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Photoinduced electron-transfer systems consisting of electron-donating pyrenes or anthracenes and benzimidazolines for reductive transformation of carbonyl compounds

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Abstract—Photoinduced electron-transfer reactions of several ketone substrates were studied to evaluate the utilities of 1,6-bis(dimethylamino)pyrene (BDMAP), 1,6-dimethoxypyrene (DMP), 9,10-bis(dimethylamino)anthracene (BDMAA), and 9,10-dimethoxyanthracene (DMA) as electron-donating sensitizers cooperating with 2-aryl-1,3-dimethylbenzimidazolines. BDMAP and DMP generally led higher conversion of ketones and better yield of reduction products compared to BDMAA and DMA.

1. Introduction

Electron transfer is a fundamental reaction process, which is operating in reduction and oxidation (redox) reactions in chemical and biological systems.[1] Single electron transfer (SET) of neutral organic molecules generates radical ions that undergo various transformations.[2] Whereas using redox reagents as well as electrochemical procedures are traditional ways to generate these reactive species, photoinduced electron-transfer (PET) is an alternative method.[1] Without a doubt, PET chemistry of organic molecules has been a central topic in organic photochemistry over the past several decades.[3] Significant progress has been accomplished in understanding PET reaction mechanisms and application of PET reactions to organic synthesis. Reactivity of radical cations generated by PET processes between electron-donating substrates and electron-accepting sensitizers has been extensively investigated.[3] On the other hand, reactivity of radical anions has been less explored in PET reactions,[4] which must be in part ascribed to the fact that practical electron-donating sensitizers are few as compared to electron-accepting sensitizers such as aromatic nitriles, quinones, and cationic salts.

In the course of our research program focused on reaction mechanism and synthetic application of carbonyl radical anions (ketyl radicals) in PET reactions,[5] we needed to find effective PET conditions to generate such radical anions. Especially, to promote reactions of substrates not efficiently absorbing light filtered by Pyrex™ of which ordinary photoreaction vessels are made, electron-donating sensitizers absorbing light of longer wavelength were desired. Related to this purpose, we have also found that some benzimidazolines act as effective electron- and proton-donors to promote PET reduction of various carbonyl compounds in which their radical anions are generated.[6] In this context, we became interested in developing electron-donating sensitizers cooperating with benzimidazolines for PET-promoted reductions of carbonyl compounds.

For this objective, we chose dimethylamino- or methoxy-substituted pyrenes or anthracenes,[7] namely 1,6-bis(dimethylamino)pyrene (BDMAP), 1,6-dimethoxypyrene

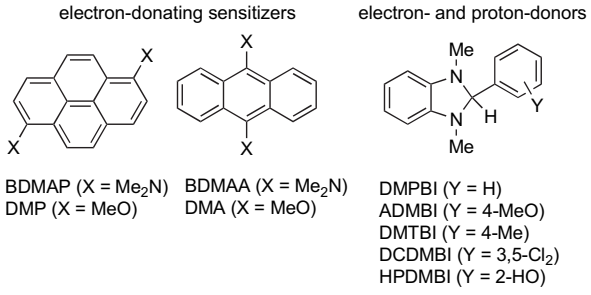

Chart 1.

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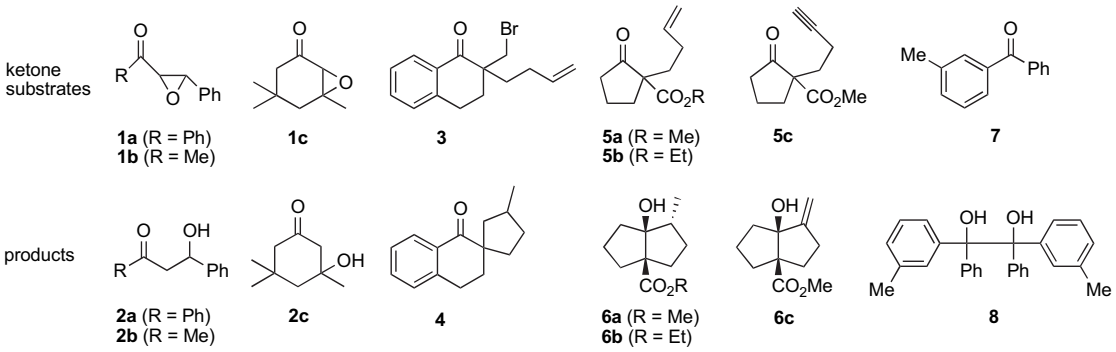


Chart 2.

(DMP), 9,10-bis(dimethylamino)anthracene (BDMAA), and 9,10-dimethoxyanthracene (DMA),[8] and five 2-aryl-1,3-dimethylbenzimidazolines (DMBIs), which are shown in Chart 1. Carbonyl substrates, epoxy ketones **1**, α-bromomethyltetralone **3**, carbon–carbon multiple bond tethered ketones **5**, and 3-methylbenzophenone **7**, and the corresponding PET reaction products **2**, **4**, **6**, and **8** are represented in Chart 2. In the reactions, unimolecular or bimolecular rearrangements of ketyl radicals of these substrates are expected to proceed, i.e., C_α–O bond cleavage of the ketyl radicals of **1**,[10] C_β–Br bond cleavage of the ketyl radical of **3**,[6e] intramolecular ketyl radical addition to C–C multiple bonds for **5**,[11] and dimerization of ketyl radical of **7**.[6g] We also conducted PET reactions using above four sensitizers with *N*,*N*-diethyl-*N*-trimethylsilylmethylamine (TMSA),[12] and using $Ru(bpy)_3Cl_2$, well-known PET sensitizer,[13] with DMBI. In this paper, we report the results obtained and discuss the features and the utilities of these PET systems.

