

## Synthesis of Azobenzenes *via* direct oxidation of Aryl amines using aqueous *tert*-Butyl HydroPeroxide

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### ABSTRACT

A new method for the direct oxidation of aromatic amines to azobenzenes employing aqueous tertiary-butyl hydrogen peroxide and potassium tertiary butoxide as an oxidant and base, respectively is described. The desired products are obtained in good yields. The developed protocol is associated with certain advantages for example free from any metal oxidants.

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## 1. Introduction

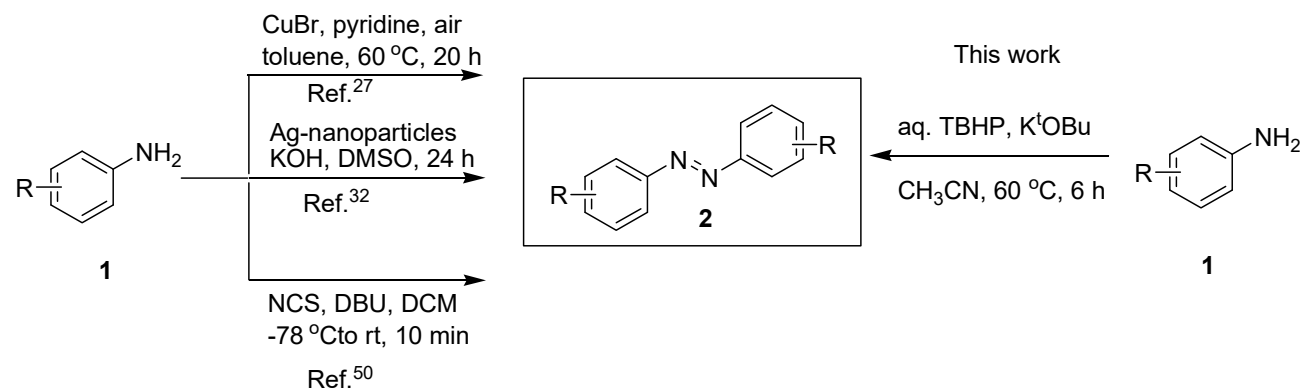
The azo compounds have been extensively investigated, due to their versatile structural features and unique  $-N=N-$  bonds.<sup>1-2</sup> Therefore the researchers in the field of chemistry and biology have made substantial efforts to develop newer methodologies for the synthesis of such compounds. Moreover, the azobenzenes has been thoroughly exploited in dyes,<sup>4-5</sup> pigments,<sup>6</sup> textiles,<sup>7</sup> polymers,<sup>8-9</sup> electronics,<sup>10-12</sup> and bioactive molecules.<sup>13-15</sup> In this context, numerous transformations have been described to accomplish direct oxidation of aromatic amines to azobenzene.<sup>16</sup> Such as BaMnO<sub>4</sub>,<sup>17</sup> Pb(OAc)<sub>4</sub>,<sup>18-19</sup> HgO/I<sub>2</sub>,<sup>20</sup> KMnO<sub>4</sub>,<sup>21-22</sup> MnO<sub>2</sub>,<sup>23</sup> Cu<sub>2</sub>Cl<sub>2</sub>-O<sub>2</sub>,<sup>24-26</sup> CuBr,<sup>27</sup> Ag<sub>2</sub>O,<sup>28</sup> Ag<sub>2</sub>CO<sub>3</sub>,<sup>29-30</sup> AgMnO<sub>4</sub>,<sup>31</sup> Ag-nanoparticles,<sup>32-33</sup> Ni peroxide,<sup>34</sup> Ce(OH<sub>3</sub>)O<sub>2</sub>H,<sup>35</sup> Co<sub>3</sub>O<sub>4</sub>-O<sub>2</sub>,<sup>36</sup> B(OH)<sub>3</sub>,<sup>37-39</sup> has been depicted in literature. However, metal oxidants would generate substantial amount of metal waste. Furthermore, the metal-free oxidative process employing PhI(OAc)<sub>2</sub>,<sup>40</sup> O<sub>2</sub>-*t*-BuOK,<sup>41</sup> KO<sub>2</sub>,<sup>42</sup> BBCP,<sup>43</sup> Ozone,<sup>44-45</sup> *t*-BuOCl/NaI,<sup>46-48</sup> CH<sub>3</sub>ONO,<sup>49</sup> NCS/DBU,<sup>50</sup> have been reported. Despite all these developments, a mild protocol with metal-free oxidants is of practical and environmental concern, thus such methods have been received a great attention. Earlier, we have reported one-pot direct oxidation of diols to carboxylic acids using TBHP as metal-free oxidant.<sup>51</sup> In this article, metal-free oxidation of aromatic amines to the corresponding azobenzenes utilizing aq. TBHP as oxidant is reported (Fig. 1).

