

Regioselective pyrrole C–benzylation using hexaethylene glycolic ionic liquids as a recyclable catalyst

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Abstract: We have thoroughly investigated the C-benzylation of pyrrole (**1**) using different second and third generation ionic liquids (ILs). The pyrrole C-benzylation is achieved with benzyl halides, mesylate, and tosylate selectively at C2 position in good yield. Moreover, minimal byproducts under relatively mild conditions in hexaethylene glycol substituted imidazolium based ILs (hexaEGILs) have been observed. 2-Benzyl pyrrole (**3**) was synthesized in high yield from pyrrole (**1**) and benzyl bromide (**2a**) in the presence of [hexaEGmim][OMs] and [dihexaEGim][OMs] as two different tailor-made ILs as catalysts (10 mol%) in MeCN at 80 °C within an hour.

Keywords: Pyrrole benzylation, benzyl bromide, ionic liquids, ethylene glycols, green chemistry; ©2025 ACG Publications. All rights reserved.

1. Introduction

The conventional nucleophilic substitution (S_N) reactions utilize the polar aprotic solvents particularly, “tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), hexamethylphosphoric triamide (HMPA)” etc.¹⁻⁶ However, from the green chemistry point of view, their adverse environmental impact make these solvents an unsuitable reaction media.^{7,8}

Over the past two decades, ILs (Figure 1a) are found to be favorable media for S_N2 reactions due to their highly charged yet non-coordinating nature.⁹⁻²¹ Because of negligible vapor pressure and magnificent thermal stabilities of ILs, it could be a potential candidate to supplant the conventional organic solvents have been used till today. However, the biphasic framework requires the use of stoichiometric amount of ILs. This brings up concerns regarding ILs price and their biodegradability data.²²⁻²⁴ The alternative to this problem is to develop some new protocols where ILs can act as a

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catalyst and not as the reaction solvent. This is often conceivable by centering the consideration of wide scientific community on the third generation tailor-made ILs.²⁵

2. Background

Recently, Kim *et al.* has designed and prepared [hexaEGILs] (Figure 1b) and developed a new catalytic system for nucleophilic fluorination reactions.^{26,27a} Binder *et al.* used glycol based ILs in copper catalyzed microwave-assisted azide/alkyne “click” reaction.^{27b} Further, amino-polystyrene supported hexaethylene glycol-bridged IL catalyst was found to be remarkably efficient at catalyzing the selective nucleophilic hydroxylation of alkyl halides.^{27c} “Eco-friendly protocol from epoxide to cyclic carbonates using tri-s-triazine terminal-linked ILs” was recently reported by Sun and coworkers.²⁸

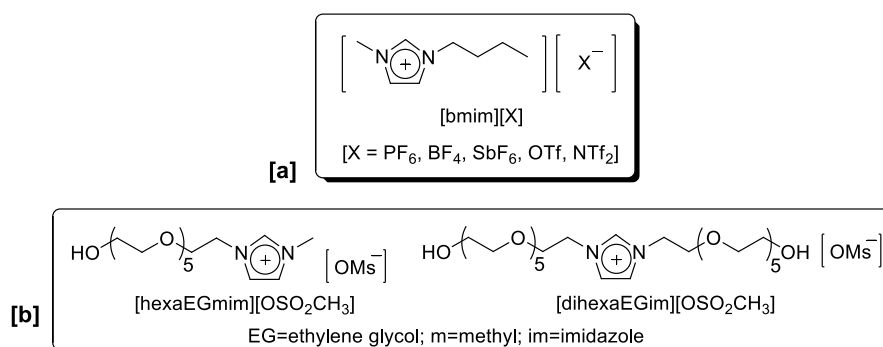
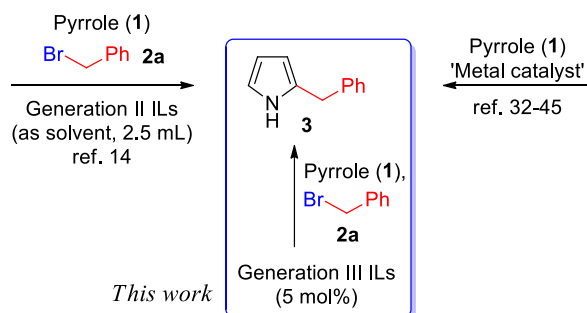


Figure 1. Second (a) and third (b) generation ILs.

