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Dehydration of 1,2,3-triaryl-3-hydroxy-1-propanones: An alternatve route for synthesis of triaryl-2-propen-1-ones

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ABSTRACT

N-Heterocyclic carbene-catalyzed reaction of aromatic aldehydes with benzyl halides leads to formation of 1,3-diaryl-3-hydroxy-2-phenylpropan-1-ones. Subsequent dehydration offers a route to 1,3-diaryl-2-phenyl-2-propen-1-ones.

Key words: *N*-heterocyclic carbene, benzyl halides, [bmim]OH, 1,2,3-triaryl-2-propen-1-ones

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INTRODUCTION

(*E*)- and (*Z*)-1,2,3-Triaryl-2-propen-1-ones obtained from aldol condensation of aryl benzyl ketone have been reported to possess potency and selectivity on COX-2 inhibition [1]. Apart from Friedel-Craft acylation of benzene derivatives with phenylacetyl chloride in the presence of $AlCl_3$, the *N*-heterocyclic carbenes (NHCs) catalyzed cross-coupling of aromatic aldehydes with benzyl halides is an alternative route for producing aryl benzyl ketones [2]. As we are interested in catalytic activity of NHC generated from *N*,*N*-dimethylbenzimidazolium iodide [3-5] and the employment of the basic ionic liquid [bmim]OH as reaction medium and base [6-10], herein we report the synthesis of triaryl propenones *via* aldol condensation of aryl benzyl ketones obtained from treatment of aromatic aldehydes with benzyl halides in the presence of *N*,*N*-dimethylbenzimidazolium iodide in [bmim]OH.

MATERIALS AND METHODS

Solvents were purified according to standard methods prior to use, while all other chemicals used were commercially available and used as received. Melting points were measured using a Sanyo Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR Spectrometer. ^{1}H and ^{13}C NMR spectra were recorded using a VARIAN MERCURY plus (400 MHz FT NMR). *N*,*N*-Dimethylbenzimidazolium iodide was prepared following our previously reported procedure [11].

General procedure for the cross-coupling of aromatic aldehydes with benzyl halides

To a stirred solution of *N*,*N*-dimethylbenzimidazolium iodide (**3**) (0.137 g, 0.5 mmol) in [bmim]OH (3.0 ml) was added an aromatic aldehyde (1.0 mmol) and a benzyl halide (2.0 mmol) at room temperature. After 8-16 hours, the completion of the reaction was indicated by TLC (10% ethyl acetate/hexane), the reaction mixture was extracted with ethyl acetate (3 × 30 ml). The combined organic layers were dried (anh.Na_2SO_4) and the solvent was removed under reduced pressure. The residue was purified by using preparative thin layer chromatography with 10% ethyl acetate /hexane as eluent to afford the 1,3-diaryl-3-hydroxy-2-phenylpropan-1-one, aroin and benzyl ester.

3-Hydroxy-1,2,3-triphenylpropan-1-one (4a)
White crystals; mp 119-120 °C; IR (KBr) (ν): 3507, 3053, 3026, 1676, 1595, 1445, 1215, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.70 (2H, d, *J* = 7.6 Hz, 2′-*H* and 6′-*H*), 7.52 (2H, d, *J* = 7.6 Hz, 2‴-*H* and 6‴-*H*), 7.37-7.45 (3H, m, Ar-*H*′), 7.23-7.34 (3H, m, Ar-*H*‴), 7.16-7.17 (3H, m, Ar-*H*″), 6.94-6.96 (2H, m, Ar-*H*″), 4.03 (1H, s, O*H*), 3.78 (1H, d, *J* = 13.6 Hz, 2-*H*), 3.52 (1H, d, *J* = 13.6 Hz, 3-*H*); ^{13}C NMR ($CDCl_3$) δ: 44.9, 82.2, 125.9, 127.0, 128.1, 128.9, 130.2, 130.4, 130.6, 130.7, 132.8, 134.7, 135.1, 142.0, 200.6.