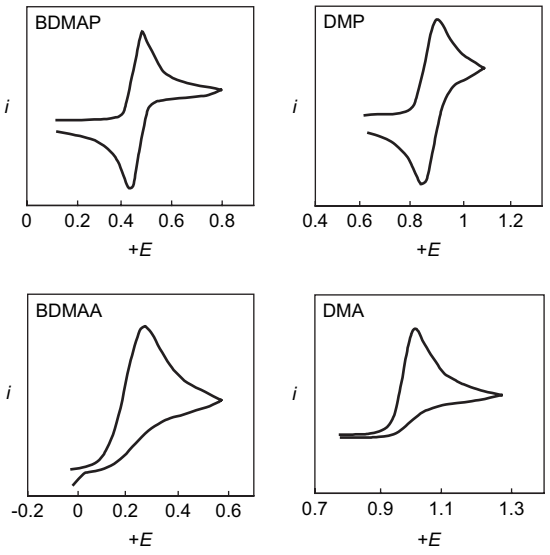


Figure 1. Cyclic voltammograms of sensitizers (*E* in V vs SCE).

2. Results and discussion

2.1. Fundamental properties of sensitizers and benzimidazolines, and basic concept of PET systems

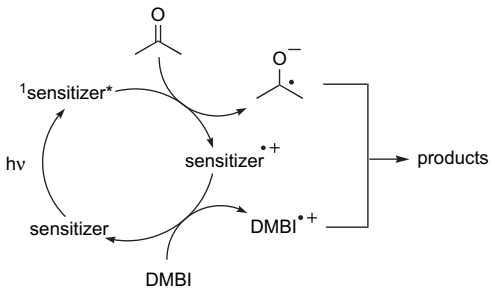
Selected photophysical and electrochemical data of the sensitizers are summarized in Table 1. These pyrenes and anthracenes can absorb the light of longer wavelength than both ketone substrates and DMBIs studied. As shown in Figure 1, cyclic voltammograms of BDMAP and DMP demonstrate reversible redox processes (differences of redox peak potentials are 56 mV and 66 mV, respectively), while those of BDMAA and DMA do not.

Expected PET reaction pathways are presented in Scheme 1. Selective photoexcitation of a sensitizer produces its singlet excited state (^{1}sensitizer*). The excited sensitizer donates single electron to a ketone within its lifetime to produce a radical cation of the sensitizer (sensitizer$^{\bullet+}$) and a radical anion of the ketone. Feasibility of this initial SET step is evaluated using the equation $\Delta G = E^{ox}_{1/2} - E_{ex} - E^{red}_{1/2} + C$, in which $E^{ox}_{1/2}$ and E_{ex} are a half-wave oxidation potential of the ground state and an excitation energy of a sensitizer, respectively, $E^{red}_{1/2}$ is a half-wave reduction potential of ketone substrate studied,[14] and *C* is the coulomb term that depends

Table 1. Photophysical and electrochemical data of sensitizers[a]

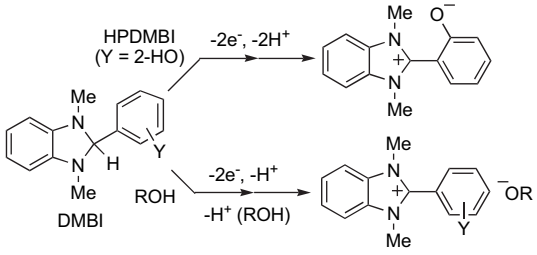
Sensitizer	λ_{max} (log ε) (nm)	λ_{end} (nm)	λ^F_{max} (nm)	τ (ns)	E_{ex} (kcal/mol)[b]	$E^{ox}_{1/2}$ in V vs SCE	E^{ox*} in V vs SCE
BDMAP	373 (4.35)	450	450	5.3[c]	64 (2.8)	+0.43[d]	−2.4
DMP	335 (4.38), 351 (4.57), 376 (4.16), 397(4.24)	420	402, 423	7.0[e]	72 (3.1)	+0.85[d]	−2.2
BDMAA	397 (3.76)	490	—[f]	—[f]	ca. 60 (2.6)[f,g]	+0.24	ca. −2.4
DMA	361 (3.79), 381 (3.95), 402 (3.87)	430	436	14.3[h]	70 (3.0)	+0.98	−2.0

[a] Measured in MeCN. λ_{max}, Absorption maximum; λ_{end}, end absorption; λ^F_{max}, fluorescence maximum; τ, lifetime; E_{ex}, excitation energy; $E^{ox}_{1/2}$, Half-wave oxidation potential of ground state and E^{ox*}, oxidation potential of the excited state that is obtained by the equation $E^{ox}_{1/2} - E_{ex}$.
[b] Values in parentheses are reported in eV.
[c] In 5% aqueous THF (Ref. 7d).
[d] Standard potential.
[e] The lifetime in DMF was 6.5 ns (this work).
[f] BDMAA was non-fluorescent.
[g] Estimated from the absorption spectrum.
[h] In heptane (Ref. 9b).



Scheme 1.

on the polarity of solvent used; the value for MeCN was reported to be −0.06 eV.[15] Formed sensitizer$^{\bullet+}$, except for BDMAA$^{\bullet+}$, is exoergonically reduced by DMBIs to its ground state because $E^{ox}_{1/2}$ of DMBIs ($E^{ox}_{1/2}$ in V vs SCE: +0.33, +0.28, +0.29, +0.40, and +0.30 for DMPBI, ADMBI, DMTBI, DCDMBI, and HPDMBI, respectively) are lower than that of each sensitizer. Then, a radical cation of DMBI (DMBI$^{\bullet+}$) and a radical anion of the ketone react with each other. For an effective sensitization (Scheme 1), a radical ion pair generated from a sensitizer and a ketone should smoothly dissociate. Therefore, a polar solvent is recommended to be used because such dissociation proceeds more efficiently in polar solvents than in nonpolar solvents.[16,17] Also noted that, in these PET reactions, HPDMBI is expected to act as a two-electron- and two-proton-donor,[6f,g] while other DMBIs are expected to perform as two-electron- and one-proton-donors that require addition of appropriate proton-donors (ROH) for reduction of ketones (Scheme 2).[6]



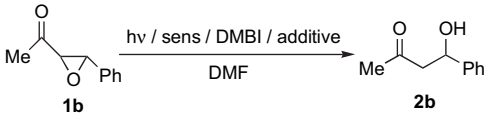
Scheme 2.

