

ORIGINAL ARTICLE

Friedel-Craft's Benzylolation and Benzoylation Using Imidazolium Protic Ionic Liquids

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ABSTRACT

Diphenylmethane, 1-benzyl-4-chlorobenzene, 1-benzyl-4-bromobenzene, 2-benzyl-naphthalene, 1-phenylethanone and diphenylmethanone are prepared via Friedel-Craft's Benzylolation and Benzoylation using the series of imidazolium protic ionic liquids (PILs) such as 2-methylimidazolium lactate ([2mim]CH₃CH(OH)COO⁻), 1-ethylimidazolium lactate ([1eim]CH₃CH(OH)COO⁻), 1-butylimidazolium lactate ([1bim] CH₃CH(OH)COO⁻), 2-methylimidazolium glycolate ([2mim] CH₂(OH)COO⁻), 1-ethylimidazolium glycolate ([1eim] CH₂(OH)COO⁻), 1-butylimidazolium glycolate ([1bim] CH₂(OH)COO⁻), as a catalyst. In comparison with the reaction performed in conventional organic solvent, faster reaction rate and higher yield of products are achieved using the said ionic liquids as a medium. Moreover, the utilized ionic liquids in the above said reactions could be conveniently recovered for recycle by distillation process and reused for another set of reactions.

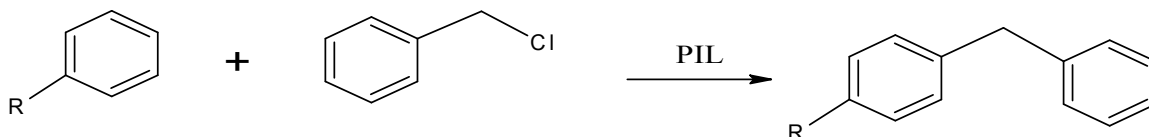
Keywords: Protic ionic liquids, Friedel-Craft's reaction, Benzylolation, Benzoylation.

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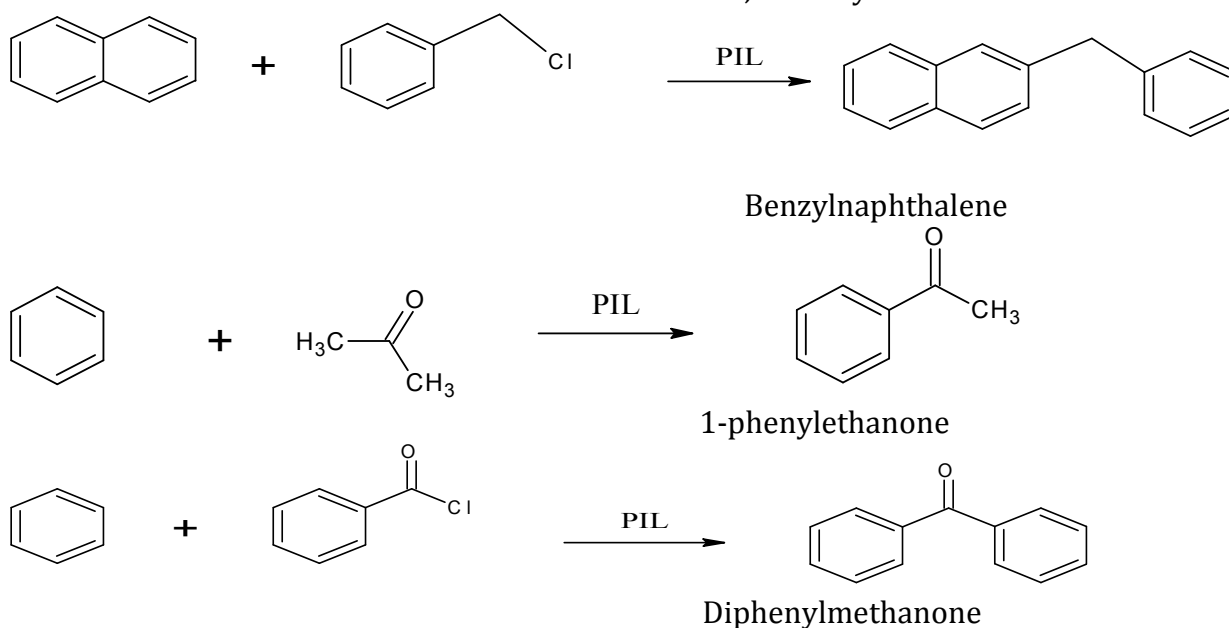
INTRODUCTION

The rudimental aim of green chemistry is to replace the hazardous volatile organic solvents required for mixing and dissolving the organic compounds in conventional organic synthesis. The recent studies and investigations show that ionic liquids are the better replacement for the hazardous volatile organic solvents because of their important attributes, such as negligible vapor pressure, excellent chemical and thermal stability, potential recoverability and ease of separation of products from reactants [1,2]. Furthermore, ionic liquids have been regarded as green solvents applied in electrochemistry [3], extraction [4,5], biocatalysis [6] and catalysis [7]. Friedel-Craft's (FC) alkylation and acylation reactions were the first reactions performed in ionic liquids as the reaction media. The Friedel-Craft's reaction is a vital process for C-C bond formation in organic chemistry. Various aromatic compounds, including benzenes with electro-donating substituent, furans, pyrroles, and indoles, have been applied successfully in numerous Friedel-Craft's reactions with diverse electrophiles. Chloroaluminate ionic liquids have been reported as both solvent and Lewis acid catalyst for Friedel-Crafts reactions [8-13], but they have a deadly deflection of moisture-sensitivity and, hence, are difficult to reuse. The FC acylation reaction has been extensively used in the synthesis of aromatic and cyclic ketones, which are important synthetic intermediates in the fine chemical and pharmaceutical industries. This paper imparts the new path for the synthesis of Diphenylmethane, 1-benzyl-4-chlorobenzene, 1-benzyl-4-bromobenzene (used in perfumery to impart an orange-blossom-like odor, catalyst for polymerization of olefins, in organic synthesis, especially as photosensitizer.), 2-benzyl-naphthalene, 1-phenylethanone (a raw material for the synthesis of some pharmaceuticals, like dextropropoxyphene and phenylpropanolamine) and diphenylmethanone (used as a photo initiator in UV-curing applications, photosensitizer in photochemistry,) are prepared via Friedel-Craft's Benzylolation and Benzoylation using the series of imidazolium protic ionic liquids as a catalyst (Scheme 1).



