

## Polymer/HIO<sub>4</sub>: An efficient catalyst for solvent-free synthesis of 2-naphthol azo dyes

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Received 25 April 2014; received in revised form 21 July 2014; accepted 31 July 2014

### ABSTRACT

A convenient, one-pot method for the synthesis of diazonium salt has been developed by the sequential diazotization of aromatic amines with NaNO<sub>2</sub>, polymer- supported periodic acid (PPIA) and 2-naphthole under solvent-free conditions at room temperature. By using this method, several types of aromatic amine, containing electron-withdrawing and electron-donating groups, were rapidly converted to the corresponding azo dyes in good to excellent yields. The ensuing aryl diazonium salts supported on polymer (aryl diazonium polymer), ArN<sub>2</sub><sup>+</sup>IO<sub>4</sub><sup>-</sup> were sufficiently stable to be kept at room temperature in the dry state. The use of mild reaction conditions and an inexpensive procedure are further advantages of this method.

**Keywords:** Azo dye, Polymer-supported periodic acid, Diazotization, Solvent-free condition.

### 1. Introduction

In recent decades, organic color chemistry is undergoing very exciting development as a result of the opportunities presented by dye applications in high technology fields: electronic devices, linear and non linear optics, reprography and sensors [1-4]. In pharmaceutical, azo compounds are well known for antifungal [5], antiviral activity [6] and some are useful as chemotherapeutic agents [7]. The azo dye sulfonamides antibacterial drugs are totally inactive *in vitro* but possess excellent activity *in vivo*. This effect is believed to be caused by broken azo links [8]. Since compounds with azo moiety and naphthalene moiety have been extensively used as dyes, but biological and antibacterial activity are less reported [9,10]. Aromatic diazonium salts are important building blocks in the preparation of azo dyes which were synthesized *via* the diazotization of aryl amines using nitrous acid. Sodium or potassium nitrites are used as nitrous acid sources because of the instability of free nitrous acid. Organic nitrite esters, such as t-butyl nitrite and ethyl nitrite have been used as alternative sources of nitrous acid in organic solvents [11,12]. Diazonium salts which are formed by liquid acids are unstable at room

temperature but by using solid acid instead of liquid acid, the stability of diazonium salts increases [13,14]. The acidic solutions result in permanent damage to our life environment and change the ecological balance. However, solid acids not only simplify experimental procedure but also are eco-friendly reagents and decrease wastes and by-products [15,16]. Recently, solvent-free synthesis of 1,4-disubstituted-1,2,3-triazoles using neat azides and alkynes and a copper (I) polymer supported catalyst (Amberlyst A21•CuI) has been reported [17]. Also it has been reported that poly vinyl pyrrolidone (PVP) supported ferric chloride catalyzes the condensation of *o*-phenylene diamines with ketones under solvent free conditions to afford the corresponding 1,5-benzodiazepine derivatives in high yields [18]. Polymer supported nitrite esters are also useful reagents in a modification of the diazotizing reaction [19]. Herein, we wish 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.

### 2. Experimental

#### 2.1. Materials and methods

Chemicals were purchased from Merck and Fluka chemical companies. All compounds were known and

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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.  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR spectra were 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 was accomplished by TLC on silica-gel polygram SIL G/UV 254 plates (from Merck Company). Preparation of poly(1,4-phenylene-2,5-pyridinedicarboxamide) was accomplished using 2,5-pyridine dicarboxylic acid, thionyl chloride and *p*-phenylenediamine according to literature [20].

## 2.2. Typical procedure of azo dyes synthesis

Aniline (1 mmol, 0.09 mL), PPIA (0.6 g) and sodium nitrite (1.2 mmol, 0.083 g) were ground in a mortar for 10 minutes to obtain a homogeneous mixture. Then, a few drops of water were gradually added to this mixture and the whole was ground for 10 min until the gas evolution released. 2-naphthol (1 mmol) was added to the diazonium salt and grinding continued for 10 min. 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 using hexane and ethyl acetate. Dye was obtained in 90 % yield, m.p. = 133-134 °C (lit [23] 134 °C).