2.2. C_α–O bond cleavage of α,β-epoxy ketones 1

The first examples of PET reactions of α,β-epoxy ketones with amines were independently reported by Cossy[10a] and us.[10b] At that moment, triethylamine was used as an electron- and proton-donor, and yields of the expected β-hydroxy ketones were moderate. Furthermore, it was found that β-diketones were major products instead of the desired β-hydroxy ketones in the reactions of 1,3-diaryl-2,3-epoxy-1-propanones (chalcone epoxides) with triethylamine.[10b] A breakthrough to solve this problem was a discovery of DMBIs, which act as effective electron- and proton-donors to give β-hydroxy ketones.[6]

First, we conducted PET reactions of epoxy ketones **1** to compare DMP, BDMAA, and DMA with previously examined BDMAP.[6] Whereas reactions of **1a** with ADMBI in DMF–AcOH afforded **2a** (86% for BDMAP, 85% for DMP, 68% for BDMAA, 62% for DMA based on the conversions of **1a**), some conversions from **1a** to **2a** were also

Table 2. PET reactions of **1b** with DMBI[a]



Exp	Sensitizer	DMBI	Additive	Conv. of **1b**[b] (%)	Yield of **2b**[b,c] (%)
1	BDMAP	ADMBI	AcOH	64	80
2	DMP	ADMBI	AcOH	67[d]	84
3	BDMAA	ADMBI	AcOH	57	—[e]
4	DMA	ADMBI	AcOH	54	64
5	BDMAP	HPDMBI	—	41	93
6	DMP	HPDMBI	—	30	86
7	BDMAA	HPDMBI	—	15	92
8	DMA	HPDMBI	—	30	90

[a] Compound **1b** (0.40 mmol), sensitizer (0.05 equiv vs **1b**), DMBI (1.2 equiv vs **1b**), AcOH (5.0 equiv vs **1b**), DMF (4 mL), λ>340 nm for 1 h.
[b] Determined on the basis of isolated compounds.
[c] Based on the conversion of **1b**.
[d] Determined with ^{1}H NMR.
[e] Detected with ^{1}H NMR but not isolated.

observed without irradiation in the cases of BDMAP and BDMAA. Therefore, we concluded that **1a** is too reactive to evaluate these sensitizers. Then, we conducted PET reactions of **1b** under two different sensitization conditions, using sensitizer–ADMBI–AcOH[6d] and sensitizer–HPDMBI (Table 2).[6f] In most of the cases, **2b** was obtained in good yields based on the conversion of **1b**. However, in the case of BDMAA with ADMBI and AcOH, **2b** could not be isolated although **1b** was consumed (exp 3). Because the decomposition of **2b** was suspected during irradiation, **2b** was subjected to the same reaction condition using BDMAA. However, **2b** was quantitatively recovered. Although this unique behavior of BDMAA could not be rationalized at the moment, combination of ADMBI and AcOH seems not to be tolerated with BDMAA (also see exp 3 in Table 6). In the reactions using HPDMBI, the conversion of **1b** in the case of BDMAA was lower than those of other sensitizers (compare exp 7 to exps 5, 6, and 8). This must be in part ascribed to endoergonic electron transfer between BDMAA$^{\bullet+}$ and DMBIs (Scheme 1).

We then studied substituent effects of the phenyl group of DMBI on PET reaction of **1c** with BDMAP under the conditions same as experiment 1 in Table 2. Plots of the conversion of **1c** versus $E^{ox}_{1/2}$ of DMBIs are presented in Figure 2. The conversion of **1c** decreased as $E^{ox}_{1/2}$ increases, being consistent with the expected SET between BDMAP$^{\bullet+}$ and DMBI (Scheme 1).

A set of $Ru(bpy)_3Cl_2$ and amines is a well-known sensitization system for reductive transformation of organic compounds,[13d–h] and $Ru(bpy)_3Cl_2$ is considered to have some advantages compared with organic sensitizers, for example, photoexcitation using longer wavelength of light is possible, and separation of $Ru(bpy)_3Cl_2$ is more easily performed. Then, we examined PET reaction of **1b** using $Ru(bpy)_3Cl_2$ with ADMBI and AcOH or with HPDMBI (Table 3). In this sensitization system, Ru(I) is an expected reducing agent. Based on the standard potential of Ru(I) (E=−1.30∼−1.33 V vs SCE),[13a–c,18] reducing ability of Ru(I) must be

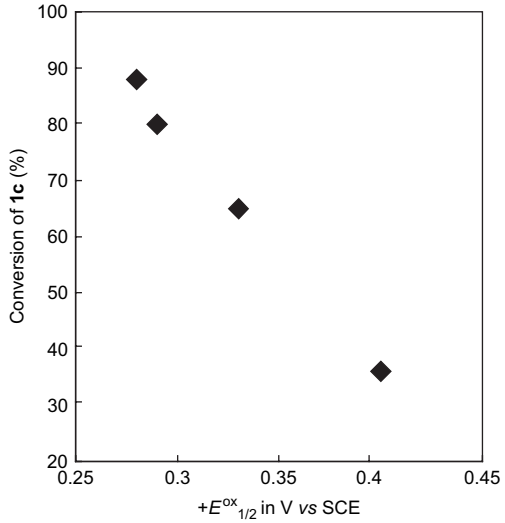
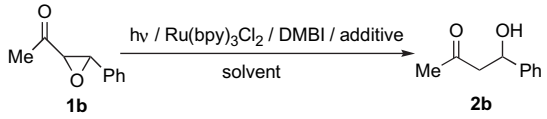


Figure 2. Plots of conversion of **1c** versus oxidation potentials of DMBIs in PET reaction of **1c** using BDMAP and DMBIs with AcOH in DMF.

