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A new nitrite ionic liquid (IL-ONO) as a nitrosonium source for the efficient diazotization of aniline derivatives and *in-situ* synthesis of azo dyes

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ABSTRACT

A new task-specific nitrite containing ionic liquid derived from the *O*-nitrosation of *N*-methyl-*N*-hydroxybutylimidazolinium chloride was synthesized and used as a source of nitrosonium ion to affect the efficient diazotization of arylamines. The diazonium salts thus obtained were coupled, using standard experimental procedures, to a range of tertiary anilines, phenols and naphthols to afford the requisite azo dyes in good yield. The diazotization and subsequent azo-coupling generated the related azo dyes at 0–5 °C in short reaction times with a simple experimental procedure.

1. Introduction

Ionic liquids are an important class of solvents which have attracted growing interest over the past few years due to their unique physical and chemical properties [1]. They usually consist of poorly coordinating ion pairs, and a classical example is the readily accessible 1-butyl-3-methylimidazolium tetrafluoroborate [bmim] BF_4, which is a colourless mobile but non-volatile liquid [2]. Recent advances in ionic liquid research provided another route for achieving task-specific ionic liquids (TSILs) in which a functional group is covalently tethered to the cation or anion of the ionic liquid, especially to the two N atoms of the imidazole ring. TSILs have been increasingly used as solvents and reagents or catalysts due to their specific properties [3–7].

In recent decades, Organic colour chemistry is undergoing very exciting developments as a result of the opportunities presented by dye applications in high technology fields e.g., electronic devices, linear and non linear optics, reprography, sensors and biomedical uses [8]. Azo dyes are very important synthetic dyes which are used extensively in industry [9]. 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 [10]. Many studies have reported the diazotization of aniline derivatives [11–15]. Lyčka and co-workers reported the synthesis of some phenylazonaphthols in 1-butyl-3-methylimidazolium tetrafluoroborate using a coupling reaction of (4-X-benzene)diazonium tetrafluoroborates (X = H and NO_2) with 1- and 2-naphthols and their sodium salts [16]. Noroozi et al. synthesized azo dyes via diazotization of aniline derivatives and subsequent azo-couplings in the presence of *p*-toluenesulfonic acid by grinding [17]. In continuation of our work on the using of task-specific phosphinite ionic liquid as solvent and catalyst/reagent for the synthesis of some heterocyclic compounds and nitrones [18–21], we now introduce a new nitrite ionic liquid (IL-ONO) that can act as nitrosonium source for the efficient conversion of aryl amines to their corresponding diazonium salts. *In situ* azo-coupling of these diazonium salts afforded the related azo dyes in good yields.

2. Experimental

2.1. Materials and instrumentation

All reagents were purchased from Merck Company and used without further purification. Infrared spectra were recorded in KBr

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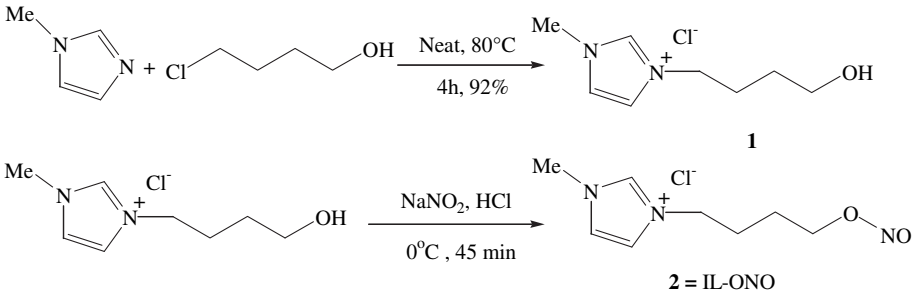


Scheme 1. Preparation of nitrite ionic liquid (IL-ONO).

and were determined on a Perkin Elmer FT-IR spectrometer. ^{1}H NMR spectra were recorded on a Bruker Avance AC- 400 MHz using DMSO-d_6 or $CDCl_3$ as the deuterated solvents and TMS as internal standard. All melting points measured in open glass-capillaries using a Stuart melting point apparatus.

