A preliminary comparative study of the Baylis-Hillman reaction in ionic liquid solution and gelled ionic liquid

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Summary: Baylis-Hillman reaction in ionic liquid ([BMIM][PF₆]) solution under stirring conditions and in the presence of a base (DABCO) can also be performed efficiently in non-stirred gel phase upon gelation of the ionic liquid using a LMW gelator (i.e., (*S*)-*N*-(1-oxo-3-phenyl-1-(tridecylamino)propan-2-yl)benzamide). In this preliminary study, we have compared both reaction media and the results showed similar behaviors. Interestingly, the ionogel was found to be slightly more effective affording the desired products with moderately higher yields within a reaction period of 24 h.

Keywords: Baylis-Hillman reaction; ionogel; supramolecular gel; ionic liquid

Introduction

Supramolecular (or physical) gels are soft materials formed by self-assembly of low molecular weight (LMW) organic compounds (so-called gelators) into 3D networks driven by various intermolecular non-covalent interactions such as hydrogen bonding, ionic, metal coordination, π - π stacking, and van der Waals interactions, among others.^[1,2] In general, the formation of supramolecular gels involves first the self-assembly of gelator molecules into 1D fibers, typically of nm diameter and mm length, followed by their physical entanglement. The solid-like appearance of the gels results from the entrapment of solvent molecules (major component) into the interstices of the 3D network *via* capillary forces and surface tension, increasing the viscosity of the medium by factors up to 10¹⁰. Due to the non-covalent nature of the interactions, most supramolecular gels display reversible *gel-to-sol* phase transitions triggered by a number of external stimuli (e.g. temperature, pH, ionic strength, irradiation, etc.).^[3,4] The practical importance of these materials is evidenced by a continuously growing number of reports dealing with their functional properties^[5,6] and applications in multiple research fields.^[7,8] An emerging application of supramolecular gels is their use as confined 3D microenvironments to

facilitate some chemical reactions under mild conditions.^[9,10] This is not surprising if we consider that natural evolution relies on the use of compartmentalized multifunctional systems such as cell organelles to facilitate challenged chemical reactions under very mild conditions and with a precise control on kinetics and selectivity. This has served as bio-inspiration to develop a number of artificial nanoreactors during the last decade.^[11-14] Within this context, we have recently demonstrated the potential of supramolecular gels as confined and compartmentalized media to carry out different air-sensitive photochemical reactions under aerobic conditions, which usually are prohibited in homogeneous solution.^[15]

The increase of environmental consciousness and governmental regulations in chemical research has motivated the development of clean procedures to avoid the use of harmful organic solvents. In this sense, room temperature (RT) ionic liquids (ILs) have attracted significant interest during the last decade, being used in numerous reactions as environmentally benign highly polar solvents and catalysts.^[16] Some of the most important features of ILs that explain these advances are their relatively low viscosity and vapor pressure, high thermal and chemical stability, wide electrochemical window (up to 3.0 V), high conductivity, inherent design flexibility, and high solubility of gases as well as inorganic, organic, and polymeric materials in them. ILs are usually made of large asymmetric organic cations and inorganic or organic anions. Among different types of ILs, 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) (*vide infra*) constitutes one of the most widely studied non-water soluble and commercially available ILs.^[16]

Among a plethora of organic reactions studied in ILs, the Baylis-Hillman reaction^[17] is an interesting example due to its atom-economy feature (i.e., all atoms from the reagents are incorporated in the product), synthetic versatility, easy preparation of starting materials, and formation of highly functionalized products in a single step. This C-C bond forming reaction occurs between the α -position of an activated alkene and a carbon electrophile such as an aldehyde in the presence of a nucleophilic catalyst (e.g., tertiary amine, phosphine). 1,4-Diazabicyclo[2.2.2]octane (DABCO) is one of the most frequently used tertiary amine catalysts employed for this reaction (Scheme 1A). Despite the above-mentioned advantages, the slow rate of the reaction for aliphatic aldehydes and electron-rich benzaldehydes (e.g., 7–14 days even in the absence of solvent and with high catalyst loading (25–200 mol %)) often limits the synthetic utility of the process under mild conditions.^[18] In 2001, Afonso, Santos and co-workers,^[19] and later Ko's group,^[20]