1,3-Di(4-chlorophenyl)-3-hydroxy-2-phenylpropan-1-one (4b)
Yellow crystals; mp 103-104 °C; IR (KBr) (ν): 3458, 3064, 2925, 2852, 1678, 1587, 1457, 1210, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.70 (2H, d, *J* = 8.4 Hz, 2′-*H* and 6′-*H*), 7.43 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*), 7.36 (2H, d, *J* = 8.8 Hz, 3‴-*H* and 5‴-*H*), 7.27 (2H, d, *J* = 8.4 Hz, 2‴-*H* and 6‴-*H*), 7.20-7.21 (3H, m, Ar-*H*″), 6.96-6.98 (2H, m, Ar-*H*″), 3.73 (1H, d, *J* = 13.6 Hz, 2-*H*), 3.68 (1H, s, O*H*), 3.40 (1H, d, *J* = 13.6 Hz, 3-*H*); ^{13}C NMR ($CDCl_3$) δ: 45.5, 82.1, 127.0, 127.4, 128.4, 128.5, 129.1, 130.7, 131.7, 132.8, 134.2, 134.5, 139.5, 140.3, 198.9.

1,3-Di(4-flurophenyl)-3-hydroxy-2-phenylpropan-1-one (4c)
White crystals; mp 98-100 °C; IR (KBr) (ν): 3466, 3068, 3032, 2928, 1679, 1598, 1454, 1232, 1158, 1091, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.78 (2H, dd, *J* = 8.8 Hz and 5.6 Hz, 2′-*H* and 6′-*H*), 7.47 (2H, dd, *J* = 8.4 Hz and 5.2 Hz, 2‴-*H* and 6‴-*H*), 7.20-7.21 (3H, m, Ar-*H*″), 7.09 (2H, t, *J* = 8.8 Hz, 3″-*H* and 5″-*H*), 6.95-7.01 (4H, m, Ar-*H*″ and Ar-*H*‴), 3.82 (1H, s, O*H*), 3.74 (1H, d, *J* = 13.6 Hz, 2-*H*), 3.45 (1H, d, *J* = 13.6 Hz, 3-*H*); ^{13}C NMR ($CDCl_3$) δ: 45.5, 82.0, 115.3, 115.5, 115.8, 116.0, 127.3, 127.4, 127.5, 128.4, 130.6, 130.8, 130.9, 133.1, 133.2, 134.6, 137.6, 137.7, 161.2, 163.7, 164.1, 166.6, 198.7.

3-Hydroxy-2-phenyl-1,3-di-*p*-tolylpropan-1-one (4d)
White crystals; mp 111-112 °C; IR (KBr) (ν): 3435, 3032, 2925, 2863, 1669, 1504, 1300, 1179, 1092, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.63 (2H, d, *J* = 8.4 Hz, 2′-*H* and 6′-*H*), 7.39 (2H, d, *J* = 8.4 Hz, 5′-*H* and 3′-*H*), 7.19 (2H, d, *J* = 8.0 Hz, 2‴-*H* and 6‴-*H*), 7.14-7.17 (3H, m, Ar-*H*″), 7.11 (2H, d, *J* = 8.4 Hz, 3‴-*H* and 5‴-*H*), 6.94-6.96 (2H, m, Ar-*H*″), 4.23 (1H, s, O*H*), 3.76 (1H, d, *J* = 13.2 Hz, 2-*H*), 3.56 (1H, d, *J* = 13.6 Hz, 3-*H*), 2.35 (3H, s, Ar-CH_3), 2.34 (3H, s, Ar-CH_3); ^{13}C NMR ($CDCl_3$) δ: 21.1, 21.6, 44.7, 81.8, 125.8, 126.9, 128.0, 128.9, 129.5, 130.5, 130.6, 132.0, 135.3, 137.8, 139.4, 143.6, 200.2.

