

Azo Dyes: Preparation Via Environmentally Benign Way

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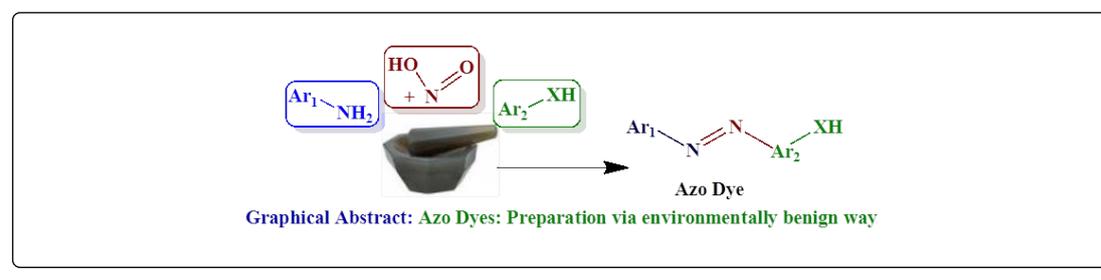
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Abstract

An environmentally benign way for the synthesis of azo dyes was carried out via grinding at room temperature. This green methodology aimed to overcome the limitations and drawbacks of that, previously reported. The new approach represented simple conditions with excellent conversions, and a low-cost practice. The environmental friendliness was evidently marked. The structure of the resulted dyes was confirmed using, elemental analysis, Mass, ¹HNMR and ¹³CNMR spectroscopy.



Keywords: Benign synthesis; Azo dyes; Grinding; Green Synthesis

Introduction

Aromatic azo dyes are important class of organic compounds that has great industrial value. It has wide applications as dyes, pigments, food additives, and drugs [1-3]. Moreover, these dyes have attracted ever growing attention due to their wide collection of color, brightness, simplicity and easiness of manufacturing and respectable dyeing performance [4-7]. They are used in high tech applications such as lasers and non-linear optical systems [8], thermal transfer printing and fuel cells [9], dye sensitized solar cells [10], photodynamic therapy [11], and metallochromic indicators [12]. Furthermore, Azo dyes are known for their medicinal importance [13-16] and to be involved in a number of biological reactivity such as inhibition of DNA, RNA and protein synthesis, carcinogenesis and nitrogen fixation [17]. In a broader sense, the azo dyes constitute the largest diverse group of all the synthetic colorants [18].

Despite their importance, the syntheses of aromatic azo compounds are carried out today using stoichiometric reagents and, frequently, environmentally unfriendly catalysts included oxidation of aromatic amino compounds with metal salts and reduction of aromatic nitro compounds with metals [19-23]. An alternative route to aromatic azo dyes entailed self-catalyzed diazotization of amino compound acidic salts under solvent-free conditions followed by coupling with electron-rich aromatic compounds [24-26].

Grindstone Chemistry opened a research window where organic compounds could be constructed under ecofriendly conditions [27-34]. Moreover, the green organic synthesis via grinding at room temperature represents a benign way towards the green and sustainable context of Chemistry [35-37].

In this work, we report a new and environmentally benign synthesis of azo dyes via grinding under solvent free condition at room temperature.

Materials and Methods

All reagents were purchased from Merck Co. Melting points were determined in open glass capillaries on a Gallenkamp melting point apparatus and uncorrected. Elemental analysis was performed on a Thermo Finnigan Flash EA 1112 Element Analyzer (Italy). ¹HNMR and ¹³CNMR spectra were recorded on a Varian Mercury 400 MHz spectrometer using TMS, Tetramethylsilane, as an internal standard and DMSO-d₆ as solvent. Mass spectra were recorded at 70 eV on a Shimadzu GCMS-QP1000EX using an inlet type injector. All reactions were monitored by TLC (silica gel, aluminum sheets 60 F254, Merck). All schemes were regenerated via Chem. Draw Ultra 12.0.2.1076.

General procedure for synthesis

The amino compound hydrochloride acidic salts 1a-c (0.001 moles) and equimolar ratio of the given phenoxide salts 2a-c were grinded in presence of Sodium nitrite (0.002 moles) by means of agate mortar and pestle under solvent free condition at room temperature, the reaction completion was monitored via means of TLC, (Thin Layer Chromatography, Alumina Sheets). The colored paste was washed thoroughly by distilled water and dried to obtain dyes 3a-i. The prepared dyes structures were confirmed.