reported that imidazolium-based IL such as [BMIM][PF₆] appeared to accelerate significantly the rates of the Baylis-Hillman reaction. Since then, a number of different ILs supporting the Baylis-Hillman reaction has been reported, being most of them imidazolium-based ILs.^[21-36] However, Aggarwal and co-workers found that [BMIM][PF₆] in the presence of bases such as DABCO can also yield a side product by reaction of the deprotonated imidazolium salt at its C-2 position with the aldehyde (Scheme 1B).^[37] The authors demonstrated that mild bases with pK_a's as low as 8–9 such as DABCO (pK_a = 8.7) are strong enough to generate the corresponding reactive carbene. This is a key observation that demonstrates that [BMIM][PF₆] is not an inert solvent under these conditions. Later, Chu and co-workers^[38] reported that, in contrast to [BMIM][PF₆], the analog IL 1-butyl-2,3-dimethylimidazolium hexafluorophosphate ([BDMIM][PF₆]) is inert, affording the desired product in higher yield under the same basic conditions.

Scheme 1. A) General preparation of functionalized allyl alcohols via Baylis-Hillman reaction between aldehydes and methyl acrylate at RT.^[19] B) Potential side product of the Baylis-Hillman reaction when carry out in IL such as [BMIM][PF₆].^[37]

In this research, and within a program focused on the study of chemical reactions in

non-conventional media,^[15] we have preliminary explored for the first time the possibility to carry out a model Baylis-Hillman reaction in a gel matrix made of a LMW compound and [BMIM][PF₆] under basic conditions. We hypothesized that the combined benefits obtained from the confinement of reactants in a supramolecular gel with those derived from the use of an IL as solvent could enhance some aspect of this type of reactions.

Results and discussion

Synthesis of LMW gelator and ionogel formation

Based on previous studies,^[39] we selected the amino acid-based amphiphilic compound **1** as LMW gelator to gel IL [BMIM][PF₆] **2** (Figure 1). Gelator **1**, bearing a benzoyl moiety at the N terminus and a long hydrophobic chain (C16) at the C terminus, was easily synthesized from L-phenylalanine in four steps following the general procedure previously described.^[39] Briefly, L-phenylalanine was *N*-Boc protected and subsequently subjected to DCC coupling with hexadecane-1-amine. Standard Boc-deprotection with TFA and DCC coupling of the free amino group with benzoic acid afforded the desired product **1** in good yield.

Ionogel formation was achieved by gently heating a mixture of a weight amount of gelator **1** and [BMIM][PF₆] **2**, following by cooling down the isotropic solution to 4 °C. The gel state was initially recognized by the absence of gravitational flow upon turning the vial upside-down (Figure 1). Gelation of [BMIM][PF₆] with **1** was previously described using 3.1 mg per 100 mg of IL.^[39] In this research we increased the amount of gelator to 3.5 mg per 100 mg of IL to slightly enhance the stability of the gel medium in the presence of reactants and catalyst required for the Baylis-Hillman reaction.

Figure 1. (Top) Chemical structures of LMW gelator **1** and ionic liquid [BMIM][PF₆] **2**. (Bottom) Illustration of ionogel formation upon mixing gelator **1** (3.5 mg) and IL **2** (100

mg) through a heating-cooling cycle (see Experimental Section).

Baylis-Hillman reaction in ionic liquid (homogeneous conditions) and in ionogel

The reaction between 4-fluorobenzaldehyde and methyl acrylate was selected as model for comparative purposes. The first approach to test the reaction in ionogel medium involved the preparation of a gel from a clear solution prepared by heating a mixture of [BMIM][PF₆] **2**, 4-fluorobenzaldehyde, methyl acrylate, and DABCO (see Experimental Section) (Figure 2). The resulting gel containing all components of the reaction was allowed to stay undisturbed for 24 h at RT prior analysis of the products. For this, the *gel-to-sol* transition was easily induced by dilution of the reaction mixture with DCM, subsequent extraction of the products with a 10% citric acid solution, and purification by column chromatography as described in the Experimental Section.

Figure 2. (Top) Scheme of a model Baylis-Hillman reaction in ionogel medium. (Bottom) Representative illustration of ionogel formation upon mixing **1** (3.5 mg) with a solution made of [BMIM][PF₆] (100 mg), DABCO (1.0 mmol), 4-fluorobenzaldehyde (1.0 mmol) and methyl acrylate (1.2 mmol). Optimization experiments with other amounts were also performed as described in the text.

