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Task Specific Dicationic Ionic Liquids: Recyclable Reaction Media for the Mononuclear Rearrangement of Heterocycles

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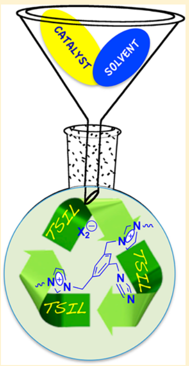
Supporting Information

ABSTRACT: Nine functionalized dicationic ionic liquids were used to study the base catalyzed mononuclear rearrangement of (*Z*)-phenylhydrazone of 3-benzoyl-5-phenyl-1,2,4-oxadiazole into the corresponding triazole at 363 K. Ionic liquids were characterized by the presence of 1-(1-imidazolylmethyl)-3,5-di[1-(3′-octylimidazolylmethyl)]benzene cation, bearing on the structure a neutral imidazole unit as basic functionality. Besides anions generally used for monocationic ionic liquids, such as [Br^-], [BF_4^-], and [NTf_2^-], also dianions having a rigid aromatic spacer such as 1,4-benzenedicarboxylate, 2,6-naphthalenedicarboxylate, and 1,5- and 2,6-naphthalenedisulfonate were taken into account. Furthermore, to have information about the effect deriving from the spacer rigidity also dianions such as 1,4-butanedicarboxylate and 1,6-hexanedicarboxylate were used. The basic strength of dicationic ionic liquids was determined using the Hammett indicator method. Data collected gave evidence that the outcome of the target reaction was affected by the nature of interactions operating between cation and anion of the ionic liquid used. Quite interestingly, solvent systems used had a good recyclability. Indeed, in some cases, they were reused for four cycles without significant loss in yield.



■ INTRODUCTION

The introduction of green chemistry twelve principles has attracted researchers to achieve a common goal, that is efficiency increase in chemical processes taking into account the environmental impact.[1,2] In this light, the choice of the right catalyst and solvent certainly plays an important role. The first one must have low toxicity and high efficiency, and it has to be recyclable. On the other hand, the second one has to provide a suitable "microenvironment" to upgrade the process. Solvent, as well as catalyst, must have low toxicity together with a low possibility to form dangerous emissions for the environment.

In the last decades, this request has been satisfied by ionic liquids (ILs), organic salts with melting points lower than 100 °C.[3] The interest in these "alternative solvents" is due to their low vapor pressure and flammability.[4] In the case of aromatic ILs, also three-dimensional organization plays a significant role. Many papers and reviews have investigated their properties and their use as reaction media.[5−8] Most of these works focus on monocationic ILs, even though nowadays attention to the class of di- and polycationic organic salts is rising.[9,10] Di- and polycationic organic salts allow several combinations of cations and anions, thanks to the possibility of changing the structure of the spacer bearing the charged heads.[11] Besides their application as reaction media, this peculiarity opens new opportunities from an applicative point of view, for example, molecular pincers for anion recognition,[12,13] host−guest complexes,[14,15] lubricants,[16] stationary phases for chromatography,[17] ionic liquid crystals,[18] gel phases,[19−23] and so on. Furthermore, di- and polycationic organic salts exhibit a thermal stability higher than that of monocationic ILs.[11,24]

Another emerging class of ILs is the one of task specific ionic liquids (TSILs).[25,26] They are so defined because it is possible to design a specific IL, bearing a functional group in the cation or in the anion, based on a user's applications. TSILs can be considered "rivals" of solid supported catalysts; indeed they can incorporate the catalyst in a solvent system. This peculiarity increases the kinetic mobility and allows a large operational surface area.[27]

On the grounds of their advantages, the combination of TSILs and di- or polycationic organic salts may form an innovative class of ILs available in several fields such as the one of catalysis. This new efficient class of organic salts presents a functional group (metal, base, or acid) incorporated in the IL. Among ILs tethered with metals, Wang et al. have recently synthesized and studied a series of NHC silver(I), palladium(II), and mercury(II) complexes with a mesitylene linker. These TSILs were fully characterized. In particular the NHC palladium(II) complex has catalyzed the Suzuki−Miyaura reaction of aryl halides (iodide, bromide, and chloride) with phenylboronic acid in good yields, using MeOH/H_2O as solvent and KOH as base in air.[28]