Table 3. PET reactions of **1b** with $Ru(bpy)_3Cl_2$ and DMBI[a]



Exp	DMBI	Solv	Additive	Conv. of **1b**[b] (%)	Yield of **2b**[b,c] (%)
1	ADMBI	DMF	AcOH	71	41
2	HPDMBI	DMF	—	45	70
3	HPDMBI	MeCN	—	41	75
4	HPDMBI	THF	—	25	71
5	HPDMBI	MeOH	—	36	72

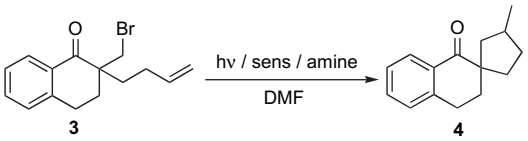
[a] Compound **1b** (0.40 mmol), $Ru(bpy)_3Cl_2$ (0.01 equiv vs **1b**), DMBI (1.2 equiv vs **1b**), AcOH (5.0 equiv vs **1b**), solvent (4 mL), λ>390 nm for 3 h.
[b] Determined with ^{1}H NMR.
[c] Based on the conversion of **1b**.

weaker than those of the excited states of above electron-donating pyrenes and anthracenes (see E^{ox*} in Table 1). As anticipated, although the reactions of **1b** proceeded, yields of **2b** were relatively low as compared to those reported in Table 2.

2.3. C_β–Br bond cleavage of α-bromomethyltetralone 3

Next, we conducted PET reactions of 2-bromomethyl-2-(3-butenyl)-1-tetralone **3** with ADMBI or TMSA (Table 4). Although yields of the expected spiro-cyclization product **4** were good in all cases, the conversions of **3** in the reactions with BDMAP or DMP were greater than those with BDMAA or DMA. This tendency was more significant in the reactions with TMSA. SET steps between ADMBI and sensitizers$^{\bullet+}$, except for BDMAA$^{\bullet+}$, are exoergonic as described above. On the other hand, calculated free energy changes for SET between TMSA ($E^{ox}_{1/2}$=+0.49 V vs SCE) and sensitizers$^{\bullet+}$ suggest that SET with DMP$^{\bullet+}$ is exoergonic (ΔG=−8.3 kcal/mol) while SET with BDMAP$^{\bullet+}$ is slightly endoergonic (ΔG=+1.4 kcal/mol). However, the conversions of **3** were not significantly different from each other (greater than 50% in both cases). This phenomena would

Table 4. PET reactions of **3** with ADMBI or TMSA[a]



Exp	Sensitizer	Amine	Conv. of **3**[b] (%)	Yield of **4**[b,c] (%)
1	BDMAP	ADMBI	83	57
2	DMP	ADMBI	70	54
3	BDMAA	ADMBI	42	53
4	DMA	ADMBI	56	59
5	BDMAP	TMSA	68	67
6	DMP	TMSA	53	59
7	BDMAA	TMSA	19	69
8	DMA	TMSA	27	46

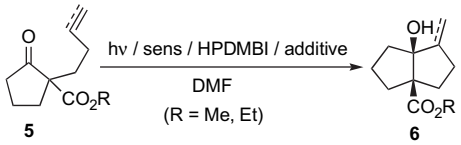
[a] Compound **3** (0.50 mmol), sensitizer (0.05 equiv vs **3**), ADMBI (1.2 equiv vs **3**), TMSA (5.0 equiv vs **3**), DMF (5 mL), λ>360 nm for 5 h.
[b] Determined with ^{1}H NMR.
[c] Based on the conversion of **3**.

be ascribed to an efficient and irreversible fragmentation of TMSA$^{\bullet+}$.[4a,19]

2.4. Intramolecular ketone–olefin or –acetylene coupling of C–C multiple bond tethered ketones 5

Cossy and co-workers reported that PET-promoted intramolecular coupling reactions of ketone carbonyls with C–C multiple bonds.[11] However, the light of shorter wavelength (254 nm) was usually used, and highly toxic hexamethylphosphoric triamide (HMPA) was in some cases required to obtain cyclization products in better yields. Therefore, we became interested in testing applicability of our PET methods to these synthetically relevant transformations. Then, we conducted reactions of **5a** with HPDMBI using four sensitizers. The results presented in Table 5 clearly indicate that both the conversion of **5a** and the yield of **6a** were essentially same regardless of the sensitizer (exps 1–4). Similar cyclization reactions of **5b** and **5c** were achieved by BDMAP with HPDMBI to produce **6b** and **6c**, respectively. Notably, addition of $Mg(ClO_4)_2$ significantly increased the

Table 5. PET reactions of **5** with HPDMBI[a]



Exp	**5**	Sensitizer	Additive	Conv. of **5**[b] (%)	Yield of **6**[b,c] (%)
1	**5a**	BDMAP	—	71	59
2	**5a**	DMP	—	72	62
3	**5a**	BDMAA	—	75	55
4	**5a**	DMA	—	78	60
5	**5b**	BDMAP	—	68	71
6	**5b**	BDMAP	$Mg(ClO_4)_2$	93	88
7	**5c**	BDMAP	—	58	86

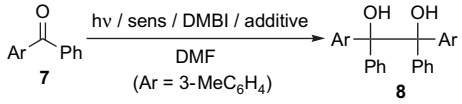
[a] Compound **5** (0.40 mmol), sensitizer (0.05 equiv vs **5a**; 0.1 equiv vs **5b** and **5c**), HPDMBI (1.2 equiv vs **5**), $Mg(ClO_4)_2$ (1.2 equiv vs **5b**), DMF (4 mL for exps 1–4; 2 mL for exps 5–7), λ>340 nm for 22 h for exps 1–5 and 7; for 16 h for exp 6.
[b] Determined with ^{1}H NMR.
[c] Based on the conversion of **5**.

conversion of **5b** and the yield of **6b** for the shorter reaction time (compare exp 6 to exp 5). This phenomenon would be rationalized by the assumption that back-electron transfer from $\mathbf{5}^{\bullet-}$ to $BDMAP^{\bullet+}$ is suppressed through ion-pair exchange with $Mg(ClO_4)_2$, and therefore the reaction is accelerated.[20]

2.5. Pinacol coupling of 3-methylbenzophenone 7

We recently found that 3-methylbenzophenone **7** was a suitable substrate to probe the mechanism of PET reactions with DMBIs.[6g] Thus, we decided to examine the PET reaction of **7** using the sensitizers with ADMBI and AcOH, or with HPDMBI (Table 6). Whereas benzpinacol **8** was obtained almost quantitatively in the case of DMP with ADMBI and AcOH (exp 2), BDMAA did not work at all (exp 3). Both BDMAP and DMA were similarly effective (exps 1 and 4). In the cases of HPDMBI, both the conversion of **7** and the yield of **8** were greater in the reactions with BDMAP and DMP than in those with BDMAA and DMA. It should also be noted that selective formation of **8** rather than benzhydrol is similar to the product selectivity observed in the PET reactions of **7** with DMPBI and AcOH or with HPDMBI without sensitizers.[6g] In the latter case, specific interactions of radical ion pairs are involved. Therefore, observed product selectivity in this work is consistent with the proposed reaction pathways in which reaction between independently generated $\mathbf{7}^{\bullet-}$ and $DMBI^{+\bullet}$ proceeds (Scheme 1).

