

entry	sensitizer (equiv *vs* **12**)	irrad wavelength	conv of **12** (%)[b]	yields (%)[b,c] **13**	**14**
1	9-MC (1.0)	$\lambda > 320$ nm	100	77	80
2	1,8-DMP (1.0)	$\lambda > 320$ nm	100	74	79
3	9-MC (0.05)	$\lambda > 340$ nm	18	6	11
4	1,8-DMP (0.05)	$\lambda > 360$ nm	100	89	~100

[a]**12** (0.02 mmol), CHD (1.0 ml), MeCN (4.0 mL), 3 h. [b]Determined by ^{1}H NMR. [c]Based on the conversion of **12**.

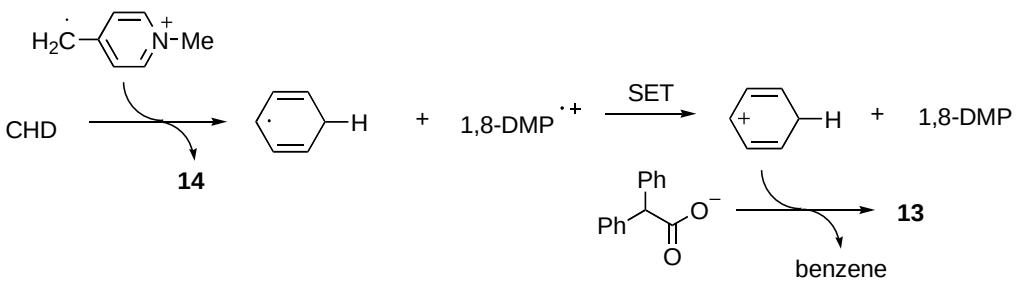
yields are detected (entries 1 and 2). However, when the quantities of the sensitizers are decreased to catalytic levels and irradiation takes place with longer wavelength light, significant differences appear between the 9-MC and 1,8-DMP promoted reactions (entries 3 and 4).

The large differences observed between PET reaction of **12** sensitized by 1,8-DMP *versus* 9-MC appears to be due to differences in their UV-VIS absorption profiles. Namely, end-absorption of 9-MC is around 360 nm while that of 1,8-DMP extends to around 400 nm in MeCN while oxidizaing abilities of their excited states are comparable.[25,36] Another notable observation is that the results of cyclic voltammometric studies show that 9-MC displays irreversible redox behavior while 1,8-DMP behaves reversibly. This finding suggests that the radical cation formed from 9-MC is less stable than that derived from 1,8-DMP. A plausible mechanistic route for PET deprotection of **12** is outlined in Scheme 6. Accordingly,[35] the radical **15**, generated from SET between 1,8-DMP* and **12** ($E^{red}_{1/2}$ = -0.95 V *vs* SCE), undergoes fragmentation to give diphenylacetate and the picolinium radical, which then abstract a respective proton and hydrogen atom to form **13** and **14**, repectively.



Scheme 6

The interesting issues in this process are, 1) what process intervenes to return 1,8-DMP$^{\bullet+}$ to its neutral form to participate in the catalytic cycle, and 2) what species donates a proton to the acetate. Unlike DMBIs, CHD does not have a sufficiently strong electron donating ability (+1.74 V *vs* SCE)[37] to transfer single electron to 1,8-DMP$^{\bullet+}$. A more plausible candidate for this role is the CHD radical that is generated by hydrogen atom transfer between CHD and the picolinium radical (Scheme 7).[38] SET between the CHD radical and 1,8-DMP$^{\bullet+}$ generates the CHD cation that should be acidic enough to protonate acetate anion and produce benzene.