A growing interest in the class of acidic and basic functionalized ILs is also developing, due to their possible use in thermoregulated catalytic systems. Indeed, thanks to their low solubility at room temperature in conventional organic solvents, it is possible to perform reactions at high temperature recycling the dicationic ILs at the end of the process. Sulfonic and carboxylic acid derivatives have been

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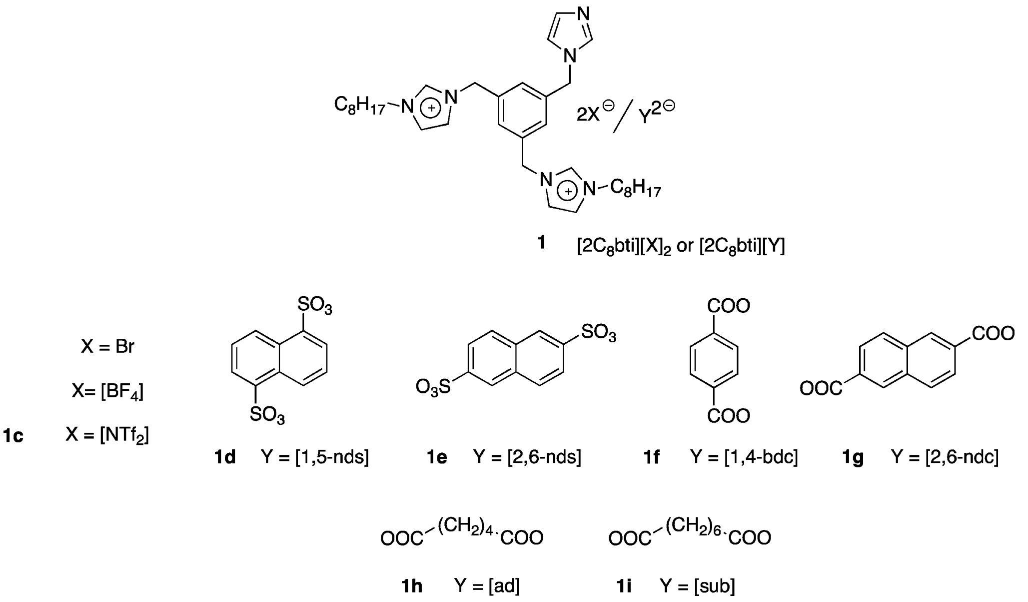
Chart 1. TSILs Used As Reaction Media



employed as acid functional moieties;[29,30] while imidazole, triazole, and pyrazine have been investigated as basic functionality.[31−33] Luo et al. recently reported a series of PEG-ILs with acidic and basic functionality, these salts were involved in the study of Knoevenagel condensation and in the synthesis of benzopyrans.[34,35]

Acidic or basic TSILs have also been used for biomass transformation in industry products, a process that requires an acidic or a basic catalyst.[36−38] An imidazolium based catalyzed system was the homogeneous reaction media in the transesterification reaction for biodiesel production from soybean oil with several alcohols.[36]

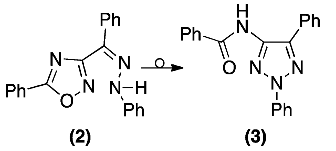
In the framework of this research field, we have recently studied a new class of dicationic imidazolium ILs. These dicationic organic salts are functionalized with a basic moiety, and they are characterized by the presence of 1-(1-imidazolylmethyl)-3,5-di[1-(3′-octylimidazolylmethyl)]benzene cation ($[2C_8bti]^{2+}$).[39] In Chart 1, ILs studied are represented.

Concerning anion properties, both mono- and dianions were used. The monoanions chosen were $[Br^-]$, $[BF_4^-]$, or $[NTf_2^-]$, which differ in size, shape, and coordination ability. Moreover, aromatic dianions with different spacers and charged heads were selected: 1,4-benzenedicarboxylate [1,4-bdc^{2-}], 2,6-naphthalenedicarboxylate [2,6-ndc^{2-}], 1,5-naphthalenedisulfonate [1,5-nds^{2-}], and 2,6-naphthalenedisulfonate [2,6-nds^{2-}]. To test the reactivity of dianions with flexible spacers, aliphatic dianions such as 1,4-butanedicarboxylate [ad^{2-}] and 1,6-hexanedicarboxylate [sub^{2-}] were also used. These dianions have chain lengths similar to those separating the charged head groups of the rigid dianions, 1,4-benzenedicarboxylate or 1,5-naphthalenedisulfonate (cf. 1,4-butanedicarboxylate) and 2,6-naphthalenedisulfonate or 2,6-naphthalenedicarboxylate (cf. 1,6-hexanedicarboxylate).

