INTRODUCTION

Recently a basic ionic liquid \([\text{bmim}]\text{[OH]}\) has been extensively used as a basic catalyst and reaction medium for various organic reactions such as Michael addition, Markovnikov addition, Knoevenagel condensation and Erlenmeyer Plochl reaction.

In our previous reports, benzoin condensation and Stetter reaction catalysed by \(N,N\)-dimethylbenzimidazolium iodide and NaOH were successfully performed in a neutral ionic liquid \([\text{bmim}]\text{[PF}_6\text{]}\). To the best of our knowledge, there is no report of the two reactions conducted in the ionic liquid \([\text{bmim}]\text{[OH]}\). Herein, as part of our continuing interest in carrying out reaction in ionic liquid as an environmentally benign solvent, we reported the use of \([\text{bmim}]\text{[OH]}\) as dual basic catalyst and reaction medium for the \(N,N\)-dimethylbenzimidazolium iodide catalysed benzoin condensation and Stetter reaction.

EXPERIMENTAL

Chemicals were purchased from Fluka, Aldrich and Merck chemical company and used without further purification. Melting points were determined on a Sanyo Gallenkamp melting point apparatus and compared with those of known...
samples. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR Spectrometer. $^1$H and $^{13}$C NMR spectra were obtained using a VARIAN MERCURY plus (400 MHz FT NMR).

$N,N$-Dimethylbenzimidazolium iodide was prepared following our previously reported reference.

**General procedure for benzoin condensation catalysed by $N,N$-dimethylbenzimidazolium iodide (2) in [bmim][OH]**

To a stirred solution of $N,N$-dimethylbenzimidazolium iodide (2) (0.055 g, 0.20 mmol) in [bmim][OH] (2 ml) was added an aromatic aldehyde (1.00 mmol) at room temperature. The temperature was raised to 80 °C and the resulting mixture was stirred for 4–8 h. After completion of the reaction, as determined by TLC (100% CH$_2$Cl$_2$), the reaction mixture was extracted with EtOAc (3x80 ml). The organic layers were combined and washed with water and dried with Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was purified using preparative thin layer chromatography on silica gel with CH$_2$Cl$_2$ as eluant.

The purified compounds (3a-d and 4a-d) with their physical data are listed below.

**Benzoin (3a).** White crystals; mp 134–136 °C (lit.$^8$ 134–136 °C). FTIR (KBr, ν, cm$^{-1}$): 3414 (O-H stretching), 3057, 3021 (aromatic C-H stretching), 2934 (aliphatic C-H stretching), 1674 (C=O stretching), 1595(arylamide C=C stretching), 1266 (C-O stretching). $^1$H NMR (CDCl$_3$, 400 MHz) δ: 7.91 (2H, d, J = 7.2 Hz, 2- and 6-H), 7.52 (1H, t, J = 7.2 Hz, 4-H), 7.39 (2H, t, J = 7.6 Hz, 3- and 5-H), 7.26–7.35 (5H, m, ArH), 5.95 (1H, s, CH$_2$), 4.54 (1H, br s, OCH$_3$); $^13$C NMR (CDCl$_3$) d: 176.2, 127.7, 128.6, 128.7, 129.1, 133.5, 133.9, 139.0, 198.9.

**4,4'-Dichlorobenzoin (3c).** White crystals; mp 87–88 °C (lit.$^8$ 88 °C). FTIR (KBr, ν, cm$^{-1}$): 3425 (O-H stretching), 3072 (aromatic C-H stretching), 2929 (aliphatic C-H stretching), 1674 (C=O stretching), 1590 (aromatic C=C stretching), 1252 (C-O stretching), 812 (C-Cl stretching). $^1$H NMR (CDCl$_3$, 400 MHz) δ: 7.75 (2H, d, J = 8.8 Hz, 2- and 6-H), 7.32 (2H, d, J = 8.4 Hz, 3- and 5-H), 7.24 (2H, d, J = 8.4 Hz, 3'- and 5'-H), 7.18 (2H, d, J = 8.4 Hz, 2'- and 6'-H), 5.81 (1H, s, CH$_2$); $^13$C NMR (CDCl$_3$) d: 75.5, 129.0, 129.2, 129.4, 130.4, 131.5, 134.8, 137.1, 140.7, 197.4.

