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Synthesis of some phenylazonaphthols in an ionic liquid

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Abstract

Several phenylazonaphthols were prepared in 1-butyl-3-methylimidazolium tetrafluoroborate (an ionic liquid) using a coupling reaction of (4-X-benzene)diazonium tetrafluoroborates (X = H and NO_2) with 1- and 2-naphthols and their sodium salts. ^1H NMR spectra of the reaction products were measured and results compared with previously published data. The reaction of benzenediazonium tetrafluoroborates with sodium salts of 1- and 2-naphthols in 1-butyl-3-methyl-imidazolium tetrafluoroborate was faster compared with that when 1- and 2-naphthols were used. 4-Nitrobenzenediazonium tetrafluoroborate was much more reactive than benzenediazonium tetrafluoroborate.

Keywords: Ionic liquid; Azo coupling

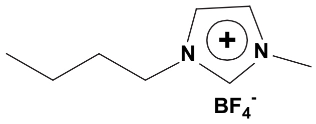
1. Introduction

Ionic liquids [1–5] – liquids consisting only of ions – have recently been attracting considerable interest. Contrary to molten salts, ionic liquids are already liquid at low temperature (below 100 °C or even at room temperature) and have relatively low viscosity. They represent a new class of solvent with non-molecular, ionic character and have been used to replace organic solvents in many technological processes and can serve as catalysts. Ionic liquids are usually good solvents for a wide range of both organic and inorganic compounds and unusual combinations of reagents can be brought into the same phase. They are often composed of poorly coordinating ions, so they have the potential to be highly polar yet non-coordinating solvents. Ionic liquids do not evaporate since they are non-volatile and can be used repeatedly [1]. Typical examples of ionic liquids are various alkylammonium, alkylphosphonium, *N,N′*-dialkylimidazolium and *N*-alkylpyridinium salts. A set of excellent books, review papers and interesting articles has appeared recently [1–11].

There are some indications that switching from a standard solvent to ionic liquids can lead to novel and unusual chemical reactivity [2,11]. This opens up a wide field for future investigations into this class of solvents. Many very interesting results have been achieved both in industrial processes scale as well as in preparation of fine chemicals [3–5].

Astolfi and Mayville [12] have recently published on the synthesis of methyl orange in ionic liquids (1-hexyl-3-methylimidazolium tetrafluoroborate and perchlorate) by coupling of appropriate diazonium salt derived from sulfanilic acid with *N,N*-dimethylaniline as the first example of application of ionic liquids in azo dye chemistry.

The aim of this paper was to describe reaction conditions for preparation of some phenylazonaphthols in an ionic liquid using a coupling reaction of (4-X-benzene)diazonium fluoroborates (X = H (**1a**) and NO_2 (**1b**)) with 1- and 2-naphthols. The reactions were carried out in 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM*BF_4).



BMIM*BF_4

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2. Results and discussion

Astolfi and Mayville [12] performed coupling reaction of diazonium salt derived from sulfanilic acid with *N*,*N*-dimethylaniline giving methyl orange in ionic liquids (1-hexyl-3-methylimidazolium tetrafluoroborate and perchlorate) by simple mixing of two reaction components. A white precipitate of diazonium salt was allowed to react with *N*,*N*-dimethylaniline to give methyl orange.

It is well known that aromatic amines undergo coupling reactions with diazonium salts in neutral or slightly acidic conditions [13] in water or water/solvent solutions. On the other hand, 1- and 2-naphthols and similar compounds usually prefer alkaline media for performing diazonium salt coupling reactions [13] under similar experimental conditions.

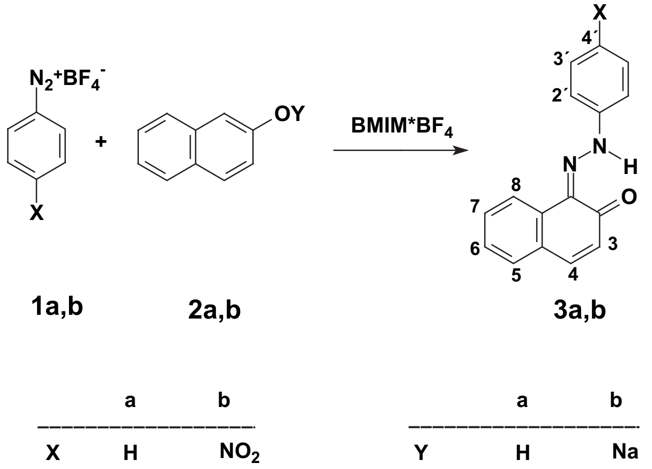
Since ionic liquids represent a very specific type of solvent for which common knowledge about acidity/basicity can hardly be easily implemented, we started our attempt to prepare phenylazonaphthols quite analogous to the procedure described by Astolfi and Mayville [12], i.e. by simple mixing of two reaction components: (4-X-benzene)diazonium tetrafluoroborates (X = H (**1a**) or NO_2 (**1b**)) and an appropriate naphthol (**2a** or **4a**) were mixed and allowed to react overnight (see Section 3). The reaction mixtures were poured into water and reaction products were isolated by suction. The ^1H NMR spectra of raw reaction products were measured and results compared with previously published data [14,15] for the same or analogous compounds prepared by standard coupling reaction procedure in water.