(3a) 4-(phenyldiazenyl)phenol

Grinding Time: 6 minutes, (Yield: 93%); M.P.: 150-153°C., Mol. F.: C₁₂H₁₀N₂O; Mol. Wt.: 198.22; m/z (FABMS): 198.08; Elemental

analysis: (Calculated %) C, 72.72; H, 5.08; N, 14.13; O, 8.07; (Found %) C, 72.68; H, 5.11; N, 14.18; O, 8.03; ¹HNMR: 7.00 (d, 2H Ar), 7.20 (t, 1H Ar) 7.55 (t, 2H Ar), 7.88 (d, 2H Ar), 8.09 (d, 2H Ar), 10.05 (s, 1H OH); ¹³CNMR: 115.80 (C₂, C₆), 122.50 (C₈, C₁₂), 122.90 (C₃, C₅), 129.70 (C₉, C₁₁), 132.20 (C₁₀), 145.10 (C₄), 150.80 (C₇), 159.00 (C₁).

(3b) 4-(phenyldiazenyl)naphthalene-1-ol

Grinding Time: 13 minutes, (Yield: 95%); M.P.: 131-133°C., Mol. F.: C₁₆H₁₂N₂O; Mol. Wt.: 248.28; m/z (FABMS): 248.09; Elemental analysis: (Calculated %) C, 77.40; H, 4.88; N, 11.28; O, 6.44; (Found %) C 77.36; H, 4.90; N, 11.32; O, 6.42; ¹HNMR: 7.18-7.28 (m, 2H Ar), 7.50-7.67 (m, 4H Ar) 7.98 (d, 2H Ar), 8.12 (d, 2H Ar), 8.59 (d, 2H Ar), 8.90 (d, 2H Ar) 10.90 (s, 1H OH); ¹³CNMR: 108.10 (C₂), 115.00 (C₃), 123.30 (C₈, C₁₂, C₁₃), 126.10 (C₁₄, C₁₅), 126.20 (C₆), 128.20 (C₁₆), 129.60 (C₅), 129.90, (C₁₀), 130.10 (C₉, C₁₁), 140.50 (C₄), 151.90 (C₇), 155.10 (C₁).

(3c) 1-(phenyldiazenyl)naphthalene-2-ol

Grinding Time: 11 minutes, (Yield: 96%); M.P.: 131-133°C., Mol. F.: C₁₆H₁₂N₂O; Mol. Wt.: 248.28; m/z (FABMS): 248.09; Elemental analysis: (Calculated %) C, 77.40; H, 4.88; N, 11.28; O, 6.44; (Found %) C 77.39; H, 4.91; N, 11.27; O, 6.43; ¹HNMR: 7.10-7.21 (m, 2H Ar), 7.48-7.52 (m, 2H Ar) 7.60 (t, 2H Ar), 8.09-8.21 (m, 5H Ar), 11.20 (s, 1H OH); ¹³CNMR: 120.00 (C₈, C₁₂), 120.20 (C₂, C₁₄), 125.60 (C₄, C₅, C₁₅), 127.00 (C₁₃), 127.20 (C₉, C₁₁), 127.40 (C₆, C₁₆), 127.90 (C₁₀), 143.00 (C₁), 150.80, (C₇), 154.90 (C₃).

(3d) 4-(p-tolydiazenyl)phenol

Grinding Time: 8 minutes, (Yield: 91%); M.P.: 192-196°C., Mol. F.: C₁₃H₁₂N₂O; Mol. Wt.: 212.25; m/z (FABMS): 212.09; Elemental analysis: (Calculated %) C, 73.36; H, 5.70; N, 13.20; O, 7.54; (Found %) C 73.31; H, 5.72; N, 13.19; O, 7.58; ¹HNMR: 2.28 (s, 3H CH₃), 7.11 (d, 2H Ar), 7.39 (d, 2H Ar), 7.80 (d, 2H Ar), 8.26 (d, 2H Ar), 10.00 (s, 1H OH); ¹³CNMR: 116.10 (C₂, C₆), 121.80 (CH₃), 121.90 (C₈, C₁₂), 122.90 (C₃, C₅), 128.90 (C₉, C₁₁), 140.00 (C₁₀), 145.30 (C₄), 149.00 (C₇), 162.30 (C₁).

