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Photochemical Reduction of Aromatic Imines by 2-Phenyl-N, N-dimethylbenzimidazoline

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Abstract: A series of aromatic imines were reduced to corresponding amines in excellent yields by 2-phenyl-N, N-dimethylbenzimidazoline (PDMBI) photochemically in the presence of magnesium perchloride ($Mg(ClO_4)_2$). A Mg^{2+} mediated photoinduced electron transfer mechanism was proposed.

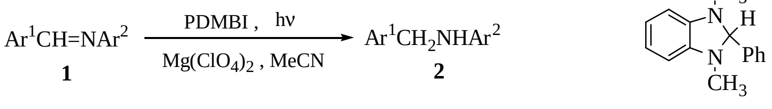
Keywords: Photoinduced electron transfer, selective reduction, imine, PDMBI.

Reduction of C=N double bonds has been recognized as an important reaction both in organic chemistry and bio-chemistry[1]. Hantzsch 1,4-dihydropyridine (HEH, one of NADH model compounds) has been reported as a reductive reagent for imines[2]. However, application of dihydropyridines as practical reducing reagents in organic synthesis is limited because of their instability[3].

Like NADH models, 2-phenyl-N, N-dimethylbenzimidazoline (PDMBI) is an efficient electron and hydrogen donor ($E_{ox} = 0.32V$ *vs* SCE)[4], but it is chemically more stable than NADH models, so it can be stored for a long time as a chemical reagent. However, the research of PDMBI was just limited in de-halogenation[5] and reduction of some C=C bonds[6]. Furthermore, its photochemistry has been paid much less attention[4].

Here, we report the photochemical reduction of imines by PDMBI. In a typical experiment, imines **1** (1 mmol), PDMBI (1.2 mmol) and magnesium perchloride (1 mmol) were dissolved in 10 ml of acetonitrile and deoxygenated by argon bubbling for 10 minutes, then irradiated with a 500 W high pressure Hg-lamp (monitored by TLC). The products amines **2** were isolated by column chromatography with neutral alumina and identified by NMR and MS. These results are summarized in **Scheme 1** and **Table 1**.

Scheme 1



$$\underset{\mathbf{1}}{Ar^1CH{=}NAr^2} \xrightarrow[Mg(ClO_4)_2\text{ , MeCN}]{\text{PDMBI , }h\nu} \underset{\mathbf{2}}{Ar^1CH_2NHAr^2}$$

PDMBI

Table 1 Photochemical reduction of aromatic imines **1a-h** to **2a-h** by PDMBI

Sub.	Ar^1	Ar^2	t/h	Conversions(%)	Products	Yields(%)
1a	Ph	Ph	1	100	**2a**	94
1b	Ph	4-Cl-C_6H_4	1	100	**2b**	92
1c	PhCH=CH	Ph	1	100	**2c**	91
1d	PhCH=CH	4-Cl-C_6H_4	1	100	**2d**	95
1e	3,4-$(CH_2O_2)C_6H_3$	Ph	1	100	**2e**	96
1f	Ph	4-$CH_3OC_6H_4$	1	100	**2f**	90
1g	4-$NO_2C_6H_4$	4-CH_3Ph	1	100	**2g**	92
1h	4-F-C_6H_4	Ph	1	100	**2h**	93

As shown in **Table 1** this is a clean and efficient reaction with excellent yield. Furthermore, it exhibits good selectivity between C=N double bond and other functional groups. The C=C double bonds of **1c** and **1d**, nitro moiety of **1g** were all kept intact and no de-halogenation took place in the case of **1b**, **1d** and **1h**.

This reaction may be initiated by photoinduced electron transfer. Magnesium ion lowers the free energy of activation for the initial single electron transfer step and makes the reduction take place[7].

In conclusion, we developed a new photochemical reductive reaction of aromatic imines by PDMBI in the presence of magnesium perchloride. Extension of this reaction is in progress.

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