Photo-assisted Oxidation of Anilines and Other Primary Aromatic Amines to Azo Compounds Using Mercury(II) Oxide as a Photo-Oxidant

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Abstract

An efficient and selective photochemical method for the oxidation of primary aromatic amines to the corresponding azoaromatic compounds with HgO as the photo-oxidant is reported. Aniline and substituted anilines were transformed to the corresponding azobenzenes by treatment with HgO in CH3CN at room temperature in high yields. Under similar conditions, diamines such as o-, m- and p-phenylenediamines gave the corresponding diaminoazo compounds. It was proposed that the photoactivated HgO effects the cleavage of one of the N–H bond of the amine to generate the aminyl radical which dimerizes to the hydrazobenzene via nitrogen-nitrogen coupling. The hydrazobenzene was then oxidized to azo product.

Keywords: Anilines, photoassisted oxidation, mercury (II) oxide, azo compounds.

1. Introduction

The oxidation of aromatic amines is an important reaction in the synthesis of various derivatives such as hydroxylamine, nitroso, nitro, oxime, azoxy and azo compounds.1 Among these derivatives, azobenzenes have gained much interest due to their characteristic color and photorespective properties. Various types of azobenzenes were prepared and studied for their possible applications in the area of nonlinear optics, optical storage media, chemosensors, liquid crystals and photochemical switches.5–12 Azo compounds are also of interest because of their physiological activity and their potential use as a diagnostic probe for the visualization of amyloid plaques in the brains of mentally deteriorating patients for a definite diagnosis of Alzheimer’s disease.13,14 Azobenzenes are commonly prepared from aromatic amines via formation of diazonium ion, followed by diazocoupling with aryl amine or alcohol.15 Less commonly used, but more effective, is the coupling of nitroso arene with arylamine.16–19

A variety of metallic and non-metallic reagents such as MnO2,20–23 Ag2CO3,24,25 Ag2O,26 AgMnO4,27 NiO2,28 NaBO3,29–31 Pb(OAc)4,32,33 BaMnO4,34 Ce(OH)1O2H,35,36 Hg(OAc)2,37 KO2,38 PhI(OAc)2,39 O2–KO–tert–Bu,40 O2–Cu2Cl2–Pyridine,41–43 O3–Co3O4,44 Peroxidase-H2O2,45 K2Fe(CN)6,46,47 Ru–H2O2,48 Mn(TPP)Cl/NaIO4,49 and K2FeO450 have been used for preparation of azobenzenes from anilines under thermal conditions. However, in comparison with these thermal oxidation methods, only a little data have been reported on photochemical oxidation of anilines to azobenzenes.51–54

In continuation of our studies on the application of photoprocesses in organic transformations using inorganic photooxidants and photocatalysts,55–57 we wish to report on the use of light-sensitive mercury (II) oxide (HgO), as an efficient and selective photo-oxidant for the oxidation of primary aromatic amines into the corresponding azo aromatic compounds under irradiation.

2. Results and Discussion

In initial experiments, we observed that when a stirred suspension of HgO in a solution of aniline (1) in acetonitrile contained in a Pyrex flask was irradiated for 4 h at room temperature with a 400 W high pressure Hg lamp, azobenzene (2) was separated as a single organic product in 86% yield. In addition to 2, the elemental mercury was
formed during irradiation as the gray precipitate according to the reaction in Scheme 1.

Blank experiments in the absence of HgO or light did not result in any oxidation of aniline. Indeed, the use of alternative Hg(II) sources such as mercury (II) halides (HgX₂, X=Cl, Br, I), Hg(NO₃)₂ and Hg(OAc)₂ did not result in conversion of 1 to 2 under our reaction conditions. Therefore, it is verified that high sensitivity of HgO to light plays an important role in this process. On the other hand, the yield of 2 did not change under aerobic (O₂) and anaerobic (N₂) conditions.

The above observation prompted us to investigate the photolysis of various substituted anilines (3) with a suspension of HgO (1 : 1; mole equiv) under the same conditions. We found that these substrates are cleanly oxidized to the corresponding azo compounds (4) in high yield. The obtained results are summarized in Table 1. These results can be explained on the basis of the reaction in Scheme 2.