The synthesis and reactions of five-membered aromatics have attracted researcher’s interest for over a century because of their medicinal and pharmacological significance.²⁹⁻³¹ The “C-alkylations of pyrrole on C2 and C5 positions from reactive halide moieties such as allyl, benzyl, and acetate” have been reported.³²⁻³⁸ The photocatalytic C2 alkylation with diazo esters was recently reported by Gryko *et al.*³⁹ Hintermann recently reported “hydrogen auto-transfer alkylation of substituted pyrroles by alkali alkoxides in alcohols at elevated temperature”.⁴⁰ The aluminum,⁴¹ cobalt,⁴² and copper-catalyzed^{43,44} direct alkylation of pyrrole using activated alkyl substituents have also been independently reported. The “role of hexameric resorcinarene capsule as a hydrogen bonding catalyst” towards the addition of heteroarenes has also been documented.⁴⁵ We have also reported highly efficient nucleophilic substitution reactions in ILs, including “pyrrole C-alkylation at C2 and C5 positions with various alkyl halides and mesylates” (Scheme 1).¹⁴

However, to the best of our understanding, no reports have been published on the regioselective benzylation of pyrrole using alkyl halides with IL as either catalysts or solvents. In this study, we present that by employing a custom-designed IL as a catalyst, significant rate enhancement of the C-benylation of pyrrole on second position can be accomplished from benzyl halides or mesylates. In this methodology preferential introduction of a benzyl group at the second position of pyrrole can be achieved with minimizing the formation of other products including dibenzylated product (Scheme 1).⁴⁶⁻⁴⁸



Scheme 1. Schematic representation of previous and this work

3. Experimental

3.1. Chemicals and Apparatus

The ^1H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer at RT and the chemical shifts are reported in δ units (ppm) relative to tetramethylsilane (TMS). TLC analysis was performed on 0.25 mm silica gel 60 aluminium sheets containing F_{254} . Column chromatography was performed using 200–400 mesh silica gel. All other known compounds including the IL, [bmim][Cl] were commercially available. Tailor-made ILs [hexaEGmim][OMs] and [dihexaEGim][OMs] were synthesized according to the reported procedure^{26, 27a} and was duly characterized before use.

3.2. Typical Procedure for Pyrrole C-Benzylolation in IL (Table 2)

In a pre-dried pressure vial benzyl halides/mesylate/tosylate (**2a**, 171 mg; **2b**, 127 mg; **2c**, 218 mg; **2d**, 186 mg; **2e**, 262 mg; 1.0 mmol), pyrrole (**1**; 0.14 mL, 2.0 mmol), NaHCO_3 (84 mg, 1.0 mmol) and [hexaEGmim][OMs] (45 mg, 0.1 mmol) or [dihexaEGim][OMs] (70 mg, 0.1 mmol) in 3.0 mL of anhydrous MeCN was heated at 80 °C in oil bath. Reaction was monitored using TLC, after completion the reaction mixture was extracted from IL phase with ethyl ether (10 mL x 3). The organic layer was dried over anhydrous Na_2SO_4 , evaporated under reduced pressure and was purified by column chromatography (5% EtOAc/hexanes) to obtain of 2-benzyl-1H-pyrrole (**3**) as colorless oil.

2-Benzyl-1H-pyrrole (3): Yield (133 mg, 85%); colorless oil; ^1H NMR (400 MHz, CDCl_3) δ , ppm: 3.97 s (2H, CH_2), 5.98–6.00 m (1H, H_{arom}), 6.13–6.15 m (1H, H_{arom}), 6.65–6.66 m (1H, H_{arom}), 7.18–7.31 m (5H, H_{arom}), 7.80 bs (NH); ^{13}C NMR (100 MHz, CDCl_3) δ , ppm: 34.0, 106.4, 108.3, 116.9, 126.4, 128.6, 128.7, 130.6, 139.5; MS (EI) 157 $[\text{M}]^+$, 80 (100). HR MS (EI) Calcd for $\text{C}_{11}\text{H}_{11}\text{N}$ $[\text{M}]^+$ 157.0891, found 157.0891; CAS Registry No. 33234-48-9.

