

Benzoin condensation of aromatic aldehydes catalysed by *N,N*-dimethylbenzimidazolium iodide and NaOH under green conditions

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Received 12 Oct 2012

Accepted 6 Dec 2012

ABSTRACT: Benzoin condensation of aromatic aldehydes catalysed by *N,N*-dimethylbenzimidazolium iodide and NaOH was performed either in ionic liquid or water or in the absence of solvent. Reusability of the catalyst mixture in all cases was demonstrated.

KEYWORDS: ionic liquid, water, solvent free condition

INTRODUCTION

As there has been a tendency to avoid hazardous substances in green chemistry, organic reactions carrying out in the absence of conventional organic solvents have received more attention. Among various reactions, the solventless benzoin condensation of benzaldehyde has been reported to proceed efficiently using sodium methoxide and several imidazolium-based ionic liquids as catalyst under microwave irradiation¹. Employing imidazolium-based ionic liquid, 1-octyl-3-methylimidazolium bromide, as solvent/catalyst under ultrasonic irradiation also provided a quantitative yield of benzoin². In addition to ionic liquids, water is a greener alternative solvent for organic reactions^{3,4}. Accordingly, benzoin condensations catalysed by *N,N*-dialkylbenzimidazolium salts in the presence of amine bases or NaOH in water gives α -hydroxy ketones in moderate to excellent yields⁵.

In our previous work, *N,N*-dimethylbenzimidazolium iodide was used as an effective and recyclable catalyst for benzoin condensation⁶. Herein we report our extended investigation of greener aspects of benzoin condensation catalysed by *N,N*-dimethylbenzimidazolium iodide and NaOH, i.e., in ionic liquid, in water, and under solvent free condition.

EXPERIMENTAL SECTION

General

Melting point were determined on Sanyo Gallenkamp melting point apparatus. IR spectra were recorded on

a Perkin Elmer Spectrum One FT-IR Spectrometer. ¹H and ¹³C NMR spectra were obtained using a VARIAN MERCURY plus (400 MHz FT NMR).

General procedure for benzoin condensation catalysed by *N,N*-dimethylbenzimidazolium iodide (2) and NaOH in [bmim][PF₆]

To a stirred solution of *N,N*-dimethylbenzimidazolium iodide (2) (0.218 g, 0.80 mmol) and NaOH (0.032 g, 0.80 mmol) in [bmim][PF₆] (5 ml) was added an aromatic aldehyde (8.00 mmol) at room temperature. The temperature was raised to 80 °C and the resulting mixture was stirred for 4.5–8 h. After completion of the reaction, as indicated by TLC (100% dichloromethane), the reaction mixture was extracted with diethyl ether (3 × 80 ml). The combined organic extract was dried (anh. Na₂SO₄) and the solvent was removed under reduced pressure. The residue was purified using preparative thin layer chromatography on silica gel with dichloromethane as eluant.

Benzoin condensation of benzaldehyde (1a)

Benzoin condensation of benzaldehyde (1a) (0.78 g, 7.36 mmol) was carried out according to the above general procedure for 5 h. Purification of the residue gave benzoin (3a) (0.65 g, 83%) and *O*-benzoylbenzoin (4a) (0.05 g, 9%).

Compound 3a was obtained as white crystals; mp 134–136 °C (lit.⁷ 134–136 °C); IR (KBr) ν_{\max} : 3414, 3057, 3021, 2934, 1674, 1595, 1449, 1266, 1205,

753 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.91 (2H, d, $J = 7.6$ Hz, 2- and 6-*H*), 7.52 (1H, t, $J = 7.6$ Hz, 4-*H*), 7.39 (2H, t, $J = 7.6$ Hz, 3- and 5-*H*), 7.26–7.33 (5H, m, Ar*H*), 5.95 (1H, s, CH), 4.54 (1H, br s, OH); ^{13}C NMR (CDCl_3) δ : 76.2, 127.8, 128.6, 128.7, 129.1, 133.5, 133.9, 139.0, 198.9.

