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Synthesis of Azo Compounds via Cu Nanoparticles Catalyzed Oxidative Coupling of Anilines

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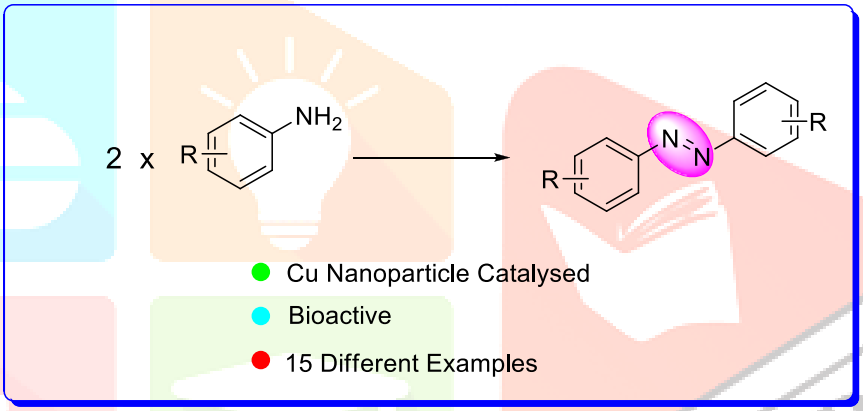
Graphical Abstract



Abstract:

Oxidative coupling of anilines gives azo compounds via mild and highly efficient Cu nanoparticles. Various aromatic anilines can be efficiently coupled under mild reaction conditions to the corresponding azo compounds in high yields. This technique gives an immediate and useful admittance to these compounds and is additionally willing to gram scale with no exceptional safeguards to exclude air or moisture.

Keywords:

Anilines, Azo compounds, Cu nanoparticles, Oxidative coupling.

Introduction:

Azo compounds are valuable compounds in view of their wide range of industrial applications in the synthesis of polymers, [1] optical materials, molecular devices, [2] and bioactive compounds. [3] Due to more usefulness, environment friendly and low cost synthesis of these compounds. On the other hand their various applications in therapeutics, [4] aromatic azo compounds are used as ligands due to ease in complex formation with metals; also it is used in various dyes and pigments [5] and as a radical initiator in Mitsunobu reaction. [6] Recently the azo compounds are used in various raw materials of polymers, drug delivery systems, optical sensing agents and smart sensors.

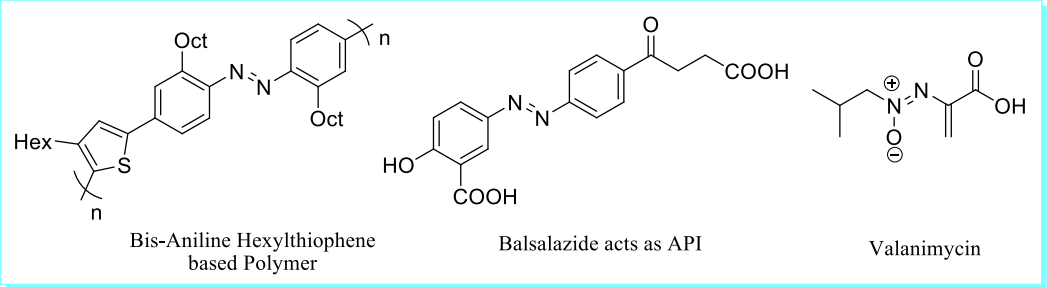
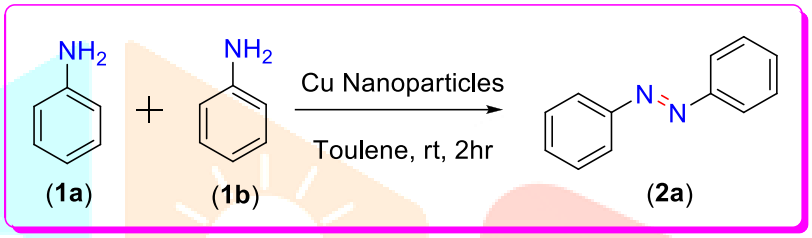


Figure: Some of the azo group containing compounds.

