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Characterizing Ionic Liquids as Reaction Media through a Chemical Probe

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Abstract: The triplet *N*,*N*-dimethylaminophenyl cation, a highly reactive but chemospecific electrophile, has been used as a probe for characterizing the properties of reaction media for a series of imidazolium ILs. With the *N*-hexyl-*N*-methyl imidazolium derivatives (*not* with the *N*-butyl analogues), hydrogen transfer leading to the aniline was the main process. Trapping by iodide occurred with an inverse dependence on viscosity. Trapping by π nucleophiles exhibited a more complex behavior. This was explained by the effect of both the bulk viscosity and the structure of the IL cation on both steps of the reaction, namely, initial electrophilic attack and ensuing cation elimination or nucleophile addition. However, with an excellent nucleophile, such as thiophene, or when the latter step was intramolecular, as with 4-pentenol, the difference was obliterated and trapping became uniform. Incorporation of the probe into the IL cation (through insertion into the C–H bond α to the imidazolium ring) was demonstrated, while no addition to the anion tested (including bis(trifluoromethanesulfonimide)) took place.

Keywords: C–C coupling · cations · ionic liquids · photochemistry · solvent effects

Introduction

Room-temperature ionic liquids (ILs) are a class of novel solvents that are attracting increasing interest as a potential "green" alternative to conventional organic media. ILs have a negligible vapor pressure[1] that, combined with excellent thermal stability and easy preparation and recycling, makes them viable ecosustainable solvents for stoichiometric and catalytic processes. Ionic liquids solubilize inorganic, organic, and polymeric materials and hence have been utilized in synthesis, catalysis, polymerization, industrial cleaning, liquid/liquid extraction, and separation as documented by the growing number of reviews and books published in recent years.[2] In particular, imidazolium salts are popular in synthetic applications, because they are easily prepared in good to quantitative yields from relatively cheap and easily available intermediates. They are chemically and thermally stable and easy recyclable materials. In addition, an appropriate choice of both the *N*-substituents and the anion enables to tailor ILs for a very wide variety of synthetic applications.[2]

However, recent studies have demonstrated some limitations to the general application of ILs in organic synthesis. Thus, toxicity to crustacean *Daphnia magna* comparable to that of common volatile organic solvents[3a] and an acute toxicity to zebrafish[3b] have been demonstrated for some of these salts.

Furthermore, the question of the chemical stability is of evident importance for evaluating the viability of ILs as solvent and should be tested by using a suitable probe. Indeed, ILs are not chemically inert and both cations and anions have been shown to react under particular conditions.[4] As an example, hydrogen abstraction from imidazolium ILs by benzophenone in the triplet state has been reported,[5] though the activation energy of the process was higher than with conventional solvents. As for the counterion, tosyl, triflyl, and trifluoroacetyl anions competed as nucleophiles in the fluorodediazoniation reaction of aromatic diazonium salts.[6a] A phenyl cation in the singlet state was the intermediate and even a non-nucleophilic anion such as $[Tf_2N]^-$ was trapped (more efficiently than Br^-).[6b] Actually, phenyl

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cations exist in two spin states, singlet and triplet. The latter states are easily accessible by photoheterolysis of electron-donating substituted aryl chlorides[7] and exhibit a peculiar reactivity. This includes addition both to π nucleophiles[7] and to inorganic anions[8] (but, characteristically, not to neutral n nucleophiles, including water), hydrogen abstraction from the medium, and intramolecular C–H insertion reactions.[9]

We reasoned that the high reactivity and selectivity of these cations would make them a convenient probe for testing the characteristics of ILs as solvents in organic reactions by studying the effect on known trapping reactions as well as any reaction with the ILs themselves.

The photoreactivity of 4-chloro-*N*,*N*-dimethylaniline (**1**), previously studied in organic solvents of different polarity,[10] was thus explored in some ILs. Specifically, we chose five methylalkylimidazolium salts (**2a–e**) as a homogeneous series with similar polarity, polarizability, and hydrogen-bond basicity and acidity by varying only the length of the alkyl chain (butyl or hexyl) and the counterion (at any rate, a non-nucleophilic anion, namely $N(SO_2CF_3)_2^-$, BF_4^-, ClO_4^-, PF_6^-) and, accordingly, the viscosity of the medium.

Results

The photochemistry of chloroaniline (**1**) was tested both in neat ILs and in the presence of selected nucleophiles, namely, an inorganic anion (I^-), an olefin (allyltrimethylsilane, ATMS), a functionalized olefin (4-penten-1-ol), an aromatic (benzene), and an heteroaromatic (thiophene), and the results were compared to the same reactions carried out in a polar nonprotic solvent such as MeCN. Contrary to the experiments in MeCN, the reactions in ILs were carried out under stirring in order to avoid inhomogeneities in such highly viscous medium. Viscosity is an important parameter that is strongly affected by the presence of water or other impurities[11] and was measured on the actually used samples. The viscosity values are reported in Table 1 and ranged from 70 cP (for **2a**) to 280 cP (**2b** and **2d**), evidently much higher than for MeCN (0.345 cP). The water content of the ILs used in this work ranged from 700 to 1000 ppm.

Irradiation of aniline **1** (0.05 M) in neat **2a–e** for 16 h caused a >90 % consumption of the starting aniline in all of the ILs considered and gave variable amounts of *N*,*N*-dimethylaniline (**3**) and 2,4′-bis(*N*,*N*-dimethylamino)biphenyl (**4**, through a "self-attack" reaction, see Scheme 1). In MeCN the amounts of **3** and **4** were roughly equimolar, whereas in ILs either reduction (in **2d**,**e**) or self-attack (in **2a–c**) largely predominated.