Inspection of the data in Table 1 clearly shows that the method can be conveniently applied to the synthesis of symmetrically substituted azobenzenes. This new system oxidized with ease a wide variety of anilines to the corresponding azo compounds. Various azobenzenes containing substituents including methyl, ethyl, methoxy, nitro, halogens, and nitrile, have been synthesized in high yields. The oxidation of amino compounds to the azo compounds was monitored by TLC and IR. The disappearance of asymmetric and symmetric stretching bands near 3450–3300 and 1450 cm⁻¹ due to the N–H bonds of NH₂ and the

Table 1 Oxidation of various primary aromatic amines to azo compounds with HgO under photoirradiation.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aromatic amine</th>
<th>Time (h)</th>
<th>Azo product a</th>
<th>Yield(b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₆H₄NH₂</td>
<td>4</td>
<td>C₆H₄N=NC₆H₄</td>
<td>87</td>
</tr>
<tr>
<td>2</td>
<td>4-MeC₆H₄NH₂</td>
<td>2.5</td>
<td>4-MeC₆H₄N=NC₆H₄(4-Me)</td>
<td>94</td>
</tr>
<tr>
<td>3</td>
<td>3-MeC₆H₄NH₂</td>
<td>2.5</td>
<td>3-MeC₆H₄N=NC₆H₄(3-Me)</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>2-MeC₆H₄NH₂</td>
<td>2.5</td>
<td>2-MeC₆H₄N=NC₆H₄(2-Me)</td>
<td>93</td>
</tr>
<tr>
<td>5</td>
<td>4-EtC₆H₄NH₂</td>
<td>2.5</td>
<td>4-EtC₆H₄N=NC₆H₄(4-Et)</td>
<td>95</td>
</tr>
<tr>
<td>6</td>
<td>4-MeOC₆H₄NH₂</td>
<td>2</td>
<td>4-MeOC₆H₄N=NC₆H₄(4-OMe)</td>
<td>96</td>
</tr>
<tr>
<td>7</td>
<td>3-MeOC₆H₄NH₂</td>
<td>2.25</td>
<td>3-MeOC₆H₄N=NC₆H₄(3-OMe)</td>
<td>88</td>
</tr>
<tr>
<td>8</td>
<td>2-MeOC₆H₄NH₂</td>
<td>2.25</td>
<td>2-MeOC₆H₄N=NC₆H₄(2-OMe)</td>
<td>90</td>
</tr>
<tr>
<td>9</td>
<td>2,4-(MeO)C₆H₄NH₂</td>
<td>2</td>
<td>2,4-(MeO)C₆H₄N=NC₆H₄(2,4-(MeO)₂)</td>
<td>94</td>
</tr>
<tr>
<td>10</td>
<td>4-NO₂C₆H₄NH₂</td>
<td>6</td>
<td>4-NO₂C₆H₄N=NC₆H₄(4-NO₂)</td>
<td>78</td>
</tr>
<tr>
<td>11</td>
<td>3-NO₂C₆H₄NH₂</td>
<td>6.5</td>
<td>3-NO₂C₆H₄N=NC₆H₄(3-NO₂)</td>
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<td>12</td>
<td>2-NO₂C₆H₄NH₂</td>
<td>6</td>
<td>2-NO₂C₆H₄N=NC₆H₄(2-NO₂)</td>
<td>78</td>
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<td>13</td>
<td>4-FC₆H₄NH₂</td>
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<td>4-FC₆H₄N=NC₆H₄(4-F)</td>
<td>76</td>
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<tr>
<td>14</td>
<td>4-CNC₆H₄NH₂</td>
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<td>4-CNC₆H₄N=NC₆H₄(4-CN)</td>
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<td>2.5</td>
<td>4-IC₆H₄N=NC₆H₄(4-I)</td>
<td>92</td>
</tr>
<tr>
<td>16</td>
<td>2-IC₆H₄NH₂</td>
<td>3</td>
<td>2-IC₆H₄N=NC₆H₄(2-I)</td>
<td>90</td>
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<tr>
<td>17</td>
<td>4-BrC₆H₄NH₂</td>
<td>2.5</td>
<td>4-BrC₆H₄N=NC₆H₄(4-Br)</td>
<td>88</td>
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<tr>
<td>18</td>
<td>2-BrC₆H₄NH₂</td>
<td>2.5</td>
<td>2-BrC₆H₄N=NC₆H₄(2-Br)</td>
<td>85</td>
</tr>
<tr>
<td>19</td>
<td>4-CIC₆H₄NH₂</td>
<td>2.5</td>
<td>4-CIC₆H₄N=NC₆H₄(4-Cl)</td>
<td>87</td>
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<tr>
<td>20</td>
<td>2-CIC₆H₄NH₂</td>
<td>2.75</td>
<td>2-CIC₆H₄N=NC₆H₄(2-Cl)</td>
<td>85</td>
</tr>
<tr>
<td>21</td>
<td>2,4-CIC₆H₄NH₂</td>
<td>3.5</td>
<td>2,4-CIC₆H₄N=NC₆H₄(2,4-Cl₂)</td>
<td>84</td>
</tr>
<tr>
<td>22</td>
<td>2,6-CIC₆H₄NH₂</td>
<td>4.5</td>
<td>2,6-CIC₆H₄N=NC₆H₄(2,6-Cl₂)</td>
<td>86</td>
</tr>
<tr>
<td>23</td>
<td>2,4-Br₂C₆H₄NH₂</td>
<td>4.5</td>
<td>2,4-Br₂C₆H₄N=NC₆H₄(2,4-Br₂)</td>
<td>88</td>
</tr>
<tr>
<td>24</td>
<td>4-NHC₆H₄NH₂</td>
<td>3</td>
<td>4-NHC₆H₄N=NC₆H₄(4-NH₂)</td>
<td>86</td>
</tr>
<tr>
<td>25</td>
<td>3-NHC₆H₄NH₂</td>
<td>4</td>
<td>3-NHC₆H₄N=NC₆H₄(3-NH₂)</td>
<td>85</td>
</tr>
<tr>
<td>26</td>
<td>2-NHC₆H₄NH₂</td>
<td>4</td>
<td>2-NHC₆H₄N=NC₆H₄(2-NH₂)</td>
<td>85</td>
</tr>
<tr>
<td>27</td>
<td>4-NeC₆H₄NH₂</td>
<td>2.25</td>
<td>4-NeC₆H₄N=NC₆H₄(4-Ne₂)</td>
<td>94</td>
</tr>
<tr>
<td>28</td>
<td>1-C₁₀H₇NH₂</td>
<td>3.5</td>
<td>1-C₁₀H₇N=NC₁₀H₇(1-C₁₀H₇)</td>
<td>76</td>
</tr>
</tbody>
</table>

