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Characterization and application of pyrazinium di(hydrogen sulfate) as a highly efficient catalyst for synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes, 9-aryl-1,8-dioxo-octahydroxanthenes and 1-amidoalkyl/carbamatoalkyl-2-naphthols

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Pyrazinium di(hydrogen sulfate) $\{PyH_2(HSO_4)_2\}$;
14-aryl-14H-dibenzo[a, j]xanthenes;
9-aryl-1,8-dioxo-octahydroxanthene;
1-amidoalkyl-2-naphthol;
1-carbamatoalkyl-2-naphthol.

Abstract. In this work, characterization of Brϕnsted acidic ionic liquid namely pyrazinium di(hydrogen sulfate) $\{PyH_2(HSO_4)_2\}$ using ^{1}H and ^{13}C NMR, mass, thermogravimetry (TG), and derivative thermogravimetry (DTG) data is achieved. Afterward, it is used as a highly efficient, green, and homogeneous catalyst to promote the following organic transformations under solvent-free conditions: (i) the synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes from 2-naphthol and arylaldehydes; (ii) the preparation of 9-aryl-1,8-dioxo-octahydroxanthenes by the reaction of dimedone (5,5-dimethyl-1,3-cyclohexanedione) with arylaldehydes, and (iii) the synthesis of 1-amidoalkyl/carbamatoalkyl-2-naphthols by the condensation of 2-naphthol with aromatic aldehydes and amide derivatives/alkyl carbamates.

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1. Introduction

Ionic Liquids (ILs) are defined as pure compounds, consisting only of cations and anions (i.e., salts), which melt at or below 100°C [1-3]. These salts have attracted rising interest in the last decades for chemists because of their unique properties such as high thermal and chemical stability, non-flammability, non-volatility, wide liquid-state temperature range, large electrochemical window, and favorable salvation behavior [3,4]. This increased interest led to an exponential growth of papers reporting on various aspects of ILs, including synthesis of various new ILs, and their application in synthetic transformations (as solvent, catalyst and reagent) [1-6], electrochemistry [3,6], spectroscopy, and extraction and separation processes [3]. Among the different kinds of ionic liquids, Br$\emptyset$nsted acidic ones have been designed to replace with solid acids and traditional mineral liquid acids like sulfuric acid and hydrochloric acid to catalyze chemical transformations [7-13]. Along this line, recently, we have synthesized some

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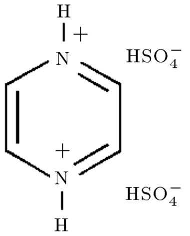


$PyH_2(HSO_4)_2$

Figure 1. The structure of pyrazinium di(hydrogen sulfate).

novel ILs with Brϕnsted acidic property, and successfully applied them as catalysts and reagents in organic synthesis [7-9,12,13]. Pyrazinium di(hydrogen sulfate) $\{PyH_2(HSO_4)_2\}$ (Figure 1) is an attractive member of acidic ILs, which we have recently prepared, and applied as a highly efficient catalyst for the synthesis of β-acetamido ketones/esters [13].

In fact, this salt is solid at room temperature, but it melts at 80-82°C; thus, according to the definition of ILs [1-3], $PyH_2(HSO_4)_2$ is an ionic liquid (in the mentioned work [13], we have introduced $PyH_2(HSO_4)_2$ as solid acid, because the reaction was carried out at room temperature, and the catalyst was solid at this temperature). We believe that this ionic liquid can be applied as efficient and homogeneous catalyst to promote different organic transformations. Herein, we have found that the synthesis of 14-aryl-14*H*-dibenzo[a, j]xanthenes, 9-aryl-1,8-dioxo-octahydroxanthenes, 1-amidoalkyl-2-naphthols, and 1-carbamatoalkyl-2-naphthols can be efficiently catalyzed by $PyH_2(HSO_4)_2$. It should be mentioned that most of the reported catalysts possessing hydrogen sulfate anion are heterogeneous metal hydrogen sulfates, and do not have the advantages of homogeneous catalysts. Homogeneous catalysts not only promote the reaction, but also create a homogenous reaction media similar to solvents [14]. In fact, these dual activation modes lead to reduced reaction times and improve products yields [14].