**4,4'-Difluorobenzoin (3d).** White crystals; mp 83–84 °C (lit.$^{11}$ 81–82 °C). FTIR (KBr, ν, cm$^{-1}$): 3451 (O-H stretching), 3075(aromatic C-H stretching), 2937 (aliphatic C-H stretching), 1677 (C=O stretching), 1597 (aromatic C=C stretching), 1232 (C-O stretching), 1156 (C-F stretching). $^1$H NMR (CDCl$_3$, 400 MHz) δ: 7.93 (2H, dd, J = 8.8 Hz and 5.2 Hz, 2- and 6-H), 7.30 (2H, dd, J = 8.8 Hz and 5.2 Hz, 2''-H and 6''-H), 7.08 (2H, t, J = 8.8 Hz, 3''-H and 5''-H), 7.02 (2H, t, J = 8.4 Hz, 3'- and 5'-H), 5.90 (1H, s, CH$_2$), 4.54 (1H, br s, OCH$_3$); $^13$C NMR d 75.3, 116.0, 116.1, 116.2, 116.3, 129.4, 129.5, 129.6, 129.7, 131.8, 131.9, 134.7, 134.8, 161.5, 164.0, 164.8, 167.3, 197.2.

**O-Benzoylbenzoin (4a).** Yellow crystals; mp 123–125 °C (lit.$^8$ 125 °C). FTIR (KBr, ν, cm$^{-1}$): 3064, 3034 (aromatic C-H stretching), 2959 (aliphatic C-H stretching), 1717, 1695 (C=O stretching), 1599 (aromatic C=C stretching), 1278, 1108 (C-O stretching). $^1$H NMR δ 8.13 (2H, d, J = 7.6 Hz, 2''- and 6''-H), 8.05 (2H, d, J = 8.0 Hz, 2- and 6-H), 7.39-7.59 (11H, m, ArH), 7.10 (1H, s, CH$_2$); $^13$C NMR d 77.9, 128.4, 128.6, 128.8, 129.1, 129.3, 129.4, 130.0, 133.3, 133.4, 133.8, 134.8, 166.0, 193.7.

**O-(4-Methylbenzoyl)-4,4'-dimethylbenzoin (4b).** Yellow liquid. FTIR (neat, ν, cm$^{-1}$): 3058, 3032 (aromatic C-H stretching), 2957 (aliphatic C-H stretching), 1707, 1690 (C=O stretching), 1610 (aromatic C=C stretching), 1283, 1114 (C-O stretching). $^1$H NMR (CDCl$_3$, 400 MHz) δ: 8.00 (2H, d, J = 8.0 Hz, 2'- and 6'-H), 7.90 (2H, d, J = 8.0 Hz, 3'- and 5'-H), 7.83 (3H, s, Ar-CH$_3$), 7.28 (3H, s, Ar-CH$_3$); $^13$C NMR (CDCl$_3$) d: 21.1, 21.7, 75.8, 127.6, 129.3, 129.4, 129.8, 131.0, 136.4, 138.3, 144.9, 198.5.
2- and 6- H), 7.45 (2H, d, J = 8.0 Hz, 3- and 5-H), 7.18 – 7.23 (6H, m, Ar H) 7.04 (1H, s, CH), 2.40 (3H, s, Ar-CH3), 2.35 (3H, s, Ar-CH3), 2.32 (3H, s, Ar-CH3); 13C NMR (CDCl3) δ: 21.2, 21.6, 21.7, 77.6, 126.8, 128.6, 129.0, 129.1, 129.3, 129.8, 130.0, 131.2, 132, 132.9, 140.2, 144.0, 144.3, 166.1, 193.4.

