



Green and Efficient Synthesis of 1-Naphthol Azo Dyes with Polymer/HIO₄ as a New Solid Acid by Grinding

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ABSTRACT

An environmentally benign and one-pot method for the synthesis of 1-naphthol azo dyes has been developed by using polymer-supported periodic acid (PPIA) as a new solid acid *via* grinding followed by a diazo coupling reaction by 1-naphthol under solvent-free conditions at room temperature. The obtained aryl diazonium salts supported on polymer (aryl diazonium polymer periodate), ArN₂⁺IO₄⁻ were sufficiently stable to be kept at room temperature in the dry state. This method has the advantages such as: eco-friendly, heterogeneous reaction conditions, simple experimental procedure, high purity. The structures of the products have been characterized by several techniques using UV-Vis, FT-IR, ¹H NMR, ¹³C NMR and mass spectra.

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Introduction

Dye is an essential property for a variety of industrial products. For example, cosmetic, textile, leather industries, electronic devices, linear and non linear optics and pharmaceutical products [1-4]. Aromatic diazonium salts are important building blocks in the preparation of azo dyes synthesized *via* the diazotization of aryl amines by using nitrous acid and strong acids [5]. Diazonium salts that are formed by liquid acids are unstable at room temperature but the use of solid acid instead of liquid acid is caused by the stability of diazonium salts [6,7]. The acidic solutions result in permanent damage to our life environment and change the ecological balance. In contrast, not only do solid acids simplify experimental procedure and they aren't harmful for environment but also are eco friendly reagents and decrease wastes and by-products [8]. There are a few reactions reported under solvent-free condition of diazo-coupling by means of solid acids or liquid acids [9,10,6]. Also polymer-supported catalysts have been favored for the wide range of organic synthesis [11]. Polymer supported periodic acid is a superior proton source and is comparable with other solid acids such as nafion-H, silica sulfuric acid, silica chloride and etc [12-15]. In this paper, it is expected to report a convenient and one-pot method for diazotization and diazo coupling reactions using polymer supported periodic acid under solvent-free conditions at room temperature by grinding.

Experimental

Materials and instruments

Chemicals were purchased from Merck and Fluka chemical companies. All compounds were known and are identified by comparison of their physical and spectroscopic data with those of authentic samples. IR spectra were recorded as KBr pellets on a Perkin-Elmer 781 spectrophotometer and an Impact 400 Nicolet FT-IR spectrophotometer. ¹H NMR was recorded on a Bruker DRX-400 Avance spectrometer with tetramethylsilane as

internal reference. Melting points obtained with a Yanagimoto micro melting point apparatus. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates (from Merck Company). Preparation of poly (1,4-phenylene-2,5-pyridinedicarboxamide) was accomplished by using 2,5-pyridine dicarboxylic acid, thionyl chloride and *p*-phenylenediamine according to the reported method [16].

Typical procedure

Aniline (1 mmol, 0.093g), PPIA (0.6g) and sodium nitrite (2 mmol, 0.138 g) were grounded in a mortar for 10 minutes to obtain a homogeneous mixture. A few drops of water were gradually added to this mixture and it was grounded for 10 minutes until the gas evolution completely stops. Then 1-naphthol (1 mmol, 0.144g) was added to the diazonium salt and grounded for another 10 minutes. The reaction progress was monitored by thin layer chromatography (TLC) using a mixture of ethyl acetate and n-hexane (1:9 v/v) as solvent. Further purification of the product was performed by flash column chromatography by using n-hexane and ethyl acetate, related azo dyes were obtained in 80% yield (product A, mp: 136 °C, lit. [21] 136 °C and product B, mp: 206 °C, lit. [21] 204 °C). The used reagent can be re-generated by reacting with a solution of HIO₄ as preliminary preparation of the reagent.

The selected spectral data

2-(2-(4-Nitrophenyl)diazenyl) naphth-1-ol. UV-Vis: λ_{max} CHCl₃ = 498, 295 nm; IR (KBr) cm⁻¹: 3441, 3030, 2935, 1609, 1512, 1442, 1332, 1270, 1110, 756 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ: 16.15 (s, 1H), 8.41 (d, *J* = 7.6 Hz, 1 H), 8.33 (d, *J* = 8.8 Hz, 2H), 7.8 (d, *J* = 7.2 Hz, 1H), 7.7 (d, *J* = 8.8 Hz, 2H), 7.55 (t, *J* = 9.2 Hz, 1H), 7.45 (t, *J* = 9.2 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H) ppm. ¹³C NMR (CDCl₃, 100 MHz) δ: 168.40, 143.59, 138.86, 138.36, 133.55, 130.19, 129.79, 128.59, 128.50, 128.03, 125.32, 124.00, 121.64, 119.18 ppm.