Currently, green synthesis of products in the absence of volatile and toxic organic solvents is the subject of considerable interest in organic synthesis. In this regard, solvent-free conditions is a helpful technique of green chemistry which often lead to shorter reaction times, increased yields, easier workup, matching with the green chemistry protocols, and may enhance the regio- and stereoselectivity of reactions [14-18].

Xanthene derivatives such as 14-aryl-14*H*-dibenzo[a, j]xanthenes and 9-aryl-1,8-dioxo-octahyd-roxanthens are of importance as they have various industrial, pharmaceutical, and biological applications [19-24]. For example, these compounds have been applied as dyes in laser technology [19], and as pH sensitive fluorescent materials for visualization of biomolecules [20]. Moreover, xanthenes derivatives have been used as antiviral [21], antitumor [22], antibacterial [23], and anti-inflammatory [24] agents. The condensation reaction between 2-naphthol (2 eq.) and arylaldehydes (1 eq.) has been used as the best protocol for 14-aryl-14*H*-dibenzo[a, j]xanthenes synthesis [25-32]. For this transformation, some catalysts have been reported, including $InCl_3$ [25], $Yb(OTf)_3$ [26], nano-TiO_2 [27], $KAl(SO_4)_2.12H_2O$ [28], $[Et_3N\text{-}SO_3H]Cl$ [29], trityl chloride [30], 1-(chloromethyl)-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) [31], and acetic acid-functionalized ionic liquids [32]. The one-pot multi-component condensation of dimedone (5,5-dimethyl-1,3-cyclohexanedione) (2 eq.) with arylaldehydes (1 eq.) has been applied as the most common synthetic route towards 9-aryl-1, 8-dioxo-oct-ahydroxanthenes [29,33-40]. Some catalysts have been employed for this reaction, e.g. $[Et_3NSO_3H]Cl$ [29], $SbCl_3/SiO_2$ [33], nano-TiO_2 [34], *N*-sulfonic acid poly(4-vinylpyridinium) chloride [35], trityl chloride [36], nano-WO_3-supported sulfonic acid [37], Fe_3O_4 nanoparticles [38], silica-supported $H_{14}[NaP_5W_{30}O_{110}]$ nanoparticles [39], and SiO_2-R-SO_3H [40].

1-Amidoalkyl-2-naphthol and 1-carbamatoalkyl-2-naphthol derivatives are significant as they can be hydrolyzed to 1-aminoalkyl-2-naphthols. 1-aminoalkyl-2-naphthols have been applied as hypotensive and bradycardiac agents [41,42]. Furthermore, 1-amidoalkyl-2-naphthols can also be easily converted to 1,3-oxazine derivatives [43] with different biological activities, such as antimalarial [44], anticonvulsant [45], antitumor [46], and analgesic [47] properties. The best synthetic route towards 1-amidoalkyl-2-naphthols is the one-pot multi-component condensation reaction of 2-naphthol with aromatic aldehydes and amide derivatives using some catalysts, e.g. sulfonic acid functionalized imidazolium salts [12], $PCl_{3-n}(SiO_2)_n$ [17], $POCl_{3-n}(SiO_2)_n$ [17], MCM-41-*N*-propylsulfamic acid [48], $ZrO(OTf)_2$ [49], copper *p*-toluenesulfonate [50], 2-methylpyridinium trifluoromethanesulfonate [51], $H_3[P(Mo_3O_{10})_4]$ [52] and polyethylene glycol based dicationic acidic ionic liquid [53]. In some methods, acetonitrile instead of amide derivatives have been used [54]. The best protocol for the preparation of 1-carbamatoalkyl-2-naphthol derivatives involves the condensation reaction between 2-napthol, aldehydes and alkyl carbamates [55-59].

Although some catalysts and methods for the preparation of 14-aryl-14*H*-dibenzo[a, j]xanthenes, 9-aryl-1,8-dioxo-octahydroxanthenes and 1-amidoalkyl (or carbamatoalkyl)-2-naphthols are known, newer catalysts and methods continue to attract attention for their difference with the others, novelty and efficacy. Moreover, most of the reported catalysts and protocols for the synthesis of the title compounds are associated with one or more of the following drawbacks: (i) Moderate yields; (ii) Long reaction times; (iii) The use of large amount of catalyst; (iv) The use of expensive, non-available or toxic catalysts; and (v) Poor agreement with the green chemistry protocols. In addition, the essential disadvantage of most protocols reported for the synthesis of 1-amidoalkyl/carbamatoalkyl-2-naphthols is harsh reaction conditions (110-120°C).