Though the developed methods for the synthesis of azo compounds are useful but they have some drawbacks like longer reaction time, critical operating reaction conditions etc. which make them inconvenient. In continuation with our work on synthesis of bioactive compounds [7, 8, 9], herewith we have reported the new method for the synthesis of azobenzenes.

Results and Discussion:

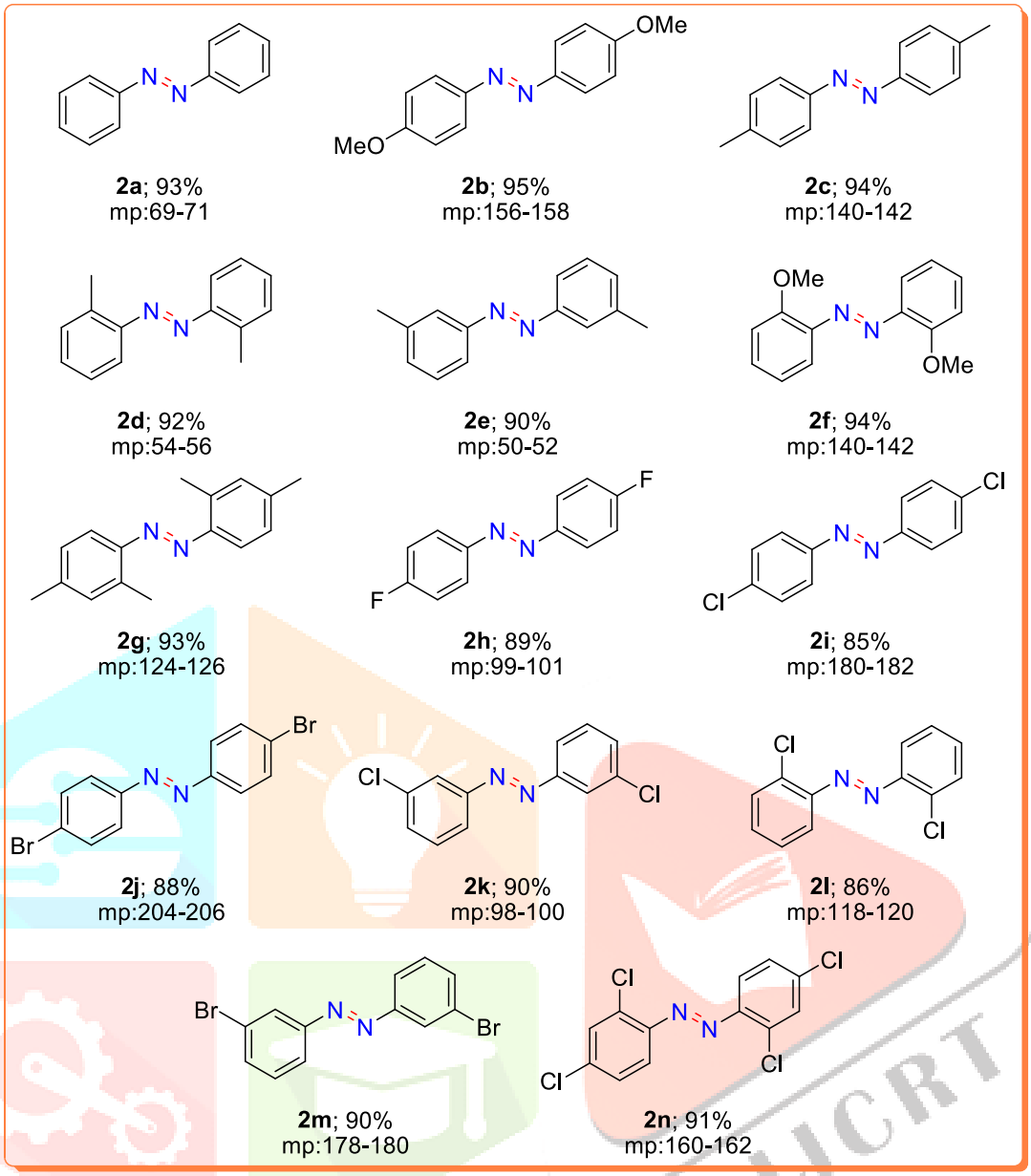


(Scheme 1)