### Selected spectral data

#### Compound (3a):

UV-Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}} = 490, 318 \text{ nm}$ . IR (KBr):  $\bar{\nu} = 3434 \text{ (w)}, 3031 \text{ (w)}, 1617 \text{ (s)}, 1447 \text{ (s)}, 1207, 1261 \text{ (s)}, 839 \text{ (s)}, 751 \text{ (s)} \text{ cm}^{-1}$ .  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 16.05 \text{ (s, 1 H, NH/OH)}, 8.37 \text{ (d, } J = 8 \text{ Hz, 1 H)}, 7.58 \text{ (d, } J = 8.4 \text{ Hz, 2 H)}, 7.56 \text{ (d, } J = 9.2 \text{ Hz, 1 H)}, 7.42 \text{ (d, } J = 8 \text{ Hz, 1 H)}, 7.36 \text{ (t, } J = 8 \text{ Hz, 1 H)}, 7.30 \text{ (t, } J = 7.2 \text{ Hz, 2 H)}, 7.21 \text{ (t, } J = 8 \text{ Hz, 1 H)}, 7.11 \text{ (t, } J = 7.2 \text{ Hz, 1 H)}, 6.68 \text{ (d, } J = 9.2 \text{ Hz, 1 H)} \text{ ppm}$ .  $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 177.88, 144.80, 140.06, 133.61, 130.08, 129.59, 128.86, 128.62, 128.07, 127.42, 125.72, 124.82, 121.73, 118.60 \text{ ppm}$ .

#### Compound (3c):

UV-Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}} = 490, 324$ . IR (KBr):  $\bar{\nu} = 3432 \text{ (w)}, 2931 \text{ (m)}, 1621 \text{ (s)}, 1492 \text{ (s)}, 1451 \text{ (s)}, 1210, 1255 \text{ (s)}, 821 \text{ (s)}, 749 \text{ (s)} \text{ cm}^{-1}$ .  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 15.60 \text{ (s, 1H, NH/OH)}, 8.65 \text{ (d, } J = 8 \text{ Hz, 1 H)}, 7.95 \text{ (d, } J = 9.6 \text{ Hz, 1 H)}, 7.88 \text{ (d, } J = 8.6 \text{ Hz, 2 H)}, 7.78 \text{ (d, } J = 7.6 \text{ Hz, 1 H)}, 7.74 \text{ (d, } J = 8.6 \text{ Hz, 2 H)}, 7.61 \text{ (t, } J = 7.6 \text{ Hz, 1 H)}, 7.46 \text{ (t, } J = 7.6 \text{ Hz, 1 H)}, 6.94 \text{ (d, } J = 9.6 \text{ Hz, 1 H)} \text{ ppm}$ .  $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta =$

170.59, 144.33, 140.10, 133.39, 133.01, 129.76, 128.94, 128.69, 128.19, 126.42, 125.89, 124.33, 121.75, 119.93 ppm.

#### Compound (3h):

UV-Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}} = 496, 322$ . IR (KBr):  $\bar{\nu} = 3437 \text{ (w)}, 3030 \text{ (w)}, 2935 \text{ (m)}, 1616 \text{ (s)}, 1501 \text{ (s)}, 1447 \text{ (s)}, 1207, 1266 \text{ (s)}, 814 \text{ (s)}, 748 \text{ (s)} \text{ cm}^{-1}$ .  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 16.2 \text{ (s, 1 H, NH/OH)}, 8.62 \text{ (d, } J = 8 \text{ Hz, 1 H)}, 7.74 \text{ (d, } J = 9.6 \text{ Hz, 1 H)}, 7.69 \text{ (d, } J = 8 \text{ Hz, 2 H)}, 7.64 \text{ (d, } J = 8 \text{ Hz, 1 H)}, 7.57 \text{ (t, } J = 7.6 \text{ Hz, 1 H)}, 7.40 \text{ (t, } J = 7.6 \text{ Hz, 1 H)}, 7.30 \text{ (d, } J = 8 \text{ Hz, 2 H)}, 6.94 \text{ (d, } J = 9.6 \text{ Hz, 1 H)}, 2.43 \text{ (s, 3 H)} \text{ ppm}$ .  $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 168.56, 143.51, 138.92, 138.35, 133.54, 130.20, 129.77, 128.61, 128.52, 128.02, 125.34, 124.04, 121.64, 119.15, 21.32 \text{ ppm}$ .

