



## Diazotization of Aniline Derivatives and Diazo Couplings in the Presence of *p*-Toluenesulfonic Acid by Grinding

N. Noroozi-Pesyan<sup>\*1</sup>, J. Khalafy<sup>2</sup>, Z. Malekpoor<sup>3</sup>

<sup>1</sup> Assistant Professor, Department of Chemistry, Faculty of Science, Urmia University, 57159, Urmia, Iran

<sup>2</sup> Professor, Department of Chemistry, Faculty of Science, Urmia University, 57159, Urmia, Iran

<sup>3</sup> M.Sc., Department of Chemistry, Faculty of Science, Urmia University, 57159, Urmia, Iran

### ARTICLE INFO

#### Article history:

Received: 4-10-2008

Accepted: 18-7-2009

Available online: 18-7-2009

#### Keywords:

Azo dyes

Solvent free

Grinding

*p*-Toluenesulfonic acid

Green chemistry.

### ABSTRACT

**T**he solid-solid reactions of electron-donor compounds, such as: barbituric acid (1a), thiobarbituric acid (1b), 1,3-dimethyl barbituric acid (1c), phenol (1d) and resorcinol (1e) with diazotized *o*-nitroaniline (3), *m*-nitroaniline (4) and *p*-nitroaniline (5) catalyzed by *p*-toluenesulfonic acid (2) afford azo dyes by grinding in good yields. This new method totally avoids the use of inorganic acids, alkalies, toxic and/or expensive solvents in diazotization and diazo coupling reactions. Prog. Color Colorants Coat. 2(2009), 61-70. © Institute for Color Science and Technology.

## 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, sensors and biomedical uses [1-4].

The diazotizing method by protonation of nitrous acid under acidic conditions is well-known [5]. The acid-base catalyzed processes are effective for the near quantitative formation of desired products. But its main limitation is their environmental incompatibility, because nowadays the prohibition of the environmental pollution is main issue in global the world [6]. In addition to the solvent case, the synthesis of azo dyes in ionic liquids is reported [7]. The solid-state diazotization and diazo coupling of some electron-rich aromatic compounds with gaseous

NO<sub>2</sub> [8], in the presence of ferric nitrate as an oxidation agent [9], via resin supported diazonium salts [10], on clays as catalyst [11] and even coupling in supercritical carbon dioxide [12] are reported. As part of our ongoing research program for exploring the catalytic properties of *p*-TsA, we herein propose a new process for diazotization and diazo coupling reactions using *p*-TsA, in which it leads to the synthesis of azo dyes.

## 2. Experimental

### 2.1. Materials and instruments

IR spectra were determined in the region 4000- 400 cm<sup>-1</sup> on a NEXUS 670 FT IR spectrometer by preparing KBr pellets. The <sup>1</sup>H NMR spectra in DMSO-*d*<sub>6</sub> were measured at 300 MHz, using Bruker 300 FT-NMR

\*Corresponding author: [n.noroozi@mail.urmia.ac.ir](mailto:n.noroozi@mail.urmia.ac.ir)

spectrometer referencing tetramethylsilane as internal standard. Compounds 1a-c were synthesized in our laboratory based on common and known methods [5]. Compounds 1d, 1e, *p*-TsA and sodium nitrite were purchased from Merck and Aldrich and used without further purification.

## 2.2. Syntheses

### General synthesis of azo dyes (6a-d-8a-d)

A general preparative procedure is described below for the preparation of 5-(4-nitro-phenylazo) pyrimidine-2,4,6-trione (8a) and all other dyes were prepared in the similar manner.

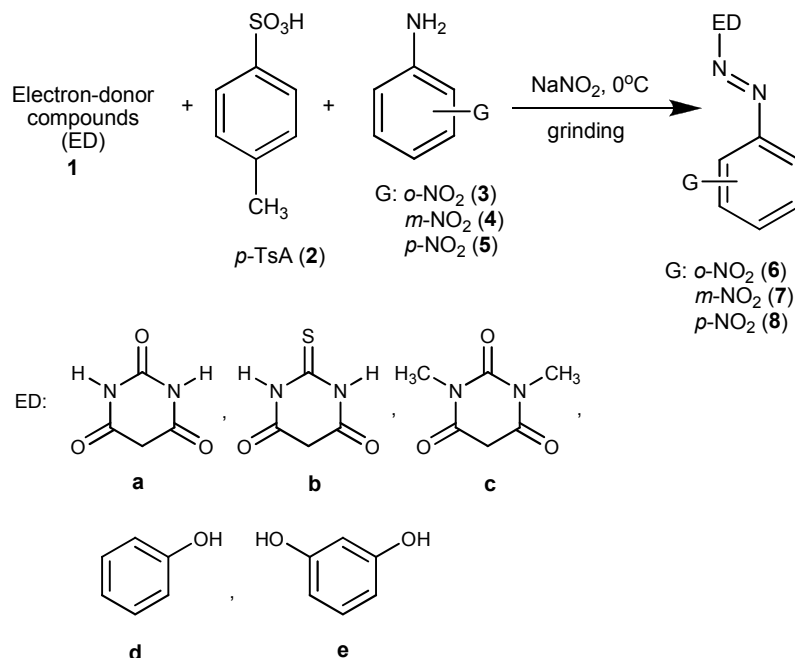
### Representative procedure for the synthesis of 5-(4-nitro-phenylazo) pyrimidine-2,4,6-trione (8a).