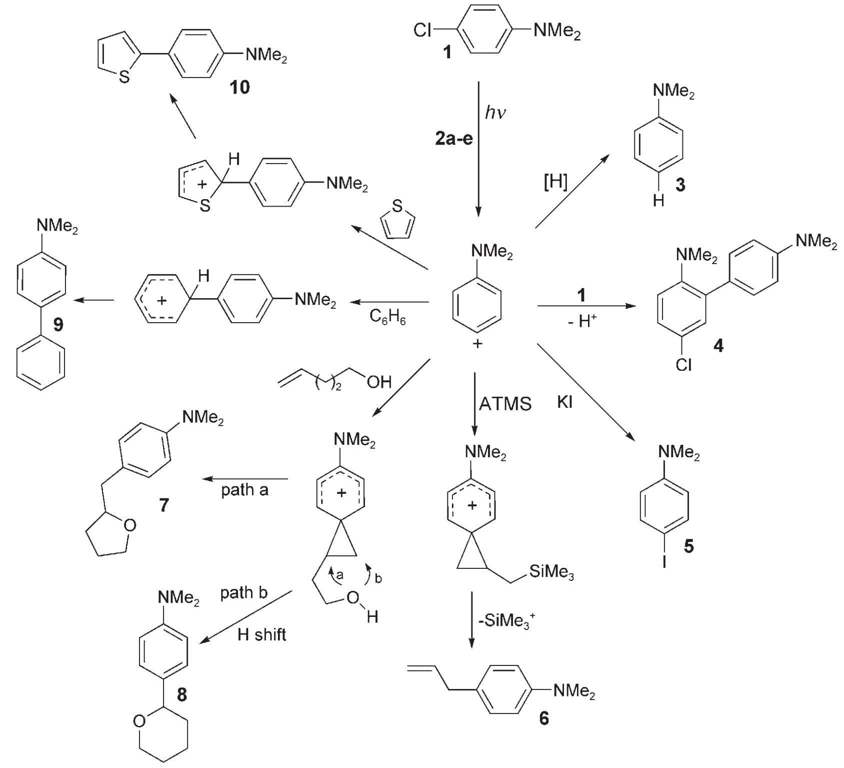
2a, R = Bu; X = NTf_2
2b, R = Bu; X = PF_6
2c, R = Bu; X = ClO_4
2d, R = Hexyl; X = ClO_4
2e, R = Hexyl; X = OMs

The limited solubility of KI in ILs (ca. 0.02 M) prevented its use in equimolecular amount with respect to **1**. Thus, the reaction was carried out in a saturated solution, by addition of 0.2 M KI, sonication, and irradiation for 16 h.[12] This gave

Table 1. Photolysis of 4-chloro-*N*,*N*-dimethylaniline (**1**; 0.05 M) in ILs **2a–e** in the presence of selected nucleophiles.

Additives		Products (% yield)[a,b]					
		[bmim][Tf_2N] (**2a**) [70][c]	[bmim][PF_6] (**2b**) [280][c]	[bmim][ClO_4] (**2c**) [160][c]	[hmim][ClO_4] (**2d**) [280][c]	[hmim][MsO] (**2e**) [180][c]	MeCN [0.345][c]
none	reduction	–	–	**3**[d] (<1)	**3** (78)	**3** (12)	**3** (45)
	self-attack	**4** (34)	**4** (29)	**4** (11)	–	–	**4** (31)
KI (satd)[e]	reduction	**3** (6)	**3** (7)	**3** (1)	**3** (59)	**3** (20)	**3** (9)
	self-attack	**4** (41)	–	–	–	**4** (6)	–
	trapping	**5** (47)	**5** (10)	**5** (6)	**5** (7)	**5** (15)	**5** (77)[f]
ATMS (0.5 M)	reduction	**3** (0, *3*)	**3** (*2*)	**3** (0, *30*)	**3** (24, *35*)	**3** (12, *14*)	**3** (5, *16*)
	self-attack	–	**4** (*2*)	**4** (0, *2*)	**4** (5, *0*)	**4** (0, *tr.*)	
	trapping	**6** (1, *30*)		**6** (0, *3*)	**6** (27, *10*)	**6** (0, *11*)	**6** (81, *53*)
4-penten-1-ol (0.5 M)	reduction	**3**[d] (0, *5*)	**3** (4)	**3** (*25*)	**3** (15, *18*)	**3**[d] (18, *16*)	**3** (6, *17*)
	self-attack	–	–	–	–	–	–
	trapping	**7** (4, *31*) **8** (0, *4*)	**7** (5)	**7** (*28*), **8** (*4*)	**7** (15, *30*), **8** (18, *4*)	**7** (28, *28*), **8** (3, *3*)	**7** (47, *22*), **8** (7, *5*)
benzene (1 M)	reduction	**3** (0, *10*)	**3** (*6*)	**3** (3, *14*)	**3** (25, *23*)	**3** (11, *21*)	**3** (20, *58*)
	self-attack	**4** (0, *5*)	**4** (*14*)	**4** (10, *3*)	**4** (4, *0*)	**4** (3, *0*)	**4** (11, *0*)
	trapping	**9** (3, *70*)	**9** (*29*)	**9** (0, *42*)	**9** (29, *22*)	**9** (19, *20*)	**9** (44, *42*)
benzene (0.5 M)	reduction	**3** (*34*)	[g]	[g]	**3** (*53*)	**3** (*56*)	**3** (*58*)
	self-attack	–	–	–	–	–	–
	trapping	**9** (*58*)	–	–	**9** (*21*)	**9** (*20*)	**9** (*21*)
thiophene (1 M)	reduction	**3** (*5*)		**3** (*16*)	**3** (*48*)	**3** (*9*)	**3** (*13*)
	self-attack	**4** (*37*)	**4** (*4*)	**4** (*18*)	**4** (*5*)	**4** (*5*)	**4** (*31*)[h]
	trapping	**10** (*47*)	**10** (*34*)	**10** (*49*)	**10** (*51*)	**10** (*39*)	**10** (*54*)

[a] GC and HPLC yields. [b] Values in italic are the yields in the presence of TEA 0.05 M. [c] The viscosity (in square brackets) is given in cP. [d] ESI-MS spectra were recorded on the IL solution after the irradiation (see text). [e] See text. [f] 70 % in a 0.02 M KI solution at 30 % aniline conversion. [g] Experiment not carried out. [h] Yields corrected with respect to that reported in reference [14].