R=H,Br,Cl

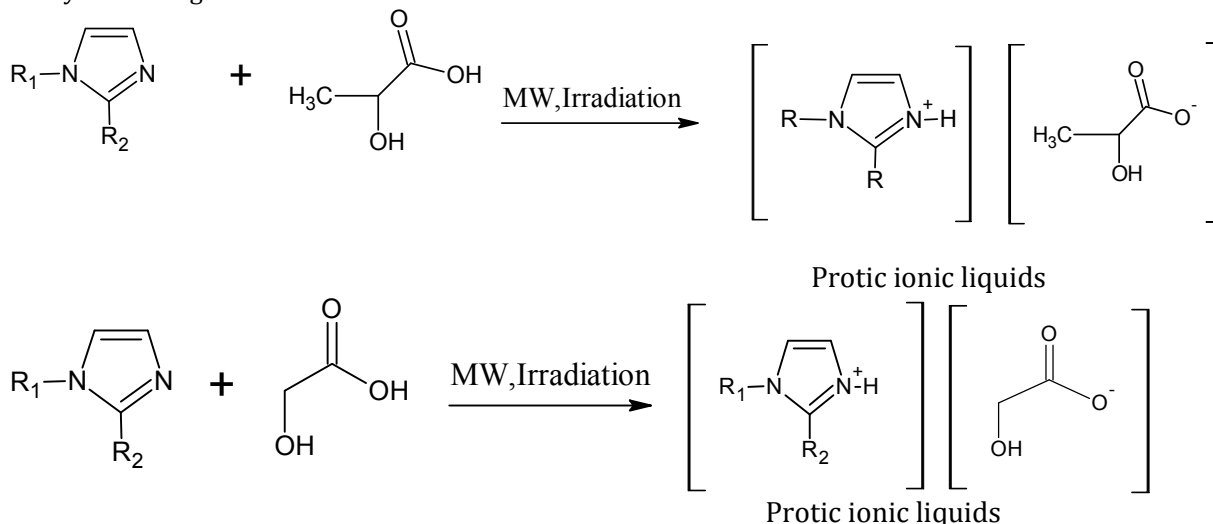
R=H, Diphenylmethane
 R=Br, 1-benzyl-4-bromobenzene
 R=Cl, 1-benzyl-4-chlorobenzene



Experimental

Synthesis of imidazolium protic ionic liquids

The imidazolium protic ionic liquids such as 2-methylimidazolium lactate, 1-ethylimidazolium lactate, 1-butylimidazolium lactate, 2-methylimidazolium glycolate, 1-ethylimidazolium glycolate, 1-butylimidazolium glycolate are synthesized according to the method outlined in the literature [14] and the synthesis is given in the scheme 2.



where R_1 -H, C_2H_5 - or C_4H_9 -. R_2 -H, CH_3

Synthesis of Dipheyl methane and its derivatives

15ml of benzene (Bromobenzene and chloro benzene for 1-benzyl-4-bromobenzene, 1-benzyl-4-chlorobenzene respectively) and 3.5ml of benzylchloride are placed in a RB flask. To this mixture 5ml of each PILs ([2mim] $CH_3CH(OH)COO^-$, [1eim] $CH_3CH(OH)COO^-$, [1bim] $CH_3CH(OH)COO^-$, [2mim] $CH_2(OH)COO^-$, [1eim] $CH_2(OH)COO^-$, [1bim] $CH_2(OH)COO^-$) is added separately for different reactions and then refluxed for the required time as mentioned in table -1. Then the mixture is allowed to cool down to attain the room temperature. 50 ml of distilled water is added to this cooled mixture and shaken well and then

transferred to the separating funnel. The lower aqueous layer (PILs and water) and the upper organic layer (benzene solution of diphenylmethane) are collected separately. The upper organic layer is washed with HCl and acetone then distilled through an air condenser for removing the impurities present in the synthesized diphenyl methane and its derivatives. The ionic liquid present in the aqueous layer is recovered by the distillation.

Synthesis of 2-benzyl-naphthalene

2 g of naphthalene and 7ml of benzylchloride are placed in a RB flask. To this mixture 5ml of each PILs([2mim]CH₃CH(OH)COO⁻, [1eim]CH₃CH(OH)COO⁻, [1bim]CH₃CH(OH)COO⁻, [2mim]CH₂(OH)COO⁻, [1eim]CH₂(OH)COO⁻, [1bim]CH₂(OH)COO⁻) is added separately for different reactions and then refluxed for the required time and it was given in table -1. Later the mixture is allowed to cool down to attain the room temperature. 50 ml of distilled water is added to this cooled mixture and stirred well. Then the solid product of 2-benzyl-naphthalene is filtered off and washed with ethanol. The ionic liquids present in the aqueous layer is recovered by the distillation.

