Photocatalyzed Oxidative Dehydrogenation of Hydrazobenzenes to Azobenzenes

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1. General Information

All commercially available reagents were obtained from commercial suppliers and used without further purification. All catalytic experiments were carried out using standard techniques. Chromatography was carried out over silica gel (Innochem 200–300 mesh) and TLC was performed using silica gel 60 F254 (Merck) plates. $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were recorded on a Bruker NMR spectrometer in CDCl$_3$ using TMS as an internal reference with chemical shift values reported in ppm. Abbreviations used in the NMR follow-up experiments: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. The blue LED [30.0 W, $\lambda_{\text{max}} = 450$ nm] was used as a visible light source. Steady-state fluorescence measurements were performed with Cary Eclipse Fluorescence Spectrophotometer NO. G9800A of Agilent technologies. High-resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique. The diphenyl hydrazine derivatives (except for commercially available 1a) were prepared by modified literature procedures. $^{1,2}$

2. Procedure for the oxidative hydrogenation of hydrazobenzenes

In an oven-dried reaction tube containing a magnetic stirring bar was charged with a solution of 10-methylacridinium perchlorate (5 mol%) in MeCN (2 ml) followed by the addition of 1,2-Diphenyl hydrazine 1a (0.3 mmol). The reaction mixture was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 25 h. After completion of the reaction (indicated by TLC), the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product 2a (54.4 mg, 99%).
3. Optimization of the reaction conditions

![Chemical structure](image)

**Table S1** Optimization of the reaction conditions

<table>
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<th>Yield (%)(^a,)(^b)</th>
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<td>Mes-Acr(^{-})-Me (10-methyl-9-mesitylacridinium)</td>
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<td>27</td>
<td>/</td>
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<td>Trace</td>
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<td>28(^d)</td>
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</tr>
<tr>
<td>29(^e)</td>
<td>Acr(^{-})-Me (10-methylacridinium)</td>
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<td>NR</td>
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\(^a\) Reaction conditions: Reaction were conducted with 1a (0.3 mmol), photosensitizer (5 mol %) in 2.0 mL of dry solvent (0.15 M) at room temperature in the open air under 30 W LED irradiated, unless otherwise noted. NR= no reaction. \(^b\) Isolated yield. \(^c\) No blue LED. \(^d\) Reaction under O\(_2\). \(^e\) Reaction under Ar.
4. The gram scale reaction

To a solution of 10-methylacridinium perchlorate (5 mol%) in MeCN (40 ml) 1,2-Diphenyl hydrazine 1a (6 mmol, 1.103 g) was added. The reaction mixture was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 25 h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product 2a in 97% yield (1.061 g).

5. UV-Visible absorption spectra of reactants and product

Figure S1 UV-Visible absorption spectra of reactants and product: (a) absorption spectra of 1,2-Diphenyl hydrazine (1a, 0.3 mml) in MeCN (2.0 ml). (b) absorption spectra of 1,2-Diphenyl hydrazine (1a, 0.3 mml) and 10-methylacridinium perchlorate(0.015 mmol) in MeCN (2.0 ml). (c) absorption spectra of diphenyldiazene(1a, 0.3 mml) in MeCN (2.0 ml).
6. Fluorescence quenching experiments

Emission intensities were recorded using a Cary Eclipse Fluorescence Spectrophotometer NO. G9800A of Agilent technologies. The photocatalyst 10-methylacridinium perchlorate (5.0 µM in MeCN) and quencher 1a (diphenyldiazene) was added into a screw-top 1.0 cm quartz cuvette in increasing concentrations of (20, 40, 60, 80 100 µM in MeCN). Each sample was irradiated at 380 nm and the emission spectrum was recorded. Plots of intensity of emission (490 nm) vs concentration of quencher are shown according to the Stern-Volmer equation.\textsuperscript{3,4}

\textbf{Figure S2.} Luminescence quenching study
7. Control experiment

7.1. Light/Dark experiments

In an oven-dried reaction tube containing a magnetic stirring bar was charged with a solution of 10-methylacridinium perchlorate (5 mol%) in MeCN (2 ml) followed by the addition of 1,2-Diphenyl hydrazine 1a (0.3 mmol). The reaction mixture was open to air and stirred under the irradiation of 30 W blue LED at room temperature. Six hours later, the light was turned off. The reaction mixture was taken and concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product 2a. After another 6 hours, the light was turned on and the reaction mixture was taken again and purified to give the desired product 2a. The procedure was repeated four times and generated the profile of the reaction under the light off/on over time.