Table 6. PET reactions of **7** with DMBI[a]



Exp	Sensitizer	DMBI	Additive	Conv. of **7**[b] (%)	Yield of **8**[b,c] (%)
1	BDMAP	ADMBI	AcOH	78	86
2	DMP	ADMBI	AcOH	100	100
3	BDMAA	ADMBI	AcOH	6	0
4[d]	DMA	ADMBI	AcOH	64	79
5	BDMAP	HPDMBI	—	34	100
6	DMP	HPDMBI	—	57	92
7	BDMAA	HPDMBI	—	17	53
8[d]	DMA	HPDMBI	—	22	77

[a] Compound **7** (0.20 mmol), sensitizer (0.05 equiv vs **7**), DMBI (1.2 equiv vs **7**), AcOH (6.6 equiv vs **7**), DMF (2 mL), λ>360 nm for 4 h.
[b] Determined with ^{1}H NMR.
[c] Based on the conversion of **7**.
[d] Benzhydrol was also obtained: 13% for exp 4 and 6% for exp 8.

3. Conclusion

We have studied PET reactions of several ketone substrates using electron-donating pyrenes or anthracenes as sensitizers with benzimidazolines as electron- and proton-donors (reducing reagents). Differences in effectiveness of these sensitizers were observed depending on the substrates and conditions. Among properties to be required for an effective sensitizer is the stability of its radical cation. Based on the cyclic voltammetry of sensitizers (Fig. 1), radical cations of the pyrenes must be more stable than those of the anthracenes in the sensitization cycle in Scheme 1, which is compatible with some of the results described above. Therefore, we would like to conclude that BDMAP and DMP are more reliable sensitizers than BDMAA and DMA. As a result, we recommend both BDMAP and DMP as visible light absorbing and electron-donating sensitizers for PET reactions. Another notable point is that DMP, unprecedented PET sensitizer, acted reasonably well in above examples. We will further explore the PET reactions of DMP and other alkoxy substituted pyrenes. The results and discussion described in this paper will hopefully provide useful information for any individual who is interested in PET chemistry to perform reductive transformation of organic compounds.

4. Experimental

4.1. General

NMR spectra were recorded in $CDCl_3$ with Me_4Si as an internal standard at 200 and 270 MHz for ^{1}H NMR, and 50 MHz for ^{13}C NMR. Uncorrected melting points are reported. Absorption and fluorescence spectra were measured in MeCN. The fluorescence lifetime was determined by time-correlated single photon counting technique based on picoseconds laser pulse excitation. Oxidation and reduction potentials in MeCN were measured with cyclic voltammetry using platinum electrodes as working and counter electrodes, Ag/0.01 M $AgNO_3$ as a reference electrode, and 0.1 M Et_4NClO_4 as a supporting electrolyte at the scan rate of 100 mV/s. Sample solutions were purged with N_2 before measurements. Ferrocene was used as a reference.[21] Standard Potentials of ferrocene/ferrocenium couple were measured to be +0.066 V and +0.439 V versus $Ag/AgNO_3$ and SCE, respectively. Then, peak potentials of sensitizers, DMBIs, and ketone substrates were converted to those against SCE. Half-wave potentials were obtained from these peak potentials by subtracting or adding 0.029 V.[22] Photoreactions were conducted in a Pyrex test tube (1.5 cm diameter) immersed in a water bath at room temperature with either a 500 W Xe lamp or 500 W Xe–Hg lamp as a light source. Column chromatography was performed with silica-gel (Wakogel C-200). Preparative TLC was performed on 20 cm×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. DMPBI,[23a] ADMBI,[6g] HPDMBI,[6g] DMTBI,[23b] and DCDMBI[23b] were prepared by the previously reported methods.[6g] BDMAP,[9a] DMP,[9a] BDMAA,[9c] DMA[9a,24] were prepared by the slight modifications of the literature procedures (see below). Substrates (**1a**,[10b] **1b**,[25] **1c**,[25] **5a**,[11] **5b**,[11] **5c**,[11] and **7**[6g]) and photoproducts (**2a**,[10b] **2b**,[25] **2c**,[25] **6a**,[11] **6b**,[11] **6c**,[11] and **8**[6g]) are known compounds. Preparation of **3** and spectral data of **3** and **4** are described below because their characterizations have not been completed.[6e]

4.2. Preparations of sensitizers

4.2.1. Preparation of BDMAP.[9a] 1,6-Diaminopyrene was prepared by the reaction of pyrene with HNO_3, followed by the reduction of 1,6-dinitropyrene with $Na_2S\cdot 9H_2O$. Then, an aqueous MeOH solution (H_2O+MeOH= 21 mL+86 mL) of 1,6-diaminopyrene (1.9 g, 8.3 mmol),

$CaCO_3$ (1.8 g, 18 mmol), and MeI (20.7 mL, 0.33 mol) was heated at 55 °C for 29 h. After addition of MeI (20.0 mL, 0.32 mol), the mixture was heated for another 36 h. Precipitated yellow solid obtained after cooling was heated with NaOEt (19.7 g, 0.29 mol) at 90 °C for 48 h. After concentration and addition of H_2O, extraction with C_6H_6 was performed. The extract was treated with H_2O, satd aqueous NaCl, and dried over anhydrous $MgSO_4$, and then concentrated. Silica-gel column chromatography (CH_2Cl_2) gave yellow solid that was recrystallized twice from EtOH to give BDMAP (709 mg, 2.5 mmol, 30%) as yellow plates: mp 163.2–164.5 °C (lit.[9a] 164–165 °C).