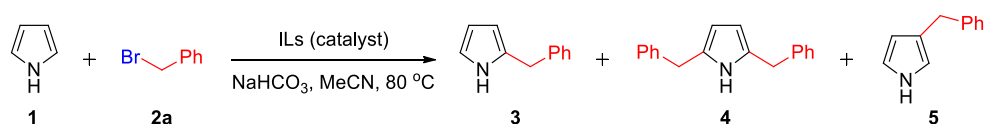
2,5-Dibenzyl-1H-pyrrole (4): light brown solid; T_{mp} 74–76 °C; ^1H NMR (400 MHz, CDCl_3) δ , ppm: 3.89 s (4H, 2CH_2), 5.85 d ($J = 2.4$ Hz, 2CH), 7.16–7.21 m (6H, H_{arom}), 7.24–7.29 m (4H, H_{arom}), 7.45 bs (NH); ^{13}C NMR (100 MHz, CDCl_3) δ , ppm: 34.1, 106.6, 126.3, 128.5, 128.6, 130.0, 139.7; MS (EI) 247 $[\text{M}]^+$, 156 (100). HR MS (EI) Calcd for $\text{C}_{18}\text{H}_{17}\text{N}$ $[\text{M}]^+$ 247.1361, found 247.1362; CAS Registry No. 850662-64-5.

3-Benzyl-1H-pyrrole (5): colorless liquid; ^1H NMR (400 MHz, CDCl_3) δ , ppm: 3.89 s (2H, CH_2), 6.10–6.12 m (1H, H_{arom}), 6.54–6.56 m (1H, H_{arom}), 6.73–6.25 m (1H, H_{arom}), 7.19–7.35 m (5H, H_{arom}), 8.02 s (NH); ^{13}C NMR (100 MHz, CDCl_3) δ , ppm: 33.3, 108.9, 115.3, 117.9, 123.1, 125.6, 128.2, 128.6, 142.2; MS (EI) 157 $[\text{M}]^+$ (100), 156 (83). HR MS (EI) Calcd for $\text{C}_{11}\text{H}_{11}\text{N}$ 157.0891 $[\text{M}]^+$ (100), found 157.0888 $[\text{M}]^+$ (100); CAS Registry No. 33234-57-0.

1-Benzyloxycarbonylpyrrole (6): colorless liquid; ^1H NMR (400 MHz, CDCl_3) δ , ppm: 5.25 s (2H, CH_2), 6.12 t (2H, H_{arom} , $J = 2.6$ Hz), 7.18 t (2H, H_{arom} , $J = 2.6$ Hz), 7.25–7.32 m (5H, H_{arom}); MS (EI) 201 $[\text{M}]^+$, 91 (100). HR MS (EI) Calcd for $\text{C}_{12}\text{H}_{11}\text{O}_2\text{N}$ 201.0790 $[\text{M}]^+$ (100), found 201.0791 $[\text{M}]^+$; CAS Registry No. 56857-08-0.

4. Present Study

To begin the investigation, we first performed the blank reaction with benzyl bromide (**2a**) as the model compound in MeCN as reaction media (Scheme 2, Table 1, entry 1). The reaction was found to be very slow and reached to completion after 36 h at 80 °C providing 65, 8, and 5% of 2-benzyl-1H-pyrrole (**3**), 2,5-bis-1H-pyrrole (**4**), and 3-benzyl-1H-pyrrole (**5**) respectively together with 4% of 1-benzyloxycarbonyl pyrrole (**6**).



Scheme 2. Pyrrole C-benylation with benzyl bromide catalyzed by hexaethylene glycolic ILs.