(3e) 4-(p-tolydiazenyl)naphthalene-1-ol

Grinding Time: 15 minutes, (Yield: 95%); M.P.: 211-213°C., Mol. F.: C₁₇H₁₄N₂O; Mol. Wt.: 262.31; m/z (FABMS): 262.11; Elemental analysis: (Calculated %) C, 77.84; H, 5.38; N, 10.68; O, 6.10; (Found %) C 77.82; H, 5.34; N, 10.71; O, 6.13; ¹HNMR: 2.30 (s, 3H CH₃), 7.01 (d, 1H Ar), 7.40 (d, 2H Ar), 7.55-7.65 (m, 2H Ar), 8.20 (d, 1H Ar), 8.45 (d, 2H Ar), 8.70 (d, 2H Ar), 11.55 (s, 1H OH); ¹³CNMR: 109.00 (C₂), 115.60 (C₃), 121.10 (CH₃), 124.80 (C₈, C₁₂, C₁₃), 124.90 (C₆, C₁₄), 126.00 (C₁₅, C₁₆), 128.10 (C₉, C₁₁), 130.20 (C₅), 140.00 (C₁₀), 143.90, (C₄), 148.70 (C₇), 157.00 (C₁).

(3f) 1-(p-tolydiazenyl)naphthalene-2-ol

Grinding Time: 15 minutes, (Yield: 97%); M.P.: 209-212°C., Mol. F.: C₁₇H₁₄N₂O; Mol. Wt.: 262.31; m/z (FABMS): 262.11; Elemental analysis: (Calculated %) C, 77.84; H, 5.38; N, 10.68; O, 6.10; (Found %) C 77.80; H, 5.341; N, 10.66; O, 6.13; ¹HNMR: 2.28 (s, 3H CH₃), 7.15 (d, 1H Ar), 7.34-7.56 (m, 4H Ar), 8.00-8.25 (m, 3H Ar), 8.46 (d, 2H Ar), 11.00 (s, 1H OH); ¹³CNMR: 121.30 (CH₃), 122.10 (C₈, C₁₂), 122.20 (C₂, C₁₄), 126.30 (C₅), 127.00 (C₄, C₁₃, C₁₅), 130.60 (C₆, C₁₆), 130.80 (C₉, C₁₁), 141.20 (C₁₀), 143.30 (C₁), 149.00, (C₇), 156.50 (C₃).

(3g) 4-(4-nitrophenyl)diazenylphenol

Grinding Time: 4 minutes, (Yield: 87%); M.P.: 235-237°C., Mol. F.: C₁₂H₉N₃O₃; Mol. Wt.: 243.22; m/z (FABMS): 243.06; Elemental analysis: (Calculated %) C, 59.26; H, 3.73; N, 17.28; O, 19.73; (Found %) C 59.31; H, 3.70; N, 17.30; O, 19.69; ¹HNMR: 7.00 (d, 2H Ar), 7.55-7.70 (m, 4H Ar), 8.25 (d, 2H Ar), 11.35 (s, 1H OH); ¹³CNMR: 115.90 (C₂, C₆), 119.50 (C₈, C₁₂), 123.60 (C₉, C₁₁), 123.80 (C₃, C₅), 143.90 (C₄), 148.90 (C₁₀), 152.10 (C₇), 160.00 (C₁).

(3h) 4-(4-nitrophenyl)diazenyl naphthalene-1-ol

Grinding Time: 9 minutes, (Yield: 89%); M.P.: 281-283°C., Mol. F.: C₁₆H₁₁N₃O₃; Mol. Wt.: 293.28; m/z (FABMS): 293.08; Elemental analysis: (Calculated %) C, 65.52; H, 3.78; N, 14.33; O, 16.37; (Found %) C 65.56; H, 3.82; N, 14.29; O, 16.33; ¹HNMR: 7.15 (d, 1H Ar), 7.50 (t, 2H Ar), 7.35 (d, 2H Ar), 8.15-8.30 (m, 3H Ar), 8.65 (d, 1H Ar), 8.95 (d, 1H Ar), 11.95 (s, 1H OH); ¹³CNMR: 108.90 (C₂), 115.00 (C₃), 120.00 (C₈, C₁₂), 123.70 (C₁₃), 123.90 (C₉, C₁₁), 124.90 (C₆, C₁₄), 127.00 (C₁₅, C₁₆), 127.20 (C₅), 143.00 (C₄), 150.50 (C₁₀), 155.00 (C₇), 156.80 (C₁).