2.2. Synthesis of 1-(4-hydroxybutyl)-3-methylimidazolium chloride

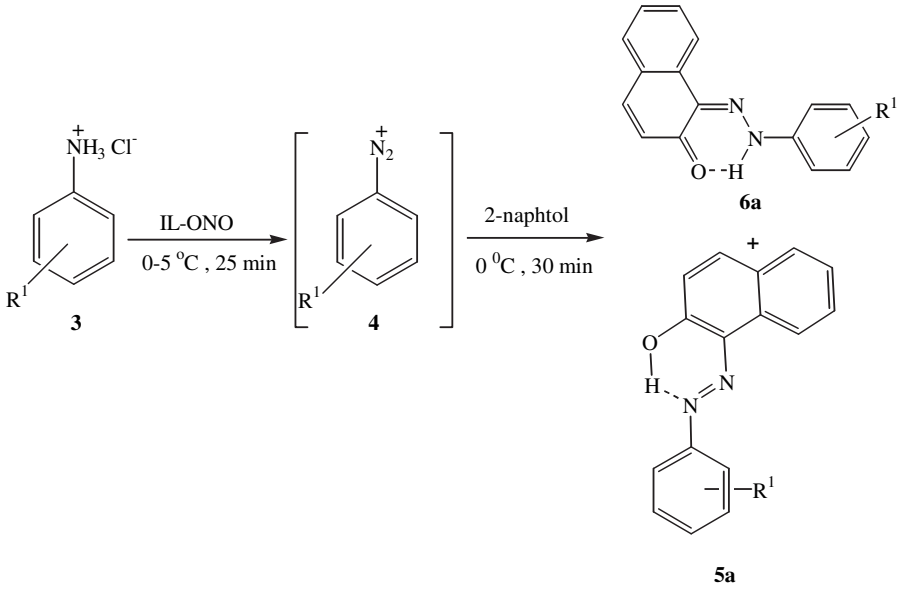
1-Methylimidazole (20 mL, 0.25 mol) and 4-chloro-1-butanol (27 mL, 0.27 mol) was stirred at 80 °C for 4 h in the absence of any catalyst and solvent. The unreacted materials were washed by diethyl ether (3 × 8 mL). The diethyl ether was removed under reduced pressure at room temperature, followed by heating under high vacuum, to yield a colourless liquid that became more viscous upon extensive drying, but did not solidify. Isolated yield was 92%. FT-IR (KBr, cm^{-1}): 3510 (bs), 1656, 1612. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (2H, m, CH_2); 1.41 (2H, m, CH_2); 2.92 (3H, s, N–CH_3); 3.84 (2H, t, N–CH_2); 4.15 (2H, dt, CH_2–OH); 5.56 (1H, t, OH); 7.76, 7.78 (2H, two singlets, C(4,5)–H); 9.09 (1H, s, C(2)–H). ^{13}C NMR (100 MHz, $CDCl_3$) 21.75 (–CH_2); 26.31 (–CH_2); 35.83 (N–CH_3); 39.54 (N–CH_2); 64.88 (CH_2(OH)); 123.16 (C(4 or 5)); 124.09 C(4 or 5)); (137.00 (C(2)). Anal. Calcd (%) for $C_8H_{15}ClN_2O$: C, 50.39; H, 7.93; N, 14.69. Found (%): C, 51.02; H, 7.95; N, 14.66.

2.3. Synthesis of Il-ONO

Freshly prepared 1-(4-hydroxybutyl)-3-methylimidazolium chloride (22 g, 0.1 mol) was added to an aqueous solution of sodium nitrite (15 mL, 7.59 g, 0.11 mol). While stirring of the mixture, 37% HCl (11 mL) was added slowly at 0 °C. While cold, the mixture was washed with cold water (20 mL) and dried under vacuum at room temperature for 4 h. Isolated yield was 87%. FT-IR (KBr, cm^{-1}): 1651, 1625, 1605. ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.27 (2H, m, CH_2); 1.43 (2H, m, CH_2); 2.89 (3H, s, N–CH_3); 3.78 (2H, t, N–CH_2); 4.23 (2H, t, CH_2–ONO); 7.75, 7.76 (2H, two singlets, C(4,5)–H); 9.15 (1H, s, C(2)–H). ^{13}C NMR (100 MHz, DMSO-d_6); 19.15 (–CH_2); 25.96 (–CH_2); 37.13 (N–CH_3); 51.50 (N–CH_2); 67.78 (CH_2(ONO)); 124.06 (C(4 or 5)); 124.42 (C(4 or 5)); 136.70 (C(2)). Anal. Calcd (%) for $C_8H_{14}ClN_3O_2$: C, 43.74; H, 6.42; N, 19.13. Found (%): C, 43.90; H, 6.46; N, 19.10.