In this work, we report our results on the use of pyrazinium di(hydrogen sulfate) $PyH_2(HSO_4)_2$ as a highly efficient, homogeneous and green catalyst to promote the following organic transformations under solvent-free conditions: (i) The synthesis of 14-aryl-14*H*-dibenzo[*a, j*]xanthenes by the condensation of 2-naphthol (2 eq.) with aromatic aldehydes (1 eq.); (ii) The preparation of 9-aryl-1,8-dioxo-octahydroxanthenes via the condensation reaction between dimedone (5,5-dimethyl-1,3-cyclohexanedione) (2 eq.) and arylaldehydes; (iii) The synthesis of 1-amidoalkyl/carbamatoalkyl-2-naphthols by the reaction of 2-naphthol with aromatic aldehydes and amide derivatives; and (iv) The synthesis of 1-carbamatoalkyl-2-naphthols by the reaction between 2-naphthol, arylaldehydes, and alkyl carbamates. These procedures have none of the above-mentioned drawbacks at all. Moreover, it is worth noting that $PyH_2(HSO_4)_2$ has catalyzed the above-mentioned organic reactions in milder conditions in comparison to most of the reported catalysts for these transformations, especially the preparation of 1-amidoalkyl/carbamatoalkyl-2-naphthol derivatives.

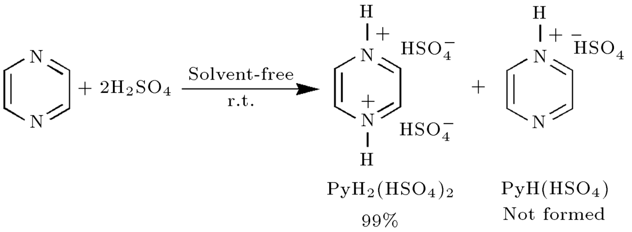
2. Results and discussion

As mentioned in the introduction section, more recently, we have reported the synthesis of $PyH_2(HSO_4)_2$ and its application as highly efficient catalyst for the synthesis of β-acetamido ketones/esters [13]. In that work [13], we have only reported the spectral data of $PyH_2(HSO_4)_2$, and have not discussed identification of the catalyst structure using spectral data. Here, we study the preparation of the catalyst, and its spectral data. Initially, ionic liquid $PyH_2(HSO_4)_2$ was synthesized by the reaction of pyrazine (1 eq.) with sulfuric acid (2 eq.) at room temperature by an easy and clean procedure (Scheme 1).

Nevertheless, the other possible product formed from the reaction of pyrazine with sulfuric acid is $PyH(HSO_4)$ (Scheme 1). To identify the real structure of the ionic liquid, we study the ^1H and ^{13}C NMR as well as mass spectral data of the product. These data include:

^1H NMR (300 MHz, DMSO-d_6): δ 8.22 (s, 4H), 10.70 (br., 4H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 141.6. MS (m/z): 276 (M^+).

The peak observed in 8.22 ppm of the ^1H NMR spectra with integral 4 is related to four equal hydrogens of the aromatic ring of the ionic liquid; the equality of the hydrogens confirmed the successful reaction of both nitrogens (not one nitrogen) of pyrazine with sulfuric acid to give $PyH_2(HSO_4)_2$, not $PyH(HSO_4)$. The other peak (10.70 ppm) of the 1H NMR spectra with integral 4 is related to four acidic hydrogens of the catalyst (2 hydrogens of HSO_4^- anion, and 2 hydrogens which bonded with the positive nitrogens). This subject also verified that the correct structure of the catalyst was $PyH_2(HSO_4)_2$, not $PyH(HSO_4)$. Observation of the acidic hydrogens in one chemical shift can be attributed to the high speed exchange of the hydrogens; NMR apparatus cannot see the hydrogens in their main positions, and sees the hydrogens in an average media. The ^{13}C NMR spectra indicated that the pyrazinium salt has one type of carbon (141.6 ppm); the equality of four carbons showed that the catalyst was correctly synthesized, and two nitrogens of pyrazine reacted with sulfuric acid to afford $PyH_2(HSO_4)_2$. In the mass spectra of the catalyst, the peak related to molecular weight of $PyH_2(HSO_4)_2$ was viewed in $m/e = 276$. The above explanations verified that the real structure of the catalyst was $PyH_2(HSO_4)_2$.



