

Synthesis, Characterization of novel Trimeric Ionic liquids and its Applications

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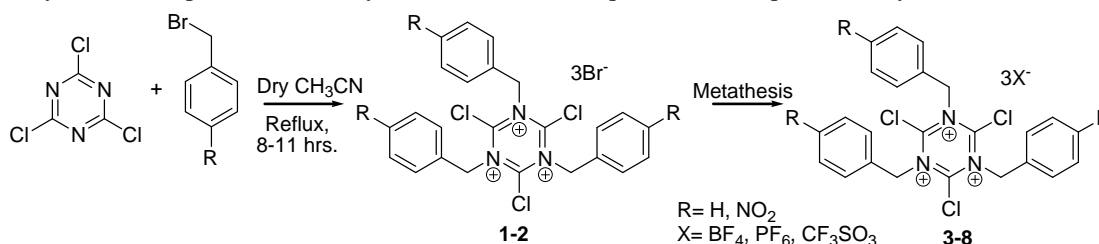
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Abstract: We have synthesized trimeric ionic liquids from substituted triazine derivatives used as a core unit and substituted aromatic halo derivatives are used as terminal units under greener approach. Our trimeric ionic liquid shows excellent catalytic activity for the synthesis of Azlactone from Erlenmeyer method.

Key words: Trimeric ionic liquids, quarternization, metathesis, greener, Azlactones

I. INTRODUCTION

Room temperature ionic liquids are plays variety of crucial roles due to their distinguishable properties such as high chemical and thermal stability, high conducting behaviors, non-flammability and very low vapor pressure; so ionic liquids extends its application.¹ One of the most attractive features of substituted, functionalized ionic liquids is that dipolar compound can be differs and modified; so that a dipolar species can be applicable in the area of catalytic activity, organic reaction transformation, ion conductive species². Zhao *et al* reported that immobilizing homogeneous catalyst to accelerate the extraction and subsequent reuse of catalyst has becomes plays important role³. Polyethylene oxide based hyperbranched polymer from triazine linkage act as a polymer electrolytes⁴. Selective oxidation of styrene catalyzed by multi carboxylic acid imidazolium halide along with transition metal afforded product with lesser yield⁵. Acetylation of variety of substituted aryl aldehyde with acidic anhydride in the presence of catalytic amount of ionic liquids afforded quantitative yield⁶



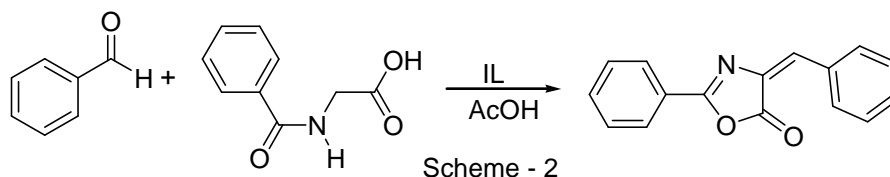
II. RESULTS AND DISCUSSIONS

Cyanuric chloride (1.0 equi.) treated with benzyl bromide / 4-nitro benzyl bromide (3.06 equi.) in the presence of dry acetonitrile under refluxing condition between 8 to 11 hours afforded compound **1** and **2** in 80 to 94 % yield. During *N*-alkylation reaction of 4-nitrobenzyl bromide completed the reaction lesser time than benzyl bromide due to presence of weaker C-Br bond. After disappearance of starting material; wash with CH₃CN to remove excess starting material. *N*-alkylated products of compound **1** and **2** followed by anion exchange reaction (metathesis) in the presence of variety of inorganic substance such as (K₄PF₆ , NaBF₄ , and LiCF₃ SO₃) with deionized water for about 1 hour will give anion exchanged compound **3-8** along with metallic bromides as a bye product. Here we have faced problem to separate ionic liquid from metallic bromide because usual extraction is not suitable for separation due to water soluble nature. To overcome this problem; we have used Soxhlet apparatus for the extraction and save the solvent ; ionic liquids with dry THF for about 2 hours extraction followed by concentration will get compound **3** to **8** in 85 to 92% yield. We have thoroughly characterized by spectral and analytical data's

Catalytic activity

Azlactones, substituted Azlactones are important precursor for the synthesis of some biologically active moieties⁷. Several methods are available for the synthesis of azlactone but that methods need very high temperature and various carcinogenic reagent⁸. We have employed simple and milder approach for the synthesis of azlactones from readily available starting material like equal molar mixture of aryl aldehyde and hippuric acid in the presence of our synthesized trimeric ionic liquids with two drops of glacial acetic acid at

room temperature will get quantitative yield of Azlactones (Scheme - 2). Azlactone was thoroughly characterized with spectral and analytical data; matched with literature⁹.