Scheme 1.

4-iodoaniline (**5**) in low-to-medium yield (5–47 %) along with compounds **3** and **4**. The highest yield of **5** (47 %) was obtained in the low viscosity IL **2a** (for which the yield of **4** remained high, however), although this was considerably lower than that in MeCN, both with KI 0.2 M (77 %) and 0.02 M (70 % at 30 % conversion, see Table 1).

Alkylaniline **6** was formed in the presence of allyltrimethylsilane and involved elimination of the trimethylsilyl cation. Since acidity was liberated in the reaction, the effect of a buffering agent (triethylamine, TEA) was tested. TEA improved the reaction mass balance (not satisfactory in the absence of bases) for reaction in *N*-butyl ILs (**2a**, **2c**), not in *N*-hexyl ILs. Even in the best cases, the yield of **6** remained far below (30 %) that obtained in MeCN (81 %).

4-Penten-1-ol was then tested as a trap. Both in fluid solvents and in ILs attack onto the double bond was followed by intramolecular nucleophilic addition of the OH group leading either to a benzyl tetrahydrofuran (**7**, path a, Scheme 1) or to a phenyl tetrahydropyran (**8**, path b).[13] The former compound largely predominated (ca. 7:1 ratio). With the *N*-butyl, but not the *N*-hexyl, ILs the presence of TEA improved the otherwise poor mass balance. TEA also affected the **7**/**8** ratio in the case of **2d**.

When turning to aromatics, we were delighted to find that the arylation of benzene gave a better yield (70 %) in **2a** than in MeCN, with a strong reduction in the yield of byproducts **3** and **4**. Generally, the arylation of benzene gave better yields with *N*-butyl than with *N*-hexyl ILs, since in the latter case more aniline **3** was formed. It is worth noting that the yield of biphenyl **9** in ILs was only slightly decreased when the amount of benzene was reduced from 1 M to 0.5 M (contrary to MeCN, for which the yield halved from 44 to 21 %), although reduction to **3** (34 to 56 %) was by far the main product under these conditions.

With heteroaromatic thiophene, arylation occurred selectively in **2**[14] to form **10** with a yield approximately constant over the series of ILs considered, at least in the presence of TEA. In **2a** self-attack was an important competitive path.

We also explored the interaction of the probe with ILs themselves. As for the anion, formation of *N*-(4-dimethylaminophenyl)bis(trifluoromethanesulfonimide) (**11**) was suspected in the experiments in **2a**, because there was a literature precedent (see above). Product **11** was synthesized (see Experimental Section) and found not to be present in the irradiation mixture. As a matter of fact, blank experiments showed that **11** was both thermally and photochemically reactive in ILs, being in part transformed into unidentified products. However, no such products were detected in the irradiated solutions in **2a**, thus excluding the formation of **11**.

The possible modification of the IL cations was explored by carrying out an ESI-MS analysis on irradiated solutions (after ethereal extraction) in representative cases in which the mass balance was low (see Experimental Section for details). As shown in Figure 1 (top), besides the [bmim]$^+$ peak at 139 *m*/*z*, after irradiation in neat **2a** an intense peak at 258 *m*/*z* corresponding to the cation incorporating the aminophenyl moiety [+(Me_2N-C_6H_4)-H] was present. This suggested that an insertion reaction of the 4-aminophenyl cation onto the [bmim]$^+$ alkyl chain had taken place, as supported by the presence of the aggregates in the spectrum. Thus, besides the [(bmim-ClO_4)$_n$-bmim] aggregates with mass 378, 616 , 855, and 1093 *m*/*z* ($n=1$–4), further peaks assigned to arylated derivatives were observed at 736 and 975 [(bmim-ClO_4)$_n$(bmim$^+$-aminophenyl)], $n=2$–3. The same 258 *m*/*z* peak was identified in the irradiation with pentenol in [bmim][Tf_2N] (Figure 1, middle), as was the hmim$^+$-aminophenyl cation (286 *m*/*z*) along with the heteroaggregates ($n=1$–5) in the pentenol [hmim][MsO] photolyzed solution (Figure 1, bottom). Furthermore, in Figure 1 (top and bottom) a small peak at 202 *m*/*z* was detected. This