Compound 4a was obtained as yellow crystals; mp 123–125 °C (lit.⁷ 125 °C); IR (KBr) ν_{max} : 3069, 2959, 1731, 1695, 1598, 1450, 1280, 1119, 957, 704 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 8.18 (2H, d, $J = 7.2$ Hz, 2''- and 6''-*H*), 8.05 (2H, d, $J = 7.6$ Hz, 2- and 6-*H*), 7.41–7.63 (11H, m, Ar*H*), 7.15 (1H, s, CH); ^{13}C NMR (CDCl_3) δ : 78.0, 128.4, 128.7, 128.9, 129.2, 129.4, 129.5, 130.0, 133.4, 133.5, 133.8, 134.8, 166.1, 193.8.

Benzoin condensation of *p*-tolualdehyde (1b)

Benzoin condensation of *p*-tolualdehyde (**1b**) (1.02 g, 8.50 mmol) was carried out according to the above general procedure for 8 h. Purification of the residue gave 4,4'-dimethylbenzoin (**3b**) (0.80 g, 78%) and *O*-(4-methylbenzoyl)-4,4'-dimethylbenzoin (**4b**) (0.09 g, 12%).

Compound 3b was obtained as white crystals; mp 73–75 °C (lit.⁸ 75–76 °C); IR (KBr) ν_{max} : 3471, 3031, 2920, 1675, 1604, 1512, 1413, 1274, 1095, 779 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.81 (2H, d, $J = 8.4$ Hz, 2- and 6-*H*), 7.21 (2H, d, $J = 8.4$ Hz, 3- and 5-*H*), 7.18 (2H, d, $J = 8.0$ Hz, 2'-*H* and 6'-*H*), 7.11 (2H, d, $J = 8.0$ Hz, 3'- and 5'-*H*), 5.89 (1H, s, CH), 2.35 (3H, s, Ar- CH_3), 2.28 (3H, s, Ar- CH_3); ^{13}C NMR (CDCl_3) δ : 21.1, 21.7, 75.8, 127.6, 129.3, 129.4, 129.8, 131.0, 136.4, 138.3, 144.9, 198.6.

Compound 4b was obtained as yellow liquid; IR (neat) ν_{max} : 2964, 2858, 1725, 1681, 1604, 1413, 1370, 1282, 1173, 1106, 751 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.92 (2H, d, $J = 8.19$ Hz, 2''- and 6''-*H*), 7.82 (2H, d, $J = 8.19$ Hz, 2- and 6-*H*), 7.37 (2H, d, $J = 8.19$ Hz, 3- and 5-*H*), 7.17–7.27 (6H, m, Ar*H*) 6.96 (1H, s, CH), 2.33 (3H, s, CH_3), 2.30 (3H, s, CH_3), 2.26 (3H, s, CH_3); ^{13}C NMR (CDCl_3) δ : 21.2, 21.6, 21.7, 77.6, 128.6, 128.9, 129.0, 129.1, 129.3, 129.7, 129.9, 130.0, 139.2, 145.1, 153.1, 153.2, 165.8, 192.1.

Benzoin condensation of *p*-chlorobenzaldehyde (1c)

Benzoin condensation of *p*-chlorobenzaldehyde (**1c**) (1.04 g, 7.40 mmol) was carried out according to the above general procedure for 7 h. Purification of the residue gave 4,4'-dichlorobenzoin (**3c**) (0.62 g, 60%) and *O*-(4-chlorobenzoyl)-4,4'-dichlorobenzoin (**4c**) (0.15 g, 19%).

Compound 3c was obtained as white crystals; mp 87–88 °C (lit.⁷ 88 °C); IR (KBr) ν_{max} : 3423, 3070, 2928, 1674, 1590, 1487, 1401, 1251, 1206, 1091, 977, 812 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.75 (2H, d, $J = 8.4$ 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); ^{13}C NMR (CDCl_3) δ : 77.3, 129.1, 129.2, 129.4, 130.4, 131.6, 134.8, 137.2, 140.7, 197.5.