Scheme 7

CONCLUSION

Electron transfer is a fundamental process that produces charged radicals that serve as intermediates in many chemical and biological reduction and oxidation (redox) reactions.[39,40] While the use of redox reagents as well as electrochemical procedures are common ways to ion radical species, reactive species in organic chemistry, PET represents a mild, practical alternative.[17] Above, we have demonstrated that DMBI and 1,8-DMP is a useful promoter system for promoting PET reductive transformations of a variety of organic compounds. Among characteristic features of the PET method based on this combination are that 1) two types of DMBIs can be chosen as reducing agents in PET promoted reductions, 2) 1,8-DMP is an effective photosensitizer that absorbs incident light near the visible region, thus avoiding unwanted photoreactions of substrates, 3) DMBIs are compatible with 1,8-DMP sensitized PET reaction conditions while DMBIs can be also used in the absence of sensitizers, 4) 1,8-DMP is not only effective with DMBIs but also with CHD, and 5) BTF, proposed as an environmentally benign solvent, can be employed in these PET reaction conditions.

EXPERIMENTAL

General procedures.

NMR spectra were recorded in $CDCl_3$ with Me_4Si as an internal standard at 200 MHz and 270 MHz for ^1H NMR, and 50 MHz and 68 MHz for ^{13}C NMR. Uncorrected melting points are reported. Absorption and fluorescence spectra were measured in MeCN. Oxidation and reduction potentials in MeCN were measured with cyclic voltammetry according to the previously reported procedure.[16] Photoreactions were conducted in a Pyrex test tube (1.5 cm diameter) immersed in a water bath at room temperature with a 500 W Xe lamp as a light source. Column chromatography was performed with silica gel (Wakogel C-200). Preparative TLC was performed on 20 cm x 20 cm plates coated with silica gel (Wakogel B-5F). Anhydrous DMF was purchased and used for the photoreactions. MeCN was distilled over P_2O_5 and subsequently with K_2CO_3. THF was distilled over sodium–benzophenone under N_2. Other reagents and solvents were purchased and used without further purification. ADMBI and HPDMBI were prepared by the previously reported methods.[15] 1,8-DMP was similarly prepared to 1,6-DMP[16] by the slight modification of the literature procedure[41] (see below). 9-MC[42] and HDHP[43] were prepared according the to literature reported procedures. Substrates (**1a**,[44] **1b**,[4] **3**,[16] **5**,[12] **7**,[32] **10**,[34] and **12**[35]) and photoproducts (**2a**,[44] **2b**,[4] **4**,[16] **6**,[12] **8**,[32] **9**,[32] **11**,[34] **13**,[35] and **14**[35]) are known compounds.

Preparation and property of 1,8-DMP.

Procedure to obtain the mixture of 1,6-pyrenedione and 1,8-pyrenedione was previously reported.[16] A typical procedure is given as follows. To the crude solid containing a mixture of 1,6-pyrenedione and

1,8-pyrenedione (13 mmol), and *n*-Bu_4NBr (419 mg, 1.3 mmol) in aqueous THF (THF + H_2O = 58 mL + 20 mL) was added $Na_2S_2O_4$ (13.6 g, 78 mmol) in H_2O (40 mL). The resulting mixture was stirred at room temperature for 1 h. Then, KOH (16.8 g, 299 mmol) in H_2O (40 mL) was added, and Me_2SO_4 (25.8 mL, 273 mmol) was slowly added in an ice–water bath. After the resulting mixture was stirred at room temperature for 22 h, addition of H_2O was followed by extraction with CH_2Cl_2. The extract was washed with H_2O and dried over anhydrous $MgSO_4$, and then concentrated *in vacuo*. Silica-gel column chromatography of the residue (CH_2Cl_2 / *n*C_6H_{14} = 1 / 2) gave a mixture of 1,6-dimethoxypyrene and 1,8-dimethoxypyrene (724 mg, 2.76 mmol, 21%). This mixture was subjected to fractional crystallization three times from C_6H_5Cl, and then 1,6-DMP (239 mg, 0.91 mmol, 7%) was obtained as yellow needles: mp 246.5–247.0 °C (lit.,[41] 244–245 °C). Then, 1,8-DMP was concentrated in the filtrate, from which 1,8-DMP (142 mg, 0.54 mmol, 4%) was obtained as yellow needles: mp 208.3-210.0 °C (lit.,[45] 201-202 °C). 1,6-DMP: IR (KBr) 2950, 1518, 1030 cm^{-1}; ^{1}H-NMR (270 MHz) ™4.17 (s, 6H), 7.54 (d, 2H, *J* = 8.37 Hz), 7.94 (d, 2H, *J* = 9.18 Hz), 8.06 (d, 2H, *J* = 8.37 Hz), 8.26 (d, 2H, *J* = 9.18 Hz); 1,8-DMP: IR (KBr) 2950, 1588, 1020 cm^{-1}; ^{1}H-NMR (270 MHz) ™4.16 (s, 6H), 7.51 (d, 2H, *J* = 8.51 Hz), 7.77 (s, 2H), 8.03 (d, 2H, *J* = 8.51 Hz), 8.41 (s, 2H); ^{13}C-NMR (68 MHz) ™56.1 (q), 108.0 (d), 120.1 (d), 120.8 (s), 124.5 (d), 124.7 (d), 125.6 (s), 125.9 (s), 152.9 (s).