3-Hydroxy-1,3-di-(4-methoxyphenyl)-2-phenylpropan-1-one (4e)
Yellow crystals; mp 91-92 °C; IR (KBr) (ν): 3458, 3064, 3031, 2925, 2852, 1678, 1587, 1454, 1249, 1210, 1093, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.95 (2H, d, *J* = 8.8 Hz, 2′-*H* and 6′-*H*), 7.74 (2H, d, *J* = 8.8 Hz, 2‴-*H* and 6‴-*H*), 7.42 (2H, d, *J* = 8.8 Hz, 3′-*H* and 5′-*H*), 7.16 (2H, d, *J* = 6.4 Hz, 2″-*H* and 6″-*H*), 6.91-6.98 (3H, m, Ar-*H*″), 6.79 (2H, d, J = 8.8 Hz, 3‴-*H* and 5‴- *H*), 4.36 (1H, s, O*H*), 3.89 (3H, s, Ar-OCH_3), 3.82 (3H, s, Ar-OCH_3), 3.73 (1H, d, *J* = 13.2 Hz, 2-*H*), 3.58 (1H, d, *J* = 13.6 Hz, 3-*H*); ^{13}C NMR ($CDCl_3$) δ: 44.7, 55.3, 55.4, 81.3, 113.5, 114.3, 127.3, 128.0, 130.6, 132.4, 132.8, 134.7, 135.3, 159.3, 163.2, 164.9, 198.9.

Benzoin (5a)
White crystals; mp 134-136 °C; IR (KBr) (ν): 3413, 3058, 3027, 2931, 1678, 1595, 1449, 1262, 1206, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.91(2H, d, *J* = 7.6 Hz, 2-*H* and 6-*H*), 7.52 (1H, t, *J* = 7.6 Hz, 4-*H*), 7.39 (2H, t, *J* = 7.6 Hz, 3-*H* and 5-*H*), 7.26-7.33 (5H, m, Ar-*H*), 5.95 (1H, s, C*H*), 4.54 (1H, br s, O*H*); ^{13}C NMR ($CDCl_3$) δ: 76.2, 127.8, 128.6, 128.7, 129.1, 133.5, 133.9, 139.0, 198.9.

4,4′-Dichlorobenzoin (5b)
White crystals; mp 87-88 °C; IR (KBr) (ν): 3425, 3072, 2929, 1674, 1590, 1488, 1401, 1252, 1207, 1093 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.75 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.32 (2H, d, *J* = 8.4 Hz, 3-*H* and 5-*H*), 7.24 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*), 7.18 (2H, d, *J* = 8.4 Hz, 2′-*H* and 6′-*H*), 5.81 (1H, s, C*H*); ^{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.

4,4′-Difluorobenzoin (5c)
White crystals; mp 81-82 °C; IR (KBr) (ν): 3450, 3074, 2927, 1676, 1596, 1506, 1231, 1156, 838 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.93 (2H, dd, *J* = 8.8 Hz and 5.2 Hz, 2-*H* 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′-*H* and 5′-*H*), 5.90 (1H, s, C*H*), 4.54 (1H, br s, O*H*); ^{13}C NMR ($CDCl_3$) δ: 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, 167.4, 197.2.

4,4′-Dimethylbenzoin (5d)
White crystals; mp 73-75 °C; IR (KBr) (ν): 3448, 3030, 2921, 1673, 1607, 1512, 1448, 1387, 1178 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.81 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.21 (2H, d, *J* = 8.4 Hz, 3-*H* 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′-*H* and 5′-*H*), 5.89 (1H, s, C*H*), 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, 198.5.

4,4′-Dimethoxybenzoin (5e)
White crystals; mp 104-106 °C; IR (KBr) (ν): 3454, 3005, 2936, 2839, 1668, 1598, 1462, 1307, 1252, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.89 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.24 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*), 6.85 (2H, d, *J* = 6.0 Hz, 2′-*H* and 6′-*H*), 6.83 (2H, d, *J* = 6.0 Hz, 3′-*H* and 5′-*H*), 5.85 (1H, s, C*H*), 3.81 (3H, s, Ar-OCH_3), 3.74 (3H, s, Ar-OCH_3); ^{13}C NMR ($CDCl_3$) δ: 55.2, 55.5, 75.2, 113.9, 114.5, 126.3, 129.0, 131.6, 131.8, 159.6, 164.0, 197.3.

Benzyl benzoate (6a)
Yellow liquid; IR (neat) (ν): 3065, 3034, 2953, 2890, 1721, 1602, 1585, 1452, 1377, 1272, 712 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.08 (2H, d, *J* = 7.6 Hz, 2-*H* and 6-*H*), 7.55 (1H, t, *J* = 7.6 Hz, 4-*H*), 7.44 (4H, m, Ar-*H*), 7.39 (2H, t, *J* = 8.4 Hz, 3′-*H* and 5′-*H*), 7.35 (1H, t, *J* = 8.4 Hz, 4′-*H*), 5.37 (2H, s, CH_2); ^{13}C NMR ($CDCl_3$) δ: 66.7, 128.1, 128.2, 128.4, 128.6, 129.7, 130.2, 133.0, 136.1, 166.4.