Compound 4c was obtained as yellow crystals; mp 125–127 °C (lit.⁹ 127–128 °C); IR (KBr) ν_{max} : 3090, 2926, 1719, 1698, 1593, 1491, 1366, 1277, 1092, 961 cm^{-1} ; ^1H NMR (CDCl_3 , 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); ^{13}C NMR (CDCl_3) δ : 77.1, 127.5, 128.9, 129.2, 129.6, 130.0, 130.1, 131.3, 131.7, 132.7, 135.8, 140.1, 140.4, 165.0, 192.1.

Benzoin condensation of furaldehyde (1d)

Benzoin condensation of furaldehyde (**1d**) (0.82 g, 8.54 mmol) was carried out according to the above general procedure for 4.5 h. Purification of the residue gave furoin (**3d**) (0.51 g, 62%) and *O*-furoylfuroin (**4d**) (0.11 g, 18%).

Compound 3d was obtained as yellow crystals; mp 137–139 °C (lit.⁷ 138–139 °C); IR (KBr) ν_{max} : 3418, 3130, 2964, 1680, 1560, 1466, 1400, 1252, 1038, 789, 735 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.61 (1H, s, 5-*H*), 7.37 (1H, s, 5'-*H*), 7.24 (1H, d, $J = 3.2$ Hz, 3-*H*), 6.53 (1H, d, $J = 3.6$ Hz, 4-*H*), 6.39 (1H, d, $J = 3.2$ Hz, 4'-*H*), 6.34 (1H, d, $J = 3.2$ Hz, 3'-*H*), 5.79 (1H, s, CH), 4.15 (1H, br s, OH); ^{13}C NMR (CDCl_3) δ : 69.2, 109.1, 110.8, 112.6, 120.1, 143.2, 147.7, 149.4, 151.2, 184.4.

Compound 4d was obtained as brown crystals; mp 118–122 °C; IR (KBr) ν_{max} : 3144, 2957, 1727, 1691, 1568, 1462, 1396, 1266, 1179, 766 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.60 (1H, d, $J = 0.8$ Hz, 5''-*H*), 7.59 (1H, d, $J = 0.8$ Hz, 5-*H*), 7.47 (1H, d, $J = 0.8$ Hz, 5'-*H*), 7.31 (1H, d, $J = 3.6$ Hz, 3''-*H*), 7.30 (1H, d, $J = 2.4$ Hz, 3-*H*), 6.96 (1H, s, CH), 6.57 (1H, d, $J = 3.2$ Hz, 4-*H*), 6.51–6.54 (2H, m, 4'- and 4''-*H*), 6.40 (1H, dd, $J = 3.2$ and 1.6 Hz, 3'-*H*); ^{13}C NMR (CDCl_3) δ : 70.6, 111.1, 112.0, 112.1, 112.5, 119.4, 119.5, 143.6, 144.3, 146.3, 147.0, 147.3, 150.2, 157.5, 179.3.

General procedure for benzoin condensation catalysed by *N,N*-dimethylbenzimidazolium iodide (2) and NaOH in water

An aromatic aldehyde (20.0 mmol) was added to a stirred solution of *N,N*-dimethylbenzimidazolium

iodide (**2**) (1.096 g, 4.00 mmol) in 0.2 M NaOH (20.0 ml, 4.00 mmol) and the resulting mixture was stirred at room temperature for 0.5–8 h. After completion of the reaction, as indicated by TLC (20% EtOAc/hexane), the crystalline powder formed was collected by filtration, washed with water and dried in open air. Mixed products was purified using preparative thin layer chromatography on silica gel with 20% EtOAc/hexane as eluant. The filtrate was washed with diethyl ether (3 × 30 ml) for reuse.