Solubilities of 1,6-DMP and 1,8-DMP in several solvents were qualitatively checked by adding DMP (1 mmol) into a solvent (1.0 mL). Both 1,6-DMP and 1,8-DMP were insoluble in MeOH. While 1,6-DMP was not completely dissolved in MeCN and BTF, 1,8-DMP was soluble in these solvents. Both 1,6-DMP and 1,8-DMP were soluble in DMF, CH_2Cl_2, and THF.

General procedure of PET reactions.

A solution of a substrate (**1**, **3**, **5**, **7**, **10**: 0.20–0.50 mmol) and DMBI (0.24–0.60 mmol) with or without 1,8-DMP (1.0–2.5 x 10^{-2} mmol) in a solvent (DMF, MeCN, CH_2Cl_2, THF, BTF 2.0–5.0 mL), in the presence or absence of AcOH (1.40 mmol) or $Mg(ClO_4)_2$ (0.24 mmol), was purged with N_2 for 5-10 min prior to irradiation. In the case of **12**, a solution of **12** (0.02 mmol), CHD (1.0 mL, 10.6 mmol) and 9-MC or 1,8-DMP (0.02 mmol or 0.001 mmol) in MeCN (4.0 mL) was purged with N_2 for 10 min before irradiation. These solutions were irradiated with the light using cut-off glass-filters (λ > 320 nm, 340 nm, and 360 nm for sensitization reactions) or not using a filter (λ > 280 nm through Pyrex) for an appropriate irradiation time. Photolysates obtained from the reactions of **1a**, **5**, **7** in DMF and 5 in BTF were subjected to the extraction with Et_2O for **1a** and EtOAc for **5**, **7**. The extracts were washed with water and satd. aqueous NaCl, and dried over anhydrous $MgSO_4$ and then concentrated. Photolysates from other reactions in MeCN, CH_2Cl_2, THF, and BTF were directly concentrated. The resulting residues were analyzed with ^{1}H-NMR using triphenylmethane for **1a**, **3**, **7**, 1,4-dimethoxybenzene for **5**, and

1,3,5-trimethoxybenze for **12** as internal standards. For reactions of **1b** and **10**, the residues were subjected to silica-gel column or TLC separation using appropriate solvents (column: CH_2Cl_2 for **1b**, TLC: EtOAc / *n*-C_6H_{14} = 1 / 3 for **10**) to give the starting materials and the products. Photoproducts were identified by analyses with their NMR and IR spectra.

ACKNOWLEDGEMENTS

We are grateful to Professor Patrick S. Mariano (University of New Mexico, USA) for his valuable comments and editing. This work was partly supported by the grant from the Uchida Energy Science Promotion Foundation.

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MeCN (see Experimental Section).

22. Polarity of the solvents estimated by E_T[30] (kcal/mol): 45.7, 43.3, 41.0, 39.3, 37.4 for MeCN, DMF, CH_2Cl_2, $C_6H_5CF_3$, THF, respectively.[24]
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