2.4. Diazotization and subsequent azo-coupling with phenolic compounds using IL-ONO, general procedure

The aniline derivative (20 mmol) was dissolved in 37% HCl (10 mL). The mixture was stirred at 0–5 °C for 5 min. While stirring of the mixture, IL-ONO (30 mmol) was added over 2 min. The diazonium salt product was assayed by well-known azo-coupling reaction with phenol or aniline derivatives. For the coupling reaction with phenolic compounds, the reaction mixture was continuously added to the solution of phenolic compound (20 mmol) and NaOH (1 g) in water (10 mL). The participated dyes were filtered and washed three times with cold water to afford the crude azo dyes. The crude dyes were purified by recrystallization on EtOH/water. For azo-coupling with aniline derivatives, the reaction mixture containing diazonium salts was continuously added to the



Scheme 2. Diazotization of anilines using IL-ONO and diazo-coupling with 2-naphtole.

Table 1
Diazotization of anilines using IL-ONO and synthesis of azo dyes.

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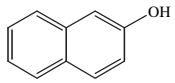
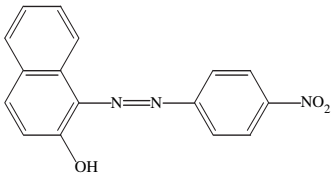
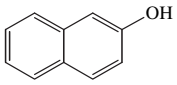
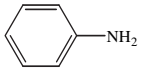
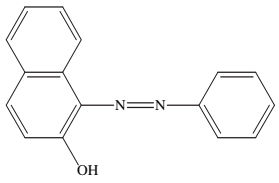
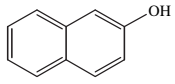
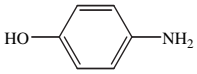
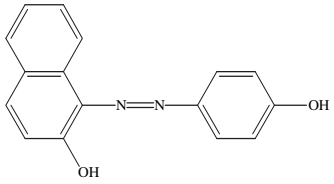
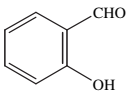
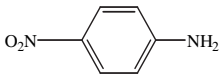
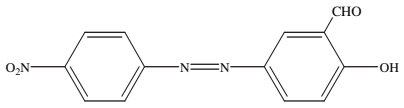
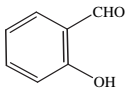
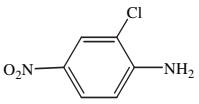
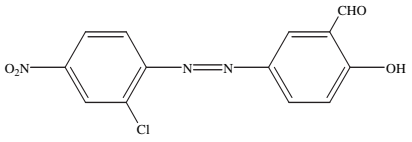
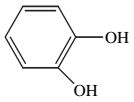
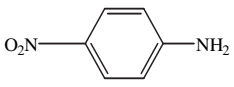
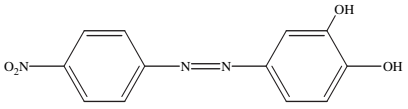
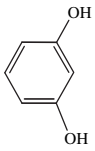
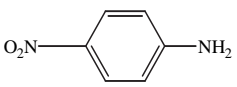
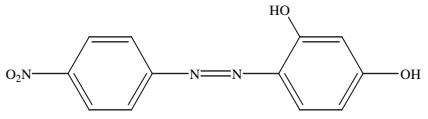
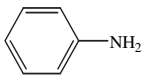
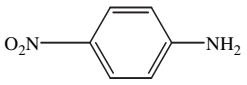
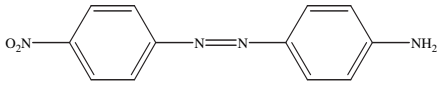
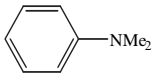
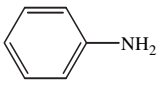
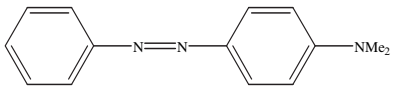
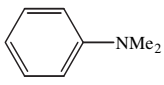
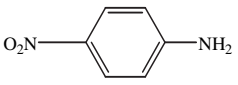
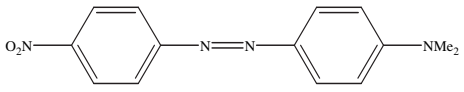
1			**3a**		**5a**
2			**3b**		**5b**
3			**3c**		**5c**
4			**3d**		**5d**
5			**3e**		**5e**
6			**3f**		**5f**
7			**3g**		**5g**
8			**3h**		**5h**
9			**3i**		**5i**
10			**3j**		**5j**