4.2.2. Preparations of DMP and DMA.[26] Pyrene (4.3 g, 21 mmol) and $K_2Cr_2O_7$ (6.2 g, 21 mmol) in 8 M H_2SO_4 (44 mL) were heated at 90 °C for 1 h and subsequently at 120 °C for 3 h. The mixture was poured into H_2O and the precipitated red-brown solid was filtered. The solid was subjected to silica-gel column separation (AcOH) to give a mixture of 1,6-pyrenedione and 1,8-pyrenedione (1.2 g, 5.2 mmol, 25%).[27] A part of the mixture (250 mg, 1.08 mmol), $Na_2S_2O_4$ (1.13 g, 6.48 mmol), and *n*-Bu_4NBr (35 mg, 0.11 mmol) in aqueous THF (H_2O+THF=4.7 mL+ 2.7 mL) were stirred at room temperature for 1 h. KOH (1.39 g, 24.8 mmol) in H_2O (3.6 mL) was added, and Me_2SO_4 (2.1 mL, 22.7 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 treated with H_2O and dried over anhydrous $MgSO_4$, and then concentrated. Silica-gel column chromatography (CH_2Cl_2) gave a mixture of 1,6-dimethoxypyrene and 1,8-dimethoxypyrene. The mixture was subjected to fractional recrystallization three times from C_6H_5Cl, and then DMP (52.7 mg, 0.20 mmol, 19%) was obtained as yellow needles: mp 250–252 °C (lit.[9a] 244–245 °C). DMA was prepared from anthraquinone (624 mg, 3.00 mmol) in the similar manner to DMP (see above). Successive recrystallization of the crude product from EtOH gave DMA (466 mg, 1.95 mmol, 65%) as pale yellow plates: mp 204–207 °C (lit.[24] 198–199 °C).

4.2.3. Preparation of BDMAA.[9c] 9,10-Diaminoanthracene was obtained by the reaction of anthraquinone (6.0 g, 29 mmol) with formamide, followed by a treatment with KOH. To the crude 9,10-diaminoanthracene were added MeOH (8 mL), MeI (8.0 mL, 129 mmol), and subsequently Na_2CO_3 (3.2 g, 30 mmol) in H_2O (8 mL). After the resulting mixture was stirred under N_2 for 16 h at room temperature and heated at 60 °C for 24 h, addition of H_2O was followed by extraction with $CHCl_3$. The extract was treated with H_2O, satd aqueous $NaHCO_3$, and dried over anhydrous $MgSO_4$, and then concentrated. Silica-gel column chromatography ($CHCl_3$/*n*-C_6H_{14}=2/1) gave yellow solids, which were recrystallized twice from EtOH to give BDMAA (552 mg, 2.09 mmol, 19% from anthraquinone) as yellow plates: mp 197–200 °C.

4.3. Preparation of 2-bromomethyl-2-(3-butenyl)-1-tetralone 3

To the mixture of NaH (ca. 66% in oil, 604 mg, 16.6 mmol) and HMPA (2.9 mL, 16.6 mmol) in THF (23 mL) was slowly added a THF solution (7 mL) of 2-(3-butenyl)-1-tetralone (1.66 g, 8.31 mmol) that was obtained through the sequence of NaH promoted reaction of 4-bromo-1-butene with ethyl 1-tetralone-2-carboxylate[28] and NaOH promoted hydrolytic decarboxylation, and stirred for 1 h under N_2. Then, CH_2Br_2 (2.9 mL, 41.6 mmol) was added and the resulting mixture was heated at 75 °C for 22 h. After addition of H_2O, extraction with Et_2O was performed. The extract was treated with satd aqueous $Na_2S_2O_3$, satd aqueous $NaHCO_3$, satd aqueous NaCl, and dried over anhydrous $MgSO_4$, and then concentrated. Silica-gel column chromatography (C_6H_6/*n*-C_6H_{14}=1/1) and subsequent distillation gave **3** (924 mg, 3.15 mmol, 38%) as colorless oil: bp 105–110 °C (0.45 mmHg); IR (Neat) 1681 cm^{-1}; ^1H NMR (270 MHz) δ 1.73–2.37 (m, 6H), 2.93–3.15 (m, 2H), 3.66 (d, J=10.4 Hz, 1H), 3.76 (d, J=10.4 Hz, 1H), 4.91–5.04 (m, 2H), 5.66–5.81 (m, 1H), 7.22–7.34 (m, 2H), 7.45–7.51 (m, 1H), 8.02–8.05 (m, 1H) ppm; ^{13}C NMR (50 MHz) δ 24.9, 27.9, 31.1, 32.5, 39.1, 48.5, 115.1, 126.8, 128.1, 128.8, 131.3, 133.6, 137.6, 142.9, 198.4 ppm. HRMS (ESI) calcd for $C_{15}H_{17}O^{79}BrNa^+$: 315.0361, found: 315.0355; $C_{15}H_{17}O^{81}BrNa^+$: 317.0341, found: 317.0335.

4.4. General procedure of PET reactions

A solution of a ketone substrate (0.20–0.50 mmol) and DMBI (0.24–0.60 mmol) or TMSA (2.50 mmol) with a sensitizer (generally $1.0–4.0\times10^{-2}$ mmol and 4.0×10^{-3} mmol for $Ru(bpy)_3Cl_2$) in DMF (2–5 mL) or other solvents (MeCN, THF, MeOH 4 mL) in the presence or absence of AcOH (1.32–2.00 mmol) or $Mg(ClO_4)_2$ (0.48 mmol) was purged with N_2 for 5 min prior to irradiation. This solution was irradiated with the light (λ>340 and 360 nm for pyrenes and anthracenes, and 390 nm for $Ru(bpy)_3Cl_2$) using a cut-off glass-filter for an appropriate irradiation time. While a photolysate without additive was concentrated, a photolysate containing AcOH or $Mg(ClO_4)_2$ was subjected to the extraction with EtOAc or C_6H_6. The extract was treated with satd aqueous $NaHCO_3$, satd aqueous NaCl, and dried over anhydrous $MgSO_4$, and then concentrated. For the reactions of **7**, the resulting residue was directly analyzed with ^1H NMR using triphenylmethane as an internal standard. For other reactions, the residues were subjected to silica-gel TLC or column separation for the reactions of **1**, **3** or **5** using appropriate mixed solvents (EtOAc/*n*-C_6H_{14} for **1**, C_6H_6/*n*-C_6H_{14} for **3**, EtOAc/C_6H_6 for **5**) to give the starting ketones and the products. Photoproducts were identified by analyses with their NMR and IR spectra. Product **4** (3/1 mixture of two diastereomers): colorless oil; IR (Neat) 1678 cm^{-1}; ^1H NMR (270 MHz) δ 1.00 (d, J=6.5 Hz, 3H, major isomer), 1.07 (d, J=6.8 Hz, 3H, minor isomer), 1.12–2.28 (m, 9H), 2.91–3.06 (m, 2H), 7.18–7.31 (m, 2H), 7.40–7.46 (m, 1H), 8.02–8.05 (m, 1H) ppm; ^{13}C NMR (50 MHz) δ 19.8, 20.2, 26.3, 26.7, 34.2, 34.3, 34.4, 34.5, 35.4, 35.7, 36.5, 42.6, 44.6, 53.4, 126.4, 127.9, 128.5, 131.5, 132.8, 143.5, 202.2 ppm. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47; found: C, 83.91; H, 8.63.