Scheme 1. Synthesis of pyrazinium di(hydrogen sulfate) $\{PyH_2(HSO_4)_2\}$.

Thermal gravimetric analysis of $PyH_2(HSO_4)_2$ was also studied. The corresponding diagram is shown in Figure 2. The Thermal Gravimetric (TG) curve of the catalyst showed main weight losses and decomposition after about 290°C.

Initially, we examined the efficacy of PyH_2 $(HSO_4)_2$ to catalyze the synthesis of 14-aryl-14*H*-

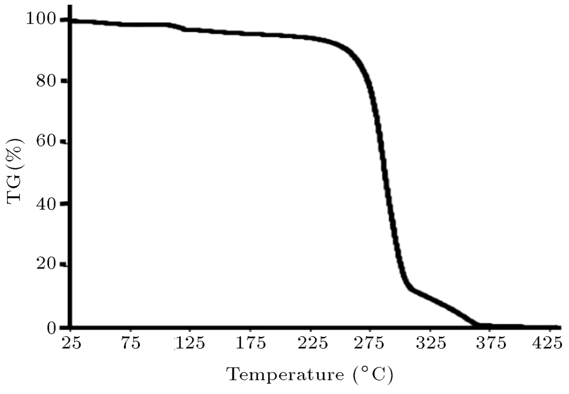
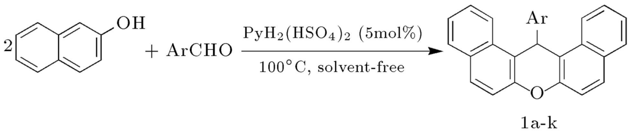


Figure 2. The TG curve of $PyH_2(HSO_4)_2$.

dibenzo[*a*, *j*]xanthenes from 2-naphthol and arylaldehydes. For this purpose, as a model reaction, the condensation of 2-naphthol (2 mmol) with benzaldehyde (1 mmol) was examined in the presence of different amounts of $PyH_2(HSO_4)_2$ at range of 80 to 105°C under solvent-free conditions (Scheme 2). The results are summarized in Table 1. As Table 1 indicates, 5 mol% of $PyH_2(HSO_4)_2$ was sufficient to catalyze the reaction efficiently at 100°C; using this amount of $PyH_2(HSO_4)_2$ yielded 14-aryl-14*H*-dibenzo[*a*, *j*]xanthene **1a** in 97% within 40 min (entry 3). Moreover, increasing the amount of $PyH_2(HSO_4)_2$ to more than 5 mol% did not improve the reaction time and yield (entry 4). In another study, when the reaction was carried out at 105°C, the product was obtained in 97% yield in slightly shorter reaction time in comparison with 100°C (entry 5). Nevertheless, we selected 100°C as optimal reaction temperature, because an important aim of this work was performing the reaction in milder reaction conditions with respect to the reported works, and this was more logical. In many of the reported methods for the synthesis of 14-aryl-14*H*-dibenzo[*a*, *j*]xanthenes, the reaction has been performed at harsher reaction conditions (110-120°C).



Scheme 2. Synthesis of 14-aryl-14*H*-dibenzo[*a*, *j*]xanthenes.

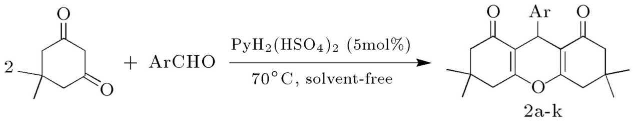
Table 1. The condensation between 2-naphthol and benzaldehyde in the presence of different molar ratios of $PyH_2(HSO_4)_2$ at range of 80 to 105°C.