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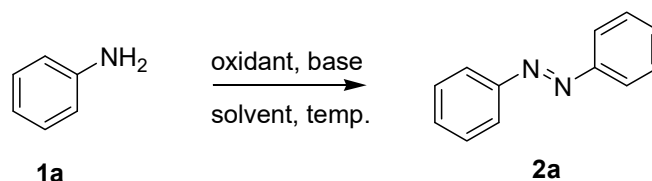


**Fig.1.** Oxidation of aryl amines to azobenzene

## 2. Results and Discussion

In order to study the suitable reaction conditions aniline was chosen as model substrate and various parameters such as oxidant, base, solvent and temperature was considered and the results are presented in Table 1. Our initial trials to convert aniline to azobenzene employing oxidants aq. 70% TBHP and 50% H<sub>2</sub>O<sub>2</sub> were not fruitful, due to heterogeneous of starting material and reagents (Table 1, entries 1-2). Screening of other solvents such as dichloromethane, ethanol, *tert*-butanol, tetrahydrofuran was also not favored the oxidation reaction (entries 3-6). As shown in entry 7, a low yield of undesired side product was obtained when pyridine was used as base and solvent. Formal screening of other oxidants such as aq. 30% H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub> and NaOCl was detrimental for oxidation (entries 8-10). Then the strong base NaOH and KOH were employed in combination with acetonitrile solvent and increase of substantial amount of oxidant produced improved yield of azobenzene in 41-64%, respectively (entries 11-13). Furthermore, it was found that potassium *tert*-butoxide (K<sup>t</sup>OBu) was the effective base in delivering the corresponding product in 76% in acetonitrile solvent (entry 14).

**Table 1.** Optimization of reaction conditions.<sup>a</sup>

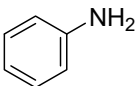
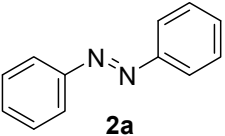
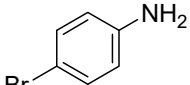
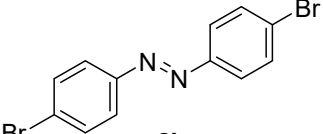
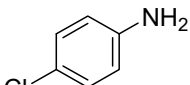
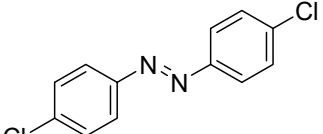
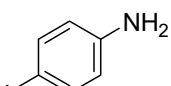
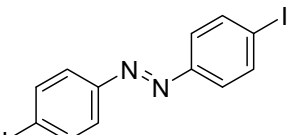
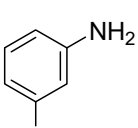
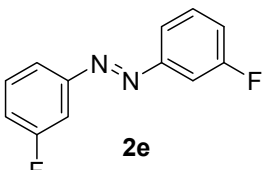
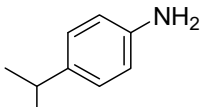
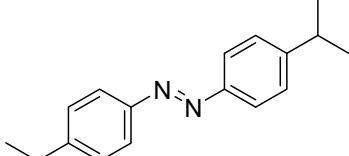