Figure S3. On/Off LED irradiation experiment for the synthesis of 2a
7.2. The model reaction was carried under Ar

In an oven-dried reaction tube containing a magnetic stirring bar was charged with a solution of 10-methylacridinium perchlorate (5 mol%) in MeCN (2 ml) followed by the addition of 1,2-Diphenyl hydrazine 1a (0.3 mmol). The reaction mixture was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 25 h. The solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent, only a trace amount of the desired product 2a was detected.

7.3. The model reaction was carried under O₂

In an oven-dried reaction tube with a magnetic stirring bar to a solution of 10-methylacridinium perchlorate (5 mol%), MeCN (2 ml) was added 1,2-Diphenyl hydrazine 1a (0.3 mmol), The reaction mixture was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 5 h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product 2a (53.7 mg, 98%).
8. Mechanistic Investigation

8.1 Singlet oxygen quenching experimental

In an oven-dried reaction tube containing a magnetic stirring bar a solution of 10-methylacridinium perchlorate (5 mol%) in MeCN (2 ml) was charged followed by the addition of 1,2-Diphenyl hydrazine 1a (0.3 mmol) and DABCO (0.45 mmol, 1.5 equiv). The reaction mixture was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 25 h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product 2a (53.1 mg, 97%).

8.2 \( \text{O}_2^- \) Radical Quenching Experiment

In an oven-dried reaction tube with a magnetic stirring bar a solution of 10-methylacridinium perchlorate (5 mol%), MeCN (2 ml), 1,2-Diphenyl hydrazine 1a (0.3 mmol) was added DPPH (0.6 mmol, 2 equiv). The reaction mixture was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 25 h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give only a trace amount of product 2a.
8.3 Test for hydrogen peroxide production

![Images of reaction mixtures]

<p>| | | | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>(a)</td>
<td>(b)</td>
<td>(c)</td>
<td>(d)</td>
</tr>
<tr>
<td>Addition of reaction mixture at 0 h to (a)</td>
<td>Addition of reaction mixture at 25 h to (a)</td>
<td>Addition of product (b)</td>
<td>Addition of $\text{H}_2\text{O}_2$</td>
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</table>

**Figure S4.** Test for production of hydrogen peroxide. (a) Reaction mixture of 0.30 mmol of 1a and 5 mol% of 10-methylacridinium perchlorate in 2.0 ml MeCN under Standard condition. (b) Reaction mixture of 0.30 mmol of diphenyldiazene 2a in 2.0 ml MeCN.
9. Characterization data for the products

1,2-diphenyldiazene (2a): Orange solid; m.p. 66-68 °C; 99% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96-7.93 (m, 4H), 7.56-7.52 (m, 4H), 7.51-7.49 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.8, 131.1, 129.2, 123.0; HRMS(EI$^+$): m/z calcd for C$_{12}$H$_{10}$N$_2$ [M]$^+$: 182.0844. Found 182.0849.

1-(4-methoxyphenyl)-2-phenyldiazene (2b): Red solid; m.p. 52-54 °C; 97% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97-7.89 (m, 4H), 7.54-7.43 (m, 3H), 7.03 (d, $J = 9.0$ Hz, 2H), 3.89 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.2, 152.9, 147.1, 130.5, 129.2, 124.9, 122.7, 114.3, 55.7; HRMS(EI$^+$): m/z calcd for C$_{13}$H$_{12}$N$_2$O[M]$^+$: 212.0950. Found 212.0945.

1-phenyl-2-($p$-tolyl)diazene (2c): Orange solid; m.p. 65-67 °C; 99% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J = 7.4$ Hz, 2H), 7.86 (d, $J = 8.4$ Hz, 2H), 7.55-7.51 (m, 2H), 7.49-7.46 (m, 1H), 7.33 (d, $J = 8.2$ Hz, 2H), 2.45 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.7, 150.7, 141.5, 130.7, 129.7, 129.0, 122.8, 122.7, 21.5; HRMS(EI$^+$): m/z calcd for C$_{13}$H$_{12}$N$_2$ [M]$^+$: 196.1000. Found 196.0997.