a All products were characterized on the basis of m.p., IR, 1H–NMR and mass spectral data and comparison with data reported in the literature. b Refer to isolated products. 1-C₁₀H₇ is 1-naphthyl.
appearance of a strong band between 1630–1565 cm\(^{-1}\) due to N=N stretching in the IR spectra clearly indicated the conversion.

As can be seen in Table 1, anilines having electron-donating groups on their phenyl ring, e. g. Me, Et and OMe groups, were converted into the corresponding azo compounds in excellent yields within 2–2.5 h (entries 2–9). Also, anilines bearing the strongly electron-withdrawing substituents such as NO\(_2\), F and CN underwent oxidation in good yield albeit after longer irradiation times of 5–6 h (entries 10–14). Halogenated anilines gave the corresponding azo compounds in moderate to high yields (entries 15–23).

An interesting electronic effect seems to exist for substituted systems. Comparing aniline (entry 1) to the anilines with electron-releasing substituents (e.g. entries 2–9), we found that the reaction times for the electron-rich arylamines were significantly shorter. Systems with electron-withdrawing groups (entries 10–14) required longer reaction times and gave lower yields when compared to more electron-rich amine substrates. Most of the reactions of these substrates did not go to completion and increasing the irradiation time did not improve the yields.

The oxidation of several aromatic diamines was also investigated. It was observed that the oxidation of \(\alpha\)-, \(m\)- and \(p\)-phenylenediamines resulted in only 2,2′-, 3,3′- and 4,4′-diaminoazobenzenes, respectively, with high yields (entries 24–26). Similarly, the irradiation of \(p\) -(\(N\),\(N\)-dimethylamino)aniline in the presence of HgO gave 4,4′-bis(\(N\),\(N\)-dimethylamino)azobenzene with excellent isolated yield (entry 27). Also, primary arylamine such as 1-naphthyl amine resulted in the corresponding azo compound under our reaction conditions (entry 28).