#### Compound (3i):

UV-Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}} = 488, 320$ . IR (KBr):  $\bar{\nu} = 3433 \text{ (w)}, 3025, 2938, 1601 \text{ (s)}, 1521 \text{ (s)}, 1441 \text{ (s)}, 1159, 1246 \text{ (s)}, 828 \text{ (s)}, 753 \text{ (s)} \text{ cm}^{-1}$ .  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 15.73 \text{ (s, 1H, NH/OH)}, 8.73 \text{ (d, } J = 8.4 \text{ Hz, 1 H)}, 7.85 \text{ (d, } J = 9.2 \text{ Hz, 2 H)}, 7.78 \text{ (d, } J = 9.2 \text{ Hz, 1 H)}, 7.71 \text{ (d, } J = 8.4 \text{ Hz, 1 H)}, 7.6 \text{ (t, } J = 8 \text{ Hz, 1 H)}, 7.41 \text{ (t, } J = 8 \text{ Hz, 1 H)}, 7.06 \text{ (d, } J = 9.2 \text{ Hz, 2 H)}, 7.04 \text{ (d, } J = 9.2 \text{ Hz, 1 H)}, 3.91 \text{ (s, 3 H)} \text{ ppm}$ .  $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 161.33, 160.67, 141.84, 136.71, 133.31, 129.53, 128.33, 128.15, 127.11, 124.80, 122.19, 122.06, 121.61, 114.78, 55.64 \text{ ppm}$ .

## 3. Results and Discussion

In continuation of our ongoing research program on the preparation and application of solid acid catalysts and supported reagents in organic synthesis,<sup>20-31</sup> in this protocol, we have reported a novel method for the conversion of primary aromatic amines to the related azo dyes. At first we prepared polymer supported periodic acid by reacting the poly (1,4-phenylene-2,5-pyridinedicarboxamide) with a 70% aqueous solution  $\text{HIO}_4$ . It was stirred at room temperature for 48 h. Then it was filtered and washed with  $\text{H}_2\text{O}$  to remove unreacted periodates. The obtained polymeric catalyst was dried to afford polymer-supported periodic acid (Fig. 1). By having weight of the polymeric reagent, we found that one gram of the polymer contains

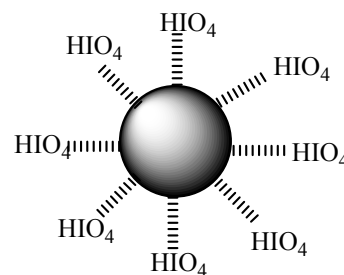


Fig. 1. The structure of polymer-supported periodic acid.

1.75 mmol  $\text{HIO}_4$ . Thus, we used 0.60 g (1.05 mmol) of the catalyst for the diazotization and azo coupling reactions. Then mixture of *p*-nitro aniline (1 mmol) and sodium nitrite (1.2 mmol) in the presence of various amounts of catalyst were ground, we have found the corresponding azo dye in excellent yield using 0.6 g of PPIA (Table 1).

We have investigated the conversion of primary aromatic amines to the corresponding azo dyes using 2-naphthol in the presence of the above mentioned catalyst under solvent free conditions by grinding (Scheme 1).

Generally, an aromatic amine (1 mmol), catalyst (0.6 g) and sodium nitrite (1.2 mmol) are ground in a mortar with a pestle for a few minutes to prepare a homogeneous mixture. Then, a few drops of water are gradually added to this mixture and then the reaction mixture is ground for 10–20 min until the gas evolution completely finished. The aryldiazonium periodate which are obtained *via* our method are sufficiently stable to be kept at room temperature in a dried state. After preparation of diazonium salts, 2-naphthol (1 mmol) was added to them and stirred for 10 minutes. The whole process of diazotization and azo

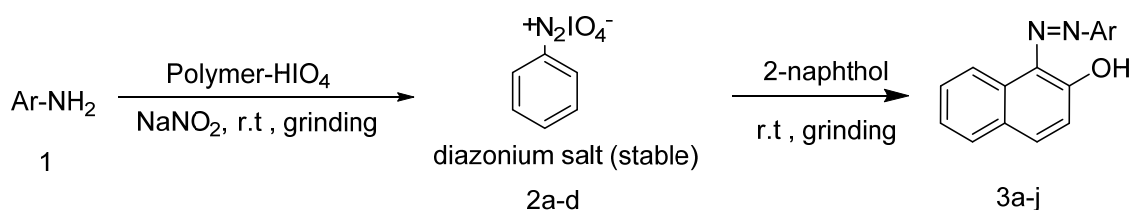
coupling were done in 30 min. The crude product was extracted with dichloromethane. Then the solvent was evaporated by rotary evaporator at reduced pressure and the crude product was purified by flash column chromatography. By this procedure, azo dyes were prepared in good to excellent yields (Table 2).