Synthesis of 1-phenylethanone

10 ml of benzene and 5 ml of acetylchloride are placed in a RB flask. To this mixture 5ml of each PILs([2mim]CH₃CH(OH)COO⁻, [1eim]CH₃CH(OH)COO⁻, [1bim]CH₃CH(OH)COO⁻, [2mim]CH₂(OH)COO⁻, [1eim]CH₂(OH)COO⁻, [1bim]CH₂(OH)COO⁻) is added separately for different reactions and then refluxed for the required time and it is given in table -1. Then the mixture is allowed to cool down to attain the room temperature. 50 ml of water is added to this cooled mixture and shaken well. Then it later transferred to the separating funnel. The lower aqueous layer (PIL and water) and the upper organic layer (benzene solution of 1-phenylethanone) are collected separately. The upper organic layer is washed with HCl and the acetone then distilled through an air condenser for removing the impurities present in the synthesized 1-phenylethanone. The ionic liquid present in the aqueous layer is recovered by the distillation.

Synthesis of diphenylmethanone.

10 ml of benzene and 5 ml of benzoylchloride are placed in a RB flask. To this mixture 5ml of each PILs([2mim]CH₃CH(OH)COO⁻, [1eim]CH₃CH(OH)COO⁻, [1bim]CH₃CH(OH)COO⁻, [2mim]CH₂(OH)COO⁻, [1eim]CH₂(OH)COO⁻, [1bim]CH₂(OH)COO⁻) is added separately for different reactions and then refluxed for the required time as mentioned in table -1. Then the mixture is allowed to cool down to attain the room temperature. 50 ml of distilled water is added to this cooled mixture and stirred well. Then the solid product of 2- diphenylmethanone is filtered off and washed with ethanol. The ionic liquids present in the aqueous layer is recovered by the distillation.

Table1: Reflux time for various substrates in PILs

S.No	Substrate	Reflux time(min)
1.	Benzene+Benzylchloride	20
2.	Bromo Benzene +Benzylchloride	45
3.	Chloro Benzene +Benzylchloride	45
4.	Naphthalene+Benzylchloride	30
5.	Benzene+Acetylchloride	110
6	Benzene+Benzoylchloride	110

Characterization

The synthesized products are confirmed by FT-IR spectral studies using the Jasco (FT-IR 460) spectrometer and ¹H NMR spectral studies by Bruker 300 MHz NMR Spectrometer using CDCl₃ as solvent. The regenerated ionic liquids are confirmed by FT -IR spectral analysis.

RESULTS AND DISCUSSION

The benzylation and benzoylation reactions are studied using six different imidazolium ionic liquids, which are acidic in nature and having lower ΔpKa value[14] (Table-2). These reactions are governed with the mechanism involving the formation of carbonium ion. The strong polarity and acidic character of the ionic liquids used here as both catalyst and reaction medium which may stabilize the positively charged intermediate carbonium ion and it results in higher conversion of product and the selectivity of the corresponding reactions. The yield of all the synthesized products using different PILs is compiled in table -3. There is a slight variations in the yield when the reactions are carried out in different PILs under the same conditions. The products are confirmed by FT-IR and ¹HNMR spectral studies (Fig1-12)

Table 2- The acidity of PILs

S.No	PILs	ΔpK_a
1.	[2mim]CH ₃ CH(OH)COO ⁻	3.84
2.	[1eim]CH ₃ CH(OH)COO ⁻	3.43
3.	[1bim]CH ₃ CH(OH)COO ⁻	3.23
4.	[2mim]CH ₂ (OH)COO ⁻	3.92
5.	[1eim]CH ₂ (OH)COO ⁻	3.46
6.	[1bim]CH ₂ (OH)COO ⁻	3.26

Table -3: The yield of different synthesized products using different PILs

S.No	Product	Yield (%)						Boiling point /Melting point °C
		PIL1	PIL2	PIL3	PIL4	PIL5	PIL6	
1.	Diphenylmethane	89	91	99	94	94	98	261(b.pt)
2.	1-benzyl-4-bromobenzene	82	79	98	81	87	91	125(b.pt)
3.	1-benzyl-4-chlorobenzene	92	97	99	98	82	99	146(b.pt)
4.	2-benzyl-naphthalene	95	98	99	98	99	98	56.5(m.pt)
5.	1-phenylethanone	79	87	99	98	85	96	200(b.pt)
6.	Diphenylmethanone	88	91	98	87	92	95	47(m.pt)

Fourier Transform-Infrared spectra of Diphenylmethane

FT-IR spectra are recorded for Diphenylmethane synthesized using all PILs and their spectral ranges were given below:

- (i) **Using 2-methylimidazolium lactate:** 3036cm⁻¹(Aromatic nucleus),753 cm⁻¹(Mono substituted benzene ring)2968 cm⁻¹(-CH₂ group),1568,1487,1448,1397 cm⁻¹(skeletal vibration of aromatic ring).
- (ii) **Using 1-ethylimidazolium lactate:** 3040cm⁻¹(Aromatic nucleus),747 cm⁻¹(Mono substituted benzene ring)2973 cm⁻¹(-CH₂ group),1560,1481,1435,1391 cm⁻¹(skeletal vibration of aromatic ring).
- (iii) **Using 1-butylimidazolium lactate:** 3034cm⁻¹(Aromatic nucleus),763 cm⁻¹(Mono substituted benzene ring)2961 cm⁻¹(-CH₂ group),1568,1490,1449,1401 cm⁻¹(skeletal vibration of aromatic ring).
- (iv) **Using 2-methylimidazolium glycolate:** 3036cm⁻¹(Aromatic nucleus),761 cm⁻¹(Mono substituted benzene ring)2963 cm⁻¹(-CH₂ group),1570,1487,1447,1398 cm⁻¹(skeletal vibration of aromatic ring).
- (v) **Using 1-ethylimidazolium glycolate:** 3037cm⁻¹(Aromatic nucleus),760 cm⁻¹(Mono substituted benzene ring)2961 cm⁻¹(-CH₂ group),1575,1482,1447,1398 cm⁻¹(skeletal vibration of aromatic ring).
- (vi) **Using 1-butylimidazolium glycolate:** 3029cm⁻¹(Aromatic nucleus),749 cm⁻¹(Mono substituted benzene ring)2973 cm⁻¹(-CH₂ group),1571,1489,1451,1401 cm⁻¹(skeletal vibration of aromatic ring).