Benzoin condensation of benzaldehyde (**1a**)

Benzoin condensation of benzaldehyde (**1a**) (2.120 g, 20.00 mmol) was carried out according to the above general procedure for 1 h. Filtration of the crystalline product gave benzoin (**3a**) (2.05 g, 97%) identical to the previously obtained sample.

Benzoin condensation of *p*-tolualdehyde (**1b**)

Benzoin condensation of *p*-tolualdehyde (**1b**) (2.40 g, 20.00 mmol) was carried out according to the above general procedure for 3 h. Filtration of the crystalline product gave 4,4'-dimethylbenzoin (**3b**) (2.31 g, 96%) identical to the previously obtained sample.

Benzoin condensation of *p*-chlorobenzaldehyde (**1c**)

Benzoin condensation of *p*-chlorobenzaldehyde (**1c**) (2.81 g, 20.00 mmol) was carried out according to the above general procedure for 3 h. Purification of the mixed products gave 4,4'-dichlorobenzoin (**3c**) (0.95 g, 34%) identical with the previously obtained sample and 4,4'-dichlorobenzil (**5c**) (1.66 g, 60%).

Compound 5c was obtained as yellow crystals; mp 197–198 °C; IR (KBr) ν_{\max} : 3093, 2936, 1660, 1587, 1486, 1401, 1316, 1211, 1173, 1096, 834 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.85 (4H, d, $J = 8.8$ Hz, 2-, 2'-, 6- and 6'-H) 7.44 (4H, d, $J = 8.8$ Hz, 3-, 3'-, 5- and 5'-H); ^{13}C NMR (CDCl_3) δ : 129.5, 131.2, 131.3, 141.9, 192.4.

Benzoin condensation of furaldehyde (**1d**)

Benzoin condensation of furaldehyde (**1d**) (1.92 g, 20.00 mmol) was carried out according to the above general procedure for 0.5 h. Purification of the mixed products gave furoin (**3d**) (0.06 g, 3%) identical with the previously obtained sample and furil (**5d**) (0.42 g, 22%).

Compound 5d was obtained as yellow crystals; mp 163–165 °C (lit.⁷ 165–166 °C); IR (KBr) ν_{\max} : 3147, 1643, 1533, 1453, 1393, 1279, 1154, 1079, 1024, 940, 813, 753 cm^{-1} ; ^1H NMR (CDCl_3 ,

400 MHz) δ : 7.78 (2H, d, $J = 0.8$ Hz, 5- and 5'-H), 7.65 (4H, d, $J = 4.0$ Hz, 3- and 3'-H), 6.64 (2H, dd, $j = 1.6$, $J = 3.6$ Hz, 4- and 4'-H); ^{13}C NMR (CDCl_3) δ : 113.1, 124.7, 149.4, 149.5, 176.9.

General procedure for benzoin condensation catalysed by *N,N*-dimethylbenzimidazolium iodide (**2**) and NaOH under solvent free condition

N,N-dimethylbenzimidazolium iodide (**2**) (0.273 g, 1.00 mmol) and NaOH (0.040 g, 1.00 mmol) and aromatic aldehyde (10.00 mmol) were ground altogether with a pestle and mortar for 10 min and heated at 80 °C for 4 h. Water (30 ml) was added to the reaction mixture and the products extracted with diethyl ether (3 × 30 ml). The combined organic extract was dried (anh. Na_2SO_4) and the solvent was removed under reduced pressure. The residue was purified using preparative thin layer chromatography on silica gel with 20% EtOAc/hexane as eluant.