The same reaction we have tried with absence of ionic liquid there is no appreciable change in TLC. Erlenmeyer synthesis of azlactones are screened by varies concentration ionic liquids like 2.404×10^{-5} , 4.808×10^{-5} , 7.212×10^{-5} , and 9.615×10^{-5} results are presented in the table-I and II. Among the four different concentrations; we optimized the catalyst concentration is 7.212×10^{-5} while increasing the concentration there is no appreciable change. So we found that Erlenmeyer method suitable concentration is 7.212×10^{-5} . We have used two types of ionic liquids like simple benzyl moiety and nitro substituted benzyl moieties containing ionic liquids; we found that 4-nitro benzyl substituted ionic liquids act as good Lewis character than simple system. We have used different anions among these; bromide containing ionic liquids shows better catalytic activity than the others; due bigger size will give better absorption results are summarized in table I and II.

TABLE I: Preparation of Azalactone from Erlenmeyer method along with benzyl moiety containing ionic liquids:

Catalytic substance	2.404×10^{-5}		4.808×10^{-5}		7.212×10^{-5}		9.615×10^{-5}	
	Time min	Yield %	Time min	Yield %	Time min	Yield %	Time min	Yield %
1	40	62	20	76	05	94	05	94
2	48	56	30	66	12	80	12	80
3	45	60	23	68	10	91	10	91
4	55	49	35	62	15	78	15	78

TABLE I: Preparation of Azalactone from Erlenmeyer method along with nitro benzyl moiety containing ionic liquids:

Catalytic substance	2.404×10^{-5}		4.808×10^{-5}		7.212×10^{-5}		9.615×10^{-5}	
	Time min	Yield %	Time min	Yield %	Time min	Yield %	Time min	Yield %
5	20	70	15	85	10	92	10	92
6	35	60	18	72	14	82	14	8
7	30	66	20	77	13	85	13	85
8	38	58	22	68	15	72	15	72

III. EXPERIMENTAL SECTION

General procedure for preparation compound 1 and 2

Cyanuric chloride (1.0g; 5.42×10^{-3} mmol) mix with benzyl bromide / 4-nitro benzyl bromide (1.65×10^{-2} mmol) in the presence of dry CH_3CN between 8 to 11 hours will give compound 1 & 2 in 94% yield. After complete the reaction followed by wash with CH_3CN to remove excess starting material.

Ionic liquid 1: Yield: 3.5g ; 94 %; Mp.: 230°C ; MS: 697; $^1\text{H NMR}$ (400MHz; D_2O); 4.62 (6H,s), 7.32(6H,d), 8.07(6H,d), $^{13}\text{C NMR}$: 54.4, 121.0, 130.0, 140.6, 145.4, 151.2; Anal. Calculated for $\text{C}_{24}\text{H}_{21}\text{Br}_3\text{Cl}_3\text{N}_3$: Cal.: C, 41.33; H, 3.03; N, 6.02; Found C, 41.24; H, 2.92; N, 5.94.

Ionic liquid 2: Yield : 4.35g; 90 %; Mp.: Liquid ; MS: 832; $^1\text{H NMR}$ (400MHz; D_2O); 4.82 (6H,s), 7.42(6H,d), 8.19(6H,d), $^{13}\text{C NMR}$: 54,8, 121.3, 131.2, 142.6, 147.4, 153.4; Anal. Calculated for $\text{C}_{24}\text{H}_{18}\text{Br}_3\text{Cl}_3\text{N}_6\text{O}_6$: Cal. C, 34.63; H, 2.18; N, 10.09; Found, C, 34.48; H, 2.08; N, 09.96.