Entry	Mol% of the catalyst	Temperature (°C)	Time (min)	Yield[a] (%)
1	-	100	240	26
2	2.5	100	70	89
3	5	100	40	97
4	7.5	100	40	97
5	5	105	35	97
6	5	80	110	82
7	5	90	70	93

[a] Isolated yield.

After optimization of the reaction conditions, 2-naphthol was reacted with different aromatic aldehydes (Table 2). As can be seen in Table 2, 2-naphthol was efficiently condensed with benzaldehyde as well as aromatic aldehydes possessing electron-withdrawing substituents, electron-releasing substituents or halogen on their aromatic rings, and the desired 14-aryl-14*H*-dibenzo[*a*, *j*]xanthene derivatives were produced in excellent yields and in relatively short reaction times.

Considering the high importance of 9-aryl-1,8-dioxo-octahydroxanthenes, in the next step, the reaction of dimedone (2 mmol) with benzaldehyde (1 mmol), to produce 9-aryl-1,8-dioxo-octahydroxanthene **2a**, was checked using different molar ratios of pyrazinium di(hydrogen sulfate) at range of 50-75°C in the absence of solvent (Scheme 3). The results



Scheme 3. Preparation of 9-aryl-1,8-dioxo-octahydroxanthenes.

Table 2. The solvent-free synthesis of 14-aryl-14*H*-dibenzo[*a*, *j*]xanthenes by the condensation of 2-naphthol with arylaldehydes using $PyH_2(HSO_4)_2$ at 100°C (Scheme 2).

Ar	Product	Time (min)	Yield[a] (%)	M.p. (°C) found (reported)
C_6H_5	**1a**	40	97	186-188 (186-188) [29]
$4\text{-}NO_2C_6H_4$	**1b**	35	98	312-314 (310-311) [25]
$3\text{-}NO_2C_6H_4$	**1c**	20	97	216-218 (213) [31]
$2\text{-}NO_2C_6H_4$	**1d**	40	94	212-214 (214-215) [25]
$4\text{-}MeC_6H_4$	**1e**	35	97	226-228 (227-228) [25]
$4\text{-}MeOC_6H_4$	**1f**	40	94	201-203 (203-205) [28]
$3\text{-}MeOC_6H_4$	**1g**	38	92	177-179 (174-176) [60]
$4\text{-}ClC_6H_4$	**1h**	30	97	284-286 (289-290) [28]
$3\text{-}ClC_6H_4$	**1i**	35	98	206-208 (207-209) [29]
$2\text{-}ClC_6H_4$	**1j**	35	97	211-213 (215) [31]
$3\text{-}BrC_6H_4$	**1k**	35	96	186-188 (190) [31]
$4\text{-}FC_6H_4$	**1l**	25	96	240-242 (238) [31]

[a] Isolated yield.

Table 3. The condensation of dimedone with benzaldehyde in the presence of different molar ratios of $PyH_2(HSO_4)_2$ at range of 50 to 75°C.

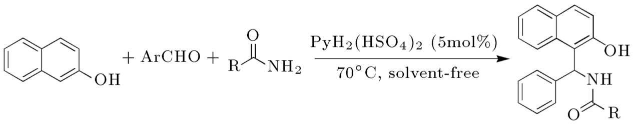
Entry	The catalyst amount (mol%)	Temperature (°C)	Time (min)	Yield^a (%)
1	-	70	240	Trace
2	2.5	70	50	93
3	5	70	35	97
4	7.5	70	30	97
5	5	75	35	97
6	5	50	120	62
7	5	60	65	76

^{a} Isolated yield.

are displayed in Table 3. As shown in Table 3, the reasonable results were obtained by using 5 mol% of the catalyst at 70°C; in these conditions, the product (**2a**) was produced in 97% yield within 35 min (entry 3). The reaction time slightly decreased by increment of the amount of the catalyst up to 7.5 mol% (entry 4); however, in this case, it is more economical and logical to use 5 mol% of the catalyst in the reaction. Moreover, the results did not improve by increment of the reaction temperature (entry 5). It is noteworthy that in the most of the reported methods for the preparation of 9-aryl-1,8-dioxo-octahydroxanthene derivatives, the reaction temperature is 80°C or higher.