Entry	Oxidant (mmol)	Base	Solvent	Temp (°C)	Yield (%) <sup>b</sup>
1	TBHP (1)	K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	25	Traces
2 <sup>c</sup>	H <sub>2</sub> O <sub>2</sub> (1)	K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	25	NR
3	TBHP (2)	K <sub>2</sub> CO <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	50	15(>5) <sup>d</sup>
4	TBHP (2)	K <sub>2</sub> CO <sub>3</sub>	EtOH	50	>7
5	TBHP (2)	K <sub>2</sub> CO <sub>3</sub>	<i>t</i> -BuOH	60	NR
6	TBHP (2)	Et <sub>3</sub> N	THF	60	NR
7	TBHP (2)	Pyridine	Pyridine	80	25 <sup>e</sup>
8	H <sub>2</sub> O <sub>2</sub> (3)	K <sup>t</sup> OBu	CH <sub>3</sub> CN	60	20 <sup>f</sup>
9	O <sub>2</sub>	KOH	CH <sub>3</sub> CN	80	NR <sup>g</sup>
10	NaOCl (3)	KOH	CH <sub>3</sub> CN	80	NR <sup>g</sup>
11	TBHP (2)	NaOH	CH <sub>3</sub> CN	60	41
12	TBHP (3)	NaOH	CH <sub>3</sub> CN	60	58
13	TBHP (3)	KOH	CH <sub>3</sub> CN	60	64
14	TBHP (3)	K <sup>t</sup> OBu	CH <sub>3</sub> CN	60	76
15	TBHP (3)	K <sup>t</sup> OBu	CH <sub>3</sub> CN	25	18

<sup>a</sup>Reaction conditions aniline (1 mmol), oxidants (mmol), base (1 mmol), solvent (2 mL), <sup>b</sup>Isolated yield <sup>c</sup>30% aq. TBHP; <sup>d</sup>Crude yield at 25 °C; <sup>e</sup>Yield corresponds to oxidation of pyridine ring; <sup>f</sup>Formation of nitrobenzene was observed, confirmed by TLC; <sup>g</sup>Starting material was recovered; NR = no reaction

Having identified the optimal reaction conditions, next the scope of substrates was examined and the results are summarized in Table 2. Anilines with halide substituents, such as bromo, chloro, iodo and fluoro tolerated the oxidative conditions to afford the corresponding azobenzenes in good yields (Table 2, entries 2-5). With substrates bearing alkyl groups such as isopropyl and methyl smoothly converted to the desired products in moderate to good yield, respectively (entries 6-7). It is important to note that strong electron-withdrawing group  $-\text{NO}_2$  was highly exothermic. However, the base sensitive substituents such as  $-\text{COOEt}$ ,  $-\text{NHCOCH}_3$  was not oxidized under these conditions, thus yielded the hydrolyzed product.

**Table 2.** Scope of substrates for the syntheses of azobenzene.<sup>a</sup>

Entry	Substrate	Product	Yield <sup>b,c</sup> (%)
1		 <b>2a</b>	76
2		 <b>2b</b>	70
3		 <b>2c</b>	74
4		 <b>2d</b>	68
5		 <b>2e</b>	62
6		 <b>2f</b>	60

7			57
8			d
9			55°
10			60°

<sup>a</sup>Reaction conditions aniline (1 mmol), aq. 70% TBHP (3 mmol), K<sup>t</sup>OBu (1 mmol), acetonitrile (2 mL), 60 °C, 6 h; <sup>b</sup>Isolated yield; <sup>c</sup>The formation of products were confirmed by FTIR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR; <sup>d</sup>The formation of product was confirmed by FTIR due to reaction highly exothermic; <sup>e</sup>Corresponding hydrolysis product was observed along with starting compound.

### 3. Conclusions

In conclusion, a direct protocol for the oxidation of aniline to azobenzenes employing aq. TBHP and potassium *tert*-butoxide (K<sup>t</sup>OBu) as oxidant and base, respectively in acetonitrile solvent has been described. This oxidative transformation is simple and free from any transition metal catalyst. Currently, we are investigating the oxidation of more challenging substrates in our laboratory.

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### 4. Experimental

#### 4.1 Materials and Methods

All the chemicals were purchased from Sigma Aldrich and Merck. Thin layer chromatography was also procured from Merck, which is pre-coated silica gel plates and visualized under UV light and iodine vapors. Melting points of the reported compounds were measured using DALAL instruments, India and are uncorrected. IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer operating at 400–4000 cm<sup>-1</sup> using KBr pellets. <sup>1</sup>H NMR spectra were recorded at 400 MHz and <sup>13</sup>C NMR spectra at 100 MHz on a Bruker AVANCE FT NMR instrument using CDCl<sub>3</sub> and DMSO-d<sub>6</sub> as standard solvents.