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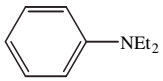
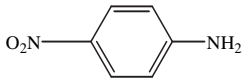
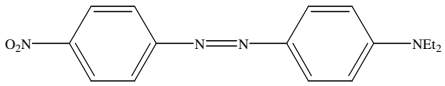
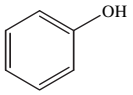
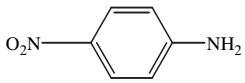
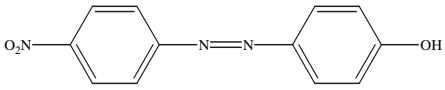
11			**3k**		**5k**
12			**3l**		**5l**

solution of aniline derivative (20 mmol) in water (10 mL) at 0–5 °C. The pH of mixture was adjusted to 6–7 by addition of NaOH solution (1 M). The participated dyes were isolated and purified as described above.

2.5. Selected spectroscopic data

Compound ***5a*** (azo): $C_{16}H_{11}N_3O_3$: FT-IR (KBr, cm^{-1}): 3409 (bs), 1665, 1621. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 12.02 (H, broad, OH); 8.42 (1H, dd, J = 8.11 and 2.03 Hz); 7.82 (2H, d, J = 7.98 Hz); 7.56 (2H, d, J = 7.98); 7.53 (1H, d, J = 7.25 Hz); 7.45 (1H, d, J = 7.25 Hz); 7.43 (1H, dd, J = 7.96 and 2.02 Hz); 7.41 (1H, dt, J = 7.65 and 1.98 Hz); 7.39 (1H, dt, J = 7.75 and 1.96 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.58, 137.45, 134.04, 130.21, 128.57, 127.18, 124.87, 121.86, 120.25, 119.50, 119.12, 117.07, 115.65, 112.32.

Compound ***6a*** (hydrazone): $C_{16}H_{11}N_3O_3$: FT-IR (KBr, cm^{-1}): 3395, 1684, 1668, 1610. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 14.16 (NH); 8.47 (1H, dd, J = 7.35 and 2.09 Hz); 7.49 (1H, d, J = 7.81 Hz); 6.59 (1H, d, J = 7.81 Hz); 7.48 (1H, dd, J = 7.54 and 2.13 Hz); 7.65 (2H, d, J = 7.65); 7.51 (1H, dt, J = 7.41 and 2.11 Hz); 7.41 (1H, dt, J = 7.48 and 2.54 Hz); 7.15 (2H, d, J = 7.65); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 158.49, 138.78, 136.54, 129.65, 128.12, 126.17, 123.68, 122.54, 122.68, 121.05, 120.97, 118.37, 116.76, 108.72.

Compound ***5b*** (azo): $C_{16}H_{12}N_2O$: FT-IR (KBr, cm^{-1}): 3420 (bs), 1660, 1605. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 12.13 (OH); 8.02 (1H, dd, J = 7.38 and 2.14 Hz); 7.65 (2H, m); 7.49 (1H, d, J = 7.82 Hz); 7.45 (1H, dd, J = 7.21 and 2.10 Hz); 7.43 (1H, dt, J = 7.73 and 2.03 Hz); 7.39 (1H, d, J = 7.82 Hz); 7.36 (1H, dt, J = 7.55 and 1.89 Hz); 7.15 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 140.01, 138.20, 135.35, 128.96, 128.31, 127.54, 124.52, 121.31, 120.28, 120.06, 119.12, 117.17, 116.29, 110.28.

Compound ***6b*** (hydrazone): $C_{16}H_{12}N_2O$: FT-IR (KBr, cm^{-1}): 3391, 1685, 1667, 1612. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 14.26 (NH); 8.42 (1H, dd, J = 7.78 and 2.35 Hz); 7.62 (1H, d, J = 7.74 Hz); 7.44 (1H, dd, J = 7.61 and 2.13 Hz); 7.41 (1H, dt, J = 7.81 and 2.42 Hz); 7.39 (1H, dt, J = 7.60 and 2.05 Hz); 7.58 (2H, m); 7.35 (3H, m); 6.70 (1H, d, J = 7.74 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.69, 139.45, 137.8 4, 130.13, 129.19, 126.23, 124.51, 122.12, 122.00, 121.56, 120.02, 117.12, 113.80, 109.28.