The mixtures of barbituric acid (0.14 g, 1.06 mmol), *p*-TsA (0.18 g, 1.06 mmol), *p*-nitroaniline (0.15 g, 1.06 mmol) and sodium nitrite (0.07 g, 1.06 mmol) were mixed, grinded in an agate mortar at 0 °C. After few minutes the color of homogenized mixture became at first yellow and then red after grinding. The reaction progress was monitored by thin layer chromatography

(TLC) using a mixture of ethyl acetate and cyclohexane (1:1; v/v) as solvent. Initially, reaction mixture was washed with water (twice) for removing of the residual sodium nitrite and *p*-TsA and then with ethanol to remove the unreacted *p*-nitroaniline. Spectroscopic data's and physical properties of the obtained azo dyes have been compared with their authentic samples and are summarized in Table 2. All the prepared azo dyes have decomposed up to 200 °C.

## 3. Results and discussion

In this article we provide a facile and novel route for the synthesis of azo dyes by grinding in the presence of solid sodium nitrite ( $\text{NaNO}_2$ ) and *p*-TsA as an acidic catalyst at 0 °C with good yields (50-80%). In this process, grinding of four components mixture, the electron-donor compounds (as a coupling agent), aniline derivative, sodium nitrite and *p*-TsA formed a colorful reaction mixture. Electron-donor compounds (1a-e) coupled with the diazotized *o*-(3), *m*-(4) and *p*-nitroaniline (5) and were afforded the corresponding azo dyes (6a-e-8a-e) (Scheme 1). The yield of azo dyes was improved by increasing of the electron-donor ability of coupling agents.

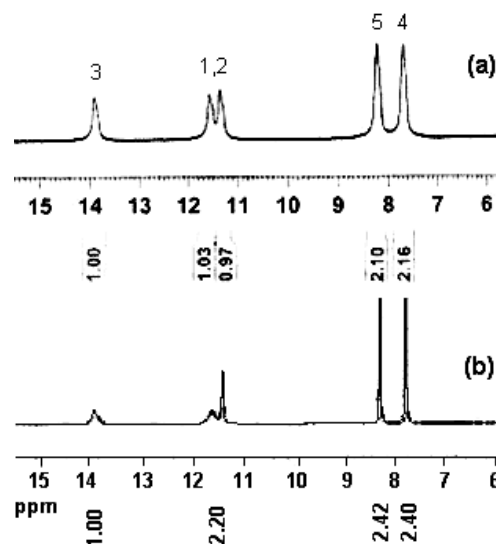


**Scheme 1:** Diazotization of aniline derivatives and coupling reaction with electron-donor compounds (1a-e) in the presence of solid sodium nitrite and 2 by grinding.

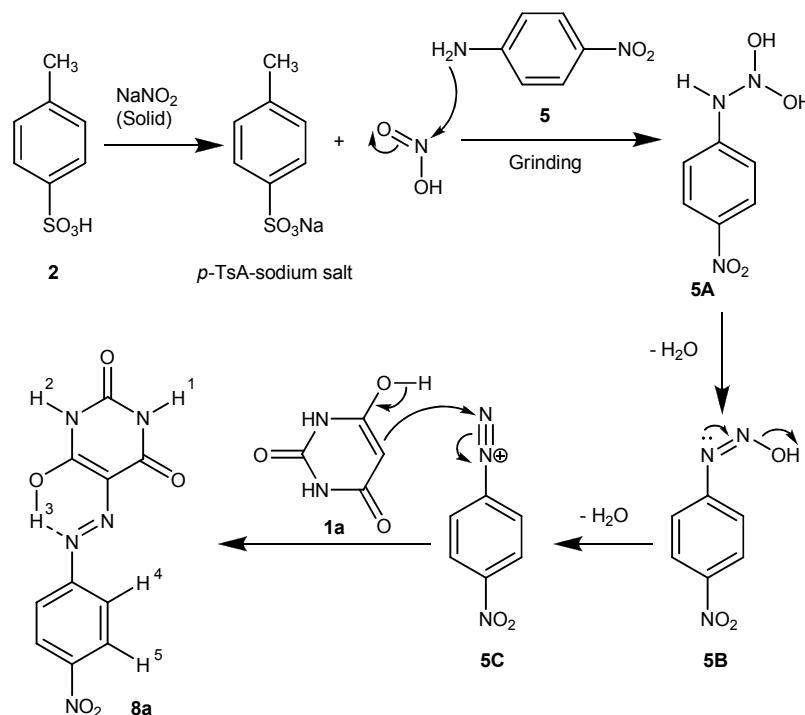
The proposed mechanism for acid-catalyzed diazo coupling reaction of diazonium salt of *p*-nitroaniline 5 with barbituric acid (1a) in the presence of solid  $\text{NaNO}_2$  was depicted in Scheme 2. Initially, *p*-TsA was converted to sodium *p*-toluenesulfonate and nitrous acid in the presence of  $\text{NaNO}_2$ . In the next step, nucleophilic addition of amino group of 5 was done by nitrous acid to produce intermediate 5A. Elimination of two molecules of water from 5A produced diazonium salt 5C. Finally, the nucleophilic attack of barbituric acid 1a to 5C forms azo dye 8a. The reaction mixture became moist due to releasing of water during the decomposition process. This observation confirmed the proposed mechanism in Scheme 2.

### 3.1. Spectral characteristics

$^1\text{H}$  NMR spectrum of the crude reaction mixture of 5-(4-nitro-phenylazo) pyrimidine-2, 4, 6-trione (8a) showed two doublets at  $\delta$  7.79 and 8.32 ppm ( $J = 9.3$  Hz), two amide protons and a highly deshielded NH/OH proton appeared at  $\delta$  11.42, 11.65 and 13.95 ppm, respectively, which all are comprised by  $^1\text{H}$  NMR data of authentic sample (Figure 1 and Table 2).