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References and notes

1. (a) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer: Berlin, 1987; (b) *Advances in Electron Transfer Chemistry*; Mariano, P. S., Ed.; JAI: Greenwich, CT, 1991–1999; Vols. 1–6; (c) *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, 2001; Vols. 1–5.
2. (a) Schmittel, M.; Burghart, A. *Angew. Chem., Int. Ed.* **1997**, *36*, 2550–2589; (b) Berger, D. J.; Tanko, J. M. *The Chemistry of Double–Bonded Functional Groups*; Patai, S., Ed.; Wiley: New York, NY, 1997; pp 1281–1354; (c) Schmittel, M.; Ghorai, M. K. *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, 2001; Vol. 2, pp 5–54.
3. (a) *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Parts A–D; (b) Kavarnos, G. J. *Fundamental of Photoinduced Electron Transfer*; VCH: New York, NY, 1993; (c) *CRC Handbook of Organic Photochemistry and Photobiology*, 1st ed.; Horspool, W. M., Song, P. S., Eds.; CRC: Boca Raton, FL, 1994, and 2nd ed.; Horspool, W. M., Lenci, F., Eds.; CRC: Boca Raton, FL, 2003.
4. Representative reviews for PET-promoted reductions of carbonyl compounds with amine donors. (a) Yoon, U. C.; Marinao, P. S.; Givens, R. S.; Atwater, B. W., III. *Advances in Electron Transfer Chemistry*; Mariano, P. S., Ed.; JAI: Greenwich, CT, 1994; Vol. 4, pp 117–205; (b) Cossy, J.; Pete, J. P. *Advances in Electron Transfer Chemistry*; Mariano, P. S., Ed.; JAI: Greenwich, CT, 1996; Vol. 5, pp 141–195.
5. Hasegawa, E. *J. Photoscience* **2003**, *10*, 61–69.
6. (a) Hasegawa, E.; Kato, T.; Kitazume, T.; Yanagi, K.; Hasegawa, K.; Horaguchi, T. *Tetrahedron Lett.* **1996**, *37*, 7079–7082; (b) Hasegawa, E.; Tamura, Y.; Tosaka, E. *Chem. Commun.* **1997**, 1895–1896; (c) Hasegawa, E.; Yoneoka, A.; Suzuki, K.; Kato, T.; Kitazume, T.; Yanagi, K. *Tetrahedron* **1999**, *55*, 12957–12968; (d) Hasegawa, E.; Chiba, N.; Nakajima, A.; Suzuki, K.; Yoneoka, A.; Iwaya, K. *Synthesis* **2001**, 1248–1252; (e) Hasegawa, E.; Takizawa, S.; Iwaya, K.; Kurokawa, M.; Chiba, N.; Yamamichi, K. *Chem. Commun.* **2002**, 1966–1967; (f) Hasegawa, E.; Chiba, N.; Takahashi, T.; Takizawa, S.; Kitayama, T.; Suzuki, T. *Chem. Lett.* **2004**, *33*, 18–19; (g) Hasegawa, E.; Seida, T.; Chiba, T.; Takahashi, T.; Ikeda, H. *J. Org. Chem.* **2005**, *70*, 9632–9635.
7. Representative examples for PET reactions using dimethylamino- or methoxy-substituted arenes as sensitizers. (a) Lee, J. A.; Israel, S. H. *J. Org. Chem.* **1983**, *48*, 4557–4563; (b) Hamada, T.; Nishida, A.; Yonemitsu, O. *J. Am. Chem. Soc.* **1986**, *108*, 140–145; (c) Nishida, A.; Hamada, T.; Yonemitsu, O. *J. Org. Chem.* **1988**, *53*, 3386–3387; (d) Okada, K.; Okamoto, K.; Oda, M. *J. Am. Chem. Soc.* **1988**, *110*, 8736–8738; (e) Pandey, G.; Rao, K. S. S. P.; Rao, K. V. N. *J. Org. Chem.* **1996**, *61*, 6799–6804; (f) Banerjee, A.; Falvey, D. E. *J. Org. Chem.* **1997**, *62*, 6245–6251; (g) Pandey, G.; Hajira, S.; Ghorai, M. K.; Kumar, K. R. *J. Am. Chem. Soc.* **1997**, *119*, 8777–8787; (h) Pandey, G.; Rao, K. S. S. P.; Rao, K. V. N. *J. Org. Chem.* **2000**, *65*, 4309–4314.
8. Although these pyrenes and anthracenes are previously known (Ref. 9) and both BDMAP (Refs. 6,7d) and DMA (Ref. 7a,h) have been used for some PET reactions, PET reactions of DMP and BDMAA have not been reported. In addition, no systematic study on the utilities of these four compounds as sensitizers for PET reactions has been conducted.
9. (a) Zweig, A.; Maurer, A. H.; Roberts, B. G. *J. Org. Chem.* **1967**, *32*, 1322–1329; (b) Dreeskamp, H.; Pabst, J. *Chem. Phys. Lett.* **1979**, *61*, 262–265; (c) Chung, Y.; Duerr, B. F.; McKelvey, T. A.; Najappan, P.; Czarnik, A. W. *J. Org. Chem.* **1989**, *54*, 1018–1032.
10. (a) Cossy, J.; Aclinou, P.; Bellosta, V.; Furet, N.; Baranne-Lafont, J.; Sparfel, D.; Souchaud, C. *Tetrahedron Lett.* **1991**, *32*, 1315–1316; (b) Hasegawa, E.; Ishiyama, K.; Horaguchi, T.; Shimizu, T. *J. Org. Chem.* **1991**, *56*, 1631–1635; (c) Cossy, J.; Bouzide, A.; Ibhi, S.; Aclinou, P. *Tetrahedron* **1991**, *47*, 7775–7782; (d) Kirschberg, T.; Mattay, J. *J. Org. Chem.* **1996**, *61*, 8885–8896; (e) Hasegawa, E.; Ishiyama, K.; Fujita, T.; Kato, T.; Abe, T. *J. Org. Chem.* **1997**, *62*, 2396–2400; (f) Zhang, J.; Jin, M.-Z.; Zhang, W.; Yang, L.; Liu, Z.-L. *Tetrahedron Lett.* **2002**, *43*, 9687–9689; (g) Recent review: Hasegawa, E.; Kamata, M. *CRC Handbook of Organic Photochemistry and Photobiology*, 2nd ed.; Horspool, W. M., Lenci, F., Eds.; CRC: Boca Raton, FL, 2003; Chapter 53, pp 1–17.
11. Belotti, D.; Cossy, J.; Pete, J. P.; Portella, C. *J. Org. Chem.* **1986**, *51*, 4196–4200.
12. (a) Hasegawa, E.; Xu, W.; Mariano, P. S.; Yoon, U. C.; Kim, J. U. *J. Am. Chem. Soc.* **1988**, *110*, 8099–8111; (b) Hasegawa, E.; Brumfield, M. A.; Yoon, U. C.; Mariano, P. S. *J. Org. Chem.* **1988**, *53*, 5435–5442.
13. Representative examples for PET reactions using $Ru(bpy)_3Cl_2$ with amines. (a) DeLaive, P. J.; Lee, J. T.; Sprinschinik, H. W.; Abruna, H.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 7094–7097; (b) Ballardini, R.; Varani, G.; Indelli, M. T.; Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1978**, *100*, 7219–7223; (c) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815–4824; (d) Pac, C.; Miyauchi, Y.; Ishitani, O.; Ihama, M.; Yasuda, M.; Sakurai, H. *J. Org. Chem.* **1984**, *49*, 26–34; (e) Ishitani, O.; Yanagida, S.; Takamuku, S.; Pac, C. *J. Org. Chem.* **1987**, *52*, 2790–2796; (f) Willner, I.; Tsfania, T.; Eichen, Y. *J. Org. Chem.* **1990**, *55*, 2656–2662; (g) Fukuzumi, S.; Mochizuki, S.; Tanaka, T. *J. Phys. Chem.* **1990**, *94*, 722–726; (h) Okada, K.; Okubo, K.; Morita, N.; Oda, M. *Chem. Lett.* **1993**, 2021–2024.
14. Reduction potentials ($E^{red}_{1/2}$ in V vs SCE) of some representative substrates are −1.59 V for **1a**, −1.82 V for **3**, and −1.78 V for **7**, respectively. In the cases of **1b**, **1c**, and **5a**, the reduction peaks were not observed below −2.3 V.
15. (a) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259–271; (b) Weller, A. *Z. Phys. Chem. Neue Folge* **1982**, *133*, 93–98.
16. In principle, a polar solvent accelerates initial PET processes (Refs. 3,15,17), and is desirable for a PET reaction involving sensitization. However, if a reaction requires a chemical process within a radical ion pair, e.g., proton transfer from a radical cation to a radical anion (Ref. 17), nonpolar solvents are in some cases more favorable to lead better yields of products