For the possible extension of the reaction, we investigated the photochemical oxidation of 2,2′-diaminobiphenyl (5) with HgO. This diamine readily underwent oxidative cyclization to dibenzopyridazine (6) in 88% isolated yield within 2.25 h irradiation (Scheme 3).

To evaluate the scope and limitations of this protocol, the oxidation of other amines was also studied. It was observed from GC analysis that aliphatic amines such as diphenyl amine (Ph\(_2\)NH) in the presence of HgO gave Ph\(_2\)N–Ph\(_2\) (88%, 2.5 h) and Hg(OH). On the other hand, tertiary amines such as triphenylamine (Ph\(_3\)N) and \(N\),\(N\)-dimethylaniline (PhNMe\(_2\)) were inert and recovered unchanged under the current reaction conditions.

Although the exact reaction mechanism is unclear and intermediates had not been observed directly, the formation of dimeric products and elemental Hg during the irradiation supports that the reaction proceeds through a light-induced electron transfer from amine into HgO. The proposed mechanism for the formation of azo compounds is indicated in Scheme 4.

In this mechanism, the reaction involves a nitrogen–nitrogen coupling of an initially formed aminyl radical (ArNH), which is probably produced by a one-electron transfer, followed by a two electron oxidation of the hydrazobenze.\(^{21,41–43,58}\) As indicated in the proposed mechanism, it seems that the formation of elemental mercury in the presence of an amine substrate involves hydrogen-atom abstraction from the NH\(_2\) group of amine by photoexcited mercuric oxide (HgO\(^3\)), followed by rapid electron transfer. On this basis, photooxidation of anilines proceeds mainly due to the hydrogen transfer, rather than electron transfer.

The following observations support this mechanism: (a) Mercuric oxide (HgO) as a reagent is not an oxidizing agent for anilines in the dark, probably can be activated to HgO\(^+\) under illumination, affording selectively azo products. (b) When the tertiary aromatic amines such as triphenylamine and \(N\),\(N\)-dimethylaniline which possess no abstractable \(N\)--H hydrogen atoms, were examined as the substrate under the our reaction conditions, the starting materials were recovered quantitatively even after 6 h irradiation. This most likely confirms that the primary reaction between photoactivated HgO and amine substrates involves hydrogen-atom abstraction rather than electron transfer. (c) On the other hand, when an equimolar mixture of two different anilines was irradiated together with HgO, two symmetrical and one unsymmetrical azobenzene were formed in moderate to low yields (less than 46%) via GC–MS analysis (Scheme 5). The formation of a mixture of products, is probably due to the coupling of various amyl radicals (Ar–NHF) during irradiation.
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(d) The initial oxidation of the amino compound to a hydrazo compound was evidenced by the isolation of hydrazobenzene (up to 35% yield) as a reaction intermediate during the course of oxidation of aniline. From this observation, we can conclude that in photooxidation of anilines the aminyl radical, \( \text{ArNH} \cdot \), was initially formed which dimerized to hydrazobenzene. (e) Also, the TLC monitoring showed that all the starting amine are first converted into the slow running spot, presumed to be hydrazobenzene based on its isolation upon workup, before subsequent transformation to the azobenzene. (f) When hydrazobenzene (PhNH–NHPh) was used as the starting material to react under the same reaction conditions, it was found to afford 82% of azobenzene within 1 h irradiation, which was similar to the reaction with aniline. This suggests that the final oxidized products were provided by oxidation of a hydrazobenzene species as the intermediate. In this case the reaction proceeds markedly faster than with the corresponding aniline.

However, whatever is the nature of the involved intermediate, this reaction offers an interesting example of application of photochemical methods in organic transformations.