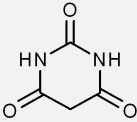
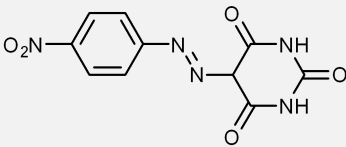
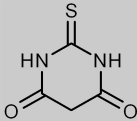
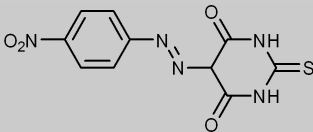
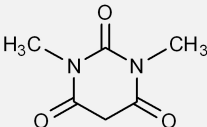
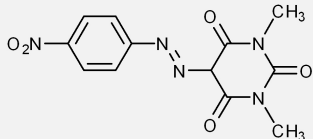
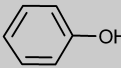
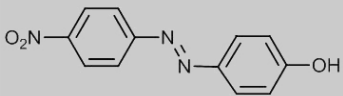
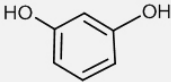
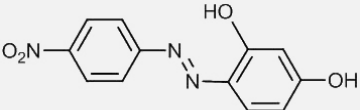


**Figure 1:**  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ) spectrum of the 8a obtained by grinding after washing with water then with ethanol, as the representative (a), is compared with the spectrum of pure 8a obtained under the solvent condition (b).



**Scheme 2:** The proposed mechanism of acid catalyzed and diazo coupling reactions by grinding. (The mechanism is assigned to compounds 5 and 1a, as the representatives).

**Table 1:** Diazotization and diazo coupling reactions of some electron-donor compounds (1a-e) with *p*-nitroaniline (5) catalyzed by *p*-TsA as the representative.

Azo dyes	Coupling agent (electron-donor)	Product	Appearance	%Yield <sup>a</sup>
8a			Yellow	70
8b			Yellow-orange	70
8c			Yellow	50
8d			Brown	70
8e			Orange-brown	80

a) Yields refer to isolated compounds.

**Table 2:** Spectroscopic data of some selected azo dyes in DMSO-*d*<sub>6</sub> as the representative.

Azo dyes	Spectral data
6a	<p>IR (KBr, cm<sup>-1</sup>): 3447.85 (m), 3072.32 (s), 1747.31 (s), 1679.78 (s), 1643.32 (m), 1488.16 (s), 1328.62 (s), 1229.67 (s), 813.81 (s)</p> <p><sup>1</sup>H NMR (300 MHz, DMSO-<i>d</i><sub>6</sub>): 15.18 (s, 1H), 11.70 (s, 1H), 11.48 (s, 1H), 8.261 (dd, <i>J</i><sub>1</sub> = 8.4 Hz, <i>J</i><sub>2</sub> = 1.2 Hz 1H), 8.08 (d, <i>J</i> = 7.8 Hz, 1H), 7.88 (t, <i>J</i> = 7.5 Hz, 1H), 7.38 (td, <i>J</i><sub>1</sub> = 7.8 Hz, <i>J</i><sub>2</sub> = 1.2 Hz).</p> <p><sup>13</sup>C NMR (75 MHz, DMSO-<i>d</i><sub>6</sub>): 161.85 (CO), 159.86 (CO), 150.17 (CO), 138.00 (C), 137.03 (C-H), 135.93 (C), 126.48 (C-H), 125.17 (C-H), 122.69 (C), 117.60 (C-H).</p>
6b	<p>IR (KBr, cm<sup>-1</sup>): 3633.07 (m), 3504.99 (m), 3137.79 (s), 1720 (s), 1700 (s), 1668.53 (s), 1606.06 (s), 1583.33 (s), 1467.49 (s), 1217.17 (s).</p> <p><sup>1</sup>H NMR (300 MHz, DMSO-<i>d</i><sub>6</sub>): 15.23 (s, 1H), 12.76 (s, 1H), 12.59 (s, 1H), 8.27 (dd, <i>J</i><sub>1</sub> = 8.4 Hz, <i>J</i><sub>2</sub> = 0.9 Hz 1H), 8.08 (d, <i>J</i> = 8.4 Hz, 1H), 7.90 (t, <i>J</i> = 7.2 Hz, 1H), 7.41 (td, <i>J</i><sub>1</sub> = 7.8 Hz, <i>J</i><sub>2</sub> = 1.2 Hz).</p> <p><sup>13</sup>C NMR (75 MHz, DMSO-<i>d</i><sub>6</sub>): 178.28 (CS), 159.78 (CO), 158.31 (CO), 137.73 (C), 137.06 (C-H), 136.15 (C), 126.52 (C-H), 125.58 (C-H), 123.19 (C), 117.80 (C-H).</p>

Table 2: Continue.