O-(4-Chlorobenzoyl)-4,4'-dichlorobenzoin (4c). Yellow crystals; mp 125-127 °C (lit.10 127-128 °C). FTIR (KBr, ν, cm⁻¹): 3095 (aromatic C-H stretching), 2925 (aliphatic C-H stretching), 1722, 1698 (C=O stretching), 1592 (aromatic C=C stretching), 1249, 1090 (C-O stretching), 757 (C-Cl stretching). 1H NMR (CDCl3, 400 MHz) δ: 7.95 (2H, d, J = 8.8 Hz, 2"- and 6"- H), 7.82 (2H, d, J = 8.4 Hz, 2- and 6- H), 7.29-7.41 (8H, m, Ar H), 6.91 (1H, s, CH); 13C NMR d 77.1, 127.5, 128.9, 129.2, 129.6, 129.9, 130.1, 131.3, 131.7, 132.7, 135.8, 140.1, 140.4, 165.0, 192.1.

O-(4-Fluorobenzoyl)-4,4'-difluorobenzoin (4d). Yellow liquid; IR (KBr, ν, cm⁻¹): 3082 (aromatic C-H stretching), 2926 (aliphatic C-H stretching), 1724, 1687 (C=O stretching), 1601, 1508 (aromatic C=C stretching), 1285, 1154 (C-O stretching), 1106 (C-F stretching). 1H NMR (CDCl3, 400 MHz) δ: 8.12 (2H, dd, J = 8.8 and 5.2 Hz, 2"- and 6"- H), 8.01 (2H, dd, J = 8.8 and 5.2 Hz, 2- and 6- H), 7.54 (2H, dd, J = 8.8 and 5.2 Hz, 2'- and 6'- H), 7.08-7.14 (6H, m, Ar H), 7.02 (1H, s, CH); 13C NMR d 76.7, 115.6, 115.8, 116.0, 116.2, 116.3, 116.5, 125.4, 128.5, 129.4, 130.2, 130.6, 130.7, 130.9, 131.0, 131.5, 131.6, 132.6, 132.7, 162.1, 164.6, 164.7, 164.9, 166.0, 167.3, 167.4, 192.0.

General procedure for Stetter reaction between either acryonitrile (5) or ethyl acrylate (7) and aromatic aldehydes catalysed by N,N-dimethylbenzimidazolium iodide (2) in [bmim] [OH].

To a stirred solution of N,N-dimethylbenzimidazolium iodide (2) (0.055 g, 0.20 mmol) in [bmim] [OH] (2 ml) was added either acryonitrile (5) or ethyl acrylate (7) (2.00 mmol) and an aromatic aldehyde (1.00 mmol) at room temperature. The temperature was raised to 80 °C and the resulting mixture was allowed to stir for 14-17 h. After completion of the reaction, as determined by TLC (100% CH2Cl2), the reaction mixture was extracted with ethyl acetate (3x80 ml). The organic layers were combined and washed with water and dried with Na2SO4 and concentrated under reduced pressure. The residue was purified using preparative thin layer chromatography on silica gel with CH2Cl2 as eluant.

The purified compounds (6a-c, 8a-c, 9d and 10d) with their physical data are listed below.

4-Phenyl-4-oxobutanenitrile (6a). White crystals; mp 75-77 °C (lit.12 76 °C). FTIR (KBr, ν, cm⁻¹): 3067 (aromatic C-H stretching), 2923, 2882 (aliphatic C-H stretching), 2252 (Ca”N stretching), 1673 (C=O stretching), 1604 (aliphatic C=O stretching). 1H NMR δ 7.96 (2H, d, J = 7.2 Hz, 2"- and 6"- H), 7.62 (1H, t, J = 7.6 Hz, 4"- H), 7.50 (2H, t, J = 7.6 Hz, 3' and 5'- H), 3.39 (2H, t, J = 7.2 Hz, CH2CH2CN), 2.78 (2H, t, J = 7.2 Hz, CH2CH2CN); 13C NMR δ 11.8, 34.2, 119.2, 128.0, 128.8, 133.9, 135.6, 195.3.