Table 1. Optimization of pyrrole C-benylation with benzyl bromide (2a).^[a]

entry	ILs (equiv)	yield of product (%) ^[b] after 30 min		yield of product (%) ^[b] after time (h)			
		3	4	time (h)	3	4	5
1 ^[c]	[blank]	-	-	36	65	8	5
2	[bmim][BF ₄] (0.11)	-	-	22	72	6	7
3 ^[d]	[bmim][BF ₄] (0.11)	6	traces ^[g]	18	68	5	5
4	[bmim][BF ₄] (1.1)	11	traces ^[g]	12	74	5	5
5 ^[e]	[bmim][OMs] (0.1)	14	traces ^[g]	6	76	4	-
6	[bmim][OMs] (1.0)	35	traces ^[g]	90 min	78	4	-
7	[hexaEGmim][OMs] (0.05)	38	-	3	85	3	-
8	[hexaEGmim][OMs] (0.10)	46	-	2	85	4	-
9	[hexaEGmim][OMs] (1.0)	80	6	30 min	80	6	-
10 ^[f]	[hexaEGmim][OMs] (1.0)	76	8	30 min	76	8	-
11	[dihexaEGim][OMs] (0.05)	36	-	3	84	4	-
12	[dihexaEGim][OMs] (0.10)	46	-	2	85	3	-

^[a]All reactions with 1.0 mmol reaction scale of benzyl bromide (2a, 171 mg) with pyrrole (1, 0.14 mL, 2.0 mmol) and NaHCO₃ (84 mg, 1.0 mmol) in acetonitrile (3.0 mL) at 80 °C. ^[b]Isolated yield.

^[c]1-Benzyloxycarbonylpyrrole (6) was obtained (8.0 mg, 4% yield). ^[d]Potassium carbonate (138 mg, 1.0 mmol) used and 1-benzyloxycarbonylpyrrole (6) was obtained (20 mg, 10% yield). ^[e]Potassium carbonate (138 mg, 1.0 mmol) used and 1-benzyloxycarbonylpyrrole (6) was obtained (24 mg, 12% yield). ^[f]In the absence of MeCN. ^[g]Observed on TLC.

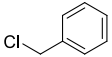
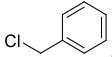
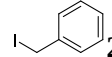
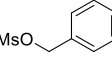
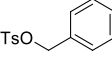
To check the catalytic behavior of IL, we conducted the reaction with approximately 10 mol% of [bmim][BF₄]. The reaction completed after 22 h to yield desired product (3) (72% yield) together with (4) (6% yield) and (5) (7% yield) (entry 2). Subsequently, in the presence of potassium carbonate, the reaction has taken similar lengths of time for completion with the good regioselectivity (entry 3). The shift of counter anion from [BF₄] to [OMs] improved the reaction time; 18 h for entry 3 and 6 h for entry 5. The objective of this report was to achieve enhanced reactivity and regioselectivity using the tailor-made ILs, so we next performed several experiments with [hexaEGmim][OMs] and [dihexaEGim][OMs]. As a catalytic amount (5-10 mol%), tailor-made IL gave desired product in short reaction time (within 2 h) than the conventional [bmim][BF₄]. With excess of ILs (1.0 equiv) without any co-solvent, the reaction was found to be much more rapid than the conventional ILs (entry 10). Subsequently, comparison was made between the two tailor-made ILs; both the ILs, [hexaEGmim][OMs] and [dihexaEGim][OMs] found to have almost similar reaction time and selectivity (entries 8 and 12).

In an effort to examine a novel method for synthesizing C-benzylated pyrrole, we have analyzed the benzylation of pyrrole using various benzyl halides or mesylates. The results reported in Table 2 shows that this approach is very successful. The yields for the 2-benzyl-1H-pyrrole (3) product vary between 70% and 85%. The benzylation of pyrrole with various good leaving groups such as chloro-, iodo-, mesylate-, and tosylate- under these conditions provided (3) in good yield (70, 80, 84, and 72%, entries 1, 3-5 respectively). Chlorides as a leaving group found to show sluggish behavior in comparison to iodo-, mesylate- and tosylate. However, use of KI (0.1 mmol) enhances the reaction rate by *in-situ* exchange of chloro to iodo; iodide is a better leaving group than chloride because it is larger and more polarizable (entry 2). The leaving group ability significantly impacts reaction rates in nucleophilic substitution. Iodide is the best leaving group within the halides (entry 3); both mesylate and tosylate groups are superior to halides (entries 4 and 5). Presumably, stronger acids

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(with lower pK_a values) form weaker conjugate bases, which are more stable and therefore better leaving groups.