Benzyl 4-chlorobenzoate (6b)
Yellow liquid; IR (neat) (ν): 3035, 2957, 2929, 1721, 1645, 1595, 1488, 1456, 1270, 758 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.01 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.39 (7H, m, Ar-*H*), 5.36 (1H, s, CH_2); ^{13}C NMR ($CDCl_3$) δ: 67.0, 128.3, 128.4, 128.6, 128.7, 129.0, 131.1, 135.8, 139.5, 165.6.

Benzyl 4-fluorobenzoate (6c)
White liquid; IR (neat) (ν): 3068, 3035, 2956, 1724, 1603, 1505, 1456, 1378, 1270, 1238, 1111, 766, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.01 (2H, dd, *J* = 8.8 Hz and 5.6 Hz, 2-*H* and 6-*H*), 7.44 (2H, d, *J* = 6.8 Hz, 2′-*H* and 6′-*H*), 7.34-7.41 (3H, m, Ar-*H*′), 7.09 (2H, t, *J* = 8.8 Hz, 3-*H* and 5-*H*), 5.35 (1H, s, CH_2); ^{13}C NMR ($CDCl_3$) δ: 66.9, 115.4, 115.6, 126.4, 126.5, 128.2, 128.3, 128.6, 132.2, 132.3, 135.9, 164.6, 165.5, 167.1.

Benzyl 4-methylbenzoate (6d)
Colorless liquid; IR (neat) (ν): 3091, 3055, 2986, 2958, 1717, 1613, 1455, 1272 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.97 (2H, d, *J* = 8.0 Hz, 2-*H* and 6-*H*), 7.44 (2H, d, *J* = 7.6 Hz, 2′-*H* and 6′-*H*), 7.45 (2H, d, *J* = 7.2 Hz, 3′-*H* and 5′-*H*), 7.35 (1H, t, *J* = 7.2 Hz, 4′-*H*), 7.23 (2H, d, *J* = 8.0 Hz, 3-*H* and 5-*H*), 5.35 (2H, s, CH_2), 2.40 (3H, s, Ar-CH_3); ^{13}C NMR ($CDCl_3$) δ: 21.7, 66.5, 127.4, 128.1, 128.2, 128.6, 129.1, 129.7, 136.2, 143.7, 166.5.

Benzyl 4-methoxybenzoate (6e)
Colorless liquid; IR (neat) (ν): 3091, 3055, 2986, 2958, 1717, 1613, 1455, 1272 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.97 (2H, d, *J* = 8.0 Hz, 2-*H* and 6-*H*), 7.44 (2H, d, *J* = 7.2 Hz, 2′-*H* and 6′-*H*), 7.45 (2H, d, *J* = 7.2 Hz, 3′-*H* and 5′-*H*), 7.35 (1H, t, *J* = 7.2 Hz, 4′-*H*), 7.23 (2H, d, *J* = 8.0 Hz, 3-*H* and 5-*H*), 5.35 (2H, s, CH_2), 2.40 (3H, s, Ar-CH_3); ^{13}C NMR ($CDCl_3$) δ: 21.7, 66.5, 127.4, 128.1, 128.2, 128.6, 129.1, 129.7, 136.2, 143.7, 166.5.

General procedure for dehydration of 1,2,3-triaryl-3-hydroxy-1-propanones
A mixture of an appropriate 1,2,3-triaryl-3-hydroxy-1-propanone (1.0 mmol) and P_2O_5 (2.0 mmol) in benzene (25 ml) was refluxed for 12-16 hours. The benzene layer was decanted and the residue was washed once with hot benzene. The combined benzene layers were washed with water, dried (anh.Na_2SO_4) and concentrated under reduced pressure. The residue was purified by using preparative thin layer chromatography with 100% dichloromethane as eluent to afford the corresponding 1,3-diaryl-2-phenyl-2-propen-1-one.