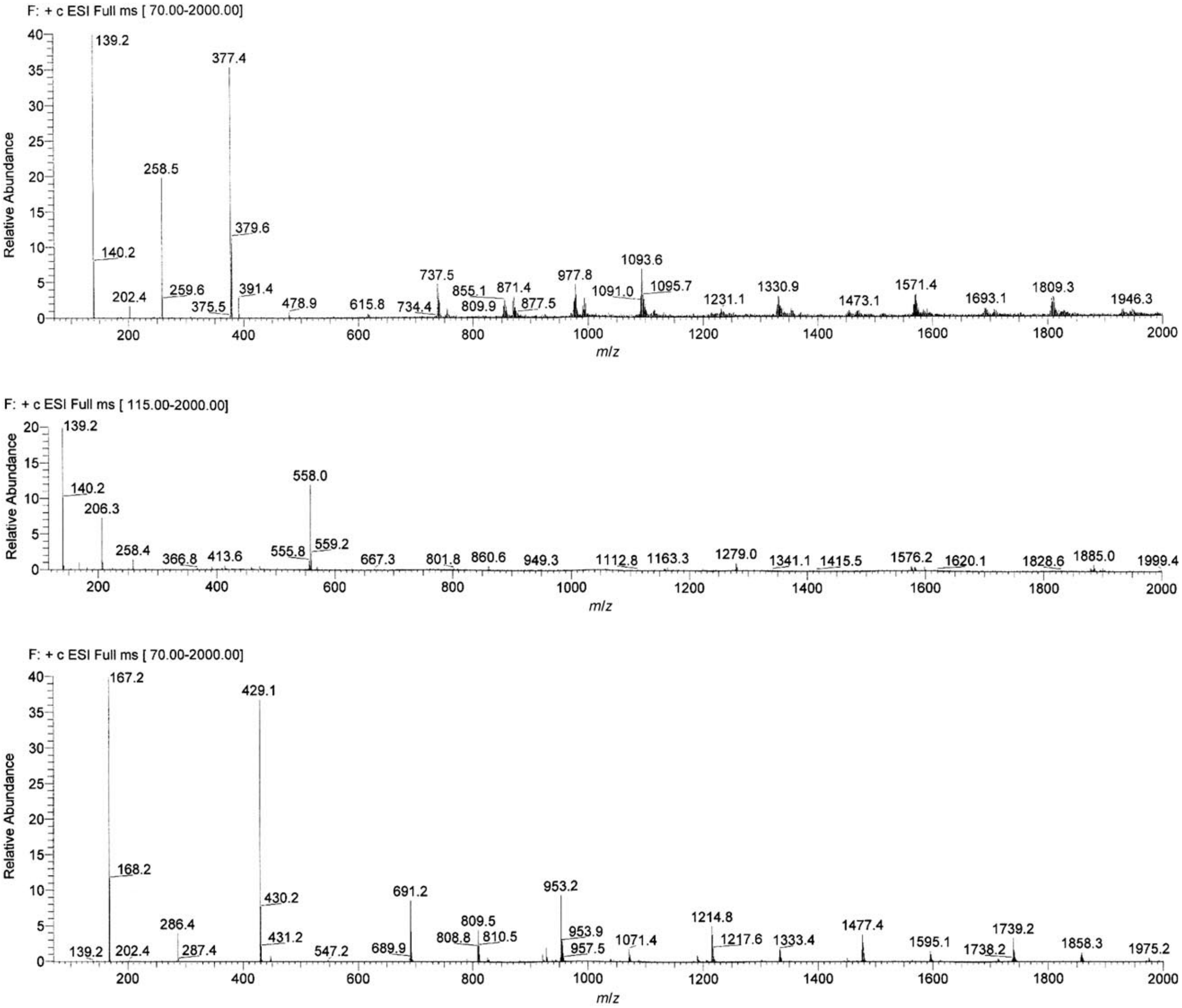


Figure 1. ESI-MS spectrum of irradiated solutions of **1** (after ethereal extraction) in neat **2a** (top), in **2a** containing 0.5 м pentenol (middle), and in **2e** containing 0.5 м pentenol (bottom).

was reasonably attributed to the loss of the alkyl chain in the arylated cation (258 (-C_4H_9) or 286 *m*/*z* (-C_6H_{13})), supporting that insertion involved (at least in part) the *N*-Me imidazolium group. ESI-MS mass spectra[15] were also measured on these solutions and the fragmentation of the [bmim]$^+$- (139 and arylated 258 *m*/*z*) and [hmim]$^+$-containing (167 and arylated 286 *m*/*z*) derivatives are shown in Figure 2. The loss of an alkyl chain (a butyl and a hexyl group, respectively) was apparent from these spectra.

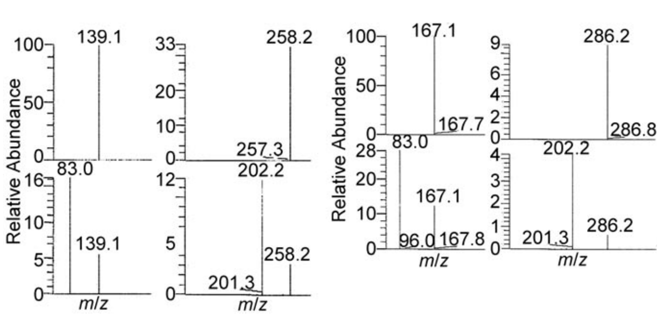


Figure 2. Selected portion of ESI-MS mass spectrum of [bmim] containing cations (left; 139 and 258 *m*/*z* from Figure 1, top) and [hmim] containing cations (right; 167 and 286 *m*/*z* from Figure 1, bottom).

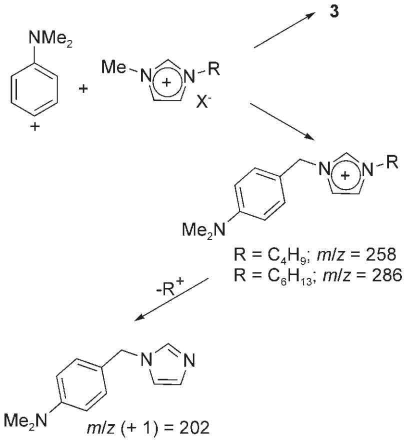
Discussion

For the reasons mentioned in the introduction, ionic liquids are regarded as "green solvents" and further it is hoped that they can be designed in such a way as to direct chemical reactions ("designer media"). This makes all important that suitable parameters are designed for characterizing ILs in view of their application in organic synthesis. Polarity has been extensively investigated by using various solvatochromic dyes,[16a,b] or by exploiting the keto–enol tautomerism of 2-nitrocyclohexanone[16c] and the association of ILs with water.[16d] Fluorescence and phosphorescence[17] from suitable lumophores have also been studied in ILs and found to be comparable to that of nonviscous solvents with a low ε,[17a] contrary to what may naively be expected. Other studies concerning the supramolecular structure of the ILs[11b,18,19a,b] and the multiple solvation interaction[19c] have recently been reported. Apart from the physical properties, a key point is evidently to assess the compatibility of ILs with charged intermediates involved in many organic reactions. This has been addressed by using a chemical probe and it has been recently found that some ILs are inert in solvolysis reactions of various triflates and mesylates via carbocations[20a] as well as to Grignard reagents via carbanions.[20b]

For photochemical reactions, ILs have been rarely employed[21] and should be sensitive to the limited molecular diffusion due to the high viscosity. This and the low oxygen solubility lead to a longer lifetime of triplet excited state with respect to common organic solvents[22] and should make them more appealing for photochemical synthesis. Most of the reported reactions involve photoinduced electron-transfer processes and ILs appear to be capable of stabilizing the radical ions formed.[22] A couple of reports concerning the photolysis of chloroaromatics in ILs have been reported, for example, the reductive dechlorination of some chlorophenols at 254 nm,[23] though at this wavelength absorption by the IL competed to some extent.