Oscillatory rheological experiments at RT confirmed the viscoelastic nature of the gel-like materials. The storage modulus (G') was found to be larger than the loss modulus (G'') in all cases. The average storage moduli were in the same range for both the pristine ionogel and the doped ionogel (i.e., ionogel having methyl acrylate, DABCO, and 4-fluorobenzaldehyde) ($G' \approx 900$ Pa). However, the dissipation factor ($\tan \delta = G''/G'$) was slightly reduced after incorporation of the Baylis-Hillman reagents (pristine ionogel: $\tan \delta = 0.57$; doped ionogel: $\tan \delta = 0.68$), suggesting that the external reagents cause a slight destabilization of the gel network.

During preliminary optimization experiments, we found that 2.0 equivalents of DABCO (a typical amount used in this transformation^[38,40,41]) induced crystallization of in the reaction mixture instead of gel formation. Therefore, we reduced the maximum amount of the base to 1.0 equiv in order to carry out the relative comparison between the reaction in solution (Table 1, entry 15) and in gel (Table 1, entries 1–14) within 24 h, which was found an optimal period of time (Table 1, entries 9, 10 and 14). A significant detriment in conversion was observed when less than 1.0 equiv of DABCO was used even for longer periods of time (Table 1, entries 1–9 vs 10). No major differences were observed with the use of higher gelator concentration (Table 1, entry 13 vs 10) or lower reaction temperature (Table 1, entry 11 vs 10). The gradual incorporation of methyl acrylate by diffusion on top of a preformed gel (i.e., gel containing gelator, IL, DABCO and aldehyde) instead of forming the gel with all components simultaneously provided also similar results in terms of conversion (Table 1, entry 12 vs 10).

Table 1. Baylis-Hillman reaction in ionogel under different conditions.^[a]

Entry	DABCO (equiv)	Reaction time	Gelator 1 (mg)	[BMIM][PF ₆] 2 (mg)	Conversion (%) ^[b]	Yield (%) ^[c]
1	0.1	1 h	3.5	100	13	5
2	0.1	24 h	3.5	100	49	30
3	0.2	1 h	3.5	100	21	9
4	0.2	24 h	3.5	100	70	48
5	0.2	48 h	3.5	100	53	36
6	0.5	1 h	3.5	100	43	27
7	0.5	24 h	3.5	100	84	65
8	0.5	48 h	3.5	100	83	63
9	1.0	1 h	3.5	100	52	37
10	1.0	24 h	3.5	100	95	74
11 ^[d]	1.0	24 h	3.5	100	95	76
12 ^[e]	1.0	24 h	3.5	100	91	72
13	1.0	24 h	10.0	100	94	73
14	1.0	48 h	3.5	100	93	72
15	1.0	24 h	--	100	96	69

^a Reaction conditions unless otherwise indicated: 4-Fluorobenzaldehyde (1.0 mmol), methyl acrylate (1.2 mmol), RT. ^b Conversion of initial aldehyde determined by NMR using dimethylacetamide as internal standard (see Experimental Section). Estimated error $\pm$ 2%. ^c Isolated yield (see Experimental Section). Estimated error $\pm$ 2%. ^d Reaction performed at 4 °C. ^e Reaction performed by adding methyl acrylate on top of a preformed gel containing gelator, IL, DABCO and aldehyde, and allowing the spontaneous diffusion through the network.

Unfortunately, no significant enantioselectivity (ee < 5%) was observed in the Baylis-Hillman reaction due to the chiral environment provided by the chiral gelator **1**. However, preliminary experiments indicated that the preparation of the reactive gel system seems to influence the enantioselectivity. For instance, the ee increased twice when the methyl acrylate was layered on top of a preformed gel (i.e., gel containing gelator, IL, DABCO and aldehyde) and allowed to diffuse through the network. These results suggest the possibility of different organization of reagents/reactants within the supramolecular gel network depending on the preparation method. Moreover, the use of higher gelator concentration and/or lower reaction temperature (i.e., 4 °C vs RT) also caused a slight increase of ee, albeit the effect was less pronounced in those cases (data not shown). This unexpected phenomenon is currently being studied in detail in our laboratory and the results will be reported in due course.

Furthermore, we were interested in comparing the prevalence of the side reaction between the IL and the aldehyde in IL (solution) vs ionogel. Thus, we monitored exclusively the reaction between [BMIM][PF₆] and 4-fluorobenzaldehyde (1 equiv) in the presence of DABCO (1 equiv) (i.e., no methyl acrylate was added in these experiments) both in homogeneous solution (i.e., absence of gelator **1**) and in the ionogel made of gelator **1** (Table 3). The potential effects of temperature, reaction time, and gelator concentration were also evaluated during this study. The results showed a significant reduction of the side product (and increase of unreactive aldehyde) with decreasing temperature both in IL (solution) and ionogel (Table 3, entries 1 vs 3, 2 vs 4, 5 vs 6). However, the ionogel medium did not contribute to the suppression of the side product (Table 3, entries 1 vs 5, 3 vs 6), regardless the gelator concentration (Table 3, entries 1 vs 2, 3 vs 4).