1,2,3-Triphenylprop-2-en-1-one (20a)
White crystals; mp 108-109 °C; IR (KBr) (ν): 3057, 3028, 2923, 2857, 1687, 1666, 1595, 1484, 1270, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.00 (2H, d, *J* = 7.2 Hz, 2′-*H* and 6′-*H*), 7.47 (2H, d, *J* = 8.8 Hz, 2″-*H* and 6″-*H*), 7.34-7.38 (5H, m, Ar-*H*), 7.28-7.31 (4H, m, Ar-*H*), 7.20 (1H, s, C*H*), 7.18 (2H, d, *J* = 7.6 Hz, 2‴-*H* and 6‴-*H*); ^{13}C NMR ($CDCl_3$) δ: 122.1, 126.3, 128.5, 128.6, 128.9, 129.0, 129.7, 130.3, 131.6, 133.9, 134.4, 136.1, 137.7, 141.7, 199.1.

1,3-Di-(4-chlorophenyl)-2-phenylprop-2-en-1-one (20b)
White crystals; mp 96-97 °C; IR (KBr) (ν): 3060, 3030, 2924, 2857, 1654, 1591, 1493, 1448, 1252, 1067 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.89 (2H, d, *J* = 8.4 Hz, 2′-*H* and 6′-*H*), 7.78 (2H, d, *J* = 8.4 Hz, 2″-*H* and 6″-*H*), 7.43 (2H, d, *J* = 8.4 Hz, 2‴-*H* and 6‴-*H*), 7.36 (1H, s, C*H*), 7.31-7.35 (3H, m, Ar-*H*), 7.24-7.26 (2H, m, Ar-*H*), 7.18-7.21 (2H, m,

Ar-*H*); ^{13}C NMR ($CDCl_3$) δ: 122.6, 127.6, 129.2, 129.4, 130.2, 131.0, 131.7, 131.8, 133.9, 134.3, 134.7, 135.8, 140.0, 140.7, 197.4.

1,3-Di-(4-fluorophenyl)-2-phenylprop-2-en-1-one (20c)

White crystals; mp 113-114 °C; IR (KBr) (ν): 3064, 3027, 2924, 2852, 1689, 1661, 1598, 1504, 1451, 1229, 1157 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 7.38 (2H, dd, *J* = 8.4 Hz and 5.6 Hz, 2′-*H* and 6′-*H*), 7.19-7.23 (3H, m, Ar-*H*), 7.10-7.17 (5H, m, Ar-*H* and C*H*), 7.05 (2H, dd, *J* = 8.8 Hz and 5.6 Hz, 2‴-*H* and 6‴-*H*), 6.78 (2H, t, *J* = 8.8 Hz, 3‴-*H* and 5‴-*H*); ^{13}C NMR ($CDCl_3$) δ: 114.9, 115.1, 115.7, 116.0, 120.3, 124.0, 125.9, 126.8, 127.0, 128.1, 128.7, 130.7, 130.8, 131.1, 131,2, 139.4, 144.6, 148.0, 160.4, 161.0, 162.8, 163.5, 198.2.

2-Phenyl-1,3-di-p-tolylprop-2-en-1-one (20d)

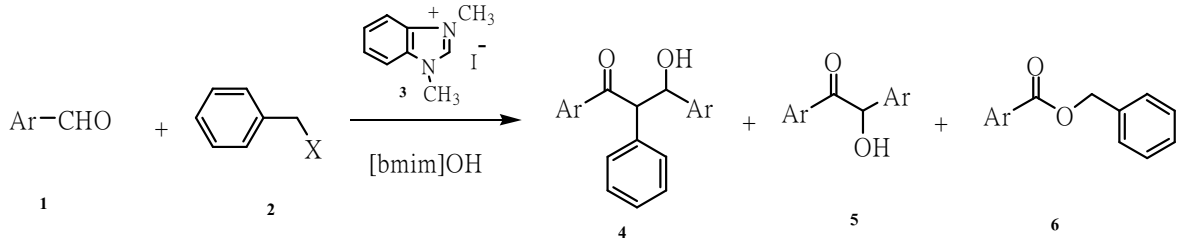
Yellow liquid; IR (neat) (ν): 3052, 3025, 2920, 2863, 1659, 1603, 1571, 1447, 1254, 1172 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 7.91 (2H, d, *J* = 7.6 Hz, 2′-*H* and 6′-*H*), 7.37 (2H, d, *J* = 8.0 Hz, 2″-*H* and 6″-*H*), 7.31 (2H, d, *J* = 7.2 Hz, 2‴-*H* and 6‴-*H*), 7.15-7.21 (8H, m, Ar-*H*, C*H*), 2.34 (6H, s, 2(Ar-C*H*$_3$)); ^{13}C NMR ($CDCl_3$) δ: 21.1, 21.7, 126.2, 127.7, 128.4, 128.7, 128.8, 129.4, 129.5, 129.8, 134.0, 135.3, 135.6, 138.1, 141.0, 141.5, 199.0.