1-(4-fluorophenyl)-2-phenyldiazene (2d): Yellow solid; m.p. 76-78 °C; 98% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98-7.91 (m, 4H), 7.55-7.47 (m, 3H), 7.24-7.18 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.5 (d, $^1J_{CF} = 250.6$ Hz), 152.6, 149.3 (d, $^4J_{CF} = 2.9$
(Hz), 131.2, 129.3, 125.0 (d, $^{2}J_{CF} = 8.9$ Hz), 123.0, 116.3 (d, $^{2}J_{CF} = 22.7$ Hz); HRMS (EI$^+$): m/z calcd for C$_{12}$H$_9$N$_2$F [M]$^+$: 200.0750. Found 200.0754.

1-(4-chlorophenyl)-2-phenyldiazene (2e): Yellow solid; m.p. 81-83 °C; 95% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94–7.91 (m, 2H), 7.88 (d, $J = 8.8$ Hz, 2H), 7.56–7.48 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.6, 151.1, 137.0, 131.4, 129.5, 129.3, 124.3, 123.1; HRMS(EI$^+$): m/z calcd for C$_{12}$H$_9$N$_2$Cl [M]$^+$: 216.0454. Found 216.0452.

1-(4-bromophenyl)-2-phenyldiazene (2f): Orange solid; m.p. 90-92 °C; 99% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94–7.91 (m, 2H), 7.81 (d, $J = 8.8$ Hz, 2H), 7.65 (d, $J = 8.8$ Hz, 2H), 7.55–7.48 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.6, 151.4, 132.5, 131.5, 129.3, 125.5, 124.5, 123.1; HRMS(EI$^+$): m/z calcd for C$_{12}$H$_9$N$_2$Br [M]$^+$: 259.9949. Found 259.9945.

1-(4-iodophenyl)-2-phenyldiazene (2g): Orange solid; m.p. 91-93 °C; 99% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94–7.91 (m, 2H), 7.88–7.86 (m, 2H), 7.67–7.65 (m, 2H), 7.55–7.48 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.5, 152.0, 138.5, 131.5, 129.3, 124.6, 123.1, 97.8; HRMS(EI$^+$): m/z calcd for C$_{12}$H$_9$N$_2$I [M]$^+$: 307.9810. Found 307.9805.

1-(4-(tert-butyl)phenyl)-2-phenyldiazene (2h): Orange solid; m.p. 51-53 °C; 93% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95–7.93 (m, 2H), 7.91–7.89 (m, 2H), 7.58–7.46 (m, 5H), 1.40 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.7, 152.9, 150.7, 130.8, 129.2,
126.2, 122.9, 122.7, 35.2, 31.4; HRMS(EI⁺): m/z calcd for C₁₆H₁₈N₂ [M⁺]: 238.1470. Found 238.1467.

1-phenyl-2-(4-(trifluoromethyl)phenyl)diazene (2i): Orange solid; m.p. 81-83 °C; 96% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.02–8.00 (m, 2H), 7.97–7.95 (m, 2H), 7.79 (d, J = 8.3 Hz, 2H), 7.58–7.52 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 154.4, 152.4, 132.2 (q, ²J_CF = 32.2 Hz), 131.8, 129.2, 126.3 (q, ³J_CF = 3.7 Hz), 123.9 (q, ¹J_CF = 270.6 Hz), 123.2, 123.0; HRMS(EI⁺): m/z calcd for C₁₃H₉N₂F₃ [M⁺]: 250.0718. Found 250.0715.

1-phenyl-2-((o-tolyl)diazene (2j): Red oil; 94% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.98–7.95 (m, 2H), 7.68 (d, J = 7.8 Hz, 1H), 7.57–7.47 (m, 3H), 7.42–7.28 (m, 3H), 2.77 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 153.1, 150.9, 138.3, 131.4, 131.1, 130.9, 129.2, 126.6, 123.1, 115.6, 17.7; HRMS(EI⁺): m/z calcd for C₁₃H₁₂N₂ [M⁺]: 196.1000. Found 196.0999.