The joint approach of TGA, DSC, and NMR investigations recently carried out on the salts evidenced their high thermal stability and the presence of conformational equilibria in solution. The distribution of conformers in solution and the thermal properties of the TSILs are influenced by the nature of the anion.[39]

In this work, the catalytic ability of the novel TSILs was tested. To pursue this goal, they were used as reaction media for a base catalyzed reaction, the mononuclear rearrangement (MHR) of (*Z*)-phenylhydrazone of 3-benzoyl-5-phenyl-1,2,4-oxadiazole (**2**) in the corresponding triazole (**3**) (Scheme 1).

Scheme 1. MHR Reaction of (*Z*)-Phenylhydrazone of 3-Benzoyl-5-phenyl-1,2,4-oxadiazole Used To Study the Catalytic Ability of TSILs



We have previously studied the rearrangement in solution of both mono- and dicationic ionic liquids.[40,41] The comparison among imidazolium, benzylimidazolium, and dicationic ILs shows that yields increased on going from imidazolium to the latter two classes of ILs. On the grounds of a combined experimental approach of different techniques, we ascribed the high efficiency of benzylimidazolium and dicationic ILs to their significant three-dimensional organization, which favors the outcome of the reaction by stabilizing the transition state.[41] In view of such results, we have chosen the novel functionalized dicationic ILs to study the target reaction.

Because the probe reaction is base catalyzed, the basic strength of the TSILs was evaluated in terms of basicity function H_-, determined using the Hammett indicator method.[36,42] The reaction time and the recyclability of each TSIL were also evaluated. Furthermore, the percentage yields obtained at two different reaction times were compared.

■ RESULTS AND DISCUSSION

According to green chemistry principles, we tried to use the smallest solvent amount allowing the substrate solubilization. Consequently, we carried out the target reaction using a solvent/substrate molar ratio equal to 4.5 (0.48 mmol of TSIL and 0.105 mmol of substrate). The reaction was performed at

363 K, and its outcome was monitored via TLC until the complete disappearance of the substrate.

In Table 1 of Supporting Information, reaction times and yields are reported as a function of different TSILs used. For a useful comparison, data previously collected by us using some mono- and dicationic [NTf_2^-]-based ILs are also reported.[41]

Perusal of data reported shows that among the dianions used, [sub^{2-}] and [ad^{2-}] anions gave the highest yields, whereas dianions bearing a naphthalene core gave the lowest ones. In this latter case, the different nature of the charged head seems to affect the outcome of the reaction, as shown by the comparison among data collected in naphthalenedicarboxylate and naphthalenedisulfonate TSILs. In the latter case, analysis of reaction mixture by TLC did not show the presence of triazole even in traces. Furthermore, concentration of substrate in the reaction mixture did not show significant decrease, as evaluated using a UV−vis calibration curve (see Experimental Section).

As far as monoanions are concerned, reaction times decreased along the following trend: [NTf_2^-] > [Br^-] > [BF_4^-]. Furthermore, only slight differences in yields were detected in [$2C_8$bti][NTf_2]$_2$ and [$2C_8$bti][Br]$_2$ (84% and 77%, respectively) notwithstanding the significantly different reaction times (7 and 2.75 h, respectively). The above trend cannot be rationalized on the grounds of the anion coordination ability, as demonstrated by β values. Indeed, this parameter changes along the following series: [Br^-] > [BF_4^-] > [NTf_2^-] (β = 0.87, 0.55, and 0.42, respectively).[43] Rather, results obtained seem better correlated with the cross-linking ability of the anion. According to data previously reported,[17] the anion ability to favor the formation of a highly organized three-dimensional network decreases on going from [BF_4^-] to [Br^-] to [NTf_2^-] and this trend perfectly parallels the ones of yields and reaction times. Comparison between data reported in this work using [$2C_8$bti][NTf_2]$_2$ and those previously collected using both mono- and dicationic [NTf_2^-]-based ILs[41] shows that in general the presence of the basic functionality on the cation favors the outcome of the reaction. Indeed, in some monocationic ILs ([bmim][NTf_2] and [Bzmim][NTf_2]) and in [*m*-Xyl-(bim)$_2$][NTf_2]$_2$, which represents the best comparison to evaluate the effect deriving from the anchoring of the basic catalyst on the structure of dicationic IL, lower yields in higher reaction times and using a higher solvent/substrate molar ratio (8/1) were obtained.