1,3-Di(4-methoxyphenyl)-2-phenylprop-2-en-1-one (20e)

Colorless liquid; IR (neat) (ν): 3058, 3008, 2958, 2840, 1652, 1594, 1505, 1454, 1251, 1163 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 7.97 (2H, d, *J* = 8.8 Hz, 2′-*H* and 6′-*H*), 7.40 (2H, d, *J* = 8.8 Hz, 2″-*H* and 6″-*H*), 7.29 (2H, d, *J* = 7.2 Hz, 2‴-*H* and 6‴-*H*), 7.13-7.20 (3H, m, Ar-*H*), 7.07(1H, s, C*H*), 6.87 (2H, d, *J* = 8.8 Hz, 3′-*H* and 5′-*H*), 6.83 (2H, d, *J* = 8.8 Hz, 3″-*H* and 5″-*H*), 3.80 (3H, s, Ar-C*H*$_3$), 3.79 (3H, s, Ar-C*H*$_3$); ^{13}C NMR ($CDCl_3$) δ: 55.3, 55.4, 114.0, 114.2, 127.5, 127.6, 127.7, 128.4, 128.7, 129.6, 130.7, 132.1, 135.7, 140.5, 159.6, 163.9, 195.1.

RESULTS AND DISCUSSION

Carrying out cross-coupling of aromatic aldehydes **1a-e** with 2 equivalents of benzyl chloride (**2a**) in the presence of 50 mol% of *N*,*N*-dimethylbenzimidazolium iodide (**3**) in [bmim]OH without additional hydroxide base at room temperature produced corresponding 1,3-diaryl-3-hydroxy-2-phenylpropan-1-ones **4a-e** in 50-83% yields as shown in Scheme 1. Additionally, aroins **5a-e** and benzyl esters **6a-e** were also obtained as side products in 4-17% yields and in 3-4 % yields respectively. Employment of benzyl bromide (**2b**) instead of benzyl chloride (**2a**) afforded the same products in similar yields.