In the present work, a phenyl cation was used as a chemical probe and generated by photolysis of 4-chloro-*N*,*N*-dimethylaniline (**1**). The main results are discussed in the following.

1) Photolysis of **1** was effective in ILs. Previous work had shown that the efficiency of this process depended on the polarity of the solvent. Thus, in this respect imidazolium ILs behave as a medium polar or polar organic solvent.
2) The chemistry occurring in ILs is the same as in common organic solvents (see Scheme 1), supporting the fact that the aminophenyl cation is again the intermediate and the differences observed can be taken as indicative of how ILs affects the chemistry of the cation. These differences highlight, we believe, some key characteristics of ILs.
3) The bulk viscosity was determining. Thus, the preferred reaction with π nucleophiles made the starting chloroaniline an evident target in the absence of a purposely added trap. This gave biphenyl derivative **4**, the yield of which showed an inverse dependence on the viscosity, a parameter depending primarily on the IL anion. This fits with the known decrease of k_{diff} (in ILs up to >20).
4) The course of the reaction was finely tuned by the IL structure, which depended on the cation. Interaction with the ILs molecules was revealed by two reactions, hydrogen transfer and insertion into a C–H bond (Scheme 2). It is apparent that hydrogen abstraction was much more effective with the *N*-hexyl-*N*-methylimidazolium salts than for the *N*-butyl-*N*-methyl analogues, indeed completely suppressing self-attack (and strongly competing with any other process, see below). Hydrogen abstraction by the phenyl cation is known to be efficient in good hydrogen donors, such as alcohols.[7] ILs are known to form an extended hydrogen-bond system in the liquid state and their structure "adapts" to many species due to the presence of hydrophobic regions.[11b] Furthermore, ILs with alkyl side chains longer than, or equal to, four carbon atoms showed an aggregation of these chains in nonpolar domains.[19b] Apparently a longer chain favored a supramolecular organization less convenient for the migration of the intermediate, resulting in easier hydrogen transfer (Scheme 2). In parallel, insertion into a C–H bond to form aminophenylalkyl imidazolium salts took place both with [bmim]$^+$ and with [hmim]$^+$ salts. As reported above, this occurred at least in part at the *N*-methyl position (see Scheme 2). This suggested that the α-position was involved in both hydrogen abstraction and insertion.[24] Returning to the reaction with trap, another important point is that with charged nucleophile such as iodide. The trapping was efficient even at the low concentration attainable in this media and the difference between [bmim]$^+$ and [hmim]$^+$ was overwhelmed, resulting in a yield of **5** that showed a simple dependence of the inverse of viscosity.
5) The ILs effect depended on the mechanism of the reaction. The π nucleophiles that we tested were in every case effective traps when used at a high concentration (0.5–1 M); diminishing the concentration made trapping less efficient, both in ILs and in MeCN, see the case of benzene in Table 1. Previous studies in organic solvents supported that addition to alkenes gave a phenonium ion and that to aromatics a Wheland cation.[7] A successful trapping depended both on the initial addition and the ensuing step of the reaction, namely (TEA-assisted) elimination. Desilylation from the initial adduct onto ATMS was apparently most demanding. The yield of allyl aniline **6** was consistently lower than in MeCN, and decreased with increasing viscosity in accord, with the idea that limits to molecular motion imposed by viscosity were significant for a case in which a more complex se-



Scheme 2.

quence was involved. In the case of pentenol the last step was an intramolecular nucleophilic attack, with closure to a five- (predominantly) or six-membered ring.[13] Accordingly, the results in ILs were similar to those in MeCN, particularly in the presence of TEA, with a similar **7**/**8** ratio. An exception was **2d**, which, in the absence of TEA, clearly forced a conformation favorable to six-mode cyclization, evidencing that ILs do affect the conformation of the dissolved species. Trapping by aromatics was more effective, a fact that may be related to a different location in the ILs. TEA was again required (at least in $[bmim]^+$ salts), but deprotonation of the Wheland cation was apparently an easier process, leaving only a small dependence on viscosity in $[bmim]^+$ ILs with benzene and none with the better nucleophile thiophene. Indeed, arylation of aromatics in ILs was appealing from the synthetic point of view reaching in some cases a yield close to, or even better than, that in MeCN.

6) That IL anions act as nucleophiles depends likewise on the medium. These anions have a key role on the reaction, since the viscosity is mainly determined by them. An excellent nucleophile such as thiophene obliterates any difference, but with alkenes the lower the viscosity was, the higher was the amount of the adduct, and the low viscosity bis(trifluoromethanesulfonimide) derivative **2a** was the only IL in the series comparable to MeCN in these bimolecular reactions. However, the feared addition of this anion on the phenyl cation intermediate did not take place, contrary to what observed when the phenyl cation was generated thermally from diazonium salts[6b,26] (in this case the unselective singlet cation is produced, not the triplet).[27] Another "innocent" anion was PF_6^-,[6b] but the high viscosity of **2b** hampered an efficient arylation reaction. As for the mesylate anion, its coupling with phenyl cation may go undetected, since 4-aminophenylmesylate undergo itself photoheterolysis[28] leading back to the cation. At any rate, no mesylate was detected. A virtually unexplored, but promising, anion in ILs chemistry is non-nucleophilic ClO_4^-.[29] It is worth noting that in the case of [hmim][ClO_4] the mass balance after irradiation of the reaction is in most cases satisfactory despite its high viscosity (280 cP). The reduction path is highly favored in this case and **2d** may find application for the photoreduction of haloaromatics.