Compound ***5c*** (azo): $C_{16}H_{12}N_2O_2$: FT-IR (KBr, cm^{-1}): 3415, 3395, 1668, 1610. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 12.12 (2H, OH); 7.65 (1H, d, J = 7.58 Hz); 7.59 (1H, d, J = 7.58 Hz); 7.51 (1H, dd, J = 7.45 and 2.13 Hz); 7.45 (1H, dt, J = 7.61 and 2.08 Hz); 7.49 (1H, dt, J = 7.59 and 2.14 Hz); 8.32 (1H, dd, J = 7.54 and 2.20 Hz); 7.65 (2H, d, J = 7.51); 7.57 (2H, d, J = 7.51); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.51, 138.90, 135.54, 129.23, 128.51, 127.11, 123.63, 122.29, 122.20, 121.56, 120.32, 116.87, 115.89, 111.23.

Compound ***6c*** (hydrazone): $C_{16}H_{12}N_2O_2$: FT-IR (KBr, cm^{-1}): 3415, 3395, 1672, 1658, 1610. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 15.1 6 (NH); 12.12 (OH); 8.42 (1H, dd, J = 7.23 and 2.23 Hz); 7.51 (1H, d, J = 7.28 Hz); 7.49 (1H, dd, J = 7.21 and 2.10 Hz); 7.40 (1H, dt, J = 7.25 and 1.98 Hz); 7.43 (1H, dt, J = 7.29 and 2.09 Hz); 7.32 (2H, d, J = 7.51); 7.15 (2H, d, J = 7.51); 6.62 (1H, d, J = 7.28 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.51, 138.90, 135.54, 129.23, 128.51, 127.11, 123.63, 122.29, 122.20, 121.56, 120.32, 116.87, 115.89, 111.23.

Compound ***5d*** (azo): $C_{13}H_9N_3O_4$: FT-IR (KBr, cm^{-1}): 3413, 3104, 1658, 1606, 1524, 1478, 1342, 1284. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 11.43 (1H, s); 10.05 (1H, s); 8.39 (2H, d, J = 7.26 Hz); 8.27 (1H, d, J = 2.21 Hz); 8.22 (1H, dd, J = 7.21, 2.21 Hz); 8.01 (2H, d, 7.26 Hz); 7.14 (1H, d, J = 7.21 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.09, 135.87, 134.14, 130.25, 129.36, 128.63, 121.54, 117.68, 112.17, 110.95.

Compound ***5g*** (azo): $C_{12}H_9N_3O_4$: FT-IR (KBr, cm^{-1}): 3460 (bs), 3380, 1628, 1611. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 12.01 (s, OH); 8.98 (s, OH); 7.81 (d, 2H, J = 8.20 Hz); 7.79 (d, 2H, J = 8.20 Hz); 7.75 (d, 1H, J = 8.15 Hz); 6.64 (dd, 1H, J = 8.15 and 2.41 Hz); 6.33 (d, 1H, J = 2.41 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.25, 149.79, 148.12, 146.06, 130.98, 128.36, 127.36, 120.98, 110.74, 105.98.

Compound ***6g*** (azo): $C_{12}H_9N_3O_4$: FT-IR (KBr, cm^{-1}): 3421 (bs), 3341, 1688, 1668. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 14.21 (s, NH); 7.72 (d, 2H, J = 7.95 Hz); 7.63 (d, 2H, J = 7.95 Hz); 6.31 (d, 1H, J = 8.12 Hz); 6.22 (d, 1H, J = 8.12 Hz); 6.05 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.15, 159.52, 142.16, 140.12, 129.63, 128.06, 111.00, 105.41, 103.32, 78.27.

Compound ***5j*** (azo): $C_{14}H_{14}N_4O_2$: FT-IR (KBr, cm^{-1}): 1611, 1519, 1475, 1531, 1345. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.78 (d, 2H, J = 8.02 Hz); 7.75 (d, 2H, J = 8.0 2); 7.70 (d, 2H, J = 7.95 Hz); 6.69 (d, 2H, J = 7.95 Hz); 3.65 (s, 6H, $-NMe_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 135.54, 128.89, 126.63, 125.54, 123.35, 120.19, 117.85, 115.12, 35.12.

