



Aryl-substituted dimethylbenzimidazolines as effective reductants of photoinduced electron transfer reactions



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ABSTRACT

Photoinduced electron transfer (PET) reactions promoted by 2-aryl substituted 1,3-dimethylbenzimidazolines (Ar-DMBIH) were investigated. Excited states of Ar-DMBIH, formed by irradiation using light above 360 nm, initiate PET reductions of various organic substrates, including transformations of epoxy ketones to aldols, free radical rearrangements such as the Dowd-Beckwith ring-expansion and 5-*exo* hexenyl cyclization, deprotection of *N*-sulfonyl-indols, and allylation of acyl formates. In these processes, Ar-DMBIH possessing 1-naphthyl, 2-naphthyl, 1-pyrenyl and 9-anthryl substituents formally act as two electron and one proton donors while the hydroxynaphthyl substituted derivative serves as a two electron and two proton donor. On the basis of the results of absorption spectroscopy studies, cyclic voltammetry and DFT calculation, a mechanistic sequence for these reduction reactions is proposed that involves initial photoexcitation of the aryl chromophore of the Ar-DMBIH followed by single electron transfer (SET) to the organic substrate to generate the radical cation of benzimidazoline and the radical anion of the substrate.

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1. Introduction

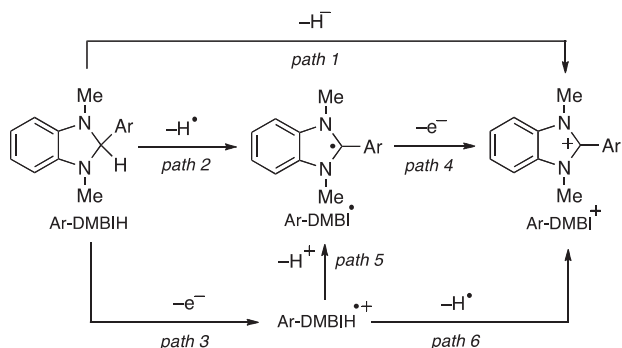
The single electron transfer (SET) reduction and oxidation (redox) abilities of electronic excited states of organic substances exceed those of their ground states. As a result, photoinduced electron transfer (PET) is a useful method to generate radical ions of organic molecules.¹ A simple way to initiate these processes is by direct photoexcitation of the organic substrate in the presence of an electron donor or acceptor co-reactant. Another approach involves the use of photosensitizers (photocatalysts), which can be designed to absorb longer wavelengths of light and whose electronic excited states can serve as electron donors or acceptors. The latter protocol has advantageous features, which include the avoidance of undesired reactions of the excited state of the substrate and secondary photoreactions of the initially formed product. In the past several years, PET reactions catalyzed by visible light absorbing transition metal complexes, such as those of ruthenium and iridium, have

received great attention in the area of synthetic organic chemistry.² More recently, metal-free protocols using organo-photocatalysts have gained interest in light of their potential application to green and sustainable synthetic transformations.³

Because amines possess relatively strong electron donating abilities compared to those of other organic substances, they have been employed often in the SET promoted reactions,⁴ and especially those initiated by PET.⁵ 2-Aryl-1,3-dimethylbenzimidazolines (Ar-DMBIH) are a family of *N*-heterocyclic aromatic amines that promote various reduction reactions by serving as hydride, hydrogen atom or electron donors (Scheme 1).⁶ Owing to their multi-donor character, Ar-DMBIH have been employed for reduction reactions of various organic substances, exemplified by their participation as hydride donors to carbocations as well as cationic salts (Scheme 1, path 1).⁷ Moreover, certain Ar-DMBIH derivatives react to produce hydrogen gas upon treatment with Brønsted–Lowry acids (path 1).⁸ Ar-DMBIH also behave as radical chain promoters through a pathway involving hydrogen atom donation followed by ET reactions (path 2 and path 4).⁹ In addition, PET reactions of various organic substances using Ar-DMBIH have been described by us and others (path 3–path 5–path 4, or path 3–path 6).^{10,11} Finally,

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the utility of Ar-DMBIH as electron donors has been expanded by their application in artificial photosynthesis systems¹² as well as organic semiconductor devices¹³ (path 3).



Scheme 1. Oxidation pathways of 2-aryl-1,3-dimethylbenzimidazole (Ar-DMBIH).

In investigations of PET promoted reduction reactions using Ar-DMBIH,¹⁰ we have employed approaches that involve both direct excitation of substrates^{10a–e,g,j,k} as well as photosensitization using electron donating pyrenes^{10d,f,h,i} or transition metal complexes.^{10h,l} As a consequence of the fact that visible light promoted organic transformations are highly attractive,^{2,3} we focused our attention on the development of Ar-DMBIH, which possess chromophores that absorb at long wavelengths so that desired PET reactions could be promoted without using expensive photocatalysts such transition metal complexes. The concept utilized to design Ar-DMBIH of this type is outlined in Fig. 1. In previous investigations, we demonstrated that phenyl-substituted DMBIH, **1a**, behaves as a two electron and one proton donor in reduction reactions of organic substrates while its phenol counterpart, **1g**, serves as a two electron and two proton donor. Based on this observation and the well-known effects of extended conjugation on the wavelength maximum for light absorption, we anticipated that Ar-DMBIH **1b–1f** (Fig. 1), in which various polycyclic aryl moieties are connected to the methylene carbon of the benzimidazole skeleton, would be suitable long wavelength absorbing PET promoters. In related studies, it has been shown that Hantzsch esters possessing aryl-substituents also are potential SET photoreductants¹⁴ although the use of these substances to promote reductive transformations has not been explored. In the study described below, we prepared the Ar-DMBIH **1b–1f** and demonstrated their utility in promoting PET transformations of the wide variety of organic substrates to form products listed in Fig. 2.