Benzoin condensation of benzaldehyde (**1a**)

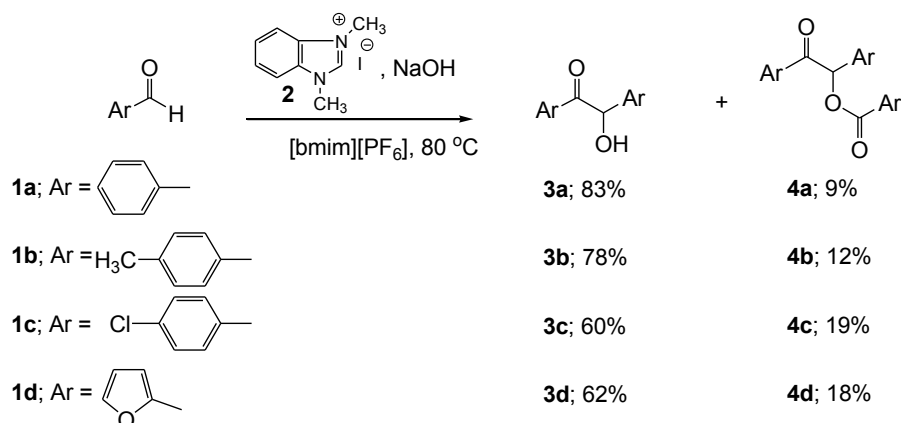
Benzoin condensation of benzaldehyde (**1a**) (1.12 g, 10.57 mmol) was carried out according to the above general procedure. Purification of the residue gave benzoin (**3a**) (0.43 g, 77%), *O*-benzoylbenzoin (**4a**) (0.06 g, 7%) and benzil (**5a**) (0.03 g, 3%). Compound **3a** and compound **4a** were identical to the previously obtained samples.

Compound 5a was obtained as yellow crystals; mp 95–96 °C (lit.⁷ 95 °C); IR (KBr) ν_{\max} : 3064, 1660, 1594, 1450, 1325, 1211, 876, 719 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.98 (4H, d, $J = 7.6$ Hz, 2-, 2'-, 6- and 6'-H), 7.66 (2H, t, $J = 7.6$ Hz, 4- and 4'-H), 7.51 (4H, t, $J = 7.6$ Hz, 3-, 3'-, 5- and 5'-H); ^{13}C NMR (CDCl_3) δ : 129.0, 129.9, 133.0, 134.9, 194.5.

Benzoin condensation of *p*-tolualdehyde (**1b**)

Benzoin condensation of *p*-tolualdehyde (**1b**) (1.18 g, 9.83 mmol) was carried out according to the above general procedure. Purification of the residue gave 4,4'-dimethylbenzoin (**3b**) (0.75 g, 64%), *O*-(4-methylbenzoyl)-4,4'-dimethylbenzoin (**4b**) (0.09 g, 10%), and 4,4'-dimethylbenzil (**5b**) (0.14 g, 12%). Compound **3b** and compound **4b** were identical to the previously obtained samples.

Compound 5b was obtained as yellow crystals; mp 97–99 °C; IR (KBr) ν_{\max} : 3047, 2916, 1662, 1602, 1571, 1328, 1222, 883, 772 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.86 (4H, d, $J = 8.0$ Hz, 2-, 2'-, 6- and 6'-H), 7.29 (4H, d, $J = 8.0$ Hz, 3-, 3'-, 5- and 5'-H); ^{13}C NMR (CDCl_3) δ : 21.8, 129.6, 129.9, 130.7, 145.9, 194.4.



Scheme 1

Benzoin condensation of *p*-chlorobenzaldehyde (**1c**)

Benzoin condensation of *p*-chlorobenzaldehyde (**1c**) (1.39 g, 9.89 mmol) was carried out according to the above general procedure. Purification of the residue gave 4,4'-dichlorobenzoin (**3c**) (0.31 g, 22%), and *O*-(4-chlorobenzoyl)-4,4'-dichlorobenzoin (**4c**) (0.16 g, 15%), and 4,4'-dichlorobenzil (**5c**) (0.65 g, 47%) identical to the previously obtained samples.