Table 2. Prevalence of side reaction in function of gelator concentration and temperature.^[a]

Entry	Gelator 1 (mg)	Temperature (°C)	Reaction time	Unreacted aldehyde (%)	Side product (%)
1	3.5	4	24 h	84	8
2	10.0	4	24 h	87	8
3	3.5	RT	24 h	72	21
4	10.0	RT	24 h	73	21
5	--	4	24 h	89	2
6	--	RT	24 h	72	18

^a Reaction conditions: 4-Fluorobenzaldehyde (1.0 mmol), DABCO (1.0 mmol), [BMIM][PF₆] (100 mg).

A direct comparison of the reaction kinetics of the Baylis-Hillman reaction in IL and ionogel indicated similar reaction rates, albeit the initial consumption of the starting material was faster in homogeneous solution probably due to slower diffusion of reagents through the gel medium (Figure 3). However, it should be noted that we performed these preliminary measurements only for one model substrate and, hence, the generality of the conclusions should be done after the evaluation of different substrates. Based on the foregoing results and our previous studies,^[15] we hypothesized that the reaction takes place within the confined pools of IL held in between the self-assembled aggregates formed by gelator **1**, where the stabilization of the zwitterionic intermediate could somehow be more effective (e.g., via a closer proximity of reactants and solvent molecules). The increase of viscosity and development of liquid interfaces upon gelation, as well as the potential increase of local concentration of substrates could also contribute to maintain the reaction rate in the non-stirred ionogel similar to that observed under vigorously stirred conditions in homogeneous solution. Nevertheless, further detailed studies are still necessary to clarify this scenario.

Figure 3. Kinetics profile of the Baylis-Hillman reaction in IL (solution) and ionogel at RT. Conditions: 4-Fluorobenzaldehyde (1.0 mmol), methyl acrylate (1.2 mmol), DABCO (1.0 mmol), [BMIM][PF₆] **2** (100 mg), gelator **1** (3.5 mg -only for the reaction in ionogel-), 24 h, RT.

The beneficial effect of confinement of the reaction in the gel network in terms of

product yield within a period of 24 h was observed with different aldehydes including aliphatic (Table 3, entry 1), aromatic (Table 3, entries 2-6), and α,β -unsaturated aldehydes. The yields observed in IL solution were in the same range than those previously reported,^[38] and moderate improvements were achieved for all cases in ionogel medium.

Table 3. Baylis-Hillman reaction of different aldehydes and methyl acrylate in IL (solution) and in ionogel.^[a]

Entry	Aldehyde RCHO	Yield (%) ^[b]	
		solution (IL 2)	Ionogel (IL 2 + gelator 1)
1	Butyraldehyde	41	50
2	4-Anisaldehyde	36	47
3	4-Fluorobenzaldehyde	69	74
4	2-Furaldehyde	36	44
5	4-Tolualdehyde	53	64
6	3,4,5-Trimethoxybenzaldehyde	66	74
7	<i>trans</i> -Cinnamaldehyde	21	38

^a Reaction conditions unless otherwise indicated: Aldehyde (1.0 mmol), methyl acrylate (1.2 mmol), DABCO (1.0 mmol), [BMIM][PF₆] **2** (100 mg), gelator **1** (3.5 mg -only for reactions in ionogel-), RT, 24 h. ^b Isolated yield (see Experimental Section). Estimated error $\pm$ 2%.

Conclusion

In conclusion, Baylis-Hillman reaction in stirred ionic liquid ([BMIM][PF₆]) solution in the presence of a base (DABCO) can also be performed efficiently in non-stirred gel phase upon gelation of the ionic liquid using a LMW gelator. The gel exhibited capability to confine the reagents (aldehydes, methyl acrylate, and DABCO), and the desired products were obtained with slightly higher yields compared to those obtained in ionic liquid solution within a period of 24 h.