Azo dyes	Spectral data
6c	<p>IR (KBr, <math>\text{cm}^{-1}</math>): 3440.00 (bm), 3088.92 (m), 2950.00 (w), 2925.00 (w), 1736.95 (s), 1680.80 (s), 1647.45 (s), 1491.56 (s), 1337.86 (s), 1230.70 (s), 747.16 (s).</p> <p><math>^1\text{H}</math> NMR (300 MHz, <math>\text{DMSO}-d_6</math>): 15.23 (s, 1H), 8.29 (d, <math>J = 8.4</math> Hz, 1H), 8.10 (d, <math>J = 8.1</math> Hz, 1H), 7.91 (t, <math>J = 7.8</math> Hz, 1H), 7.41 (t, <math>J = 8.1</math> Hz, 1H), 3.24 (s, 3H), 3.23 (s, 3H)</p> <p><math>^{13}\text{C}</math> NMR (75 MHz, <math>\text{DMSO}-d_6</math>): 160.31 (CO), 158.75 (CO), 150.92 (CO), 137.82 (C), 137.08 (C-H), 136.10 (C), 126.51 (C-H), 125.44 (C-H), 121.90 (C), 117.66 (C-H), 28.74 (<math>\text{CH}_3</math>), 27.93 (<math>\text{CH}_3</math>).</p>
7a	<p>IR (KBr, <math>\text{cm}^{-1}</math>): 3194.63 (s), 3074.07(s), 1755.13 (s), 1729.67 (s), 1665.42 (s), 1519.42 (s)1355.94 (s), 1249.74 (s), 814.03 (s).</p> <p><math>^1\text{H}</math> NMR (300 MHz, <math>\text{DMSO}-d_6</math>): 13.92 (bs, 1H), 11.39 (bs, 2H), 8.44 (t, <math>J = 2.1</math> Hz, 1H), 8.03 (d, <math>J = 2.1</math> Hz, 1H), 8.00 (d, <math>J = 2.1</math> Hz, 1H), 7.71 (t, <math>J = 8.4</math> Hz).</p> <p><math>^{13}\text{C}</math> NMR (75 MHz, <math>\text{DMSO}-d_6</math>): 162.02 (CO), 160.09 (CO), 150.20 (CO), 149.11 (C), 143.42 (C), 131.44 (C-H), 123.32 (C-H), 120.10 (C-H), 119.88 (C), 111.40 (C-H).</p>
7b	<p>IR (KBr, <math>\text{cm}^{-1}</math>): 3194.63 (s), 3074.07(s), 1755.13 (s), 1729.67 (s), 1665.42 (s), 1519.42 (s)1355.94 (s), 1249.74 (s), 814.03 (s).</p> <p><math>^1\text{H}</math> NMR (300 MHz, <math>\text{DMSO}-d_6</math>): 13.92 (bs, 1H), 11.39 (bs, 2H), 8.44 (t, <math>J = 2.1</math> Hz, 1H), 8.03 (d, <math>J = 2.1</math> Hz, 1H), 8.00 (d, <math>J = 2.1</math> Hz, 1H), 7.71 (t, <math>J = 8.4</math> Hz).</p> <p><math>^{13}\text{C}</math> NMR (75 MHz, <math>\text{DMSO}-d_6</math>): 178.16 (CS), 159.83 (CO), 158.55 (CO), 149.09 (C), 143.23 (C), 131.49 (C-H), 123.61 (C-H), 120.58 (C), 120.49 (C-H), 111.78 (C-H).</p>
7c	<p>IR (KBr, <math>\text{cm}^{-1}</math>): 3436.00 (bs), 3100.00 (w), 2920.00 (w), 2960.00 (w), 1727.63 (s), 1677.71 (s), 1648.60 (s), 1516.46 (s) 1451.76 (s), 1352.64 (s), 1245.80 (s), 750.75 (s).</p> <p><math>^1\text{H}</math> NMR (300 MHz, <math>\text{DMSO}-d_6</math>): 14.023 (s, 1H), 8.50 (t, <math>J = 2.1</math> Hz, 1H), 8.06 (m, 2H), 7.73 (t, <math>J = 8.4</math> Hz, 1H), 3.22 (s, 6H).</p> <p><math>^{13}\text{C}</math> NMR (75 MHz, <math>\text{DMSO}-d_6</math>): 160.32 (CO), 158.96 (CO), 151.01 (CO), 149.12 (C), 143.43 (C), 131.48 (C-H), 123.46 (C-H), 120.29 (C-H), 119.26 (C), 111.65 (C-H), 28.64 (<math>\text{CH}_3</math>), 27.73 (<math>\text{CH}_3</math>).</p>
8a	<p>IR (KBr, <math>\text{cm}^{-1}</math>): 3569.22 (s), 3460.47 (s), 3202.46 (s), 3064.62 (m), 1710.99 (s), 1697.96 (s), 1670.99 (m), 1611.43 (m), 1510.06 (s), 1446.78 (s), 1336.69 (s), 1246.96 (s).</p> <p><math>^1\text{H}</math> NMR (300 MHz, <math>\text{DMSO}-d_6</math>): 13.95 (bs, 1H), 11.65 (bs, 1H), 11.42 (s, 1H), 8.32 (d, <math>J = 9.3</math> Hz, 2H), 7.79 (d, <math>J = 9.3</math> Hz, 2H).</p> <p><math>^{13}\text{C}</math> NMR (75 MHz, <math>\text{DMSO}-d_6</math>): 162.00 (CO), 159.97 (CO), 150.20 (CO), 147.44 (C), 144.29 (C), 126.07 (C-H), 121.29 (C), 117.17 (C-H).</p>
8b	<p>IR (KBr, <math>\text{cm}^{-1}</math>): 3524.00 (s), 3434.03 (s), 3257.04 (s), 3088.14 (s), 1705.60 (s), 1664.05 (s), 1609.92 (s), 1494.20 (s), 1339.63 (s), 1240.07 (s).</p> <p><math>^1\text{H}</math> NMR (300 MHz, <math>\text{DMSO}-d_6</math>): 14.03 (s, 1H), 12.69 (s, 1H), 12.53 (s, 1H), 8.32 (d, <math>J = 9.3</math> Hz, 2H), 7.81 (d, <math>J = 9.3</math> Hz, 2H).</p> <p><math>^{13}\text{C}</math> NMR (75 MHz, <math>\text{DMSO}-d_6</math>): 178.23 (CS), 159.85 (CO), 158.42 (CO), 147.17 (C), 144.56 (C), 126.05 (C-H), 121.86 (C), 117.54 (C-H).</p>

Table 2: Continue.