Benzoin condensation of furaldehyde (**1d**)

Benzoin condensation of furaldehyde (**1d**) (1.04 g, 10.83 mmol) was carried out according to the above general procedure. Purification of the residue gave furoin (**3d**) (0.27 g, 26%), *O*-furoylfuroin (**4d**) (0.12 g, 16%), and furil (**5d**) (0.41 g, 40%) identical to the previously obtained samples.

RESULTS AND DISCUSSION

In our recent report, we demonstrated that Stetter reactions were accompanied by benzoin condensations when aromatic aldehydes were treated with ethyl acrylate in the presence of 20 mol% of *N,N*-dimethylbenzimidazolium iodide (**2**) and NaOH in ionic liquid, [bmim][PF₆], at 80 °C¹⁰. We, therefore, carried out benzoin condensation of aromatic aldehydes **1a-d** catalysed by 20 mol% of the benzimidazolium salt **2** and NaOH in [bmim][PF₆] at 80 °C. As shown in Scheme 1, the expected aroins **3a-d** were obtained as major products together with the aroylaroins **4a-d** as minor products. The aroylaroins **4a-d** were resulted from further transformation of the corresponding aroins **3a-d** by the mechanism reported⁹.

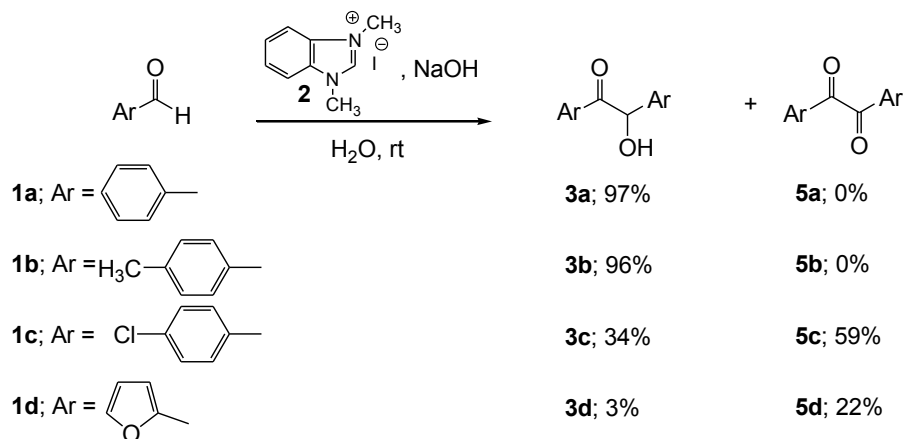
After extraction of the products thus obtained

with diethyl ether, the ionic liquid containing *N,N*-dimethylbenzimidazolium iodide (**2**) and NaOH could be reused, even after the third run without loss of activity, the same products were obtained with no obvious decrease in their yields.