Fourier Transform -Infrared spectra of 1-benzyl-4-bromobenzene

FT-IR spectra are recorded for bromodiphenylmethane synthesized using all PILs and their spectral ranges are given below:

- (i) **Using 2-methylimidazolium lactate:**2927 cm⁻¹ (-CH₂ group),1606 cm⁻¹ (Phenyl nucleus),3038 cm⁻¹ (Aromatic -CH stretching),857 cm⁻¹ (C-H out of plane bending for 1,4 disubstituted benzene ring),600(C-Br stretching), 749 cm⁻¹(Mono substituted benzene ring),1547 cm⁻¹,1436 cm⁻¹,1439 cm⁻¹,1414 cm⁻¹ (skeletal vibration of aromatic ring).
- (ii) **Using 1-ethylimidazolium lactate:**2959 cm⁻¹ (-CH₂ group),1629 cm⁻¹ (Phenyl nucleus),3018 cm⁻¹ (Aromatic -CH stretching),853 cm⁻¹ (C-H out of plane bending for 1,4 disubstituted benzene ring),574(C-Br stretching),740 cm⁻¹(Mono substituted benzene ring),1543 cm⁻¹,1446 cm⁻¹,1429cm⁻¹,1410 cm⁻¹ (skeletal vibration of aromatic ring).
- (iii) **Using 1-butylimidazolium lactate:**2982 cm⁻¹ (-CH₂ group),1639 cm⁻¹ (Phenyl nucleus),3148 cm⁻¹ (Aromatic -CH stretching),823 cm⁻¹ (C-H out of plane bending for 1,4 disubstituted benzene ring),600(C-Br stretching), 670 cm⁻¹(Mono substituted benzene ring), 755cm⁻¹(Mono substituted benzene ring),1540cm⁻¹,1429cm⁻¹,1401 cm⁻¹,1390 cm⁻¹ (skeletal vibration of aromatic ring).

(iv) **Using 2-methylimidazolium glycolate:** 2964 cm⁻¹ (-CH₂ group), 1660 cm⁻¹ (Phenyl nucleus), 3122 cm⁻¹ (Aromatic -CH stretching), 869 cm⁻¹ (C-H out of plane bending for 1,4 disubstituted benzene ring), 541 (C-Br stretching), 739 cm⁻¹ (Mono substituted benzene ring), 1570 cm⁻¹, 1449 cm⁻¹, 1421 cm⁻¹, 1401 cm⁻¹ (skeletal vibration of aromatic ring).

(v) **Using 1-ethylimidazolium glycolate:** 2976 cm⁻¹ (-CH₂ group), 1593 cm⁻¹ (Phenyl nucleus), 3096 cm⁻¹ (Aromatic -CH stretching), 810 cm⁻¹ (C-H out of plane bending for 1,4 disubstituted benzene ring), 541 (C-Br stretching), 739 cm⁻¹ (Mono substituted benzene ring), 1536 cm⁻¹, 1431 cm⁻¹, 1414 cm⁻¹, 1398 cm⁻¹ (skeletal vibration of aromatic ring).

(vi) **Using 1-butylimidazolium glycolate:** 2991 cm⁻¹ (-CH₂ group), 1590 cm⁻¹ (Phenyl nucleus), 3079 cm⁻¹ (Aromatic -CH stretching), 841 cm⁻¹ (C-H out of plane bending for 1,4 disubstituted benzene ring), 543 (C-Br stretching), 739 cm⁻¹ (Mono substituted benzene ring), 1548 cm⁻¹, 1451 cm⁻¹, 1429 cm⁻¹, 1411 cm⁻¹ (skeletal vibration of aromatic ring).

Fourier Transform -Infrared spectra of 1-benzyl-4-chlorobenzene

FT-IR spectra are recorded for chlorodiphenylmethane synthesized using all PILs and their spectral ranges are given below:

(i) **Using 2-methylimidazolium lactate:** 3017 cm⁻¹ (-CH₂ group), 1616 cm⁻¹ (Phenyl nucleus), 3045 cm⁻¹ (Aromatic -CH stretching), 847 cm⁻¹ (C-H out of plane bending for 1,4 disubstituted benzene ring), 792 (C-Cl stretching), 749 cm⁻¹ (Mono substituted benzene ring), 1549 cm⁻¹, 1436 cm⁻¹, 1456 cm⁻¹, 1424 cm⁻¹ (skeletal vibration of aromatic ring).

(ii) **Using 1-ethylimidazolium lactate:** 2995 cm⁻¹ (-CH₂ group), 1601 cm⁻¹ (Phenyl nucleus), 3016 cm⁻¹ (Aromatic -CH stretching), 851 cm⁻¹ (C-H out of plane bending for 1,4 disubstituted benzene ring), 774 (C-Cl stretching), 741 cm⁻¹ (Mono substituted benzene ring), 1563 cm⁻¹, 1406 cm⁻¹, 1396 cm⁻¹, 1417 cm⁻¹ (skeletal vibration of aromatic ring).