3. Results and discussions

The IL-OH, 1-(4-hydroxybutyl)-3-methylimidazolium chloride **1** was prepared by the efficient alkylation of the 3-methylimidazole with 4-chlorobutanole at 80 °C in 92% yield. The resulting ionic liquid when left in contact with 3 M $NaNO_2$ and HCl (1:1) solution at 0 °C was transformed into the ester-ionic liquid **2** in 87% yield (Scheme 1). Synthesis of nitrite ionic liquid **2** was confirmed by its FT-IR spectrum. The broad band at 3510 cm^{-1} arising from O–H stretching vibration in compound **1** was disappeared and a new band emerged around 1605 cm^{-1} can be ascribed to the asymmetrical stretching of the nitrite ester group, which is characteristic for nitrite esters group [22].

The new nitrite ionic liquid was used for the diazotization of aniline derivatives at 0–5 °C in the presence of HCl. In a pilot experiment, the mixture of freshly prepared nitrite ionic liquid and 4-nitroaniline **3a** was stirred with 37% HCl for 25 min to obtain the 4-nitrodiazonium intermediate **4a** (R^1 = 4-NO_2). The 4-nitrodiazonium intermediate was not isolated. The mixture of reaction

Table 2
Comparison of the reaction times and yields with the reported values.

Entry	Structure number	Reaction time (min)		M.P (°C)		Yield (%)	
		Found	Reported [Ref.]	Found	Reported [Ref.]	Found	Reported [Ref.]
1	**5a**	22	30 [23]	250–252	248–252 [24]	89	83 [23]
2	**5b**	25	–	131–132	131–132 [25]	87	–
3	**5c**	20	–	196–199	192–193 [26]	85	–
4	**5d**	24	–	185–186	184–186 [27]	84	93.7 [26]
5	**5e**	22	–	126–128	127–128 [28]	90	–
6	**5f**	20	–	187–190	188–190 [29]	88	–
7	**5g**	25	–	196–198	185 [29]	89	80 [14]
8	**5h**	25	–	199–202	200 [29]	90	–
9	**5i**	25	20 [23]	108–112	111 [29]	84	81 [23]
10	**5j**	20	30 [23]	218–222	225–228 [30]	83	85 [23]
11	**5k**	25	–	145–146	[a]	85	–
12	**5l**	22	30 [23]	203–204	207 [30]	86	86 [23]

[a] The melting point of this product was not found in the literature.

was added to the solution of β-naphthol sodium salt to obtain the azo dye **5a** via the well-known azo-coupling reaction with diazonium intermediate (Scheme 2). The structure of azo dye **5a** was characterized by comparing its (^{1}H, ^{13}C NMR and IR) spectroscopic data and melting point with literature values.

Optimization of the reaction conditions was studied with different molar ratios of the aniline, ionic liquid and β-naphthol. The best ratio was found to be 1:1.5:1. Increasing the amount of ionic liquid led to the mixture of products and low yield of azo dye was obtained. In this method the IL-ONO acts as a nitrosonium source reagent. This ionic liquid was then used for diazotization of aniline derivatives and subsequent transformation to azo dyes via the reaction with a variety of phenolic compounds and aniline derivatives (Table 1). The *in-situ* azo-coupling reaction product of *p*-nitrobenzodiazonium chloride, benzenediazonium chloride and *p*-hydroxybenzodiazonium chloride with β-naphthol existed as a mixture of (**5a** and **6a** in molar ratio 1.2:0.1), (**5b** and **6b** in molar ratio 1:0.1) and (**5c** and **6c** in molar ratio 1.2:0.1) respectively. The molar ratios of the isomers were determined by ^{1}H NMR spectroscopy by comparison of the relative integrals of the OH/NH signals of the respective isomers. As can be seen from Table 1, electron withdrawing or releasing groups on both reactants have no significant effect on the reaction times and yields of products in this procedure. All of the products were characterized by comparing their (^{1}H, ^{13}C NMR and IR) spectroscopic data and melting points with literature values.

We also compared the results (reaction times and yields of products) of the preparation of selected products via present method with those reported in the literature. As shown in Table 2, azo dyes were prepared in yields comparable with those obtained by traditional routes reported in the literature.

In conclusion, using new and easily prepared nitrite ionic liquid as a nitrosonium source provides an attractive and practical method for the clean diazotization and subsequent azo-coupling for the preparation of azo dyes. To our knowledge, this is the first report concerning the diazotization of anilines in TSILs under mild conditions.

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