Table 2. Benzylation of pyrrole with various benyl halides/mesylate/tosylate in [hexaEGmim][OMs].^[a]

entry	compound	time (h)	yield (%) ^[b]	
			3	4
1	 2b	24	70	10
2 ^[c]	 2b	2	82	6
3	 2c	1.5	80	6
4 ^[d]	 2d	45 min	84	5
5 ^[d]	 2e	30 min	72	9

^[a]All reactions with 1.0 mmol reaction scale of benzyl halides/mesylate (OMs)/tosylate (OTs) (**2**), pyrrole (**1**, 0.14 mL, 2.0 mmol), NaHCO₃ (84 mg, 1.0 mmol) and [hexaEGmim][OMs] (45 mg, 0.1 mmol) in MeCN (3.0 mL) at 80 °C. ^[b]Isolated yield. ^[c]KI (17 mg, 0.1 mmol) was used. ^[d]Reaction temp. (70 °C).

Up to several rounds of recycling and reuse of [HexaEGmim][OMs] are possible without a discernible loss in IL activity and regioselectivity. Pyrrole C-benylation reaction with 10 mol% [hexaEGmim][OMs] in MeCN afforded (**3**) in high yield even after five runs (Table 3; Figure 2).

Table 3. Catalyst recycling ability.^[a]

Run	0	1	2	3	4	5
yield (%) ^[b]	85	85	84	85	83	84

^[a]All reactions with 2.0 mmol reaction scale of benzyl bromide (**2a**, 342 mg), pyrrole (**1**, 0.28 mL, 4.0 mmol), NaHCO₃ (168 mg, 2.0 mmole) and [hexaEGmim][OMs] (90 mg, 0.2 mmol) in MeCN (6.0 mL) at 80 °C for 2 h. ^[b]Isolated yield of (**3**).

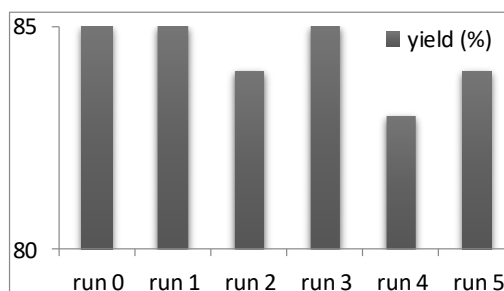
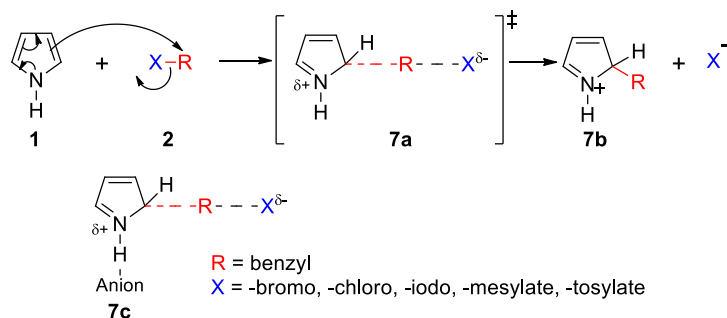


Figure 2. Catalyst recycling ability

The pyrrole C-benylation in the ILs media is likely caused by the following mechanism (Scheme 3). The pyrrole alkylation activated complex demonstrates that the N atom gains a positive charge as the pyrrole attacks the carbon centre, enhancing the N–H proton's capacity to donate H-bond. The positively charged species (**7b**) in turn is stabilized by the counter anion of IL.^{26,27,49} The hexaethylene glycol substituted Imidazolium salt core might have a phase-transfer catalyst like activity.²⁶ Further, the terminal hydroxyl group might have initial interaction by H-bonding with N–H thereby enhancing the pyrrole attack on the carbon centre.



Scheme 3. Plausible mechanism.

5. Conclusion

In summary, hexaEGILs acts as an important driving force in regioselective C-benylation of pyrrole. The experimental procedure is very simple and convenient. Moreover, our methodology did not require any aqueous work-up thereby avoiding the generation of toxic waste. It is noteworthy that our procedure need not require any Lewis acid/base catalyst. Further studies on the development of more efficient green protocols (broader substrate applicability, lower reaction temperature, shorter reaction time, etc.) for C-benylation of pyrrole using smart IL are in progress in our laboratories. Studies towards the development of novel IL for more effective nucleophilic substitutions are currently underway.

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Supporting Information

Supporting information accompanies this paper on <http://www.acgpubs.org/journal/organic-communications>

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