The reusability of catalyst was investigated for several times which indicated no significant decrease in catalytic activity (Fig. 2).

**Table 1.** Preparation of azo dye in the presence of various amount of catalyst<sup>a</sup>.

Entry	Catalyst (g)	Yield (%)
1	0.1	15
2	0.2	30
3	0.3	37
4	0.4	55
5	0.5	80
6	0.6	95
7	0.7	95

<sup>a</sup>*p*-nitroaniline (1 mmol) and sodium nitrite (2 mmol) were used.



**Scheme 1.** Azo dyes preparation based on 2-naphthol in the presence of polymer-supported periodic acid.

**Table 2.** Preparation of azo dyes based 2-naphthol in the presence of polymer-supported periodic acid at room temperature.<sup>a</sup>

Entry	Substrate	Product	Yield (%)	m.p. (°C)	
				Found	Reported <sup>b</sup>
1	Aniline	3a	90	134	134
2	<i>p</i> -Chloro aniline	3b	93	160	161
3	<i>p</i> -Bromo aniline	3c	85	155	154
4	<i>o</i> -Nitro aniline	3d	92	243	245
5	<i>p</i> -Nitro aniline	3e	95	255	256
6	<i>o</i> -Chloro aniline	3f	83	162	166
7	<i>o</i> -Methyl aniline	3g	83	130	131
8	<i>p</i> -Methyl aniline	3h	88	140	142
9	<i>p</i> -Methoxy aniline	3i	89	178	180
10	3,4-Dimethoxy aniline	3j	70	195	198

<sup>a</sup>The ratio of amine (mmol),  $\text{NaNO}_2$  (mmol), 2-naphthol (mmol) and PPIA (g) is 1:1.2:1:0.6.

<sup>b</sup>Reported m.p. from Ref. [32].

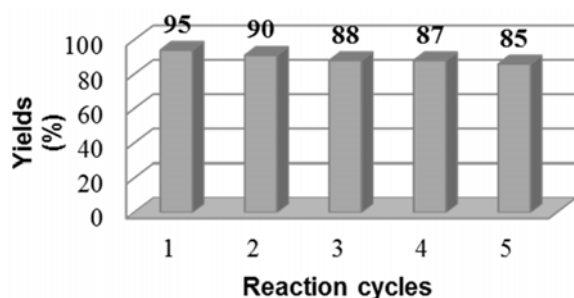


Fig. 2. Reusability of catalyst.

For determining the stability of the diazonium salts, some aryl diazonium polymer-supported periodates were stored in a desiccator at room temperature. After the specified times, 2-naphthol was added to each salt and the reaction mixture was ground at room temperature for 10 minutes. The products were extracted and the yield of azo dyes compared with the product provided with the related fresh diazonium salts (Table 3). As shown in table 2, aryl diazonium polymer periodates 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 [14].

#### 4. Conclusions

In conclusion various aromatic amines were rapidly and efficiently converted to the corresponding of azo dyes. The solvent free conditions employed in the present method, which make it environmentally friendly and make it useful for industrial applications. This method is a novel route for solvent-free synthesis of azo dyes. Furthermore, it has other advantages such as mildness, short reaction times, low cost, ease of handling and simple experimental procedure. It is pointed out that the *in vitro* antibacterial activity of some azo dyes were studied [9].

#### Acknowledgment

The authors are grateful to University of Kashan for supporting this work by Grant No (159189/15).

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Table 3. The stability study of some aryl diazonium polymer-supported periodate at room temperature.<sup>a</sup>

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

<sup>a</sup>The yields refer to the isolated pure products after adding 2-naphthol into their related diazonium salts within the specified time.

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