4-(4-Tolyl)-4-oxobutanenitrile (6b). White crystals; mp 75-77 °C (lit.13 75 °C). FTIR (KBr, ν, cm⁻¹): 3040 (aromatic C-H stretching), 2924, 2853 (aliphatic C-H stretching), 2251(Ca”N stretching), 1673 (C=O stretching), 1606 (aromatic C=C stretching). 1H NMR δ 7.86 (2H, d, J = 8.0 Hz, 2' and 6'- H), 7.29 (2H, d, J = 8.0 Hz, 3' and 5'- H), 3.37 (2H, t, J = 7.2 Hz, CH2CH2CN), 2.77 (2H, t, J = 7.2 Hz, CH2CH2CN); 13C NMR δ 11.8, 29.7, 34.1, 119.2, 128.1, 129.5, 133.2, 144.9, 201.4.

4-(4-Chlorophenyl)-4-oxobutanenitrile (6c). White crystals; mp 70-72 °C (lit.14 72-73 °C). FTIR (KBr, ν, cm⁻¹): 3091, 3060 (aromatic C-H stretching), 2924 (aliphatic C-H stretching), 2250 (Ca”N stretching), 1675 (C=O stretching), 1590 (aromatic C=C stretching), 772 (C-Cl stretching). 1H NMR δ 7.89 (2H, d, J = 8.4 Hz, 2' and 6'- H), 7.47 (2H, d, J = 8.4 Hz, 3' and 5'- H), 3.35 (2H, t, J = 7.2 Hz, CH2CH2CN), 2.77 (2H, t, J = 7.2 Hz, CH2CH2CN); 13C NMR δ 11.7, 34.2, 119.0, 129.2, 129.4, 133.9, 140.5, 194.1.

Ethyl 4-phenyl-4-oxobutanolate (8a). Yellow liquid. FTIR (neat, ν, cm⁻¹): 3063 (aromatic C-H stretching), 2983, 2933 (aliphatic C-H stretching), 1733, 1687(C=O stretching), 1597 (aromatic C=C stretching), 1219, 1031 (C-O stretching). 1H NMR δ 7.97 (2H, d, J = 7.2 Hz, 2' and 6'- H), 7.55 (1H, t, J = 7.2 Hz, 4'- H), 7.45 (2H, t, J = 7.2 Hz, 3'- and
5'-H), 4.15 (2H, q, J = 7.2 Hz, OCH$_2$CH$_3$), 3.30 (2H, t, J = 6.8 Hz, CH$_2$CH$_2$CO$_2$CH$_3$), 2.75 (2H, t, J = 6.8 Hz, CH$_2$CH$_2$CO$_2$CH$_3$), 1.25 (3H, t, J = 7.2 Hz, CO$_2$CH$_2$CH$_3$). $^{13}$C NMR δ 14.2, 28.2, 33.3, 60.7, 128.0, 128.6, 133.2, 136.6, 172.9, 198.1.

4-(4'-Toly)-4-oxobutanoate (8b). White crystals; mp 64-65 °C; IR (KBr, v, cm$^{-1}$): 3091 (aromatic C-H stretching), 2981, 2930 (aliphatic C-H stretching), 1732, 1671 (C=O stretching), 1589 (aromatic C=C stretching), 1174, 1089 (C-O stretching). $^1$H NMR δ 7.85 (2H, d, J = 8.4 Hz, 2'- and 6'-H), 7.37 (2H, d, J = 8.4 Hz, 3'- and 5'-H), 4.09 (2H, q, J = 7.2 Hz, CO$_2$CH$_2$CH$_3$), 3.21 (2H, t, J = 6.4 Hz, CH$_2$CH$_2$CO$_2$CH$_3$), 2.69 (2H, t, J = 6.4 Hz, CH$_2$CH$_2$CO$_2$CH$_3$), 2.10 (3H, s, Ar-CH$_3$), 1.20 (3H, t, J = 7.2 Hz, CO$_2$CH$_2$CH$_3$). $^{13}$C NMR δ 14.2, 28.2, 30.9, 33.0, 60.7, 128.9, 129.4, 134.9, 139.6, 172.7, 196.9.