With the only exception of [ad^{2-}] and [sub^{2-}] anions, for the other dianions, reaction times were equivalent to the one detected in the presence of [NTf_2^-]. Furthermore, comparison between [NTf_2^-] and [2,6-ndc^{2-}] derivatives shows that, at equivalent reaction time, the yield decreased on going from mono- to dianion.

As for dianions, in general, data indicate that an increase in the spacer rigidity on going from [ad^{2-}] and [sub^{2-}] to [1,4-bdc^{2-}] and [2,6-ndc^{2-}], induced a parallel increase in reaction time and a decrease in yields. Moreover, a negative effect seems also to be played by the increase in the π-surface area of the spacer, as demonstrated by data collected in the presence of [1,4-bdc^{2-}] and [2,6-ndc^{2-}] anions.

To have a better comparison among data collected in different TSILs, we performed the reaction using equivalent reaction times. In particular, we used the shortest (0.5 h) and the longest (7 h) reaction time, and data collected are reported in Table 1.

Perusal of data shows that only in the case of [$2C_8$bti][ad] the increase in reaction time, on going from 0.5 to 7 h, caused a small decrease in yield. Probably, this accounts for a slow decomposition of the reaction product as a consequence of the extended contact with the basic reaction media (slow hydrolysis of the amide bond in side chain could be supposed). Regardless of the reaction time used, [Br^-] and [BF_4^-] derivatives were the most reactive TSILs bearing monoanions, whereas [$2C_8$bti][ad] and [$2C_8$bti][sub] were the most suitable reaction media. Data collected at equivalent reaction time (7 h) assert an influence of the different nature of the anionic head, as demonstrated by higher reactivity of [2,6-ndc^{2-}] with respect to [2,6-nds^{2-}] derivative. Furthermore, they also shed light on the negative effect exerted by the increase in π-surface area of the anion on going from [1,4-bdc^{2-}] to [2,6-ndc^{2-}] and on the positive one derived from the flexibility of anion spacer, as testified by the comparison among data collected using aromatic and aliphatic dicarboxylate anions.

Table 1. Yields in Triazole at 363 K at Equivalent Reaction Times (0.5 and 7 h) as a Function of TSIL Used

TSIL	yield$_{0.5h}$ (%)[a]	yield$_{7h}$ (%)[a]
[$2C_8$bti][Br]$_2$	52	87
[$2C_8$bti][BF_4]$_2$	79	89
[$2C_8$bti][NTf_2]$_2$	0	84
[$2C_8$bti][1,5-nds]	0	0
[$2C_8$bti][2,6-nds]	0	0
[$2C_8$bti][1,4-bdc]	26	83
[$2C_8$bti][2,6-ndc]	28	63
[$2C_8$bti][ad]	95	83
[$2C_8$bti][sub]	87	90

[a] Yields were reproducible within 4%.

To have a better understanding of the data, we bore in mind data previously obtained about MHR reaction both in conventional organic solvents and in IL solution. As previously stated, the target reaction is a base catalyzed reaction, and its rate is significantly affected by the nature of catalyst used.[44] Furthermore, a previous computational investigation demonstrated that this reaction proceeds through a cyclic quasi-aromatic transition state.[45] In view of this, data previously collected in IL solution have shown that the outcome of this reaction highly benefits from the use of aromatic ILs.[40,41,46] Indeed, the thick network of cation−cation and cation−anion interactions is able to induce a significant structural order degree in the solvent system that stabilizes the transition state mainly by π−π interactions.