To assess the efficiency and capacity of $PyH_2(HSO_4)_2$ in the synthesis of 9-aryl-1,8-dioxo-octahydroxanthenes, dimedone was reacted with various aromatic aldehydes (bearing electron-withdrawing substituents, electron-releasing substituents or halogen on their aromatic rings) under the optimized reaction conditions. The results are shown in Table 4. As it is clear from Table 4, all reactions proceeded efficiently and the corresponding xanthene derivatives were obtained in excellent yields and in short reaction times.

After the successful application of $PyH_2(HSO_4)_2$ in the synthesis of 14-aryl-14*H*-dibenzo[*a, j*]xanthenes and 9-aryl-1,8-dioxo-octahydroxanthenes, we decided to examine its applicability for the preparation of 1-amidoalkyl-2-naphthols and 1-carbamatoalkyl-2-naphthols by the reaction of 2-naphthol with aromatic aldehydes and amide derivatives or alkyl carbamates, under solvent-free conditions (Scheme 4). Thus, the reaction of 2-naphthol (1 mmol) with benzaldehyde (1 mmol) and acetamide (1.2 mmol), to produce compound **3a**, was selected as a model reaction, and its behavior was studied in the presence of different amounts of $PyH_2(HSO_4)_2$ at range of 60-75°C under solvent-free conditions (Table 5). As Table 5 shows, the reasonable results were obtained when the reaction was carried out using 5 mol% of $PyH_2(HSO_4)_2$ at 70°C (entry 3). Increasing the amount of the catalyst up to 7.5 mol% did not advance the results; in these conditions, a little amount of a by-product was produced (entry 4). In addition, the reaction time and the yield did not change by enhancing the reaction temperature (entry 5).



3a-o

Scheme 4. The synthesis of 1-amidoalkyl-2-naphthols and 1-carbamatoalkyl-2-naphthols.

Table 4. The $PyH_2(HSO_4)_2$-catalyzed preparation of 9-aryl-1,8-dioxo-octahydroxanthenes via the reaction of dimedone with arylaldehydes at 70°C in solvent-free conditions (Scheme 3).

Aldehyde	Product	Time (min)	Yield^a (%)	M.p. (°C) found (reported)
C_6H_5	**2a**	35	97	199-201 (204-205) [40]
$4\text{-}NO_2C_6H_4$	**2b**	25	98	225-227 (224-226) [29]
$3\text{-}NO_2C_6H_4$	**2c**	30	98	164-166 (165-166) [33]
$2\text{-}NO_2C_6H_4$	**2d**	35	97	257-259 (259-261) [61]
$3,4,5\text{-}(MeO)_3C_6H_2$	**2e**	30	91	192-194 (190-192) [34]
$4\text{-}MeOC_6H_5$	**2f**	35	91	243-245 (248-250) [39]
$4\text{-}MeC_6H_4$	**2g**	30	97	216-218 (219-221) [39]
$4\text{-}ClC_6H_4$	**2h**	25	98	229-231 (231-233) [39]
$3\text{-}ClC_6H_4$	**2i**	30	97	185-157 (183-185) [33]
$2\text{-}ClC_6H_4$	**2j**	35	85	224-226 (223-225) [29]
$4\text{-}Br\text{-}C_6H_4$	**2k**	27	94	242-244 (242-244) [29]
$4\text{-}FC_6H_4$	**2l**	35	90	226-228 (223-225) [38]

^{a} Isolated yield.

Table 5. Effect of amount of the catalyst and temperature on the condensation of 2-naphthol with benzaldehyde and acetamide.

Entry	**The catalyst amount (mol%)**	**Temperature (°C)**	**Time (min)**	**Yield[a] (%)**
1	-	70	240	19
2	2.5	70	75	95
3	5	70	40	95
4	7.5	70	35	94
5	5	75	40	95
6	5	60	70	90

[a] Isolated yield.