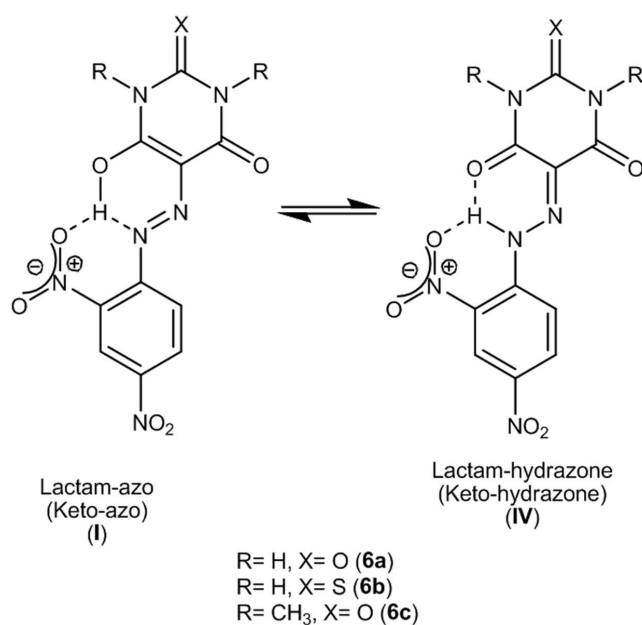
Azo dyes	Spectral data
<b>8c</b>	IR (KBr, $\text{cm}^{-1}$ ): 3399.72 (bw), 3082.44 (m), 2943.78 (w), 2900.0 (w), 1730.66 (s), 1681.01 (s), 1643.49 (s), 1517.90 (s), 1455.18 (s), 1343.52 (s), 1248.28 (s), 746.58 (s). $^1\text{H}$ NMR (300 MHz, $\text{DMSO}-d_6$ ): 13.99 (s, 1H), 8.32 (d, $J = 9.0$ Hz, 2H), 7.83 (d, $J = 9.0$ Hz, 2H), 3.23 (s, 3H), 3.21 (s, 3H). $^{13}\text{C}$ NMR (75 MHz, $\text{DMSO}-d_6$ ): 160.50 (CO), 159.79 (CO), 150.75 (CO), 145.49 (C), 143.95 (C), 126.06 (C-H), 119.09 (C), 117.39 (C-H), 28.70 ( $\text{CH}_3$ ), 27.80 ( $\text{CH}_3$ ).
<b>8d</b>	IR (KBr, $\text{cm}^{-1}$ ): 3413.45 (m), 1604.42 (m), 1585.47 (s), 1504.07 (s), 1336.12 (s), 1282.93 (m), 1139.09 (s), 1108.58 (w). $^1\text{H}$ NMR (300 MHz, $\text{DMSO}-d_6$ ): 10.56 (s, 1H), 8.35 (d, $J = 8.4$ Hz, 2H), 7.94 (d, $J = 8.4$ Hz, 2H), 7.84 (d, $J = 8.4$ Hz, 2H), 6.94 (d, $J = 8.4$ Hz, 2H). $^{13}\text{C}$ NMR (75 MHz, $\text{DMSO}-d_6$ ): 162.75 (C), 155.98 (C), 148.18 (C), 145.82 (C), 126.22 (C-H), 125.43 (C-H), 123.40 (C-H), 116.65 (C-H).
<b>8e</b>	IR (KBr, $\text{cm}^{-1}$ ): 3467.92 (m), 1602.42 (m), 1526.61 (s), 1503.24 (s), 1342.03 (m), 1271.31 (m), 1140.41 (s). $^1\text{H}$ NMR (300 MHz, $\text{CDCl}_3$ ): 8.71 (t, $J = 1.8$ Hz, 1H), 8.28-8.32 (m, 1H), 8.23 (t, $J = 7.2$ Hz, 1H), 7.95 (d, $J = 8.7$ Hz, 2H), 7.69 (t, $J = 8.1$ Hz, 1H), 6.99 (d, $J = 8.7$ Hz, 2H), 5.37 (bs, 1H, OH). $^{13}\text{C}$ NMR (75 MHz, $\text{CDCl}_3$ ): 163.66 (C), 157.03 (C), 150.97 (C), 149.07 (C), 132.82 (C), 130.54 (C-H), 127.19 (C-H), 121.60 (C-H), 109.81 (C-H), 103.44 (C-H).

The (NH/OH) signal of the dyes released from *o*-nitroaniline (3) are deshielded more than those of *m*- (4) and *p*-nitroaniline (5), due to bifurcated intramolecular hydrogen bonds which are examples of hydrogen bonds involving one proton and two acceptors [13,14]. For instance, the  $^1\text{H}$  NMR spectra of dyes 6a, 6b and 6c show a signal at  $\delta$  15.18, 15.23 and 15.23 ppm, respectively. These chemical shifts may be attributed to bifurcated hydrogen bonded NH/OH protons (Scheme 3 and Table 2).