To evaluate the role played by each of the above factors, we first measured the basicity of TSILs in methanol solution, determining the H_- basicity function and using the Hammett indicator method.[33,42] This method has been recently used to assess the basicity of functionalized dicationic ILs.[36] We are aware of the fact that the situation detected in methanol solution could be different with respect to that occurring in the neat IL. Indeed, taking into account solvent polarity and alkyl chain length of our salts, in methanol solution they could be present as contact ion pairs. However, determination of the H_- function could allow having general information about basic strength of solvent media able to promote the target reaction. In our case, because the nature of anions used gave rise to different basic strengths, H_- values were determined using as acidic indicators both *p*-nitrophenol and bromocresol green. It is worth mentioning that in the case of [$2C_8$bti][2,6-ndc] we were not able to measure the H_- value as a consequence of the strong absorption band of this IL. The UV−vis spectra

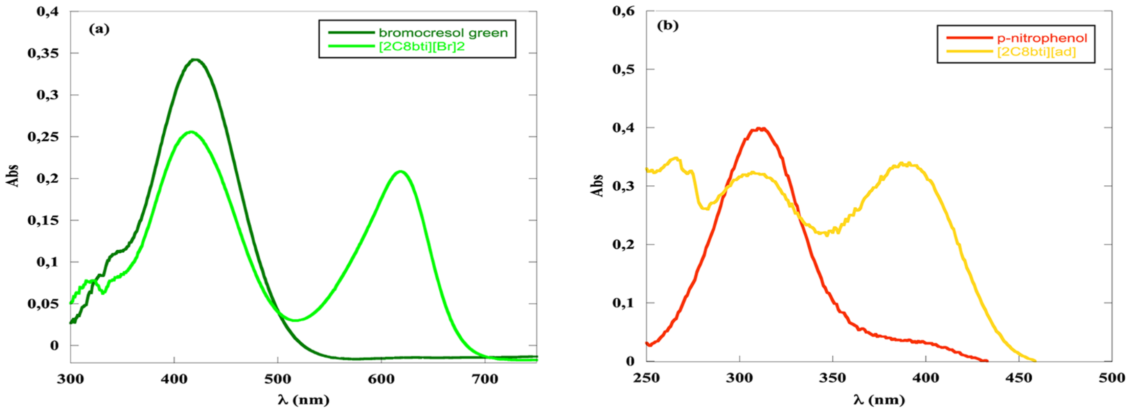


Figure 1. UV−vis spectra recorded at 298 K for (a) bromocresol green/[2C_8bti][Br]$_2$ and (b) *p*-nitrophenol/[2C_8bti][ad] systems in methanol solution.

recorded to determine H_- values in the case of [2C_8bti][Br]$_2$ and [2C_8bti][ad] are presented in Figure 1. The H_- values as a function of different TSILs are reported in Table 2.

Table 2. H_- Values Determined for TSILs at 298 K Using the Method of Hammett Indicator

TSIL	H_-[a]
Bromocresol Green[b]	
[2C_8bti][Br]$_2$	9.3
[2C_8bti][BF_4]$_2$	9.0
[2C_8bti][NTf_2]$_2$	8.5
[2C_8bti][1,5-nds]	8.9
[2C_8bti][2,6-nds]	8.6
p-Nitrophenol[c]	
[2C_8bti][1,4-bdc]	10.7
[2C_8bti][ad]	10.7
[2C_8bti][sub]	10.5

[a] H_- values were reproducible within ±0.1. [b] pK_a(MeOH) = 9.80.[47] [c] pK_a(MeOH) = 11.30.[47]

Analysis of the data shows that [2C_8bti][ad], [2C_8bti][sub], and [2C_8bti][1,4-bdc] have the highest basicity; whereas [2C_8bti][NTf_2]$_2$ and [2C_8bti][2,6-nds] have comparable basicity and are the least basic TSILs used in this work. This latter result does not account for the experimental trend obtained. Indeed, it does not allow us to explain the triazole formation in [2C_8bti][NTf_2]$_2$ solution. On the other hand, in the case of [2C_8bti][1,4-bdc], [2C_8bti][ad], and [2C_8bti][sub], significant differences detected both in yields and in reaction times cannot be explained on the grounds of H_- values. Similar conclusions can be drawn by the comparison between data in [2C_8bti][BF_4]$_2$ and [2C_8bti][NTf_2]$_2$ solution. All of the above data indicate that in our case, although basicity plays an important role in determining the outcome of the reaction, it is not able to explain alone the experimental trend. Analysis of data previously reported in the literature about correlation between basicity or acidity and reactivity of functionalized ILs demonstrates that different behaviors can be detected for varying ILs and reaction nature. Indeed, a result similar to ours was previously obtained by Chen et al. studying catalytic performance of acidic dicationic ILs in the Beckmann rearrangement.[48] In that case, comparable yields in amides were collected regardless of the acidic strength of ILs as indicated by H_0 values. Similarly, Deng et al. did not find a clear relationship between catalytic performance and acidic strength of some Brønsted acidic ILs used to catalyze production of γ,γ-bishydroxyphenyl valeric acid from renewable levulinic acid.[38] On the other hand, Zhang et al. detected a little bit different situation studying biodiesel production in the presence of dicationic basic ILs. Indeed, in this latter case, trend in yields was partly ascribed to alkali amount.[36]