## 4.2 General procedure for the synthesis of azobenzenes

A 50 mL round bottom flask was charged with aniline (1 mmol) followed by addition of acetonitrile 2 mL. The solution was allowed to stir at 25 °C. To this solution aq. 70% TBHP (3 mmol) was added carefully followed by addition of base K<sup>t</sup>OBu (3 mmol) and further stirred at 25 °C for 10 min. Then the whole reaction mixture was heated at 60 °C for 6 h. The oxidation process was observed by TLC. After completion of the reaction, the flask was cooled down to 25 °C followed by quenching with cold water. Then, the reaction mixture was transferred to separatory funnel and extracted with chloroform (2 × 15 mL). The combined organic layers were washed with dil. NH<sub>4</sub>Cl and water, and organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Obtained organic layer was evaporated under reduced pressure to give crude azobenzene. Further purification of compound was achieved by column chromatography technique EtOAc-*n*-hexane as eluent to yield azobenzene in 76% yield (0.140 g).

## 4.3 Spectral Data

### 1,2-diphenyl diazene (**2a**, Table 2, entry 1)

Yellow solid; mp 67-68 °C [lit.<sup>47</sup>; 67-68 °C]; FTIR KBr (cm<sup>-1</sup>): 640, 768, 920, 1061, 1286, 1445, 1475, 1580, 1610; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 7.49–7.52 (m, 6 H), 7.92–7.94 (m, 4 H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 122.7, 128.8, 130.7, 152.2.

### 1,2-bis(4-bromophenyl)diazene (**2b**, Table 2, entry 2)

Orange solid; mp 201-203 °C [lit.<sup>47</sup>; 201.3-203.7 °C]; FTIR KBr (cm<sup>-1</sup>): 709, 833, 1004, 1062, 1269, 1396, 1469, 1568, 1726; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 7.69 (d, J = 8 Hz, 4H), 7.85 (d, J = 8 Hz, 4H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 124.3, 125.7, 132.3, 151.0.

### 1,2-bis(4-chlorophenyl)diazene (**2c**, Table 2, entry 3)

Solid; mp 181-182 °C [lit.<sup>47</sup>; 182.0-184.5 °C]; FTIR KBr (cm<sup>-1</sup>): 715, 825, 842, 1002, 1082, 1103, 1475, 1571; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 7.59 (d, J = 8 Hz, 4H), 7.96 (d, J = 8 Hz, 4H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 124.1, 129.3, 137.1, 150.6.

### 1,2-bis(4-iodophenyl)diazene (**2d**, Table 2, entry 4)

Red solid; mp 241-243 °C [lit.<sup>47</sup>; 242.4-244.8 °C]; FTIR KBr (cm<sup>-1</sup>): 713, 810, 1001, 1049, 1095, 1296, 1390, 1467, 1560; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 7.65 (d, J = 8 Hz, 4H), 7.88 (d, J = 8 Hz, 4H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 98.1, 124.5, 138.4, 151.8.

### 1,2-bis(3-fluorophenyl)diazene (**2e**, Table 2, entry 5)

Solid; FTIR KBr (cm<sup>-1</sup>): 511, 685, 1144, 1327, 1610; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 7.32-7.54 (m, 2H), 7.60-7.68 (m, 4H), 7.80 (d, J = 8 Hz, 2H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 110.5, 117.2, 118.4, 129.8, 153.3, 162.7.

### 1,2-bis(4-isopropylphenyl)diazene (**2f**, Table 2, entry 6)

Orange solid; mp 145-147 °C [lit.<sup>33</sup>; 146 °C]; FTIR KBr (cm<sup>-1</sup>): 958, 1112, 1171, 1501, 1602, 2933; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 1.25 (d, J = 6 Hz, 12 H), 2.90-3.10 (m, 2H), 7.30-7.38 (m, 4H), 7.83 (d, J = 8 Hz, 4H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 23.8, 34.1, 122.8, 127.0, 151.2, 152.0.

### 1,2-bis(4-methylphenyl)diazene (**2g**, Table 2, entry 7)

Orange solid; mp 139-140 °C [lit.<sup>47</sup>; 137.6-140.9]; FTIR KBr (cm<sup>-1</sup>): 823, 945, 1109, 1151, 1501, 1597, 2922; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ 2.41 (s, 6H), 7.23 (d, J = 8 Hz, 4H), 7.76 (d, J = 8 Hz, 4H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 21.6, 122.6, 129.6, 141.1, 150.7.

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