4-(4'-Dichlorophenyl)-4-oxobutanoate (8c). White crystals; mp 56-58 °C (lit. 58-59 °C). FTIR (KBr, v, cm$^{-1}$): 3003 (aromatic C-H stretching), 2950, 2846 (aliphatic C-H stretching), 2249, 1749, 1659 (C=O stretching), 1598 (aromatic C=C stretching), 1270, 1105 (C-O stretching), 775 (C-Cl stretching). $^1$H NMR δ 7.85 (2H, d, J = 8.8 Hz, 2c- and 6c-H), 7.37 (2H, d, J = 8.8 Hz, 3c- and 5c-H), 4.09 (2H, q, J = 7.2 Hz, CO$_2$CH$_2$CH$_3$), 3.20 (2H, t, J = 6.8 Hz, CH$_2$CH$_2$CO$_2$CH$_3$), 2.68 (2H, t, J = 6.8 Hz, CH$_2$CH$_2$CO$_2$CH$_3$), 1.20 (3H, t, J = 7.2 Hz, CO$_2$CH$_2$CH$_3$). $^{13}$C NMR δ 14.2, 28.2, 33.3, 60.7, 128.9, 129.4, 134.9, 139.6, 172.7, 196.9.

4,5-Di(4-fluoro)-4-hydroxy-5-oxopentane (9d). Colourless liquid. FTIR (neat, n, cm$^{-1}$): 3428 (O-H stretching), 3030 (aliphatic C-H stretching), 2249 (Ca$^+$N stretching), 1677 (C=O stretching), 1606 (aromatic C=C stretching), 1255 (C-O stretching), 1183 (C-F stretching). $^1$H NMR δ 7.79 (2H, dd, J = 8.4 and 5.6 Hz, 2- and 6-H), 7.41 (2H, dd, J = 8.4 and 5.2 Hz, 2c- and 6c-H), 7.11 (2H, t, J = 8.4 Hz, 3- and 5-H), 7.02 (2H, t, J = 8.8 Hz, 3’- and 5’-H), 2.56-2.69 (2H, m, CH$_2$CH$_2$CN), 2.38-2.46 (1H, m, HCH$_2$CN), 2.19-2.27 (1H, m, HCH$_2$CN). $^{13}$C NMR δ 11.8, 34.9, 80.6, 115.7, 116.0, 116.2, 116.4, 118.1, 119.2, 127.2, 127.3, 129.5, 132.9, 133.0, 135.8, 159.9, 161.5, 163.9, 167.0 198.0.

4,4'-Difluorobenzil (10d). White crystals; mp 119-121 °C (lit. 115-117 °C). FTIR (KBr, v, cm$^{-1}$): 3076 (aromatic C-H stretching), 1664 (C=O stretching), 1598 (aromatic C=C stretching), 1157 (C-F stretching). $^1$H NMR δ 8.02 (4H, dd, J = 8.8 Hz and 5.2 Hz, 2-H, 6-H, 2'-H and 6'-H), 7.20 (4H, t, J = 8.4 Hz, 5-H, 3-H, 5'-H and 3'-H). $^{13}$C NMR δ 116.4, 116.6, 128.8, 129.4, 132.8, 132.9, 165.6, 168.2, 192.2.

RESULTS AND DISCUSSION

Benzoin condensation and Stetter reaction were carried out under similar conditions as previously reported$^{6}$ except for the using of 20 mol% of $N,N$-dimethylbenzimidazolium iodide (2) in basic ionic liquid [bmim][PF$_6$] at 80 °C. As shown in Scheme I, benzoin condensation of aromatic aldehydes 1a-d proceeded very efficiently in [bmim][OH]. Similar to our previous results using [bmim][PF$_6$], arions 3a-d underwent further transformation to the corresponding aroylaroins 4a-d by the mechanism reported by Miyashita et al.$^{10}$

Stetter reaction between acrylonitrile (5) and aromatic aldehydes 1a-c in [bmim][OH] gave the corresponding adducts 4-aryl-4-oxobutanenitriles 6a-c, in satisfactory yields as illustrated in Scheme 2. Unlike our previous reactions in [bmim][PF$_6$], benzoin condensation was the only side reaction as evidenced by isolation of the corresponding arions 3a-c as minor products.

Similar results were also obtained upon carrying out Stetter reaction using a less electrophilic double bond, i.e., ethyl acrylate (7). Benzoin condensation, however, became the more competitive side reaction. While the percent yields of ethyl 4-aryl-4-oxobutanenitriles 8a-c decreased, percent yields of arions 3a-c increased significantly as illustrated in Scheme 3.