Bearing this in mind, we took into account the effect exerted on the target reaction by the structure of the IL,[40,41,46] and we considered again information recently obtained about the properties of TSILs used in this work.[39] Indeed, as above stated, using a combined approach of DSC, TGA, and NMR investigations, we demonstrated that these TSILs were characterized by the presence of different cation conformers whose distribution was heavily affected by the nature of the anion. In particular, [nds] and [ndc] anions were able to form the tightest ion pairs. In these cases, the anion was situated in the near environment of the cation, as demonstrated by cross peaks detected in 2D NOESY spectra, precluding variation in the cation conformation.[39] This result was also supported by a previous computational investigation showing that in the case of 3,3′-dioctyl-1,1′(1,3-phenylenedimethylene)diimidazolium [1,5-nds], the optimized geometry bore the anion embedded in a kind of closed cage formed by two aromatic rings of cation.[19] If this geometry is effective also in this case, it could hamper the inclusion of the transition state between two parallel planes of cations and consequently the formation of stabilizing $\pi-\pi$ interactions. It is worth noting that we previously claimed the occurrence of these interactions, on the grounds of activation parameters detected for the target reaction in solution of aromatic and aliphatic monocationic ILs.[46] The above hypothesis should explain why more flexible [ad^{2-}] and [sub^{2-}] anions, proved to be the most active solvent media. Furthermore, this could also account for significant differences in yields and reaction times detected among [2C_8bti][1,4-bdc], [2C_8bti][ad], and [2C_8bti][sub] notwithstanding comparable basicity.

Analysis of the above data also sheds light on the different behavior of mono- and dianionic TSILs. Indeed, the thick reticulation of solvent induced by the presence of the [BF_4^-] anion did not hamper cation−transition state interactions able to favor the outcome of the reaction.

As above stated, one of the main advantages in using TSILs is represented by the possibility of reusing both solvent system and catalyst avoiding problems due to their leaching. To test the possibility of recycling our TSILs, after extraction of the product, the solvent system was dried and reused. In Table 3, yields obtained after each cycle are reported as a function of TSIL.

Table 3. Yields in Triazole, Reaction Times and Catalytic Cycles as a Function of TSIL Used

TSIL	catalytic cycle	time (h)	yield (%)[a]
$[2C_8bti][Br]_2$	I	2.75	77
	II	2.75	84
	III	2.75	67
$[2C_8bti][BF_4]_2$	I	1	96
	II	1	90
	III	1	88
	IV	1	91
$[2C_8bti][NTf_2]_2$	I	7	84
$[2C_8bti]$[1,5-nds]	I	7	0
$[2C_8bti]$[2,6-nds]	I	7	0
$[2C_8bti]$[1,4-bdc]	I	5.5	86
	II	5.5	90
	III	5.5	74
$[2C_8bti]$[2,6-ndc]	I	7	63
	II	7	56
$[2C_8bti]$[ad]	I	0.5	95
	II	0.5	83
	III	0.5	86
	IV	0.5	88
	V	0.5	78
$[2C_8bti]$[sub]	I	0.5	87
	II	0.5	85
	III	0.5	88
	IV	0.5	76

[a] Yields were reproducible within 4%.

In general, due to low solubility of TSILs in diethyl ether, after each recycle loss in weight of the IL was lower than 5%. It is worth noting that further recycling was avoided if drop in yields higher than 10% or loss in IL weight higher than 5% were detected.