3. Experimental

3.1. General

All chemicals and solvents were purchased from Merck or Fluka and used as received. 2,2’-Diaminobiphenyl (5) was prepared according to literature method.\(^{39}\) The light source was a 400 W high-pressure mercury lamp (HPML, \( \lambda > 320 \text{ nm} \)). \(^1\text{H}-\text{NMR}\) spectra were recorded on a Bruker 500 MHz instrument. \(^{13}\text{C}-\text{NMR}\) spectra were recorded at 75 MHz. Infrared spectra were recorded on FT-IR 8400 spectrophotometer using KBr pellets. Elemental analysis was performed using a Carlo Erba 1106 instrument. Mass spectra were measured on a Fining matt spectrometer with fast atom bombardment (FAB) method. Melting points were obtained using an Electrothermal-9200 instrument. All products were characterized by comparison of melting points and IR, \(^1\text{H}\) and \(^{13}\text{C}-\text{NMR}\) and/or MS data with those of authentic samples or literature data.\(^{20–48, 60–62}\)

3.2. General Procedure for Photoassisted Oxidation of Primary Aromatic Amines with \( \text{HgO} \)

In a Pyrex flask equipped with a magnet bar, a solution of primary aromatic amine (2 mmol) in acetonitrile (20 mL) was prepared. To this solution \( \text{HgO} \) (red, 2 mmol) was added. The reaction mixture was irradiated with a 400 W high pressure Hg lamp in a Pyrex water bath thermostated at 25 ± 2 °C. The progress of the reaction can be easily followed by TLC and or GC. After an irradiation time of 2–6.5 h, depending on the nature of amine, the irradiation was stopped and the resulting gray to near black precipitate of mercury separated by filtration. The filtrate was concentrated and chromatographic purification of products were performed on a silica-gel plate or silica gel column using hexane-EtOAc (1–5:1) as the eluting solvent. Yields of azo products are shown in Table 1. Selected physical and spectral data for some of products listed in Table 1 are as follows:

**Azobenzene** (Table 1, entry 1): an orange solid. Mp: 66–68 °C (68 °C\(^{60}\)); Elemental Anal. Calc. for \( \text{C}_{12}\text{H}_{10}\text{N}_{2} \): C 79.13, H 5.50, N 15.38. Found: C 79.0, H 5.53, N 15.40%; FT-IR (KBr, cm\(^{-1}\)): \( \nu(N=N) 1582 \); \(^1\text{H}-\text{NMR}\) (CDCl\(_3\)) \( \delta \) ppm: 7.92 (d, 4H), 7.50 (m, 4H), 7.45 (d, 2H); \(^{13}\text{C}-\text{NMR}\) (CDCl\(_3\)) \( \delta \) ppm: 152.66 (2C), 130.94 (2C), 129.04 (2C), 122.94 (2C), 120.44 (2C).

**3,3’-dimethylazobenzene** (Table 1, entry 3): a yellow solid. Mp: 55–56 °C (55 °C\(^{60}\)); Elemental Anal. Calc. for \( \text{C}_{14}\text{H}_{14}\text{N}_{2} \): C 80, H 6.66, N 13.34. Found: C 80, H 6.69, N 13.37%; FT-IR (KBr, cm\(^{-1}\)): \( \nu(N=N) 1606 \); \(^1\text{H}-\text{NMR}\) (CDCl\(_3\)) \( \delta \) ppm: 7.37-7.31 (m, 4H), 7.30 (m, 4H), 7.27 (s, 2H), 2.44 (s, 6H, 2CH\(_3\)); \(^{13}\text{C}-\text{NMR}\) (CDCl\(_3\)) \( \delta \) ppm: 152.82 (2C), 138.87 (2C), 131.64 (2C), 128.85 (2C), 122.94 (2C), 120.44 (2C), 21.31 (2C); FAB/MS: 182 (M\(^+\)), 105 (M–C\(_6\)H\(_3\)).

**4,4’-dimethoxyazobenzene** (Table 1, entry 6): a yellow solid. Mp: 140–141 °C (140 °C\(^{60}\)); Elemental Anal. Calc. for \( \text{C}_{14}\text{H}_{14}\text{O}_{2} \): C 69.42, H 5.79, N 11.57. Found: C 69.51, H 5.80, N 11.63%; FT-IR (KBr, cm\(^{-1}\)): \( \nu(N=N) 1600 \);
1H-NMR (CDCl3) δ ppm: 7.88 (d, 4H), 7.00 (d, 4H), 3.88 (s, 6H, 2OCH3); 13C-NMR (CDCl3) δ ppm: 161.50 (2C), 147.10 (2C), 114.10 (2C), 55.50 (2C); FAB/MS: 242 (M⁺), 135 (MeOC₆H₄N₂), 92 (C₆H₃NH₂).