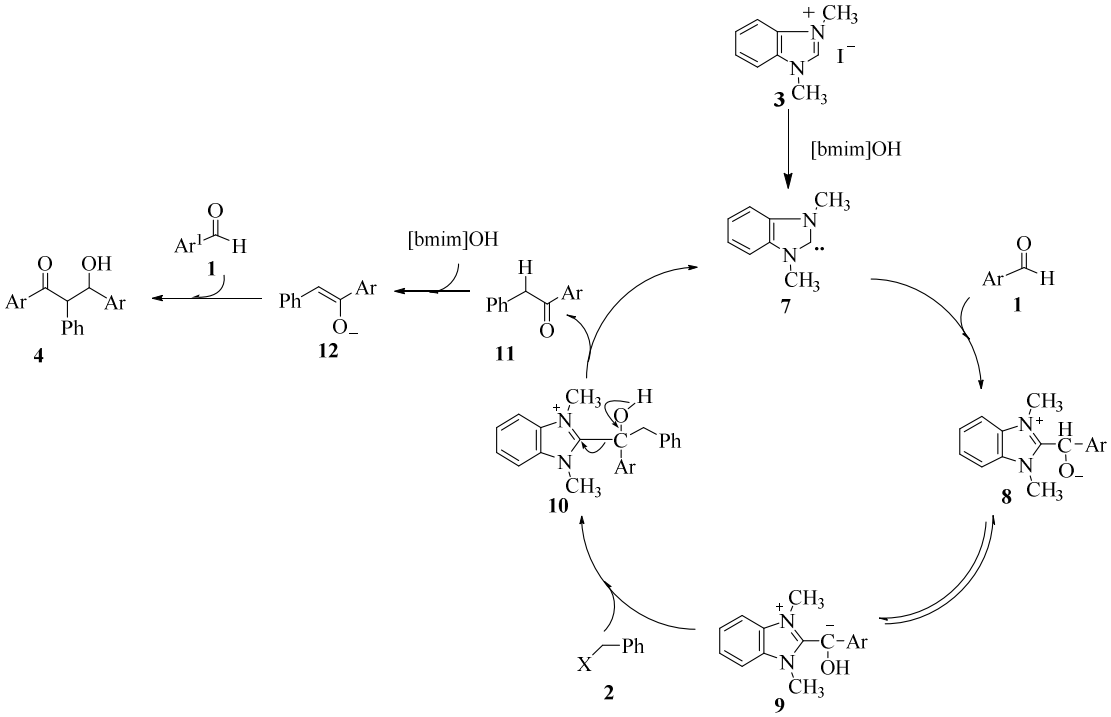


1, **2**, **3**, **4**, **5**, **6**

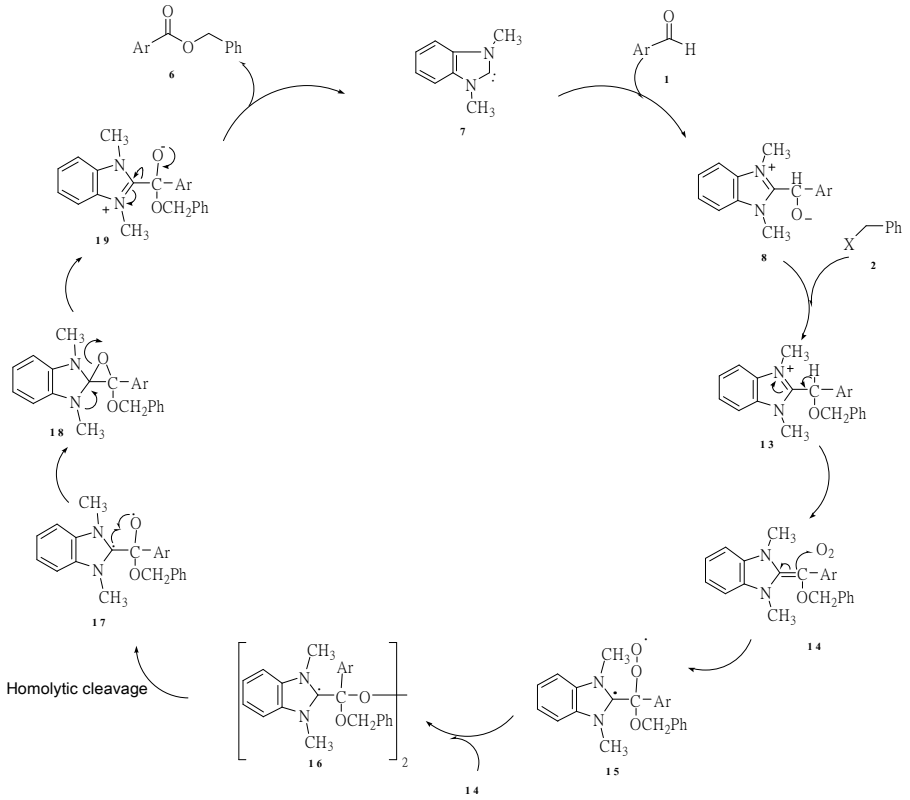
1a; Ar = C_6H_5	**2a**; X = Cl	**4a**; 67%	**5a**; 10%	**6a**; 4%
1b; Ar = 4-ClC_6H_5	**2a**; X = Cl	**4b**; 82%	**5b**; 4%	**6b**; 4%
1c; Ar = 4-FC_6H_5	**2a**; X = Cl	**4c**; 82%	**5c**; 4%	**6c**; 4%
1d; Ar = 4-$CH_3C_6H_5$	**2a**; X = Cl	**4d**; 66%	**5d**; 17%	**6d**; 4%
1e; Ar = 4-$CH_3OC_6H_5$	**2a**; X = Cl	**4e**; 50%	**5e**; 10%	**6e**; 3%
1a; Ar = C_6H_5	**2b**; X = Br	**4a**; 73%	**5a**; 15%	**6a**; 4%
1b; Ar = 4-ClC_6H_5	**2b**; X = Br	**4b**; 82%	**5b**; 8%	**6b**; 4%
1c; Ar = 4-FC_6H_5	**2b**; X = Br	**4c**; 83%	**5c**; 6%	**6c**; 4%
1d; Ar = 4-$CH_3C_6H_5$	**2b**; X = Br	**4d**; 73%	**5d**; 13%	**6d**; 4%
1e; Ar = 4-$CH_3OC_6H_5$	**2b**; X = Br	**4e**; 66%	**5e**; 11%	**6e**; 3%