Analysis of results shows that TSILs used in this work can be recycled for at least two cycles without significant decrease in yield. In this measure, the nature of the anion seems to play a significant role. Indeed, among anions used, the ones giving rise to the most active solvent media, namely, $[BF_4^-]$, $[ad^{2-}]$, and $[sub^{2-}]$, give also highly recyclable TSILs. These solvent media were reused for at least four cycles, and the highest decrease in yield was equal to 9%. On the other hand, $[2C_8bti][NTf_2]_2$ and $[2C_8bti]$[2,6-ndc] proved to be the worst solvent media. Indeed, the first one precluded the possibility of recycling; whereas in the second case a significant drop in yield was detected after the second cycle. Finally, an intermediate behavior was detected in the case of $[2C_8bti][Br]_2$ and $[2C_8bti]$[1,4-bdc].

CONCLUSIONS

The use of TSILs has allowed performance of the MHR reaction with good yields and, at least in three cases, with short reaction time. Solvent systems used had a good recyclability. Indeed, in general, they could be reused for at least three or four cycles without significant loss in yield. This result constitutes a further support to the possibility of lowering the environmental impact of chemical processes.

Data collected demonstrate that the catalytic ability of these functionalized ILs is heavily affected by the anion nature. Indeed, although in two of three cases detected, the most reactive solvent systems were the ones having the highest basicity, they were also ILs having the most flexible anions. A joint action of anion flexibility and IL basicity seems to be determinant in favoring the outcome of the reaction. Indeed, only in cases in which the tightness of the cation−anion ion pair allows the formation of cation−transition state stabilizing interactions can the target reaction occur with high yields and low reaction time regardless of IL basicity.

EXPERIMENTAL SECTION

Materials and Measurements. TSILs **1a**−**1i** were prepared as previously reported.[39] (*Z*)-Phenylhydrazone of 3-benzoyl-5-phenyl-1,2,4-oxadiazole was synthetisized according to previous reports.[49] *p*-Nitrophenol, bromocresol green, diethyl ether, methanol, and 1,4-dioxane were analytical reagents purchased from commercial sources and used as received.

Product or substrate concentrations in the reaction mixture were determined with a common UV−vis spectrophotometer using calibration curves in 1,4-dioxane ($\lambda_{max,(3)}$ = 291 nm; $\lambda_{max,(2)}$ = 367 nm).

Reaction Conditions. All of the catalytic reactions were performed using a TSIL/substrate molar ratio of 4.5. In a typical experiment, 0.48 mmol of TSIL was weighed into a 4 mL screw capped vial, and its temperature was stabilized for 30 min at 90 °C. Subsequently (*Z*)-phenylhydrazone of 3-benzoyl-5-phenyl-1,2,4-oxadiazole (36 mg; 0.105 mmol) was added into the vial. The reaction was conducted under magnetic stirring at 363 K evaluating the disappearance of the substrate via TLC (eluent, petroleum ether/ethyl acetate 10/1).

One milliliter of H_2O was added to the reaction mixture; then the reaction product was extracted with diethyl ether. The organic phase was concentrated in vacuum and solubilized in 1,4-dioxane to determine the percentage yields of the reaction. In order to recycle the TSIL, the water phase was concentrated in vacuum and reused several times.

Base Strength. A suitable amount of TSIL was added to a methanol solution of the indicator. After the addition, color change of the indicator solution was observed. The resulting solution was analyzed by means of UV−vis spectroscopy. The indicators used, the relative concentrations, and the TSIL concentration were as follows: *p*-nitrophenol (pK_{HI} = 11.30; [HI] = 2×10^{-4} M; [TSIL] = 2×10^{-3} M); bromocresol green (pK_{HI} = 9.8; [HI] = 1×10^{-4} M; [TSIL] = 5×10^{-4} M). Basic strength was expressed by a basicity function (H_-), defined by the following eq 1.

$$H_- = pK_{HI} + \log[I^-]/[HI] \quad (1)$$

where pK_{HI} is the logarithm of the dissociation constant of the indicator used, and [HI] and $[I^-]$ are the concentration of the indicator and its conjugated base, respectively. The $[I^-]/[HI]$ ratio was determined spectrophotometrically after the evaluation of indicator ε value.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Table of yields in triazole and reaction times obtained in different TSILs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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