(iii) **Using 1-butylimidazolium lactate:** 2982 cm⁻¹ (-CH₂ group), 1598 cm⁻¹ (Phenyl nucleus), 3148 cm⁻¹ (Aromatic -CH stretching), 817 cm⁻¹ (C-H out of plane bending for 1,4 disubstituted benzene ring), 801 (C-Cl stretching), 659 cm⁻¹ (Mono substituted benzene ring), 745 cm⁻¹ (Mono substituted benzene ring), 1540 cm⁻¹, 1439 cm⁻¹, 1418 cm⁻¹, 1398 cm⁻¹ (skeletal vibration of aromatic ring).

(iv) **Using 2-methylimidazolium glycolate:** 3014 cm⁻¹ (-CH₂ group), 1616 cm⁻¹ (Phenyl nucleus), 3107 cm⁻¹ (Aromatic -CH stretching), 855 cm⁻¹ (C-H out of plane bending for 1,4 disubstituted benzene ring), 791 (C-Cl stretching), 749 cm⁻¹ (Mono substituted benzene ring), 1570 cm⁻¹, 1429 cm⁻¹, 1411 cm⁻¹, 1398 cm⁻¹ (skeletal vibration of aromatic ring).

(v) **Using 1-ethylimidazolium glycolate:** 2998 cm⁻¹ (-CH₂ group), 1598 cm⁻¹ (Phenyl nucleus), 3056 cm⁻¹ (Aromatic -CH stretching), 826 cm⁻¹ (C-H out of plane bending for 1,4 disubstituted benzene ring), 791 (C-Cl stretching), 739 cm⁻¹ (Mono substituted benzene ring), 1535 cm⁻¹, 1413 cm⁻¹, 1406 cm⁻¹, 1398 cm⁻¹ (skeletal vibration of aromatic ring).

(vi) **Using 1-butylimidazolium glycolate:** 3016 cm⁻¹ (-CH₂ group), 1616 cm⁻¹ (Phenyl nucleus), 3059 cm⁻¹ (Aromatic -CH stretching), 849 cm⁻¹ (C-H out of plane bending for 1,4 disubstituted benzene ring), 798 (C-Cl stretching), 739 cm⁻¹ (Mono substituted benzene ring), 1560 cm⁻¹, 1414 cm⁻¹, 1409 cm⁻¹, 1398 cm⁻¹ (skeletal vibration of aromatic ring).

Fourier Transform -Infrared spectra of Benzyl naphthalene

FT-IR spectra are recorded for benzyl naphthalene synthesized using all PILs and their spectral ranges are given below:

(i) **Using 2-methylimidazolium lactate:** 840 cm⁻¹ (m, C-H out of plane bending of two adjacent H,β-substituted naphthalene), 744 cm⁻¹ (monosubstituted benzene ring), 3100 cm⁻¹ (Aromatic -CH stretching), 1605 cm⁻¹ (Phenyl nucleus), 2961 cm⁻¹ (-CH₂ group).

(ii) **Using 1-ethylimidazolium lactate:** 831 cm⁻¹ (m, C-H out of plane bending of two adjacent H,β-substituted naphthalene), 751 cm⁻¹ (monosubstituted benzene ring), 3071 cm⁻¹ (Aromatic -CH stretching), 1616 cm⁻¹ (Phenyl nucleus), 2977 cm⁻¹ (-CH₂ group).

(iii) **Using 1-butylimidazolium lactate:** 831 cm⁻¹ (m, C-H out of plane bending of two adjacent H,β-substituted naphthalene), 753 cm⁻¹ (monosubstituted benzene ring), 3091 cm⁻¹ (Aromatic -CH stretching), 1601 cm⁻¹ (Phenyl nucleus), 3001 cm⁻¹ (-CH₂ group).

(iv) **Using 2-methylimidazolium glycolate:** 829 cm⁻¹ (m, C-H out of plane bending of two adjacent H,β-substituted naphthalene), 766 cm⁻¹ (monosubstituted benzene ring), 3087 cm⁻¹ (Aromatic -CH stretching), 1613 cm⁻¹ (Phenyl nucleus), 2960 cm⁻¹ (-CH₂ group).

(v) **Using 1-ethylimidazolium glycolate:** 826 cm⁻¹ (m, C-H out of plane bending of two adjacent H,β-substituted naphthalene), 745 cm⁻¹ (monosubstituted benzene ring), 3077 cm⁻¹ (Aromatic -CH stretching), 1625 cm⁻¹ (Phenyl nucleus), 2977 cm⁻¹ (-CH₂ group).

(vi) **Using 1-butylimidazolium glycolate:** 841 cm^{-1} (m , C-H out of plane bending of two adjacent H, β -substituted naphthalene) 766 cm^{-1} (monosubstituted benzene ring), 3060 cm^{-1} (Aromatic -CH stretching), 1607 cm^{-1} (Phenyl nucleus), 2960 cm^{-1} (-CH₂ group).

Fourier Transform -Infrared spectra of 1-phenylethanone

FT-IR spectra are recorded for 1-phenylmethanone synthesized using all PILs and their spectral ranges are given below:

(i) **Using 2-methylimidazolium lactate:** 3031 cm^{-1} (Aromatic -CH stretching), 1399 cm^{-1} (-CH₃-CO group) 762 cm^{-1} (monosubstituted benzene ring), 1605 cm^{-1} (Phenyl nucleus)

(ii) **Using 1-ethylimidazolium lactate:** 3061 cm^{-1} (Aromatic -CH stretching), 1379 cm^{-1} (-CH₃-CO group) 751 cm^{-1} (monosubstituted benzene ring), 1615 cm^{-1} (Phenyl nucleus).