Conclusion

As it had been hoped, the use of a highly reactive, yet chemoselective probe such as the 4-*N*,*N*-dimethylaminophenyl cation was informative about the characteristics of ILs as reaction media. These are indeed convenient media for carrying out syntheses involving highly reactive intermediates, provided that the concentration of the traps and of other reagents required are high enough to avoid undesired side reactions. Importantly, the choice of the IL and thus the supramolecular organization of this medium can have a key effect on the products distribution, while maintaining, with a sensible arrangement, a good material balance. The effect is in part due to the viscosity, and in part to the specific interaction with the ILs, which depend on the specific structure. This becomes apparent when complex conformation changes are involved in the reaction, for example, in the reactions with alkenes. Furthermore, insertion into a C−H bond of the imidazolium *N*-alkyl chain was observed for the first time and the non-negligible hydrogen-donor ability of ILs cation was confirmed. Thus, the use of a triplet phenyl cation as a probe also evidences the limits of the use of ILs. The above unprecedented insertion into ILs cation along with the recently reported trapping of an intermediate by an IL anion show that ILs are not necessarily innocent bystanders in organic reactions. These results are expected to help prediction of the course of a reaction of known mechanism in a given IL, and thus help to devise tailor-made ILs.

Experimental Section

General: NMR spectra were recorded on a 300 MHz spectrometer. The attributions were made on the basis of ^1H and ^{13}C NMR, chemical shifts are reported in ppm downfield from TMS. The viscosity measurements were performed at 25 °C by a rotational viscosimeter Rheotec RC20 (RheoTec, Germany), in constant shear stress mode, by using a measuring cone CC25 DIN. The data were best fitted with the Rheo 2000 v2.7 software.

Positive ESI mass spectra were collected on a LCQ Advantage Finningan mass spectrometer (I spray voltage: 3.44 kV; capillary voltage: 10.83 V) at different capillary temperature $T = 280–175\,°C$. The sample was dissolved in 80/20/0.2 % vol of $MeOH/H_2O/CH_3COOH$ at concentration of $1\,mg\,mL^{-1}$, and was introduced continuously at a flow rate of $20\,\mu L\,min^{-1}$. The water content of each IL was measured using a coulometric Karl Fischer titrator (Metrohm 684 KF Coulometer). Samples were prepared by dissolving 0.250–0.350 g of IL in anhydrous acetonitrile in a 2 mL calibrated flask and duplicate determinations were performed on each sample with results agreeing to within 5 %.

The photochemical reactions were performed under stirring in quartz tubes by using nitrogen-purged solution and a multilamp reactor fitted with four 15-W phosphor-coated lamps (maximum of emission 310 nm) for the irradiation. The yields of the end products were determined by GC and HPLC techniques by comparison with authentic samples. The amount of **4** formed was determined by HPLC (AQUASIL C18 (250x4.6 mm) column, MeCN/water 60:40, flux 1 mL/min) with UV detection at $\lambda = 270$ nm.

ILs **2a** and **2b** were commercially available, while **2c**[30] and **2d**[31] were obtained by known procedures. In all cases, ILs were dried under vacuum (60–70 °C at <0.001 mmHg) for 6 h before use.

Synthesis of 1-hexyl-3-methylimidazolium methanesulfonate $[hmim]^+$ $MeSO_3^-$ (2e): *n*-Hexyl methanesulfonate[32] (18.03 g, 0.1 mol) and *N*-methyl imidazole (8.46 g, 0.103 mol) were placed in a 100 mL round-bottomed flask, fitted with a reflux condenser and a $CaCl_2$ drying tube. The mixture was then heated at 90 °C under stirring for 20 h until the methanesulfonate disappeared (the progress of the reaction was monitored by GC), dissolved in CH_2Cl_2 (80 mL), washed with a solution of saturated Na_2SO_4 containing 5 % methanesulfonic acid (2×5 mL) and then with saturated Na_2SO_4 (3×5 mL) until neutrality. The organic phase was dried over anhydrous Na_2SO_4, concentrated by using a rotary evaporator and dried under vacuum (60–70 °C at <0.001 mmHg) for 6 h, obtaining 23.62 g (90 % yield) of a very hygroscopic oil. $\rho^{25} = 1.112\,g\,mL^{-1}$; $\rho^{60} = 1.098\,g\,mL^{-1}$; $[\alpha]_D^{20} = 1.4816$; ^1H NMR ($CDCl_3$; 300 MHz): $\delta = 9.81$ (s, 1 H;

NCHN), 7.41 (A part of an AB system, d, $J = 1.53$ Hz, 1H), 7.33 (B part of an AB system, d, $J = 1.53$ Hz, 1H), 4.19 (t, $J = 6.53$ Hz, 2H; NCH_2-), 3.99 (s, 3H; NCH_3), 2.72 (s, 3H; OSO_2CH_3), 1.83–1.79 (m, 2H; CH_2), 1.30–1.25 (m, 6H; $(CH_2)_3$), 0.81 ppm (t, 3H; CH_3); MS(ES^+): *m*/*z*: 167.3 (100) $[hmim]^+$, 429.6 (50) $[(hmim)_2CH_3SO_3]^+$.