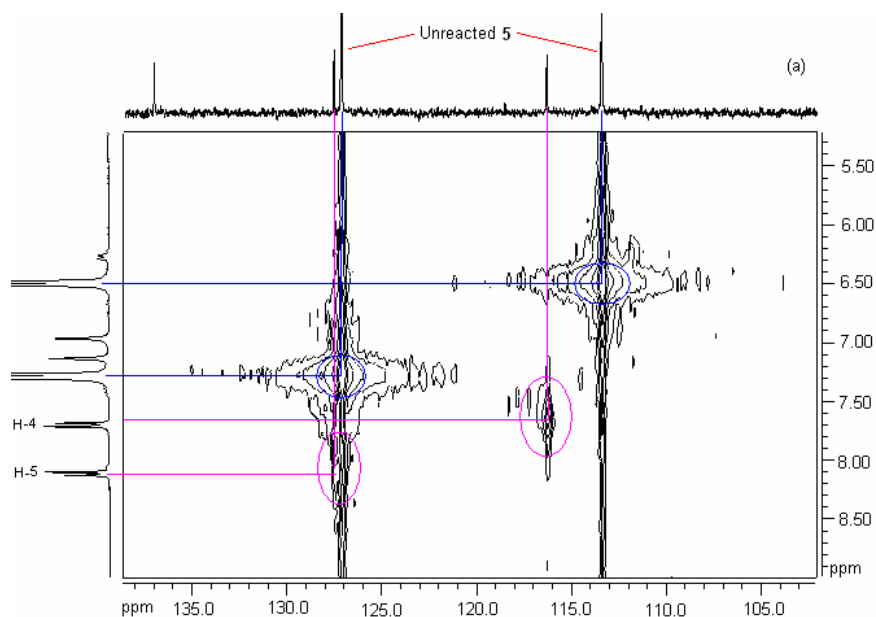
The  $^1\text{H}$ - $^{13}\text{C}$  HETCOR spectrum of 8a shows obviously, two doublets at  $\delta$  7.79 and 8.32 ppm which are in correlation with two carbon-13 signals at  $\delta$  117.17 and 126.07 ppm, respectively (Figure 2). The  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of the crude 8a shows a doublet at  $\delta$  7.79 ppm which is in correlation with doublet at  $\delta$  8.32 ppm. These observations are the other evidences for the formation of 8a under the solvent free condition.

The azo-dyes prepared in this study may exist in tautomeric forms (A and B) as shown in Scheme 4. The

infrared spectra of A and B (for 8a as representative) show three intense carbonyl absorptions at 1711, 1698 and 1671  $\text{cm}^{-1}$  for A and at 1730 and 1681  $\text{cm}^{-1}$  for B. Two absorptions at 3569 and 3460  $\text{cm}^{-1}$  (broadened) are due to the frequency of O-H vibrations, and correspond to intermolecular and intramolecular hydrogen bonds of hydroxyl groups for A, respectively (forms II and III). A broadened bond at 3400  $\text{cm}^{-1}$  is also attributed to the intramolecular hydrogen bond of hydroxyl groups for B (form II). Therefore, on the basis of IR data, we conclude that they may exist in various tautomeric forms (II, III and IV of A) in the solid state [15, 16]. The broad bands in the region of 3064-3202  $\text{cm}^{-1}$  are due to the frequency of N-H vibration. The low frequency and the broadening of these bands suggest that these compounds have strong hydrogen bonds (N-H/O) in the solid state [17-22]. The other characteristic peaks of the B appearing at 1643 and 1344  $\text{cm}^{-1}$  are attributed to the frequencies of C=N and C-N groups, respectively.



**Scheme 3:** Existence of bifurcated intra-molecular hydrogen bonds in dyes 6a-c.



**Figure 2:** Expanded  $^1\text{H}$ - $^{13}\text{C}$  HETCOR spectrum of the mixture of 5 and 8a in aromatic region (after washing with water and removing the residual of 1a and *p*-TsA).

It is well known that hydrogen bonded OH proton resonance appears at lower field than that of the NH proton. Furthermore, Song et al. [15, 23] have reported that azo pyrimidine derivatives exist in the azo form in

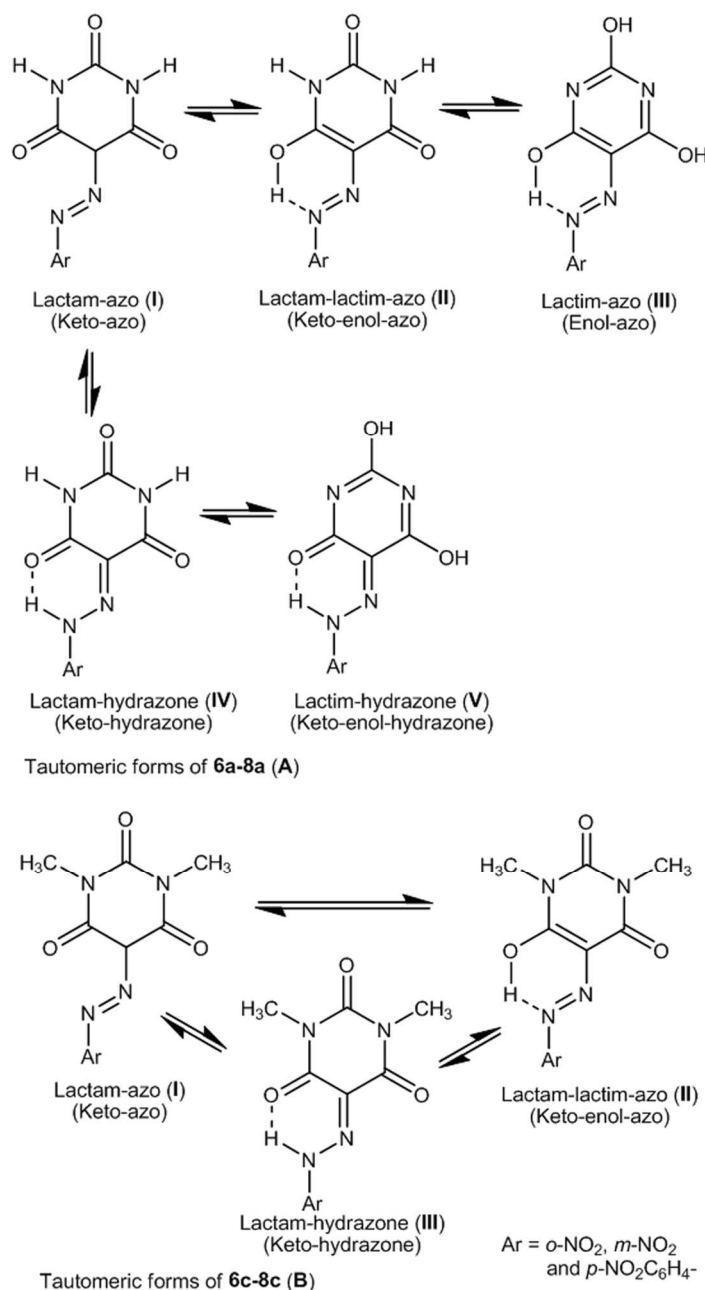
the absolute solvents. Therefore, it may be concluded that these compounds exist in the azo form (III) in solutions. For example, in the  $^1\text{H}$  NMR spectrum of A in 6a, the two singlets at  $\delta$  11.70 and 11.48 ppm are due to NH