as compared to polar solvents (Ref. 10e). Therefore, a choice of a suitable solvent for each case is important for preparative PET reactions.

17. Devadoss, C.; Fessenden, R. W. *J. Phys. Chem.* **1991**, *95*, 7253–7260.
18. Tokel-Takvoryan, N. E.; Hemingway, R. E.; Bard, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 6582–6589.
19. (a) Zhang, X.; Ye, S. R.; Hong, S.; Freccero, M.; Albini, A.; Falvey, D. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1994**, *116*, 4211–4220; (b) Su, Z.; Mariano, P. S.; Falvey, D. E.; Yoon, U. C.; Oh, S. W. *J. Am. Chem. Soc.* **1998**, *120*, 10676–10686.
20. Representative examples of inorganic salt effects on PET reactions. (a) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 4875–4882; (b) Mizuno, K.; Ichinose, N.; Otsuji, Y. *Chem. Lett.* **1985**, 455–458; (c) Review: Loupy, A.; Tchoubar, B.; Astruc, D. *Chem. Rev.* **1992**, *92*, 1141–1165.
21. (a) Gritzne, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 461–466; (b) Workentin, M. S.; Parker, V. D.; Morkin, T. L.; Wayner, D. D. M. *J. Phys. Chem. A* **1998**, *102*, 6503–6512.
22. Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker: New York, NY, 1970.
23. (a) Chikashita, H.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1747–1752; (b) Lee, I.-S. H.; Jeoung, E. H.; Kreevoy, M. *J. Am. Chem. Soc.* **1997**, *119*, 2722–2728.
24. Meek, J. S.; Monroe, P. A.; Bouboulis, C. J. *J. Org. Chem.* **1963**, *28*, 2572–2577.
25. Hasegawa, E.; Ishiyama, K.; Kato, T.; Horaguchi, T.; Shimizu, T.; Tanaka, S.; Yamashita, Y. *J. Org. Chem.* **1992**, *57*, 5352–5359.
26. Kraus, G. A.; Man, T. O. *Synth. Commun.* **1986**, *16*, 1037–1042.
27. Fatiadi, A. J. *J. Chromatogr.* **1965**, *20*, 319–324.
28. Bowman, W. R.; Westlake, P. J. *Tetrahedron* **1992**, *48*, 4027–4038.