Stetter reaction between either acrylonitrile (5) or ethyl acrylate (7) and 4-fluorobenzaldehyde (1d) on the other hand gave different results. As shown in Scheme 4, treatment of acrylonitrile (5) with 4-fluorobenzaldehyde (1d) gave 5-oxonitrile 9d and aril 10d as the only isolated products. Contrastingly, when ethyl acrylate (7) was employed as electrophilic...
Scheme 1:

\[
\begin{align*}
\text{ArCH}_2\text{H} & \xrightarrow{[\text{bmim}][\text{OH}]} \text{ArCH}_2\text{Ar} + \text{ArCH}_2\text{Ar} \\
1a; \text{Ar} = & \begin{array}{c}
\begin{array}{c}
\text{H} \\
\text{Cl} \\
\text{F}
\end{array}
\end{array} & 3a; 87\% & 4a; 7\%
1b; \text{Ar} = & \begin{array}{c}
\begin{array}{c}
\text{H}_3\text{C} \\
\text{OH}
\end{array}
\end{array} & 3b; 62\% & 4b; 37\%
1c; \text{Ar} = & \begin{array}{c}
\begin{array}{c}
\text{Cl} \\
\text{OH}
\end{array}
\end{array} & 3c; 76\% & 4c; 21\%
1d; \text{Ar} = & \begin{array}{c}
\begin{array}{c}
\text{F} \\
\text{OH}
\end{array}
\end{array} & 3d; 83\% & 4d; 12\%
\end{align*}
\]

Scheme 2:

\[
\begin{align*}
\text{XCHO} + & \text{CN} & \xrightarrow{[\text{bmim}][\text{OH}]} \text{XCOCH} &= \text{CN} + \text{XCOCH} &= \text{CN} \\
1a; X = & \text{H} & 5 & 6a; 68\% & 3a; 24\%
1b; X = & \text{CH}_3 & & 6b; 40\% & 3b; 38\%
1c; X = & \text{Cl} & & 6c; 71\% & 3c; 18\%
\end{align*}
\]

Scheme 3:

\[
\begin{align*}
\text{XCHO} + & \text{CN} & \xrightarrow{[\text{bmim}][\text{OH}]} \text{XCOCH} &= \text{CN} + \text{XCOCH} &= \text{CN} \\
1a; X = & \text{H} & 5 & 6a; 68\% & 3a; 24\%
1b; X = & \text{CH}_3 & & 6b; 40\% & 3b; 38\%
1c; X = & \text{Cl} & & 6c; 71\% & 3c; 18\%
\end{align*}
\]
double bond the Stetter adduct could no longer be detected. Only arin 3d and aril 10d were the two isolated products.

Formation of 5-oxonitrile 9d was resulted from further reaction of 4-oxonitrile 6 (X = F) by the mechanism proposed in our previous report [6]. Further oxidation of arin 3d by the mechanism suggested by our group was responsible for the formation of aril 10d. Treatment of ethyl acrylate (7) with 4-fluorobenzaldehyde (1d) gave none of the Stetter adduct because 4-fluorobenzaldehyde (1d) was a much better acyl anion receptor than ethyl acrylate (7), therefore, the cross-coupling reaction between ethyl acrylate (7) and 4-fluorobenzaldehyde (1d) could not efficiently proceed.

It was also found that the recycled reaction media from either benzoin condensation or Stetter reaction, containing benzimidazolium salt, can be reused in the same type of reaction for up to at least 3 cycles. The same product distributions without significant decreasing in their yields were obtained.

**CONCLUSION**

Benzoin condensation of aromatic aldehydes catalysed by \( N,N \)-dimethylbenzimidazolium iodide in [bmim][OH] proceeded very well with no additional hydroxide base. Aroylaroins were found as the only minor products. Stetter reaction between either acrylonitrile or ethyl acrylate and aromatic aldehydes catalysed by benzimidazolium salt also performed well in [bmim][OH], although benzoin condensation occurred competitively. No Stetter reaction was observed upon treatment of ethyl acrylate with 4-fluorobenzaldehyde.

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