Scheme 1 Products from coupling of aromatic aldehydes with benzyl halides

Our plausible mechanistic pathway responsible for the formation of 1,3-diaryl-3-hydroxy-2-phenylpropan-1-ones **4a-e** is illustrated in Scheme 2. Accordingly, *N*,*N*-dimethylbenzimidazol-2-ylidene (**7**) generated *in situ* from deprotonation of benzimidazolium salt **3** reacts with aromatic aldehyde **1** to give the Breslow intermediate **9** which then reacts with benzyl halide **2** to give aryl benzyl ketone **11**. Deprotonation of **11** follows by addition of the enolate anion **12** to aromatic aldehyde **1** produces 1,3-diaryl-3-hydroxy-2-phenylpropan-1-one **4**.



Scheme 2 Proposed mechanism for the formation of 3-hydroxy-1,2,3-triarylpropan-1-ones 4

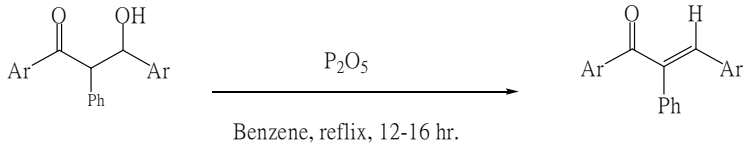


Scheme 3 Proposed mechanism for the formation of benzyl esters 6

Aroins **5a-e** were obtained from benzoin condensation. Benzyl esters **6a-e** probably occurred through the mechanism involving oxygenation with molecular oxygen. As illustrated in Scheme 3, intermediate **8** reacts with benzyl halide **2** to give a benzyl ether **13**. Deprotonation of **13** gives enol ether **14** which undergoes oxygenation to give peroxy radical **15**. Subsequent coupling with another equivalent of **14** provides peroxide **16**. Homolytic

cleavage and intramolecular coupling of the diradical **17** gives epoxide **18** which is then subjected to epoxide ring opening to give esters **6a-e** after the departure of benzimidazol-2-ylidene **7**.

Dehydration of 1,3-diaryl-3-hydroxy-2-phenylpropan-1-ones **4a-e** with phosphorus pentoxide at 80 °C in benzene [12] gave good yields of 1,3-diaryl-2-phenyl-2-propen-1-ones **20a-e** as shown in Scheme 4.



4a; Ar = C_6H_5
4b; Ar = 4-ClC_6H_4
4c; Ar = 4-FC_6H_4
4d; Ar = 4-MeC_6H_4
4e; Ar = 4-$MeOC_6H_4$

20a; 78%
20b; 87%
20c; 91%
20d; 73%
20e; 68%

Scheme 4 Dehydration of 1,3-diaryl-3-hydroxy-2-phenylpropan-1-ones 4a-e

CONCLUSION

Treatment of aromatic aldehydes with benzyl halides in the presence of *N*,*N*-dimethylbenzimidazolium iodide in [bmim]OH at room temperature produced good yields of the corresponding 1,3-diaryl-3-hydroxy-2-phenylpropan-1-ones along with aroins and benzyl esters as minor side products. Mechanisms for the formation of 1,3-diaryl-3-hydroxy-2-phenylpropan-1-ones and benzyl esters are suggested. Dehydration of 1,3-diaryl-3-hydroxy-2-phenylpropan-1-ones using phosphorus pentoxide in benzene provided 1,3-diaryl-2-phenyl-2-propen-1-ones in good yields.

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