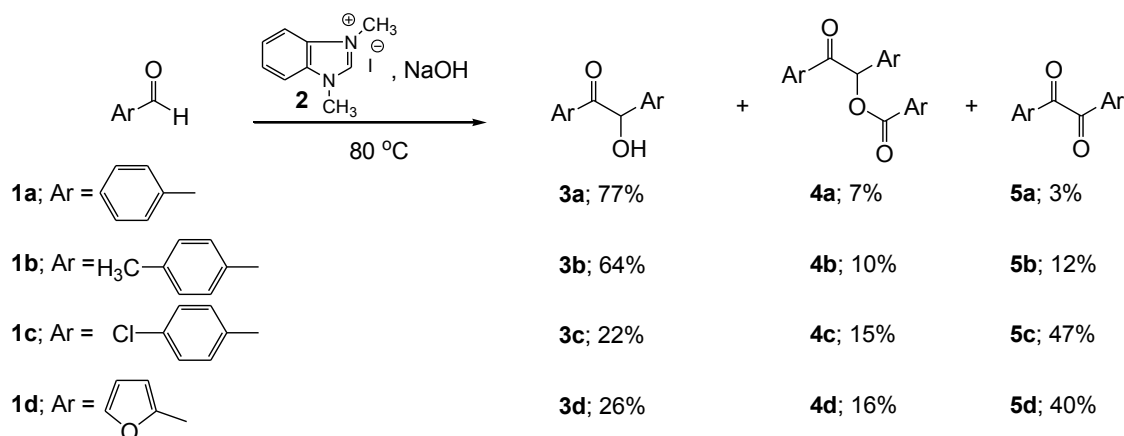
Next, we investigated benzoin condensation of aromatic aldehydes **1a-d** in water. Although it has been reported that effective self-condensation of benzaldehyde (**1a**) catalysed by *N,N*-dialkylbenzimidazolium salts required long *N*-alkyl chain⁵, however, in our hands this was not the case. Upon stirring either benzaldehyde (**1a**) or *p*-tolualdehyde (**1b**) in the aqueous solution of 20 mol% of *N,N*-dimethylbenzimidazolium iodide (**2**) in 0.2 M NaOH at room temperature, self-condensation proceeded efficiently to give the corresponding aroin **3a** or **3b** as the sole product in nearly quantitative yields as illustrated in Scheme 2. Self-condensation of *p*-chlorobenzaldehyde (**1c**) and furaldehyde (**1d**), on the other hand, gave 34% yield of aroin **3c** and 3% yield of aroin **3d** along with the corresponding arils **5c** and **5d** in 59 and 22% yields, respectively. Formation of arils **5c** and **5d** were resulted from subsequent oxidation of the corresponding aroins **3c** and **3d** by the mechanism suggested in our previous paper⁶. As has been previously pointed out¹¹, the poor overall yield of furoin (**3d**) and furil (**5d**) was owing to the formation of unidentified coloured byproduct.

The aqueous layer, after washing with diethyl ether, was reused in the self-condensation of benzaldehyde (**1b**) and *p*-tolualdehyde (**1b**) for three times, giving in each time similar yields of the corresponding aroins **3a** and **3b**.

Benzoin condensation catalysed by *N,N*-dimethylbenzimidazolium iodide (**2**) and NaOH was also found to proceed quite efficiently in the absence



Scheme 2



Scheme 3

of solvent. This was illustrated by heating a grinding mixture of an aromatic aldehyde and 20 mol% of *N,N*-dimethylbenzimidazolium iodide (**2**) and NaOH at 80 °C for 4 h. As shown in Scheme 3, the condensation of aromatic aldehydes **1a-d** under solvent free condition gave the corresponding aroins **3a-d**. In addition to aroins, both aroylaroins and aroils, which occurred when condensations were carried out in [bmim][PF₆] and in water, respectively, were also found under solvent free condition. The amount of aroylaroins **4a-d** isolated from solvent free condition were similar to those found from conducting the reaction in [bmim][PF₆]. Since we also found that aroin **3c** could simply and quantitatively transformed to aril **5d** by heating its powder at 80 °C for 4 h, formation of aroils **5a-d** under solvent free condition should have resulted, at least in part, from air oxidation of their corresponding aroins **3a-d** at elevated temperature.

N,N-dimethylbenzimidazolium iodide (**2**) employed under solvent free condition could be recov-

ered by the method previously reported⁶.

CONCLUSIONS

Benzoin condensation of aromatic aldehydes catalysed by 20 mol% of *N,N*-dimethylbenzimidazolium iodide and NaOH could be carried out either in ionic liquid or water or under solvent free condition. Aroylaroins and arils were also obtained as minor products. Reusability of [bmim][PF₆] containing *N,N*-dimethylbenzimidazolium iodide and NaOH as well as its corresponding aqueous solution were demonstrated. The benzimidazolium salt employed under solvent free condition could also be recovered for reuse.

Acknowledgements: Financial support from the Centre of Excellence for Innovation in Chemistry (PERCH-CIC), Office of the Higher Education Commission, Ministry of Education is gratefully acknowledged.

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