(iii) **Using 1-butylimidazolium lactate:** 3082 cm^{-1} (Aromatic -CH stretching), 1390 cm^{-1} (-CH₃-CO group) 762 cm^{-1} (monosubstituted benzene ring), 1607 cm^{-1} (Phenyl nucleus).

(iv) **Using 2-methylimidazolium glycolate:** 3045 cm^{-1} (Aromatic -CH stretching), 1389 cm^{-1} (-CH₃-CO group) 749 cm^{-1} (monosubstituted benzene ring), 1616 cm^{-1} (Phenyl nucleus).

(v) **Using 1-ethylimidazolium glycolate:** 3037 cm^{-1} (Aromatic -CH stretching), 1399 cm^{-1} (-CH₃-CO group) 751 cm^{-1} (monosubstituted benzene ring), 1592 cm^{-1} (Phenyl nucleus).

(vi) **Using 1-butylimidazolium glycolate:** 3096 cm^{-1} (Aromatic -CH stretching), 1401 cm^{-1} (-CH₃-CO group) 749 cm^{-1} (monosubstituted benzene ring), 1610 cm^{-1} (Phenyl nucleus).

Fourier Transform- spectra of Diphenylmethanone

FT-IR spectra are recorded for diphenylmethanone synthesized using all PILs and their spectral ranges are given below:

(i) **Using 2-methylimidazolium lactate:** 3107 cm^{-1} (Aromatic -CH stretching), 1640 cm^{-1} (Phenyl nucleus), 1205 cm^{-1} (Diarylketone, C-CO-C stretching)

(ii) **Using 1-ethylimidazolium lactate:** 3098 cm^{-1} (Aromatic -CH stretching), 1617 cm^{-1} (Phenyl nucleus), 1218 cm^{-1} (Diarylketone, C-CO-C stretching).

(iii) **Using 1-butylimidazolium lactate:** 3078 cm^{-1} (Aromatic -CH stretching), 1616 cm^{-1} (Phenyl nucleus), 1231 cm^{-1} (Diarylketone, C-CO-C stretching).

(iv) **Using 2-methylimidazolium glycolate:** 3078 cm^{-1} (Aromatic -CH stretching), 1609 cm^{-1} (Phenyl nucleus), 1225 cm^{-1} (Diarylketone, C-CO-C stretching).

(v) **Using 1-ethylimidazolium glycolate:** 3030 cm^{-1} (Aromatic -CH stretching), 1630 cm^{-1} (Phenyl nucleus), 1201 cm^{-1} (Diarylketone, C-CO-C stretching).

(vi) **Using 1-butylimidazolium glycolate:** 3047 cm^{-1} (Aromatic -CH stretching), 1606 cm^{-1} (Phenyl nucleus), 1217 cm^{-1} (Diarylketone, C-CO-C stretching).

¹H NMR spectra of synthesized products

¹H NMR spectra are recorded for synthesized products using all PILs and their chemical shift values are given below

Diphenylmethane

7.273(1H,d), 7.189(1H,m, adjacent to C-CH₂), 4.107(2H -CH₂ proton, s)

1-benzyl-4-bromobenzene

7.75(1H,d, adjacent to -C-Br), 7.21(1H,m, adjacent to C -CH₂), 4.15(2H -CH₂ proton, s)

1-benzyl-4-chlorobenzene

7.380(H,d, adjacent to -C-Cl), 7.29(1H,m, adjacent to C-CH₂), 4.41(2H -CH₂ proton, s)

Benzyl naphthalene

8.102(1H(naphthalene), s), 7.652(1H(naphthalene), m), 7.461(1H,m, adjacent to C -CH₂), 4.05(2H -CH₂ proton, s), 7.27(1H(phenyl), adjacent to -CH₂, m),

1-phenylethanone

7.652(1H adjacent to -CO-CH₃, s), 7.456(1H, s), 2.059(3H, -CO-CH₃, s)

Diphenylmethanone

7.820(1H adjacent to -CO-C₆H₅, d) 7.553(1H(phenyl), m), 7.453(1H, s)

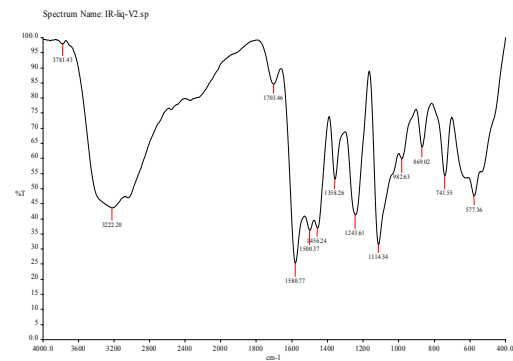
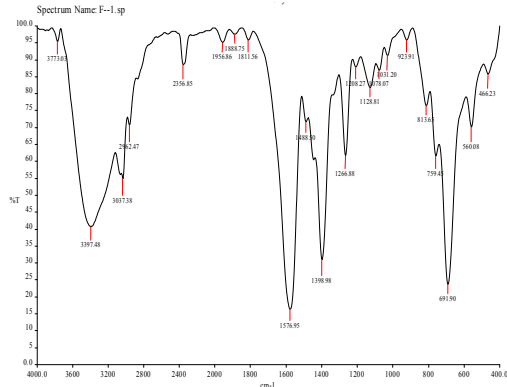
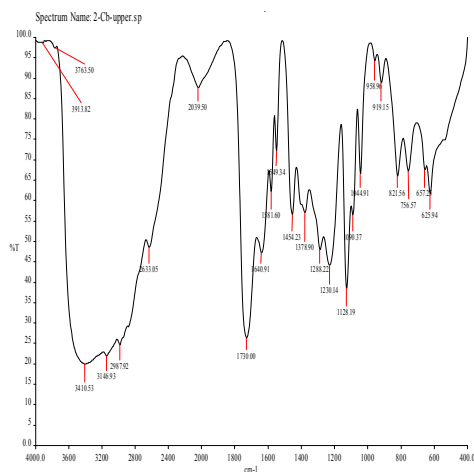