Synthesis of *N*-(4-dimethylaminophenyl)bis(trifluoromethanesulfonimide) (11): Compound **11** was obtained in 20% yield (light yellow solid) after purification by column chromatography starting from 4-(dimethylamino)aniline by known procedure.[33] This sulfonimide is quite unstable upon dissolution in organic solvents. M.p. 91–94°C; ^1H NMR ($CDCl_3$): $\delta = 3.00$ (s, 6H), 6.60 (d, $J = 8.6$ Hz, 2H), 7.10 ppm (d, $J = 8.6$ Hz, 2H; ArH); ^{13}C NMR ($CDCl_3$): $\delta = 40.3$ (CH_3), 112.5 (CH), 120.0 (q, $J = 320$ Hz), 121.2, 127.5 (CH), 150.2 ppm; IR (neat): $\tilde{\nu} = 966$, 1139, 1197, 1460, 1516, 2923 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{22}F_6N_4O_4S_2$: C 40.30, H 4.13; found: C 40.6, H 4.0.

Irradiation of 1 in ionic liquids 2a–e—general procedure: 4-Chloro-*N*,*N*-dimethylaniline (**1**, 8 mg, 0.05 mmol, 0.05 M) was placed in a quartz tube; the ionic liquid (**2a–e**, 1 mL) and the nucleophile (from 0.2 to 1 M) were then added. The resulting mixture was sonicated for a few minutes to allow the dissolution of the reagents and then flushed with nitrogen and irradiated. The resulting mixture (16 h; consumption of **1** $>90\%$) was then extracted with diethyl ether (4×1 mL) and analyzed by GC and HPLC technique. When **2a** was used as the solvent, a cyclohexane/ethyl acetate (4:1) mixture was used.

Compounds 7 and 8: Compounds **7** and **8** were obtained from the irradiation of **1** in MeCN/water 1:5[34] and used as standard.

*2-(4-*N,N*-dimethylbenzyl)tetrahydrofuran (7)*: Data for **7**: oil; ^1H NMR ($CDCl_3$): $\delta = 1.55$–1.65 (m, 1H), 1.85–2.00 (m, 3H), 2.65–2.80 (dd, $J = 7$, 13 Hz, 1H), 2.85–2.95 (dd, $J = 7$, 13 Hz, 1H), 2.95 (s, 6H), 3.70–3.80 (m, 1H), 3.90–3.95 (m, 1H), 4.00–4.05 (quintet, $J = 7$ Hz, 1H), 6.70–7.15 ppm (AA′BB′, 4H); ^{13}C NMR ($CDCl_3$): $\delta = 25.5$ (CH_2), 30.7 (CH_2), 38.7 (CH_2), 40.8 (CH_3), 67.8 (CH_2), 80.3 (CH), 113.3 (CH), 113.5, 129.8 (CH), 149.1 ppm; IR (neat): $\tilde{\nu} = 2956$, 1616, 1524, 1061, 975, 803 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{19}NO$: C 76.06, H 9.33; found: C 75.1, H 9.1.

*3-(4-*N,N*-dimethylphenyl)tetrahydropyran (8)*: Data for **8**: oil; ^1H NMR ($CDCl_3$): $\delta = 1.55$–1.70 (m, 3H), 1.85–1.95 (m, 3H), 3.60–3.70 (m, 1H), 4.05–4.20 (m, 2H), 6.70–7.15 ppm (AA′BB′, 4H); ^{13}C NMR ($CDCl_3$): $\delta = 24.0$ (CH_2), 25.9 (CH_2), 33.5 (CH_2), 40.8 (CH_3), 68.9 (CH_2), 79.9 (CH), 112.5 (CH), 114.5, 126.8 (CH), 149.1 ppm; IR (neat): $\tilde{\nu} = 2957$, 1621, 1522, 1059, 978, 799 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{19}NO$: C 76.06, H 9.33; found: C 76.3, H 9.4.

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[1] Note, however, that dialkylimidazolium cations have been revealed in the vapor phase upon heating ILs. See: H. Chen, Z. Ouyang, R. Graham Cooks, *Angew. Chem.* **2006**, *118*, 3738–3742; *Angew. Chem. Int. Ed.* **2006**, *45*, 3656–3660.

[2] a) *Green Industrial Applications of Ionic Liquids* (Eds.: R. D. Rogers, K. R. Seddon, S. Volkov), Kluwer, Dordrecht, **2003**; b) "Ionic liquids as Green Solvents: Progress and Prospects":*ACS Symp. Ser.* **2003**, *856*, whole volume; c) T. Welton, *Coord. Chem. Rev.* **2004**, *248*, 2459–2477; d) C. Chiappe, D. Pieraccini, *J. Phys. Org. Chem.* **2005**, *18*, 275–297; e) N. Jain, A. Kumar, S. Chauhan, S. M. S. Chauhan, *Tetrahedron* **2005**, *61*, 1015–1060; f) S. Lee, *Chem. Commun.* **2006**, 1049–1063.

[3] a) R. J. Bernot, M. A. Brueseke, M. A. Evans-White, G. A. Lamberti, *Environ. Toxicol. Chem.* **2005**, *24*, 87–92; b) C. Pretti, C. Chiappe, D. Pieraccini, M. Gregori, F. Abramo, G. Monni, L. Intorre, *Green Chem.* **2006**, *8*, 238–240.

[4] See for example: J. Dupont, J. Spencer, *Angew. Chem.* **2004**, *116*, 5408–5409; *Angew. Chem. Int. Ed.* **2004**, *43*, 5296–5297.

[5] M. J. Muldoon, A. J. McLean, C. M. Gordon, I. R. Dunkin, *Chem. Commun.* **2001**, 2364–2365.

[6] a) K. K. Laali, V. J. Gettwert, *J. Fluorine Chem.* **2001**, *107*, 31–34; b) R. Bini, C. Chiappe, E. Marmugi, D. Pieraccini, *Chem. Commun.* **2006**, 897–899.

[7] a) M. Fagnoni, A. Albini, *Acc. Chem. Res.* **2005**, *38*, 713–721; b) M. Fagnoni, *Lett. Org. Chem.* **2006**, 3, 253–259.