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Experimental Section

Material and methods

All reagents and starting materials were commercially purchased from Acros, Aldrich, Fluka, Merck and TCI. They were used as received without further purification. ^1H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker Avance 300 spectrometer in CDCl_3 as solvent, and chemical shifts are reported relative to Me_4Si ($\delta = 0$). Reaction conversion and yields were calculated by NMR using *N,N*-dimethylacetamide an internal standard (i.e., 1.0 mmol was added to the vial and mixed with the reaction before an NMR measurement was made). Thin-layer chromatography (TLC) was carried out on Merck Aluminum sheets coated with silica gel 60 F₂₅₄. Visualization was performed with phosphomolybdic acid in ethanol with heating. Chromatographic purifications were conducted by column chromatography using silica gel (0.063-0.200 mm) obtained from Merck Compounds. Oscillatory rheology was performed with an AR 2000 Advanced rheometer (TA Instruments) equipped with a Julabo C cooling system. A 500 or 1000 μm gap setting and a torque setting of 40,000 dynes/cm² at 25 °C were used for the measurements in a plain-plate (40 mm, stainless steel). Gels made of gelator **1** (3.5 mg) and IL **2** (100 mg), with and without Baylis-Hillman reagents (i.e., 4-fluorobenzaldehyde (1.0 mmol), methyl acrylate (1.2 mmol), DABCO (1.0 mmol), were prepared as indicated below and equilibrated at RT for 24 h before measurements. Spectroscopic data of isolated compounds were identical to those reported in the literature (Table 3, entries 1,^[42] 2,^[43] 3,^[44] 4,^[43] 5,^[45] 6,^[19] 7,^[43]).

Synthesis of (S)-N-(1-(hexadecylamino)-1-oxo-3-phenylpropan-2-yl)benzamide (1): Gelator **1** was synthesized in four steps from L-phenylalanine following the procedure previously reported in the literature with slight modifications.^[14] Briefly, L-phenylalanine was first protected with di-*tert*-butyl dicarbonate. In a second step, the *tert*-butyloxycarbonyl (Boc)-protected L-amino acid was coupled with hexadecan-1-amine using *N,N'*-dicyclohexylcarbodiimide (DCC, 1.0 equiv) in dry dichloromethane (DCM). After column chromatography (*n*-hexane/AcOEt 8/2 v/v), trifluoroacetic acid (TFA, 3.0 equiv) was used for deprotection in dry DCM during 2 h. Finally, the free amine group was coupled with benzoic acid using DCC (1.0 equiv) in dry DCM. The desired product was purified by column chromatography (AcOEt/toluene 2/1 v/v), and displayed identical spectroscopic data to those reported in the literature.^[14] ^1H NMR (300 MHz, CDCl_3) δ (ppm) 7.8–7.3 (m, 10H), 7.0–6.9 (d, 1H), 5.7 (br, 1 H), 4.8–4.7 (m, 1 H), 3.3–3.2 (m, 2H), 3.2–3.0 (m, 2H), 1.4 (m, 2 H), 1.3–1.6 (br, 26H), 0.9 (t, 3H).

Preparation of ionogels

Gelator **1** (3.5 mg, 7.1×10^{-3} mmol) was mixed with ionic liquid [BMIM][PF₆] **2** (100 mg, 0.35 mmol), and the mixture was gently heated with a heat-gun for 30 s. The obtained isotropic solution was stored in the refrigerator at 4 °C affording an opaque gel within 3 min.

General procedure for Baylis-Hillman reaction in ionic liquid

To a mixture containing the desired aldehyde (1.0 mmol), methyl acrylate (103.3 mg, 107 μ L, 1.2 mmol) and DABCO (112.2 mg, 1.0 mmol), ionic liquid [BMIM][PF₆] **2** (100 mg, 0.35 mmol) was added and the resulting homogeneous solution was stirred for 24 h at RT. After this time, the mixture was diluted with DCM and extracted with 10% citric acid solution (x 3). The water layers were combined and extracted with DCM (x 3). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc 5/1 v/v).

General procedure for Baylis-Hillman reaction in ionogel

To a mixture containing gelator **1** (3.5/10.0 mg, 7.1×10^{-3} /0.02 mmol), methyl acrylate (103.3 mg, 107 μ L, 1.2 mmol) and DABCO (112.2 mg, 1.0 mmol), ionic liquid [BMIM][PF₆] **2** (100 mg, 0.35 mmol) and the desired aldehyde (1.0 mmol) were added. The mixture was heated for ca. 30 s and the resulting yellowish solution was cooled down to RT to induce the gel formation. The obtained gel was allowed to stay undisturbed for 24 h at RT. Finally, the gel was destroyed by mixing it with DCM and the mixture was extracted with 10% citric acid solution (x 3). The water layers were combined and extracted with DCM (x 3). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc 5/1 v/v).

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