4-(2-(4-Nitrophenyl)diazenyl) naphth-1-ol. UV-Vis: λ_{\max} CHCl₃ = 490, 315 nm; IR (KBr): 3441, 3033, 1635, 1444, 1526, 1352, 1188, 1266, 756, 827 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 8.53 (s, 1H), 8.4 (d, *J* = 7.6 Hz, 1H), 8.33 (d, *J* = 8.41 Hz, 2H), 8.09 (d, *J* = 9.6 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.58 (t, *J* = 9.2 Hz, 1H), 7.42 (t, *J* = 9.2 Hz, 1H), 7 (d, *J* = 8.41 Hz, 2H), 6.7 (d, *J* = 9.6 Hz, 1H) ppm; mass spectra: 294 (M⁺+1, 10), 293 (M⁺, 48), 263 (12), 171 (10), 143 (92), 115 (61), 92 (17), 76 (9), 65 (12) m/z.

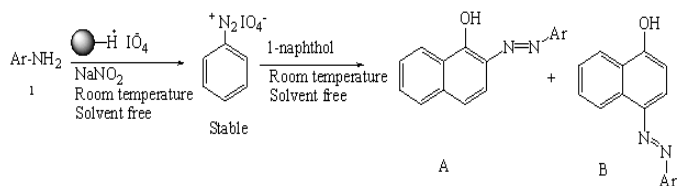
2-(2-(4-Chlorophenyl)diazenyl) naphth-1-ol. IR (KBr) cm⁻¹: 3438, 3032, 1626, 1491, 1448, 1209, 1254, 1096, 822, 749; ¹H NMR (400 MHz, CDCl₃) δ : 16.11 (s, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.31-7.25 (m, 2H), 7.04-6.83 (dd, *J* = 9.6 Hz, 2H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ : 172.29, 145.75, 142.19, 131.69, 130.21, 127.63, 125.56, 124.75, 124.19, 123.62, 122.59, 120.73, 119.15, 116.53 ppm.

4-(2-(4-Chlorophenyl)diazenyl) naphth-1-ol. IR (KBr) cm⁻¹: 3438, 3032, 1618, 1491, 1448, 1209, 1254, 1096, 822, 749; ¹H NMR (400 MHz, CDCl₃) δ : 8.83 (s, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.31-7.25 (m, 2H), 6.57 (d, *J* = 8.8 Hz, 1H) ppm. ¹³C NMR (CDCl₃, 100 MHz) δ : 170.59, 144.33, 140.10, 133.39, 133.01, 129.76, 128.94, 128.69, 128.19, 125.89, 124.33, 121.75, 119.93 ppm.

4-(2-Phenyl)diazenyl) naphth-1-ol. IR (KBr) cm⁻¹: 3441, 3033, 1635, 1444, 1526, 1352, 1188, 1266, 756, 827. ¹H NMR (400 MHz, CDCl₃) δ : 15.69 (s, NH), 8.18 (d, *J* = 7.6 Hz, 1H), 8.11 (d, *J* = 9.2 Hz, 2H), 7.50 (m, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 9.2 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 9.6 Hz, 1H), 6.82 (d, *J* = 9.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ : 161.33, 160.67, 141.84, 136.71, 133.31, 129.53, 128.33, 128.15, 124.80, 122.19, 122.06, 121.61, 114.78, 55.64 ppm. Mass spectra: 249 (M⁺+1, 22), 248 (M⁺, 95), 171 (25), 144 (14), 145 (88), 115 (59), 77 (31), 51 (10) m/z.

Results and Discussion

In continuation of our ongoing research program on the preparation and application of supported reagents in organic synthesis¹⁶⁻²⁰, a novel method has been reported for the conversion of primary aromatic amines to the related 1-naphthol azo dyes. At first, we have supported periodic acid on the poly (1,4-phenylene-2,5 pyridine dicarboxamide) according to our previous work. By obtaining their weight of the polymeric reagent, it has been realized that each gram of the reagent contains 1.75 mmol HIO₄. Thus, 0.60 g (1.05 mmol) of the PPIA was used for conversion of 1 mmol aromatic amines to related diazonium salts and azo dyes. The conversion of aromatic amines to the related azo dyes was investigated by using this polymeric reagent and sodium nitrite under solvent-free conditions at room temperature by grinding (Scheme 1).