The scope of newly developed protocol was extended to primary aromatic amines to produce a series of diverse azo compounds under optimized reaction conditions (**Table**). In case of aromatic amines the corresponding azo compounds were obtained in excellent yield (85-95%). When aniline (**1a**) is reacted with another molecule of aniline (**1b**) in presence of Cu nanoparticles at room temperature under atmospheric air for 2 h, the product azobenzene (**2a**) is formed and isolated in 93% yield (**Scheme 1**). Similarly, the electron donating group methyl at para position of aniline gave the corresponding azo compound (**2c**). Likewise the other electron donating group i.e. methyl and methoxy, situated at ortho, meta and para gives corresponding azo compounds (**2b**, **2d**, **2f**, **2g**, **2e**) in high yields. The halo- substituted anilines (F, Cl and Br) also gives the corresponding azo compounds (**2h**, **2i**, **2j**. **2k**, **2l**, **2m**, **2n**) in moderate to high yields. Remarkably in all above cases only azo products were formed selectively and no other by-products such as Ullman coupling, N-oxides and hydroxyl amines were noticed. [10]

All the newly synthesized compounds have been characterized using their IR, ^{1}H NMR and ^{13}C NMR spectral data. The IR spectrum of compound (**2a**) indicates the formation of product as it shows a characteristic absorption peak at 1582 cm^{-1} which corresponds to the N=N of azobenzene. The ^{1}H NMR spectrum of compound (**2a**) displays peaks, a multiplets at δ 7.97-7.89 ppm for four hydrogen atoms and 7.58-7.45 ppm due to six hydrogen atoms of aromatic ring. The four carbon signals are observed at δ 152.8, 131.2, 129.3, 123.1 ppm in ^{13}C NMR spectrum of (**2a**) owing clearly indicates the formation of azobenzene.

Table: Scope of Cu Nanoparticle Catalysed Oxidative Coupling of Anilines.



2a; 93%
mp:69-71

2b; 95%
mp:156-158

2c; 94%
mp:140-142

2d; 92%
mp:54-56

2e; 90%
mp:50-52

2f; 94%
mp:140-142

2g; 93%
mp:124-126

2h; 89%
mp:99-101

2i; 85%
mp:180-182

2j; 88%
mp:204-206

2k; 90%
mp:98-100

2l; 86%
mp:118-120

2m; 90%
mp:178-180

2n; 91%
mp:160-162

Experimental:

The chemicals used were of laboratory grade. Melting points of all the synthesized compounds were determined in open capillary tubes and are uncorrected. The IR spectra were recorded on Brukar FT-IR spectrometer.^{1}H NMR spectra were recorded on a Brukar DRX-300 spectrometer using tetramethylsilane (TMS) as an internal standard and chemical shifts are in δ (ppm). ^{13}C NMR spectra were recorded on a Brukar DRX-75 in $CDCl_3$/DMSO-d_6. The purity of the title and intermediate compounds was checked by thin-layer chromatography (TLC).

General Procedure for the synthesis of (2a-m)

Aniline (**1**) (2 mol) was stirred in presence of Cu nanoparticles (20 mol %) in toluene at room temperature. The progresses of the reactions were monitored by TLC. After completion of reactions (2-3h), the cu nanoparticles were separated by filtration. The filtrate was extracted with ethyl acetate and washed with water. The organic layer was dried over sodium sulphate; finally the resulting solution was purified by column chromatography using petroleum ether and ethyl acetate as solvent.

Procedure for Synthesis of Copper Nanoparticles

In a typical synthesis, 1.08 g of copper chloride and 3.65 g of sodium oleate were dissolved in a mixture of hexane, ethanol, and distilled water. The solution was heated and refluxed during 4 h, and later it was transferred to a separation funnel to eliminate the aqueous residues. The organic phase with copper-oleate complex and hexane was washed three times with distilled water. Afterwards the copper-oleate complex was transferred to a Petri dish to help evaporate the residual solvent. Next 3.6 g of copper-oleate complex was mixed with 1.14 g of oleic acid and 20 g of phenyl ether at room temperature. The solution was heated at 250°C for 30 min. During the course of the reaction, the solution turned brown in color indicating the formation of Cu NPs. The resulting mix was cooled at room temperature and the precipitate was washed a few times with ethanol to eliminate solvent and residues; finally the NPs were collected by centrifugation. [11]