**4,4'-dinitroazobenzene** (Table 1, entry 10): an orange-red solid. Mp: 223–225 °C (222 °C 60); Elemental Anal. Calc. for C₁₂H₈N₂I₂: C 33.22, H 1.85, N 6.45. Found: C 33.18, H 1.83, N 6.46; FT-IR (KBr, cm⁻¹): ν(N=N) 1561; 1H-NMR (CDCl3) δ ppm: 7.80 (d, 4H), 7.65 (d, 4H); 13C-NMR (CDCl3) δ ppm: 152.10 (2C), 138.7 (4C), 124.74 (4C), 98.3 (2C); FAB/MS: 343 (M⁺), 231 (IC₆H₄N₂), 203 (IC₆H₃).

**3. 4. Oxidation of Mixture of Anilines**

Following the general procedure for oxidation of anilines, irradiation of a mixture of 4-nitroaniline (1 mmol) and 1,4-diaminoaniline (1 mmol) with mercury(II) oxide (2 mmol) in acetonitrile (20 mL) and work-up in the usual manner, employing chromatography on silica-gel, gave 4,4'-diaminoazobenzene (46%), 4-aminoo-4'-nitroazobenzene (31%), and 4,4'-dinitroazobenzene (14%). Also, irradiation of the mixture of aniline (1 mmol) with 4-iodoaniline (1 mmol) in the presence of HgO (2 mmol) gave 4,4'-diiodoazobenzene (32%), 4-iodoazobenzene (23%), and azobenzene (18%).

**4-amino-4'-nitroazobenzene**: a deep-orange solid. Mp: 214–216 °C (216 °C60); Elemental Anal. Calc. for C₁₂H₉N₂O₃: C 59.50, H 4.13, N 23.14. Found: C 59.44, H 4.20, N 23.25%; FT-IR (cm⁻¹, KBr): ν(N=N) 1587; 1H-NMR (CDCl3) δ ppm: 4.2 (bs, 2H, D₂O exchange), 6.75 (d, 2H), 7.85 (d, 2H), 7.98 (d, 2H), 8.34 (d, 2H); 13C-NMR (CDCl3) δ ppm: 156.15 (1C), 154.50 (1C), 153.80 (2C), 137 (2C), 118.10 (2C) 116.10 (2C) 115.10 (2C); FAB/MS: 320 (M⁺), 174 (Cl₂C₆H₄N₂), 146 (Cl₂C₆H₃).

**4,4'-diaminoazobenzene** (Table 1, entry 21): a green-yellow solid. Mp: 248–251 °C (250 °C60); Elemental Anal. Calc. for C₁₂H₉N₂Cl₂: C 67.93, H 5.66, N 26.42. Found: C 67.84, H 5.61, N 26.40%; FT-IR (KBr, cm⁻¹): ν(N=N) 1575; 1H-NMR (CDCl3) δ ppm: 7.75 (d, 4H), 3.92, 6.74 (d, 4H), (bs, 4H, D₂O exchange); 13C-NMR (CDCl3) δ ppm: 154.10 (2C), 145.80 (2C), 127 (4C), 114.90 (4C); FAB/MS: 212 (M⁺), 120 (NH₂C₆H₄N₂), 92 (C₆H₃NH₂).

**3. 3. Oxidation of 2,2'-diaminobiphenyl (5)**

In a similar manner as the above, treatment of 2,2'-diaminobiphenyl (1 mmol) with mercury(II) oxide (2 mmol) in acetonitrile (20 mL) under irradiation for 2.25 h and work-up in the usual manner, employing chromatography on silica-gel, gave 0.32 g (88%) of dibenzopyridazine (6) as an orange solid. Mp: 156–157 °C (157–158 °C60); Elemental Anal. Calc. for C₁₂H₁₁N₂ (M⁺=180): C 80, H 4.45, N 15.56. Found: C 79.88, H 4.43, N 15.60%; FT-IR (KBr, cm⁻¹): ν(N=N) 1585; 1H-NMR (CDCl3) δ ppm: 8.74–8.80 (m, 2H), 8.58–8.64 (m, 2H), 7.90–7.96 (m, 4H); 13C-NMR (CDCl3) δ ppm: 150.20 (2C), 130.94 (2C), 129.04 (2C), 128 (2C), 124.25 (2C), 121.34 (2C); FAB/MS: 180 (M⁺), 90 (C₆H₃N₂), 77 (C₆H₃).