Scheme 1: General preparation procedure of azo dyes

Then the mixture of *p*-nitro aniline (1 mmol), sodium nitrite (2 mmol) and PPIA (0.6 g) were grounded in a mortar with a pestle for a few minutes at room temperature to obtain a homogeneous mixture. Then, a few drops of water were gradually added to this mixture and then the reaction of the mixture is grounded for 10 minutes. The aryldiazonium

periodates that have been prepared were sufficiently stable to be kept at room temperature in a dried state. Then 1-naphthol (1mmol) was added to the formed diazonium salt and grinding continues for another 10 minutes. The whole process of diazotization and diazo coupling reaction were performed in 30 minutes. The crude product was extracted with ethanol or acetone. Then solvent was evaporated by rotary evaporator at reduced pressure and the crude product was purified by short column chromatography. By this method, corresponding azo dyes were obtained with 92% isolated yield. The same conditions have been used for the conversion of other aromatic amines to the corresponding azo dyes and the products have been obtained from good to excellent yields (Table 1).

Table 1: Diazotization and diazo coupling reactions of some amines with 1-naphthol at room temperature

Entry	Amines	Yield (%) ^a	Yield (%) ^b	Time (min)	Mp(°C) Found Reported[21]
1	C ₆ H ₅ NH ₂	80	80	30	A:135 A:136 B:207 B:204
2	<i>p</i> -ClC ₆ H ₄ NH ₂	85	85	25	A:163 A:162 B:178 B:176
3	<i>o</i> -ClC ₆ H ₄ NH ₂	80	78	27	A:156 A:153 B:176 B:178
4	<i>o</i> -NO ₂ C ₆ H ₄ NH ₂	80	76	23	A:172 A:175 B:285 B:284
5	<i>p</i> -NO ₂ C ₆ H ₄ NH ₂	92	92	30	A:184 A:183 B:291 B:295
6	<i>p</i> -MeOC ₆ H ₄ NH ₂	79	76	27	A:156 A:159 B:196 B:194
7	<i>p</i> -BrC ₆ H ₄ NH ₂	72	70	26	A:186 A:188 B:267 B:269
8	<i>o</i> -MeC ₆ H ₄ NH ₂	88	82	30	A:165 A:168 B:246 B:249
9	<i>p</i> -MeC ₆ H ₄ NH ₂	79	69	28	A:177 A:180 B:288 B:285

^{a,b} The ratio of amine (mmol), NaNO₂ (mmol), 1-naphthol (mmol) and PPIA (g) is 1: 2: 1: 0.6

^{a,b} Isolated yields

For consideration the stability of the diazonium salts, some aryl diazonium polymer-supported periodates were stored in a desiccator at room temperature. After some times, 2-naphthol was added to each salt and the reaction mixture was grounded at room temperature. The crude products were extracted and the yield of azo dyes were compared with the product provided with the related fresh diazonium salts (Table 2). As it is shown in table 2, aryl diazonium polymer-supported periodate with electron-withdrawing groups on aromatic ring, are more stable

than those with electron donating groups because of the instability of the resulting aryl cation [6]. Also, we have compared the stability of aryl diazonium polymer periodates versus aryl diazonium silica sulfates that previously published by Zarei et al [6] and found that the diazonium polymer-supported periodates have more stability.

Table 2. The stability study of some aryl diazonium polymer-supported periodate at room temperature

Diazonium salt	Yield (%) after						
	30 min	1 day	2 days	3 days	4 days	5 days	6 days
	90	87	82	79	75	58	31
	89	85	80	77	73	54	25
	93	90	88	82	79	73	68
	95	92	87	80	77	70	65

^aThe yields refer to the isolated pure products after adding 2-naphthol into their related diazonium salts within the specified time

Conclusion

In conclusion, different aromatic amines were rapidly and efficiently converted to the related azo dyes under solvent-free conditions at room temperature by grinding. This method has many merits, including efficient and environmentally more benign route for solvent-free synthesis of azo dyes. And also it has other advantages such as mildness, short reaction times and simplicity of methodology.

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