(*E*)-1,2-Diphenyldiazene (2a): Orange Solid; M. P. 69-71 ^{0}C; IR (film) 1582, 1483, 1453, 1299 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97-7.89 (m, 4H), 7.58-7.45 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8, 131.2, 129.3, 123.1.[12]

(*E*)-1,2-Bis(4-methoxyphenyl)diazene (2b): Yellow Solid; M. P. 156-158 ^{0}C; IR (film) 1657, 1597, 1580, 1499, 1455, 1441 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, J = 8.7 Hz, 4H), 7.01 (d, J = 8.7 Hz, 4H), 3.88 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.8, 147.3, 124.5, 114.4, 55.7. [12]

(*E*)-1,2-Di-*p*-tolyldiazene (2c): Orange Solid; M. P. 140-142 ^{0}C; IR (film) 1600, 1503, 1414, 1154 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, J = 7.2 Hz, 4H), 7.40 (d, J = 7.2 Hz, 4H), 2.46 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.0, 141.4, 129.9, 122.9, 21.7. [12]

(*E*)-1,2-Di-*o*-tolyldiazene (2d): Orange Red Solid; M. P. 54-56 ^{0}C; IR (film) 1596, 1478, 1455, 1376 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, J = 8.1 Hz, 2H), 7.41-7.33 (m, 4H), 7.32-7.24 (m, 2H), 2.76 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.3, 138.2, 131.5, 130.9, 126.6, 116.0, 17.8. [12]

(*E*)-1,2-Di-*m*-tolyldiazene (2e): Orange Solid; M. P. 50-52 ^{0}C; IR (film) 1605 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76-7.69 (m, 4H), 7.42 (t, J = 8.1 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 2.47 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 139.1, 131.9, 129.1, 123.1, 120.7, 21.6. [12]

(*E*)-1,2-Bis(2,4-dimethylphenyl)diazene (2g): Orange Solid; M. P. 124-126 ^{0}C; IR (film) 1605, 1485, 1451, 1373 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 7.8Hz, 2H), 7.18 (s, 2H), 7.10 (d, J = 7.8 Hz, 2H), 2.75 (s, 6H), 2.42 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4, 140.9, 138.0, 132.0, 127.3, 115.9, 21.6, 17.8. [12]

(*E*)-1,2-Bis(4-fluorophenyl)diazene (2h): Orange Solid; M. P. 99-101 ^{0}C; IR (film) 1593, 1499, 1415, 1232 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98-7.79 (m, 4H), 7.28-7.09 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6 (d, J = 250.6 Hz), 149.2, 125.0 (d, J = 9.2 Hz), 116.3 (d, J = 22.8 Hz). [12]

(*E*)-1,2-Bis(4-chlorophenyl)diazene (2i): Orange Solid; M. P. 180-182 ^{0}C; IR (film) 1587, 1547, 1478, 1402 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 7.66 (d, J = 8.7 Hz, 4H), 7.09 (d, J = 8.7 Hz, 4H); ^{13}C NMR (75 MHz, C_6D_6) δ 151.0, 137.3, 129.5, 124.4. [12]

(*E*)-1,2-Bis(4-bromophenyl)diazene (2j): Orange Solid; M. P. 204-206 ^{0}C; IR (film) 1570, 1472, 1398 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 7.57 (d, J = 8.7 Hz, 4H), 7.25 (d, J = 8.7 Hz, 4H); ^{13}C NMR (75 MHz, C_6D_6) δ 151.3, 132.4, 125.8, 124.5. [12]

(*E*)-1,2-Bis(3-chlorophenyl)diazene(2k): Orange Yellow Solid; M. P. 98-100 ^{0}C; IR (film) 1585, 1568, 1463, 1416 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92-7.88 (m, 2H), 7.87-7.79 (m, 2H), 7.51-7.42 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3, 135.4, 131.4, 130.4, 122.8, 122.1; [12]