The reaction product of benzenediazonium tetrafluoroborate (**1a**) coupling with 2-naphthol (**2a**) existed as a viscous oil consisting of compound **3a** and starting 2-naphthol in molar ratio 0.1:1. Analogously, 1-naphthol (**4a**) reacted with benzenediazonium tetrafluoroborate (**1a**) to give solid raw reaction product containing compounds **5a** and **6a** and again non-reacted 1-naphthol in molar ratio 1:0.22:0.43. During the reactions appropriate amount of acid was released that could influence the reaction medium.

The coupling reaction of 4-nitrobenzenediazonium tetrafluoroborate (**1b**) with 2-naphthol (**2a**) as well as with 1-naphthol (**4a**) gave expected products, i.e. compound **3b**, and a mixture of compounds **5b** and **6b** (ratio 1:0.11), respectively (Schemes 1, 2). The molar ratios of compounds were determined from integral intensities of OH/NH signals in ^1H NMR spectra.

In the next step, we wanted to perform the coupling reaction in ionic liquid only (to avoid a necessity to use another solvent) and, again, by mixing two solid reaction components. That is why we prepared sodium salts of naphthols (**2b** and **4b**) by dissolving 1- and 2-naphthols in equimolar amount of sodium methoxide in methanol and subsequent evaporation of solvent in vacuo.

The (4-X-benzene)diazonium tetrafluoroborates (X = H (**1a**) or NO_2 (**1b**)) and an appropriate sodium salt of 1- or 2-naphthol (**2b** and **4b**) were mixed and allowed to react for 1 h. The mixtures were poured into water and reaction products were isolated by suction. Both benzenediazonium tetrafluoroborate (**1a**) and 4-nitrobenzenediazonium tetrafluoroborate (**1b**) reacted smoothly to give compounds **3a**,**b** and mixtures of compounds **5a**,**b** and **6a**,**b**, respectively. The ^1H NMR spectra of raw reaction products were measured and analysed as described above. For results see Section 3.



Scheme 1. Predominant tautomeric forms shown.

We can conclude that the reaction of benzenediazonium tetrafluoroborates with sodium salts of 1- and 2-naphthols in 1-butyl-3-methylimidazolium tetrafluoroborate was faster compared with that when 1- and 2-naphthols are used. The 4-nitrobenzenediazonium tetrafluoroborate reacted faster compared with benzenediazonium tetrafluoroborate. Regardless of the fact that 1-butyl-3-methylimidazolium tetrafluoroborate is a completely different type of solvent compared with water the diazonium salt coupling reactions can be performed, from the viewpoint of passive component, under similar conditions to those in water. On the other hand, the reaction mechanism seems to be different [16].