protons at 1- and 3-positions of the pyrimidine ring. Appearance of the two characteristic singlets for the CH<sub>3</sub> groups at the 1- and 3-positions of the pyrimidine ring at  $\delta$  3.24 and 3.23 ppm for 6c and at  $\delta$  3.23 and 3.21 ppm for 8c, indicate that these compounds exist in two tautomeric forms in DMSO as solvent (forms II and III of B) (Scheme 4). Instead, the appearance of a singlet for CH<sub>3</sub> groups in 7c at  $\delta$  3.22 ppm indicates that two methyl groups are equivalent in chemical shift which are based

on our experiments (Table 2).

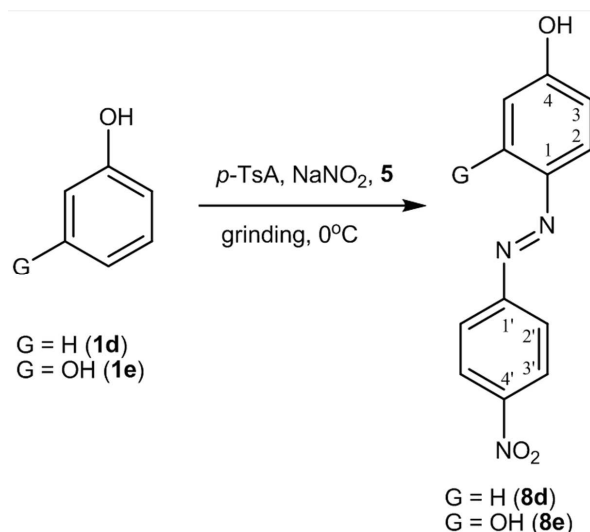
We performed diazotization and diazo coupling of phenol, 1d and resorcinol, 1e in the presence of *p*-TsA, aniline derivatives and sodium nitrite by grinding (Schemes 1 and 5).

The structures of azo dyes 8a-e, and their appearance and yields are summarized in Table 1. The spectroscopic data of the azo dyes 6a-c, 7a-c and 8a-e are summarized in Table 2.



**Scheme 4:** Tautomeric forms of some azo dyes based on barbituric acids [24, 25].





**Scheme 5:** Diazo coupling of phenol **1d** and resorcinol **1e** with diazonium salt of **5** catalyzed by *p*-TsA and followed by grinding.

#### 4. Conclusions

We have developed an efficient “green” method for the synthesis of azo dyes based on electron-donor compounds, aniline derivatives, sodium nitrite and *p*-TsA by grinding in good yield. Diazotization of amino group in *ortho*-, *meta*- and *para*-nitroaniline catalyzed by *p*-TsA in the presence of sodium nitrite. The yields increase with increasing of electron-donor ability of coupling agent. This method totally avoids the use of strong

inorganic acids, alkalis or toxic solvents in diazotization and diazo coupling reactions. The main advantage of this process is the use of water and alcohols (ethanol or methanol) for removing the most of unreacted materials.

#### Acknowledgements

We thank the Urmia University Research Council for supporting this work.

#### 5. References

1. H. Zollinger. Color chemistry, synthesis, properties and application of organic dyes and pigments. 3rd ed. Weinheim, Wiley VCH, 2003, Chapters 12-14, 413-537.
2. P. Gregory. High-Technology Applications of Organic Colorants. New York, Plenum press, 1991, Chapters 3-5, 27-52.
3. G. Viscardi, P. Quagliotto, C. Barolo, G. Caputo, G. Digilio, I. Degani, E. Barni. Structural characterisation of nitrazine yellow by NMR spectroscopy. *Dyes Pigments*. 57(2003), 87-95.
4. A. Fraleoni-Morgera, C. Della-Casa, P. Costa-Bizzarri, M. Lanzi, A. Missiroli. Completely soluble azo-dye-substituted thiophenic copolymers through proper molecular design. *Macromolecules*. 38(2005), 3170-3175.
5. A. Vogel. Textbook of Practical Organic Chemistry Including Qualitative Organic Analysis (VOGELE'S). 4<sup>th</sup> Ed. Longman, New York. 1978, 718.
6. J. H. Clark. Chemistry of Waste Minimization. Chapman and Hall, London. 1995, Chapter 3, 66-85.
7. A. Lyčka, A. Koloničný, P. Šimůnek, V. Macháček. Synthesis of some phenylazonaphthols in an ionic