1,2-Bis(2-chlorophenyl)diazene (2l): Orange Red Solid; M. P. 118-120 ^{0}C; IR (KBr, cm^{-1}) 3087, 1582, 1466, 1442, 1254, 1060, 764, 726; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 2H), 7.44 (m, 2H), 7.56 (m, 2H), 7.78 (m, 2H). [13]

(E)-1,2-bis(2-methoxyphenyl)diazene (2f): Yellow Solid; M. P. 140-142 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.1 Hz, 2H), 7.56 (t, J = 8.9, 8.7 Hz, 2H), 7.12-7.04 (m, 4H), 3.98 (s, 6H). [14]

(E)-1,2-bis(3-bromophenyl)diazene (2m): Yellow Solid; M. P. 178-180 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 2H), 7.88 (d, J = 8.6 Hz, 2H), 7.68 (d, J = 9.0, 2H), 7.47 (t, J = 8.6, 9.0, 2 H). [14]

(E)-1,2-bis(2,4-dichlorophenyl)diazene (2n): Yellow Solid; M. P. 160-162 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$); δ 7.87 (d, J = 8.8, 2H), 7.56 (s, 2H), 7.34 (d, J = 8.8, 2H). [14]

Conclusions:

We have developed a novel oxidative coupling of anilines using Cu nanoparticles as catalyst. Different primary and secondary anilines can be effectively coupled under mild conditions to give the corresponding azo compounds in high yields. This reaction is simple, clean and is manageable to gram scale. It is feasible to perform the reaction at room temperature. This protocol gives target molecules with no side products.

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Conflict of Interest:

The authors declare no conflict of interest.

References:

1. H.T. Nguyen, O. Coulembier, K. Gheysen, J. C. Martins, P. Dubois, *Macromolecules* **2012**, 45,9547-9550.
2. M. Kamenjicki, S. A. Asher, *Macromolecules* **2004**, 37, 8293–8296.
3. M. Pangerl, C.C. Hughes, D. Trauner, *Tetrahedron* **2010**, 66, 6626- 6631.
4. A. Jain, Y. Gupta, S.K. Jain, *Crit. Rev. Ther. Drug Carrier Syst.* **2006**, 23, 349-400.
5. K.Hunger, Industrial Dyes: Chemistry, Properties, Applications; *Wiley- VCH: Weinheim, Germany* **2003**.
6. T.Y.S. But, P.H. Toy, *J. Am. Chem. Soc.* **2006**, 128, 9636-9637.
7. P. S. Phatak, B. P. Sathe, S. T. Dhumal, N. N. M. A. Rehman, P. P. Dixit, V. M. Khedkar, K. P. Haval, *J. Heterocycl. Chem.* **2019**, 56, 1928.

8. P. S. Phatak, R. D. Bakale, S. T. Dhumal, L. K. Dahiwade, P. B. Choudhari, V. S. Krishna, D. Sriram, K. P. Haval, *Synth. Commun.* **2019**, 49, 2017.
9. P. S. Phatak, R. D. Bakale, R. S. Kulkarni, S. T. Dhumal, P. P. Dixit, V. S. Krishna, D. Sriram, V. M. Khedkar, K. P. Haval, *Bioorg. Med. Chem. Lett.* **2020**, 22, 127579.
10. E. Sperotto, G.P.M. van Klink, G. van Koten, J. G. de Vries, Dalton Trans **2010**, 39, 10338-10351.
11. R. Betancourt-Galindo, P.Y. Reyes-Rodriguez, B.A. Puente-Urbina, C.A. Avila-Orta, O.S. Rodríguez-Fernández, G. Cadenas-Pliego, R.H. Lira-Saldivar, L.A. García-Cerda, *J. Nanomater.* **2014**.
12. Y. Zhu and Y. Shi, *Org. Lett.* **2013**, 15, 1942-1945.
13. M. Zhang, R. Zhang, A. Q. Zhang, X. Li, H. Liang, *Syn. Comm.* **2009**, 39, 3428-3435.
14. A. R. Patel, G. Patel, G. Maity, S. P. Patel, S. Bhattacharya, A. Putta, S. Banerjee, *ACS Omega* **2020**, 5, 30416-30424.