Fig.1. FT-IR Spectrum of Diphenylmethane Fig.2. FT-IR Spectrum of 1-benzyl-4-bromo benzene



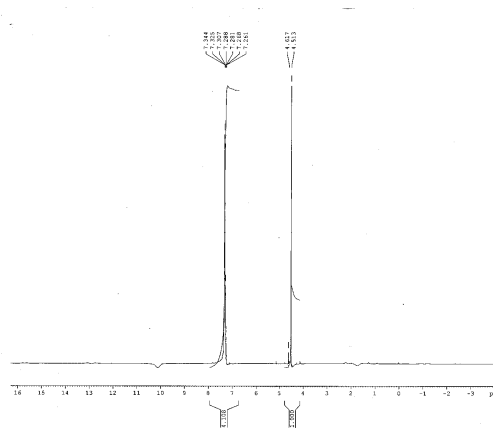
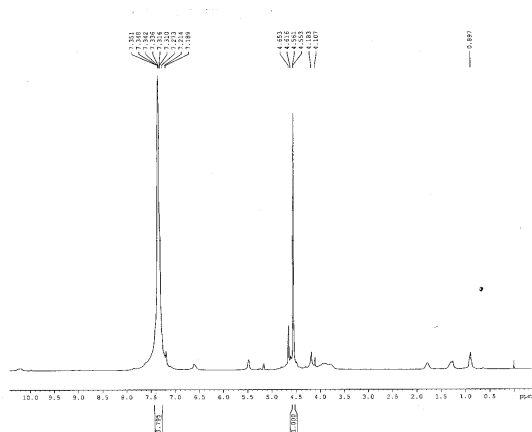


Fig.7. ¹H NMR spectrum of Diphenylmethane Fig.8. ¹H NMR spectrum of 1-benzyl-4-bromobenzene

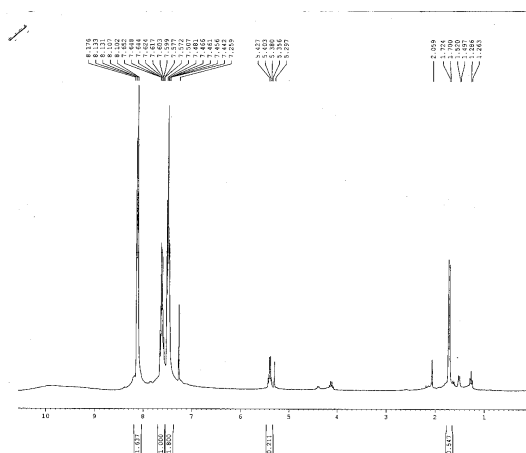
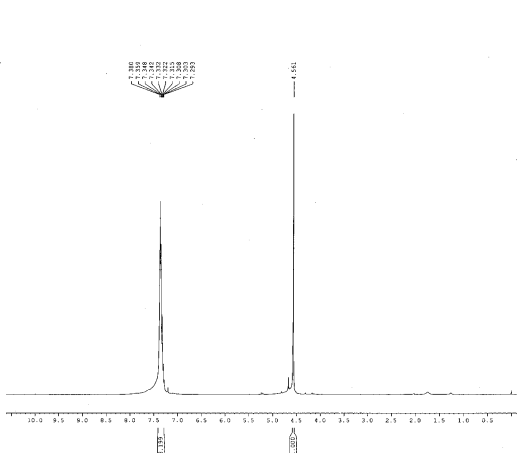


Fig.9: ¹H NMR spectrum of 1-benzyl-4-chlorobenzene Fig.10. ¹H NMR spectrum of Benzyl naphthalene

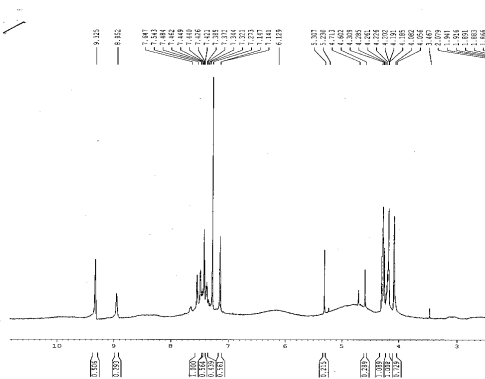
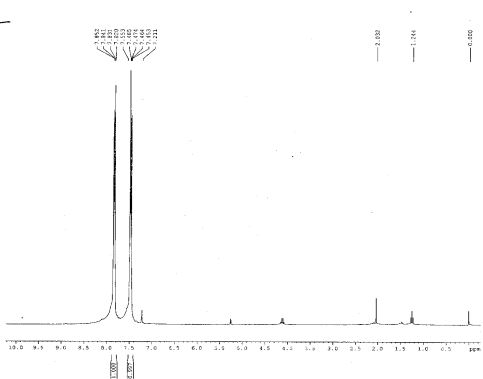


Fig.11. ¹H NMR spectrum of 1-phenylethanone Fig.12. ¹H NMR spectrum of diphenylmethanone

The prime advantage of using ionic liquids as reaction medium is that it can be regenerated after completion of the reaction and reused for another cycle of reaction. The above said argument is proved by comparing the FT-IR spectra of both the initial and regenerated one (fig13-18). It is clear from the figures that the used ionic liquids are regenerated as such without any deformation.