1-phenyl-2-((m-tolyl)diazene (2k): Red oil; 97% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.94–7.92 (m, 2H), 7.76–7.74 (m, 2H), 7.55–7.46 (m, 3H), 7.42 (t, J = 8.3 Hz, 1H), 7.32–7.30 (m, 1H), 2.77 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.9, 152.8, 139.1, 131.9, 131.0, 129.2, 129.0, 123.0, 122.9, 120.7, 21.5; HRMS(EI⁺): m/z calcd for C₁₃H₁₂N₂ [M⁺]: 196.1000. Found 196.0995.
1-(3-bromophenyl)-2-phenyldiazene (2l): Orange solid; m.p. 62-64 °C; 97% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.08–8.07 (m, 1H), 7.95–7.88 (m, 3H), 7.62–7.48 (m, 4H), 7.41 (t, $J$ = 8.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.6, 152.4, 133.7, 131.7, 130.6, 129.3, 124.7, 123.3, 123.2, 123.2; HRMS(EI$^+$): m/z calcd for C$_{12}$H$_9$N$_2$Br $[M]^+$: 259.9949. Found 259.9946.

![1-(3-bromophenyl)-2-phenyldiazene](image)

1-(2-bromophenyl)-2-phenyldiazene (2m): Red oil; 84% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01–7.98 (m, 2H), 7.77–7.75 (m, 1H), 7.70–7.67 (m, 1H), 7.58–7.48 (m, 3H), 7.42–7.30 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.7, 149.8, 133.9, 132.0, 131.7, 129.3, 128.1, 125.9, 123.6, 117.9; HRMS(EI$^+$): m/z calcd for C$_{12}$H$_9$N$_2$Br $[M]^+$: 259.9949. Found 259.9943.

![1-(2-bromophenyl)-2-phenyldiazene](image)

1,2-di-p-tolyldiazene (2n): Orange solid; m.p. 140-142 °C; 96% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J$ = 8.0 Hz, 4H), 7.33 (d, $J$ = 8.4 Hz, 4H), 2.46 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 150.9, 141.3, 129.8, 122.9, 21.6; HRMS(EI$^+$): m/z calcd for C$_{14}$H$_{14}$N$_2$ $[M]^+$: 210.1157. Found 210.1161.

![1,2-di-p-tolyldiazene](image)

1,2-bis(4-(tert-butyl)phenyl)diazene (2o): Orange solid; m.p. 182-184 °C; 99% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J$ = 8.4 Hz, 4H), 7.54 (d, $J$ = 8.4 Hz, 4H), 1.38 (s, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.4, 150.9, 126.1, 122.6, 35.1, 31.4; HRMS(EI$^+$): m/z calcd for C$_{26}$H$_{26}$N$_2$ $[M]^+$: 294.2096. Found 294.2095.

![1,2-bis(4-(tert-butyl)phenyl)diazene](image)
1,2-bis(4-fluorophenyl)diazene (2p): Red solid; m.p. 93-95 °C; 92% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.93\) (dd, \(J = 5.2\)Hz, \(J = 8.4\)Hz, 4H), 7.20 (t, \(J = 8.6\) Hz, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 164.5\) (d, \(^1J_{\text{CF}} = 251.4\) Hz), 149.1 (d, \(^4J_{\text{CF}} = 2.3\) Hz), 125.0 (d, \(^3J_{\text{CF}} = 9.1\) Hz), 116.2 (d, \(^1J_{\text{CF}} = 23.0\) Hz); HRMS(El\(^+\)): m/z calcd for C\(_{12}\)H\(_8\)N\(_2\)F\(_2\) [M\(^+\): 218.0656. Found 218.0651.

\[\begin{array}{c}
\text{F}_2\text{C} \\
\text{N} \quad \text{N} \\
\text{C} \quad \text{F}_3
\end{array}\]

1,2-bis(4-(trifluoromethyl)phenyl)diazene (2q): Red solid; m.p. 110-112 °C; 99% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.03\) (d, \(J = 8.0\) Hz, 4H), 7.80 (d, \(J = 8.3\) Hz, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 154.2, 133.1\) (q, \(^2J_{\text{CF}} = 32.4\) Hz), 126.6 (q, \(^3J_{\text{CF}} = 3.8\) Hz), 123.9 (q, \(^1J_{\text{CF}} = 270.6\) Hz), 123.5; HRMS(El\(^+\)): m/z calcd for C\(_{14}\)H\(_8\)N\(_2\)F\(_6\) [M\(^+\): 318.0592. Found 318.0584.

10. References


11. NMR spectra of for the products