After optimization of the reaction conditions, the scope and efficacy of the catalyst was studied by the reaction of 2-naphthol with aryl aldehydes and different amide derivatives. The results are summarized in Table 6. As shown in Table 6, using ionic liquid $PyH_2(HSO_4)_2$, 2-naphthol was efficiently condensed with all aldehydes (including benzaldehyde as well as aromatic aldehydes possessing electron-withdrawing substituents, electron-releasing substituents or halogens on their aromatic rings) and aliphatic, alkenyl or aromatic amides to afford the desired 1-amidoalkyl-2-naphthols in excellent yields and in short reaction times (Table 6, compounds **3a-k**). $PyH_2(HSO_4)_2$ was also successfully applied for the condensation of 2-naphthol with arylaldehydes and methyl carbamate; in these conditions, 1-carbamatoalkyl-2-naphthols **3l-o** were produced in excellent yields and short reaction times.

The above observations confirmed the high efficiency and the generality of our catalyst, PyH_2 $(HSO_4)_2$. According to these excellent results, we anticipate that this new Brϕnsted acidic ionic liquid can catalyze a wide range of organic transformations.

In another study, to confirm that the catalyst could not be converted to pyrazine and H_2SO_4 during the reaction, the solvent-free reaction of dimedone (2 mmol) with benzaldehyde (1 mmol) was examined in the presence of 5 mol% of H_2SO_4 (the predicted amount of sulfuric acid produced from $PyH_2(HSO_4)_2$) at 70°C in which the desired product was produced in 61% after 35 min (the yield and time for this reaction in the presence of $PyH_2(HSO_4)_2$ were 97% and 35 min, respectively). Moreover, the TLC of the reaction mixture did not indicate presence of pyrazine during the reaction (consequently, H_2SO_4 could not be produced). The TG and DTG diagrams of the catalyst showed that it is stable up to 290°C (the reactions temperatures for this work were 70 and 100°C). Considering these subjects, the catalyst could not be converted to pyrazine and H_2SO_4 during the reactions.

As previously shown, pyrazinium di(hydrogen sulfate) was highly efficient and general for the synthesis of four important classes of biologically

Table 6. The $PyH_2(HSO_4)_2$-catalyzed reaction of 2-naphthol with arylaldehydes and amides (or methyl carbamate) leading to 1-amidoalkyl (or carbamatoalkyl)-2-naphthols at 70°C in the absence of solvent (Scheme 4).

Ar	**R**	**Product**	**Time (min)**	**Yield[a] (%)**	**M.p. (°C) found (reported)**
C_6H_5	Me	**3a**	40	95	237-239 (238-240) [17]
$4\text{-}NO_2C_6H_4$	Me	**3b**	30	96	246-248 (245-247) [17]
$3\text{-}NO_2C_6H_4$	Me	**3c**	35	92	238-240 (238-240) [12]
$3,4\text{-}(MeO)_2C_6H_3$	Me	**3d**	55	88	232-234 (232-234) [54]
$4\text{-}MeC_6H_4$	Me	**3e**	40	94	223-225 (223-225) [12]
$4\text{-}ClC_6H_4$	Me	**3f**	25	96	220-222 (220-222) [54]
C_6H_5	$CH_2{=}CH$	**3g**	45	94	243-245 (247-249) [52]
$4\text{-}NO_2C_6H_4$	$CH_2{=}CH$	**3h**	40	95	217-21 (223-225) [53]
$4\text{-}MeC_6H_4$	$CH_2{=}CH$	**3i**	40	92	214-216 (214-216) [53]
$4\text{-}NO_2C_6H_4$	C_6H_5	**3j**	30	96	234-236 (237-239) [50]
$4\text{-}MeOC_6H_4$	C_6H_5	**3k**	35	93	201-203 (208-210) [50]
C_6H_5	MeO	**3l**	15	96	220-222 (217-218) [56]
$4\text{-}NO_2C_6H_4$	MeO	**3m**	10	96	203-205 (205-207) [56]
$3\text{-}NO_2C_6H_4$	MeO	**3n**	12	95	248-250 (253-255) [57]
$3\text{-}ClC_6H_4$	MeO	**3o**	40	94	199-201 (196-198) [56]

[a] Isolated yield.

interesting organic compounds including 14-aryl-14*H*-dibenzo[a, j]xanthenes, 9-aryl-1,8-dioxo-octahydroxanthenes, 1-amidoalkyl-2-naphthols, and 1-carbamatoalkyl-2-naphthols. To raise the catalyst worth, its recoverability and reusability was studied. For this purpose, the reaction of dimedone with benzaldehyde using $PyH_2(HSO_4)_2$ was carried out several times, and the reaction mixtures were combined. Afterward, H_2O was added to the combined reaction mixtures, stirred for 3 min, and filtered (the catalyst is soluble in H_2O; however, the reaction mixture is not soluble in H_2O). The filtrate (containing the catalyst) was washed with $CHCl_3$ (two times), and the water of the aqueous phase was evaporated under vacuum to give pure $PyH_2(HSO_4)_2$. It was recovered and reused three times with no significant loss of its catalytic activity.