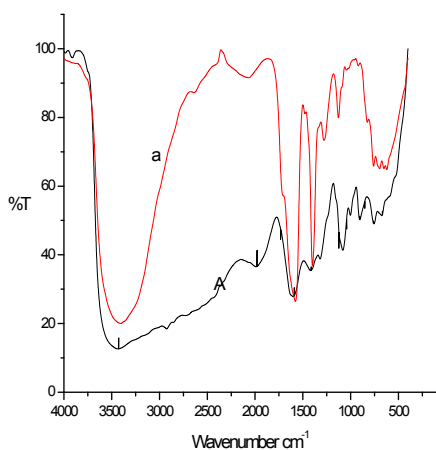


Fig 13.

FT-IR spectrum of initial(A) and regenerated(a)[2mim]CH₃CH(OH)COO⁻

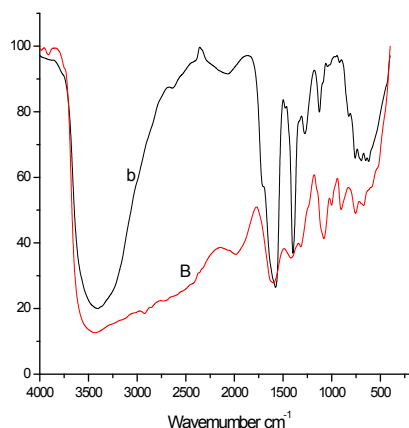


Fig14

FT-IR spectrum of initial (B) and regenerated (b)[1eim]CH₃CH(OH)COO⁻

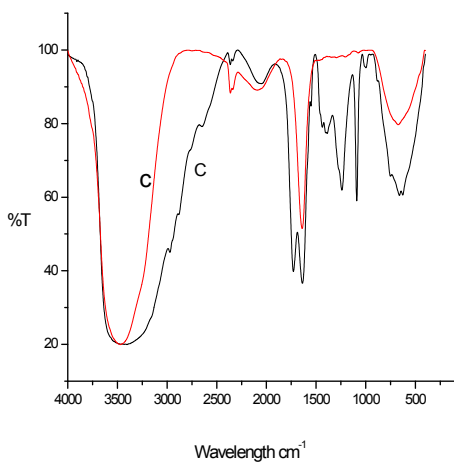


Fig 15

FT- IR spectrum of initial (C)and regenerated(c) [1bim]CH₃CH(OH)COO⁻

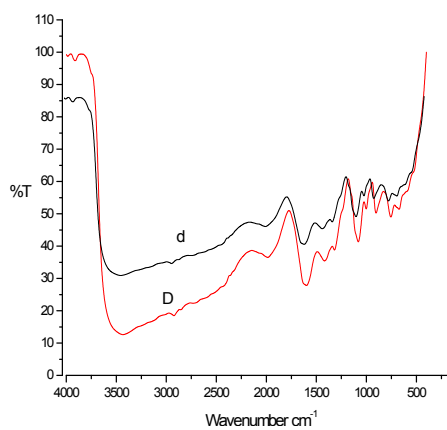


Fig 16.

FT- IR spectrum of initial (D) and regenerated (d) [2mim]CH₂(OH)COO⁻

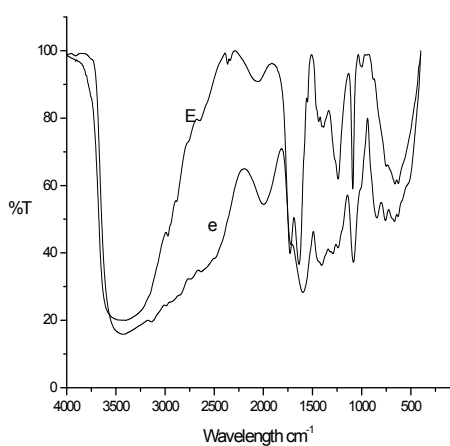


Fig 17.

FT- IR spectrum of initial (E) and regenerated(e)[1eim]CH₂(OH)COO⁻

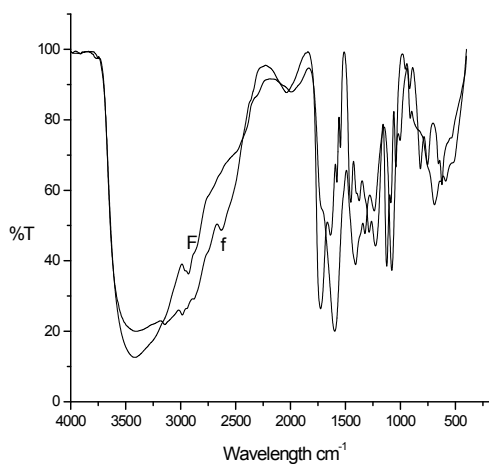


Fig 18

FT- IR spectrum of initial (F) and regenerated(f) [1bim] CH₂(OH)COO⁻

CONCLUSION

The Friedel-Craft's benzoylation and benzoylation reactions are carried out using six different imidazolium protic ionic liquids are the facile method for the synthesis of various organic compounds such as Diphenylmethane, 1-benzyl-4-chlorobenzene, 1-benzyl-4-bromobenzene, 2-benzyl naphthalene, 1-phenylethanone and diphenylmethanone. The PILs employed in these reactions are found to be novel reaction media and acid catalyst. These PILs show higher yield of products and fast reaction rate. Moreover the experimental procedure employed is quite simple and convenient. Of all the advantages the main benefit of using PILs in these reactions is the regeneration of PILs could be achieved after the completion of the reaction and reused in other processes. Thus these PILs reaction media are expected to be promising replacement of toxic organic solvents and used in wide number of organic synthesis.

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