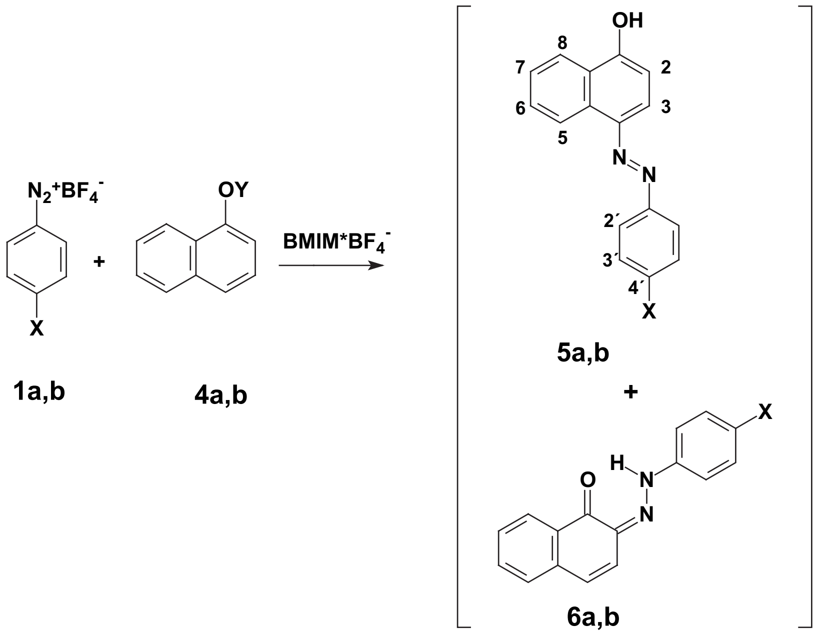
3. Experimental

3.1. Synthesis

1-Butyl-3-methylimidazolium tetrafluoroborate ($BMIM*BF_4$) was a commercial product bought from Solvent Innovations. Benzenediazonium tetrafluoroborate and 4-nitrobenzenediazonium tetrafluoroborate were prepared as described previously [17]. Sodium salts of 1- or 2-naphthol were obtained by dissolving 1- or 2-naphthol in equimolar amount of sodium methoxide in methanol and evaporating in vacuo.

*3.1.1. Preparation of compounds **3a**,**b**, **5a**,**b** and **6a**,**b***

*3.1.1.1. Preparation of compounds from naphthols (**2a** and **4a**).* 1- or 2-naphthol of 288 mg (2 mmol) was placed into 4 ml of 1-butyl-3-methylimidazolium tetrafluoroborate and 2 mmol of (4-X-benzene) diazonium fluoroborates (X = H (**1a**), 383.8 mg) or NO_2 (**1b**, 473.8 mg) in 2 ml of 1-butyl-3-methylimidazolium tetrafluoroborate was added. The reaction



	a	b
X	H	NO_2

	a	b
Y	H	Na

Scheme 2. Predominant tautomeric forms shown. Compound **5b** exists, contrary to **5a**, in hydrazone form.

mixtures were stirred overnight at laboratory temperature. The mixtures were poured into 100 ml of water. Solid compounds were isolated by suction and rinsed with distilled water several times. Yields: 360 mg of **3a** and 2-naphthol (oil, ratio 0.1:1), 490 mg of **5a**, **6a** and 1-naphthol (ratio 1:0.22:0.43), 405 mg of **3b**, 510 mg of **5b** and **6b** (ratio 1:0.11).

*3.1.1.2. Preparation of compounds from sodium naphtholates (**2b** and **4b**).* Sodium salts of 1- or 2-naphthol of 332 mg (2 mmol) were placed into 4 ml of 1-butyl-3-methylimidazolium tetrafluoroborate and 2 mmol of appropriate (4-X-benzene) diazonium tetrafluoroborate (X = H (**1a**), 383.8 mg, or X = NO_2 (**1b**), 473.8 mg) in 2 ml of 1-butyl-3-methylimidazolium tetrafluoroborate was added. The reaction mixture was stirred for 1 h at laboratory temperature. The mixture was poured into 100 ml of water. Solid compounds were isolated by suction and rinsed with distilled water several times. Yields of raw products: 305 mg of **3a**, 505 mg of **3b**, 410 mg of **5a** and **6a** (ratio 1:0.12), 520 mg of **5b** and **6b** (ratio 1:0.11).

All raw samples contain small amount of ionic liquid ($<5\%$) as well as some decomposition products.

3.2. NMR spectroscopy

The ^{1}H NMR spectra and gradient-selected H,H-COSY spectra of raw reaction products were measured on a Bruker Avance 500 spectrometer equipped with 5 mm broadband probe at 500.13 MHz in deuteriochloroform (compounds **3a**,**b**) or hexadeuteriodimethyl sulfoxide (compounds **5a**,**b** and **6a**,**b**) at ambient temperature. The ^{1}H chemical shifts were referred to the signal of internal TMS ($\delta(^1H) = 0.00$). Positive values of chemical shifts denote high frequency shifts with respect to the standard.

The ^{1}H chemical shifts of compound **3a**: 16.26 (NH), 7.71 (H3), 6.86 (H4), 7.59 (H5), 7.40 (H6), 7.55 (H7), 8.57 (H8), 7.70 (H2′), 7.48 (H3′), 7.28 (H4′); compound **3b**: 16.14 (NH), 7.69 (H3), 6.70 (H4), 7.54 (H5), 7.44 (H6), 7.56 (H7), 8.42 (H8), 7.69 (H2′), 8.32 (H3′); compound **5a**: 11.22 (OH), 7.07 (H2), 7.93 (H3), 8.94 (H5), 7.65 (H6), 7.76 (H7), 8.29 (H8), 8.03 (H2′), 7.65 (H3′), 7.53 (H4′); compound **5b**: 12.01 (OH), 6.83 (H2), 8.32 (H3), 8.54 (H5), 7.82 (H6), 7.64 (H7), 8.32 (H8), 7.74 (H2′), 8.32 (H3′); compound **6a**: 14.78 (NH); compound **6b**: 15.14 (NH).

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