General procedure for metathesis reaction: Quaternized ammonium bromide (1.0 equi.) mix with inorganic salt (3.03 equi.) in the presence of deionized water at room temperature for about one hour will give ion exchanged products. After the metathesis reaction followed by Soxhlet extraction removes metallic bromide to get ionic liquids compound 3 to 8.

Ionic liquid 3: 0.4g; Yield: 80 %; Liquid; MS: 718; ¹H NMR (400MHz; D₂O) 4.61 (6H, s), 7.39 (6H, d), 8.14(6H, d), ¹³C NMR: 55.3, 122.6, 133.1, 143.6, 148.7, 154.1; Anal. Calculated for C₂₄H₂₁B₃Cl₃F₁₂N₃: Cal.: C, 40.14; H, 2.95; N, 5.85 Found C, 40.06; H, 2.88; N, 5.80.

Ionic liquid 4: Yield: 0.3g; 60 %; Liquid; MS: 892; ¹H NMR (400MHz; D₂O); 4.66 (6H,s), 7.32 (6H,d), 8.07 (6H,d), ¹³C NMR: 55.2, 121.0, 130.0, 140.6, 145.4, 149.8; Anal. Calculated for C₂₄H₂₁Cl₃F₁₈N₃P₃: Cal.; C, 32.29; H, 2.37; N, 4.71; Found: C, 32.20; H, 2.28; N, 4.62.

ionic liquid 5: 0.45g Yield : 90 %; Mp.: 260⁰C ; MS: 863; ¹H NMR(400MHz;D₂O) ;4.71 (6H,s), 7.42(6H,d), 8.16(6H,d), ¹³C NMR: 55.2, 122.2, 134.6, 143.4, 147.0, 156.3; Anal. Calculated for C₃₃H₂₁Cl₃F₃N₃O₉S₃: Cal.:C, 45.92; H,2.45; N, 4.87; Found: C, 45.80; H,2.33; N, 4.76.

Ionic liquid 6: Yield :0.41g; 82 %; Liquid ; MS: 853; ¹H NMR(400MHz;D₂O); 4.66 (6H, s), 7.32(6H,d), 8.07(6H,d), ¹³C NMR : 55.8, 123.2, 134.4, 145.8, 148.2, 159.5; Anal. Calculated for C₂₄H₁₈B₃Cl₃F₁₂N₆O₆: Cal.: C;33.79; H;2.13; N;9.85; Found C;33.64; H;2.06; N;9.73.

Ionic liquid 7: Yield: 0.45g 90 %; Liquid; MS: 832; ¹H NMR (400MHz; D₂O); 4.79 (6H,s), 7.49 (6H,d), 8.27 (6H,d), ¹³C NMR: 55.2, 122.6, 132.4, 141.6, 147.4, 155.6; Anal. Calculated for C₂₄H₁₈Cl₃F₁₈N₆O₆P₃: Cal.: C, 28.05; H, 1.77; N, 8.18; Found: C, 27.92; H, 1.64; N, 8.10.

Ionic liquid 8: Yield: 0.45g; 90 %; Liquid; MS: 1040; ¹H NMR (400MHz; D₂O); 4.72 (6H,s), 7.39 (6H,d), 8.19(6H,d), ¹³C NMR: 56.4, 122.5, 132.0, 144.6, 148.4, 157.6; Anal. Calculated for C₂₇H₁₈Cl₃F₉N₆O₁₅S₃: Cal.: C, 31.18; H, 1.74; N, 8.08; Found: C, 31.08; H, 1.68; N, 7.96.

IV. CONCLUSION

We have synthesized variety trimetric ionic liquids from readily available starting material by nucleophilic substitution reaction followed by greener approach (metathesis) will give ionic liquids with quantitative yields. We have prepared Azalactone from Erlenmeyer method with our synthesized trimetric ionic liquids. 4-Nitro benzyl ionic liquid shows better catalytic activity than simple ionic liquids. Based on anion catalytic activity will differ; bromide containing ionic liquids shows better Lewis character than PF₆⁻ > BF₄⁻ > CF₃ SO₃⁻ due to size of anions.

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