[8] V. Dichiarante, M . Fagnoni, A. Albini, *Chem. Commun.* **2006**, 3001–3003.

[9] E. Fasani, F. F. Barberis Negra, M. Mella, S. Monti, A. Albini, *J. Org. Chem.* **1999**, *64*, 5388–5395.

[10] M. Freccero, M. Fagnoni, A. Albini, *J. Am. Chem. Soc.* **2003**, *125*, 13182–13190.

[11] a) K. R. Seddon, A. Stark, M. J. Torres, *Pure Appl. Chem.* **2000**, *72*, 2275–2287; b) M. Antonietti, D. Kuang, B. Smarsly, Y. Zhou, *Angew. Chem.* **2004**, *116*, 5096–5100; *Angew. Chem. Int. Ed.* **2004**, *43*, 4988–4992.

[12] During this period the salt dissolved completely.

[13] Notice the formation of tetrahydropyrane **8** requires Wagner–Meerwein migration, a process previously observed in the phenyl cation addition; see reference [7b].

[14] B. Guizzardi, M. Mella, M. Fagnoni, A. Albini, *Tetrahedron* **2000**, *56*, 9383–9389.

[15] For related ESI-MS mass experiments on imidazolium ILs, see: F. C. Gozzo, L. S. Santos, R. Augusti, C. S. Consorti, J. Dupont, M. N. Eberlin, *Chem. Eur. J.* **2004**, *10*, 6187–6193.

[16] a) M. J. Muldoon, C. M. Gordon, I. R. Dunkin, *J. Chem. Soc. Perkin Trans. 2* **2001**, 433–435; b) C. Reichardt, *Green Chem.* **2005**, *7*, 339–351; c) G. Angelini, C. Chiappe, P. De Maria, A. Fontana, F. Gasparrini, D. Pieraccini, M. Pierini, G. Siani, *J. Org. Chem.* **2005**, *70*, 8193–8196; d) T. Köddermann, C. Wertz, A. Heintz, R. Ludwig, *Angew. Chem.* **2006**, *118*, 3780–3785; *Angew. Chem. Int. Ed.* **2006**, *45*, 3697–3702.

[17] a) P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.* **1996**, *35*, 1168–1178; b) K. A. Fletcher, S. Pandey, I. K. Storey, A. E. Hendricks, S. Pandey, *Anal. Chim. Acta* **2002**, *453*, 89–96.

[18] A. Mele, G. Romanò, M. Giannone, E. Ragg, G. Fronza, G. Raos, V. Marcon, *Angew. Chem.* **2006**, *118*, 1141–1144; *Angew. Chem. Int. Ed.* **2006**, *45*, 1123–1126.

[19] a) J. Dupont, *J. Braz. Chem. Soc.* **2004**, *15*, 341–350; b) J. N. A. Canongia Lopes, A. A. H. Pádua, *J. Phys. Chem. B* **2006**, *110*, 3330–3335; c) J. L. Anderson, J. Ding, T. Welton, D. W. Armstrong, *J. Am. Chem. Soc.* **2002**, *124*, 14247–14254.

[20] a) X. Creary, E. D. Willis, M. Gagnon, *J. Am. Chem. Soc.* **2005**, *127*, 18114–18120; b) M. C. Law, K.-Y. Wong, T. H. Chan, *Chem. Commun.* **2006**, 2457–2459.

[21] "Photochemistry in Ionic Liquids"R. M. Pagni, C. M. Gordon, in *Handbook of Organic Photochemistry and Photobiology*, 2nd ed. CRC , Boca Raton, **2004**.

[22] M. Alvaro, B. Ferrer, H. Garcia, M. Narayana, *Chem. Phys. Lett.* **2002**, *362*, 435–440.

[23] Q. Yang, D. D. Dionysiou, *J. Photochem. Photobiol. A* **2004**, *165*, 229–240.

[24] *N*-Dealkylation of a $[bmim]^+$ ion has been previously reported to occur upon addition of the bmim cation to a Pd^{II} complex to form bis(methylimidazole) dichloropalladate. See: J. E. L. Dullius, P. A. Z. Suarez, S. Einloft, R. F. de Souza, J. Dupont, *Organometallics* **1998**, *17*, 815–819.

[25] It has been proposed that benzene and arenes were staggered through π–π sandwich interactions between two bmim cations; see reference [19a].

[26] D. J. Moody, N. A. Hamill (Avecia Pharmaceuticals), WO 2004108633, **2004**.

[27] This highlights again the carbene character at C_1 of the triplet phenyl cation, as opposed to the localized cation at C_1 of the singlet,

as formed, for example, from the photolysis of phenyl diazonium salts.

[28] M. De Carolis, S. Protti, M. Fagnoni, A. Albini, *Angew. Chem.* **2005**, *117*, 1258–1262; *Angew. Chem. Int. Ed.* **2005**, *44*, 1232–1236.

[29] a) L. Cammarata, S. G. Kazarian, P. A. Salter, T. Welton, *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192–5200; b) D. Landini, A. Maia, *Tetrahedron Lett.* **2005**, *46*, 3961–3963.

[30] L. Cammarata, S. G. Kazarian, P. A. Salter, T. Welton, *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192–5200.

[31] D. L. Astolfi, F. C. Mayville, Jr., *Tetrahedron Lett.* **2003**, *44*, 9223–9224.

[32] H. R. Williams, H. S. Mosher, *J. Am. Chem. Soc.* **1954**, *76*, 2984–2990.

[33] C. W. Y. Chung, P. H. Toy, *Tetrahedron* **2005**, *61*, 709–715.

[34] The yield of tetrahydrofurans or -pyrans of structures **7** and **8** from the irradiation of **1** or other chloroaromatics dramatically depends on the solvent used. This topic is currently under investigation.

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