(3i) 1-(4-nitrophenyl)diazenyl naphthalene-2-ol

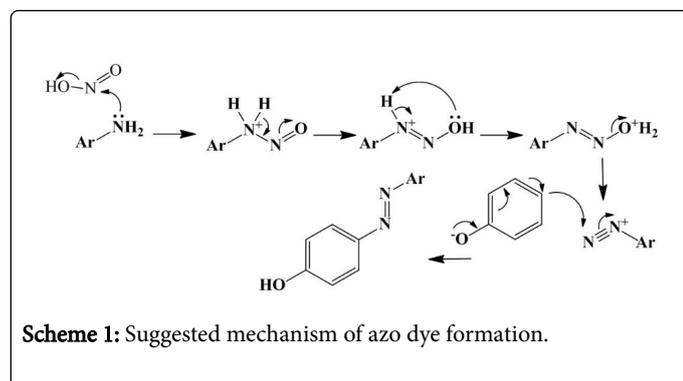
Grinding Time: 8 minutes, (Yield: 91%); M.P.: 274-277°C., Mol. F.: C₁₆H₁₁N₃O₃; Mol. Wt.: 293.28; m/z (FABMS): 293.08; Elemental analysis: (Calculated %) C, 65.52; H, 3.78; N, 14.33; O, 16.37; (Found %) C 65.51; H, 3.80; N, 14.29; O, 16.40; ¹HNMR: 7.20 (d, 1H Ar), 7.45 (m, 2H Ar), 7.80 (d, 2H Ar), 8.05-8.25 (m, 3H Ar), 8.45 (d, 2H Ar), 12.25 (s, 1H OH); ¹³CNMR: 120.00 (C₈, C₁₂), 122.50 (C₂, C₁₄), 124.95 (C₉, C₁₁), 125.90 (C₅), 126.10 (C₄, C₁₅), 127.20 (C₁₃), 129.10 (C₆, C₁₆), 145.00 (C₁), 149.80 (C₁₀), 154.70, (C₇), 156.00 (C₃).

Results and Discussion

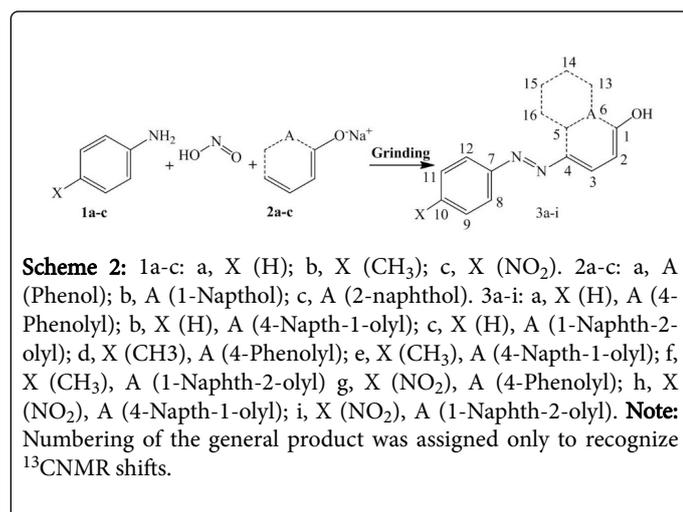
Azo dyes that represent an important class of industrial dyes were established via a two steps reaction mechanism. The first one was diazotization between an aromatic amine and nitrous acid salt, followed by the next coupling step with another electron rich aromatic system.

Initially, the aromatic amine reacted with nitrous acid salt affording the highly reactive diazonium cation with electron deficient Nitrogen that struggled to complete the octet. Therefore, the diazonium ion, incidentally, would be attacked by electron rich aromatic system that was susceptible for electrophilic aromatic substitution and the azo dye was the product, Scheme 1.

In our current work, the reactants were grinded together, via means of agate mortar and pestle, in a solvent free facile synthesis. The completion of the reaction was recognized, and the resulted azo dyes were achieved through an efficient short time and benign experiment, Scheme 2.



Remarkably, the grinding process, supplied a gentle and an adequate activation energy via frictions that was sufficient for the three reactants to interact. Accordingly, the grinding time was largely affected by the susceptibility of the electron rich aromatic system and the structure-reaction time relationship was largely pronounced. Hence, the grinding time was minimized, if compared to the conventional methods, offering an efficient green and sustainable process [38,39].



Furthermore, the results revealed excellent conversion and high yield practice that optimized the atom economy of the whole experiment, hence, reinforced the green context of the synthesis.

Additionally, the simplicity of the synthesis opened a research window for more advances in synthesis of such important organic compounds via environmentally benign pathways with safer handling and easier processing.

Conclusion

The present study developed the former synthetic pathways of azo dyes, via grinding at room temperature and under solvent free conditions. The implemented method showed a benign research that enhanced the atom efficiency, minimized the reaction time and afforded a relatively high reaction yield. Finally, this method opened research window for forthcoming methodologies to green, sustainable, and benign practices that strengthen environmental impacts of manufacturing valuable organic compounds.

Acknowledgment

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