**4,4'-dicyanoazobenzene** (Table 1, entry 14): an orange solid. Mp: 230–231 °C (232 °C60); Elemental Anal. Calc. for C₁₂H₈N₂Cl₂: C 45.0, H 1.86, N 7.86. Found: C 44.90, H 2.01, N 8.71%; FT-IR (KBr, cm⁻¹): ν(N=N) 1584; 1H-NMR (CDCl3) δ ppm: 7.05–6.74 (m, 4H), 6.59 (s, 2H); 13C-NMR (CDCl3) δ ppm: 151.10 (2C), 142.80 (2C), 137 (2C), 118.10 (2C) 116.10 (2C) 115.10 (2C); FAB/MS: 232 (M⁺), 130 (ClC₆H₄N₂),102 (ClC₆H₃).

**2,2',4,4'-tetrachloroazobenzene** (Table 1, entry 21): an orange solid. Mp: 164–166 °C (161–162 °C60); Elemental Anal. Calc. for C₁₂H₉Cl₄: C 45.0, H 1.86, N 8.76. Found: C 44.90, H 2.01, N 8.71%; FT-IR (KBr, cm⁻¹): ν(N=N) 1584; 1H-NMR (CDCl3) δ ppm: 7.05–6.74 (m, 4H), 6.59 (s, 2H); 13C-NMR (CDCl3) δ ppm: 151.10 (2C), 142.80 (2C), 137 (2C), 118.10 (2C) 116.10 (2C) 115.10 (2C); FAB/MS: 320 (M⁺), 174 (Cl₂C₆H₄N₂), 146 (Cl₂C₆H₃).

**4,4'-diaminobenzene** (Table 1, entry 24): a golden-yellow solid. Mp: 248–251 °C (250 °C60); Elemental Anal. Calc. for C₁₂H₉N₂: C 67.93, H 5.66, N 26.42. Found: C 67.84, H 5.61, N 26.40%; FT-IR (KBr, cm⁻¹): ν(N=N) 1575; 1H-NMR (CDCl3) δ ppm: 7.75 (d, 4H), 3.92, 6.74 (d, 4H), (bs, 4H, D₂O exchange); 13C-NMR (CDCl3) δ ppm: 154.10 (2C), 145.80 (2C), 127 (4C), 114.90 (4C); FAB/MS: 212 (M⁺), 120 (NH₂C₆H₄N₂), 92 (C₆H₃NH₂).

**4. Conclusions**

We have introduced a novel, efficient and selective photochemical method for oxidation of primary aromatic amines to azo compounds by using an inexpensive, available and light-sensitive inorganic oxide (HgO), which acts as the photo-oxidant under photoirradiation. This photoassisted oxidation can be used in synthetic transformations and it could be useful for synthetic organic chemists.
5. Acknowledgment

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6. References

Povzetek

V prispevku je predstavljena učinkovita in selektivna fotokemična metoda za oksidacijo primarnih aromatskih aminov v odgovarjajoče azoaromatske spojine z HgO kot fotoooksidantom. Anilin in substituirani anilini se pretvorijo v odgovarjajoče azobenzene z visokimi izkoristi v pri sobni temperaturi v prisotnosti HgO in CH₃CN kot topilu. Pod podobnimi pogoji reagirajo tudi diamini kot so orto-, meta- in para-fenilendiamini do odgovarjajočih diaminoazono spojin. V predlaganem mehanizmu reakcije fotoaktivirani HgO povzroči cepitev ene od N–H vezi v aminu, pri čemer se število aminilnih radikal, ki dimerizira do hidrazina z N–N sklopitvijo. Hidrazin se nato nadalje oksidira v azo produkt.