3. Experimental

3.1. General

All chemicals were purchased from Merck or Fluka Chemical Companies. All known compounds were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by TLC using silica gel SIL G/UV 254 plates. The ^1H NMR (250, 300, 400 or 500 MHz) and ^{13}C NMR (62.5, 75, 100 or 125 MHz) were run on Bruker Avance DPX, FT-NMR spectrometers (δ in ppm). Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

3.2. Preparation of pyrazinium di(hydrogen sulfate) $\{PyH_2(HSO_4)_2\}$

A 25 mL flask charged with sulphuric acid 98% (2.50 g, containing 25 mmol of the acid) was put into an ice-bath, and pyrazine (1.00 g, 12.5 mmol) was added to it in portions over a period of 5 min. The resulting mixture was stirred for 20 min, and then $CHCl_3$ (30 mL) was added to it, and stirred for 3 min. The resulting solid was filtered, washed with $CHCl_3$, and dried to give $PyH_2(HSO_4)_2$ (3.42 g, 99%) as a pale yellow solid [13].

3.3. General procedure for the synthesis of 14-aryl-14H-dibenzo[a, j]xanthenes 1a-l

A mixture of 2-naphthol (0.288 g, 2 mmol), aldehyde (1 mmol) and $PyH_2(HSO_4)_2$ (0.014 g, 0.05 mmol), in a test tube, was firstly stirred magnetically, and after solidification of the reaction mixture, was stirred with a small rod, at 100°C. After completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature, H_2O (3 mL) was added to it, stirred for 3 min, and filtered to separate the catalyst. Then, the solid residue was recrystallized from EtOH (95%) to give the pure product.

3.4. General procedure for the synthesis of 9-aryl-1,8-dioxo-octahydroxanthenes 2a-l

To a mixture of dimedone (0.28 g, 2 mmol) and aldehyde (1 mmol) in a test tube, $PyH_2(HSO_4)_2$ (0.014 g, 0.05 mmol) was added. The resulting mixture was firstly stirred magnetically, and after solidification of the reaction mixture, was stirred with a small rod at 70°C, and the reaction progress was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature, H_2O (3 mL) was added to it, stirred for 3 min, and filtered to separate the catalyst. The solid residue was recrystallized from EtOH (95%) to give the pure product.

3.5. General procedure for the synthesis of 1-amidoalkyl-2-naphthols 3a-k and 1-carbamatoalkyl-2-naphthols 3l-o

To a well-ground mixture of 2-naphthol (0.144 g, 1 mmol), aldehyde (1 mmol) and amide derivative or alkyl carbamate (1.2 mmol) in a test tube, $PyH_2(HSO_4)_2$ (0.014 g, 0.05 mmol) was added and the resulting mixture was firstly stirred magnetically, and after solidification of the reaction mixture it was stirred with a small rod at 70°C. After completion of the reaction, as monitored with TLC, the reaction mixture was cooled to room temperature, H_2O (3 mL) was added to it, stirred for 3 min, and filtered to separate the catalyst. The solid residue (crude product) was recrystallized from EtOH (95%) to give the pure product.

4. Conclusions

In summary, we have developed highly efficient new methods for the synthesis of important organic compounds, 14-aryl-14*H*-dibenzo[a, j]xanthenes,9-aryl-1,8-d ioxo-octahydroxanthenes and 1-amido-alkyl/carbamatoalkyl-2-naphthols using Brϕnsted acidic ionic liquid $PyH_2(HSO_4)_2$. Some promising points for the presented methods are efficiency, generality, high yields, relatively short reaction times, cleaner reaction profile, simplicity, ease of preparation of the catalyst, and compliance with the green chemistry protocols.

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