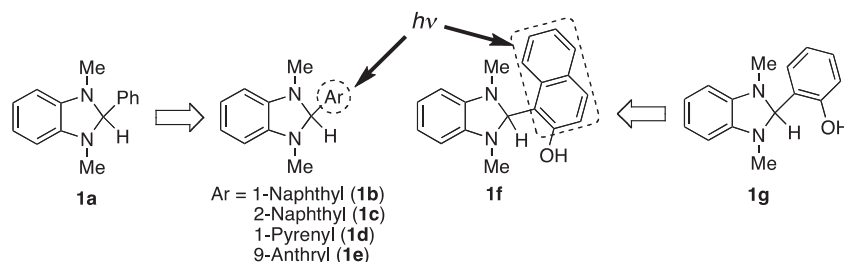


Fig. 1. 2-Aryl substituted 1,3-dimethylbenzimidazoles (Ar-DMBIH) (**1**).

2. Results and discussion

Analysis of the absorption spectra of Ar-DMBIH **1a–1g** displayed in Fig. 3 and Fig. 4, shows that these substances at 0.1 M concentrations absorb light at wavelengths >360 nm, which are attained by irradiation using Glass Filter L-39.¹⁵ Absorption spectroscopic data for **1** are accumulated in Table 1. Because 1,2-diaminobenzene

has an absorption maximum around 300 nm,¹⁶ the longer wavelength absorption bands at 313 nm for **1a** and 305 nm for **1g** are a consequence of the presence of the benzimidazole chromophore. In the absorption spectra of **1b**, **1c** and **1f**, the maxima present in the 307–314 nm range are attributed to both the naphthalene and benzimidazole chromophores.¹⁶ On the other hand, characteristic absorption bands associated with the pyrene¹⁷ and anthracene rings are present in the spectra of **1d** and **1e**, respectively.¹⁶ Under the >360 nm irradiation conditions used in the PET reactions explored (see below), the pyrene moiety of **1d**, anthracene moiety of **1e**, and benzimidazole moieties of **1a** and **1g** absorb the incident light. On the other hand, competitive absorption by naphthalene and benzimidazole chromophores is possible for **1b**, **1c** and **1f**.

Based on the results of previous studies, we concluded that reductive ring opening reactions of epoxy ketones **2** (Fig. 2) and radical rearrangement reactions of halo-alkyl substituted cyclic ketones **4** and **8** would serve as model processes to evaluate the Ar-DMBIH based PET protocol described above.^{10a–f,h–j,l} In PET promoted reductive ring opening reactions of epoxy ketones **2** that form the corresponding hydroxyl ketones **3**, two hydrogen atoms are formally transferred to the substrates (Scheme 2).^{10a,c,d,f,h,i} Because **1a–1e** are expected to serve as a two electron and one proton donors, PET reactions of epoxy ketones promoted by these substances require the participation of another proton donor.

To test these proposals, photoreactions of chalcone epoxide **2a** with **1** under the various conditions were explored (Table 2). Ar-DMBIH **1b–1e** were found to serve as photoreductants for reactions of epoxy ketone **2a** in THF containing AcOH that are induced by irradiation with light of wavelengths >360 nm (Xe lamp). The yields of these reactions, which are ca. 90% based on the conversion of **2a**, are much higher than those in which the phenyl-substituted benzimidazole **1a** was employed as the promoter (compare entries 2, 11, 12 and 14 to entry 1). Detailed studies using **1b** as the photoreductant unveiled several characteristic features of the epoxide ring opening reaction. For example, PhCO₂H as well as PhOH serves as proton donors for the reductive ring opening process (entries 3 and 4, also see entries 13 and 15). Moreover, reactions of **2a** in CH₂Cl₂ and DMF proceeded smoothly to generate **3a** in good to excellent yields (entries 5 and 8). Extending the irradiation time does not cause decomposition of **3a** (compare entry 6 to entry 5). Furthermore, decomposition products such as chalcone, acetophenone and benzaldehyde and not **3a** are produced when the photoreactions are conducted in solvents that do not contain proton donors (entry 7). In addition, reactions of **2a** promoted by **1b** using PhCO₂H (entry 9) or PhOH (entry 10) under solvent free

conditions formed **3a** with low to moderate efficiencies. Finally, good yields of **3a** are associated with reductive ring opening reactions of **2a** in THF, CH₂Cl₂ or PhCH₃ solutions not containing proton donating additives, which are promoted by **1f** and **1g** that contain respective naphthol and phenol proton donor moieties (entries 16–22). It should be noted that these two electron and two proton-donors **1f** and **1g** have some advantage compared to the

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