- liquid. *Dyes Pigments*. 72(2007), 208-211.
8. G. Kaupp, M. A. Metwally, F. A. Amer, E. Abdelatif. Quantitative gas-solid diazotization of 3-aminopyrazolo[3,4-*b*] pyridine derivatives and azo dye syntheses by means of solid-solid reactions. *European J. Org. Chem.* (2003), 1545-1551.
  9. C. Wang, Y. Wang, X. Wang, X. Wang, H. Wang. A practical procedure for the solid-phase synthesis of azo compounds in the undergraduate organic laboratory. *J. Chem. Educ.* 77(2000), 903.
  10. J. Merrington, M. James, M. Bradley. Supported diazonium salts-convenient reagents for the combinatorial synthesis of azo dye. *Chem. Commun.* (2002), 140-141.
  11. H. A. Dabbagh, A. Teimouri, A. Najafi Chermahini. Green and efficient diazotization and diazo coupling reactions on clays. *Dyes Pigments*. 73(2007), 239-244.
  12. J. Hooker, D. Hinks, G. Montero, C. Conlee. Synthesis of *N,N*-diethyl-*N*-{4-[(*E*)-(4-nitrophenyl)-diazenyl]phenyl}amine via *in situ* diazotisation and coupling in supercritical carbon dioxide. *Coloration Tech.* 118(2002), 273-276.
  13. P. Gregory, Azo dyes: Structure-carcinogenicity relationships. *Dyes Pigments*. 7(1986), 45-56.
  14. T. Steiner, The hydrogen bond in the solid state, *Angew. Chem. Int. Ed.* 41(2002), 48-76.
  15. H. Song, K. Chen, D. Wu, H. Tian. Synthesis and absorption properties of some new azo-metal chelates and their ligands. *Dyes Pigments*. 60(2004), 111-119.
  16. R. Gupta, T. P. Lal, R. Mukherjee. Synthesis and properties of  $[\text{Cu}(\text{L}^5)_2][\text{ClO}_4]_2 \cdot \text{H}_2\text{O}$  having square planar and pseudo-octahedral geometries in the same unit cell, and anion-bound complexes  $[\text{Cu}(\text{L}^5)_2\text{X}][\text{ClO}_4]$  ( $\text{X}=\text{Cl}^-$ ,  $\text{NCS}^-$ ,  $\text{N}_3^-$ ) [ $\text{L}^5=2$ -(3,5-dimethylpyrazol-1-ylmethyl)pyridine]. *Polyhedron*. 21(2002), 1245-1253.
  17. S. Wang, S. Shen, H. Xu. Synthesis, spectroscopic and thermal properties of a series of azo metal chelate dyes. *Dyes Pigments*. 44(2000), 195-198.
  18. M. Adachi, T. Bredow, K. Jug. What is the origin of color on metal complex dyes? Theoretical analysis of a Ni-coordinate azo dye. *Dyes Pigments*. 63(2004), 225-230.
  19. R. Chandra, N. N. Ghosh. Thermal and  $^1\text{H}$  NMR studies on some azo derivatives of barbituric acid. *Thermochim. Acta*. 189(1991), 83-89.
  20. M. S. Masoud, G. B. Mohamed, Y. H. Abdul-Razek, A. E. Ali, F. N. Khairy. Spectral, magnetic, and thermal properties of some thiazolylazo complexes. *J. Korean Chem. Soc.* 46(2002), 99-116.
  21. D. Maiti, H. Paul, N. Chanda, S. Chakraborty, B. Mondal, V. G. Puranik, G. K. Lahiri. Synthesis, structure, spectral and electron-transfer properties of octahedral- $[\text{Co}^{\text{III}}(\text{L})_2]^+ / [\text{Zn}^{\text{II}}(\text{L})_2]$  and square planar- $[\text{Cu}^{\text{II}}(\text{L})\{\text{OC}(=\text{O})\text{CH}_3\}]$  complexes incorporating anionic form of tridentate bis(8-quinolyl)amine  $[\text{N}^1\text{C}_9\text{H}_6\text{-N}^2\text{-C}_9\text{H}_6\text{N}^3, \text{L}^-]$  ligand. *Polyhedron*. 23 (2004), 831-840.
  22. N. Ertan, P. Gürkan. Synthesis and properties of some azo pyridone dyes and their Cu(II) complexes. *Dyes Pigments*. 33(1997), 137-147.
  23. H. Song, K. Chen, H. Tian. Synthesis of novel dyes derived from 1-ethyl-3-cyano-6-hydroxy-4-methyl-5-amino-2-pyridone. *Dyes Pigments*. 53(2002), 257-262.
  24. R. Gup, E. Giziroglu, B. Kirkan. Synthesis and spectroscopic properties of new azo-dyes and azo-metal complexes derived from barbituric acid and aminoquinoline. *Dyes Pigments*. 73(2007), 40-46.
  25. R. Gup, B. Kirkan. Synthesis of new azo dyes and Copper(II) complexes derived from barbituric acid and 4-aminobenzoylhydrazone. *Turkish J. Chem.* 32 (2008), 9-17.