SUPPORTING INFORMATION

Selective Iododeamination of Electron Deficient Anilines Using Task-Specific Nitrite and Iodide-Based Ionic Liquids

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Synthesis of ionic liquid, 1-butyl-3-methylimidazolium iodide:

The freshly prepared 1-butyl-3-methylimidazolium chloride and an excess amount of KI were added into the dichloromethane and stirred for 24 h at room temperature. KCl which was prepared during the exchange of chloride anion with iodide was removed by filtering. The dichloromethane was removed under reduced pressure at room temperature, followed by heating under high vacuum, to yield a Low viscosity yellow iodide-based ionic liquid in 90% yield.

Selected spectroscopic data:

1-Butyl-3-methylimidazolium iodide: FT-IR (KBr, cm^{-1}): 1651, 1624, 1609. ^1H NMR (400 MHz, DMSO-d_6) δ 1.22(3H, t, CH_3); 1.33 (2H, m, CH_2); 1.49 (2H, m, CH_2); 2.91 (3H, s, N- CH_3); 3.83 (2H, t, N- CH_2); 7.73, 7.74 (2H, two singlets, C(4,5)-H); 9.12 (1H, s, C(2)-H). ^{13}C NMR (100 MHz, DMSO-d_6); δ 18.3 (CH_3), 21.1 ($-\text{CH}_2$); 26.1 ($-\text{CH}_2$); 38.1 (N- CH_3); 54.5 (N- CH_2); 123.0 (C(4 or 5)); 125.4 (C(4 or 5)); 138.0 (C(2)). Anal. calcd. (%) for $\text{C}_8\text{H}_{15}\text{N}_2\text{I}$: C, 36.09; H, 10.52; N, 5.64. Found (%): C, 35.98; H, 10.45; N, 5.66.

Characterization Data for some compounds in Tabe II:

4-Nitroiodobenzene (2b):

Light brown solid (yield 80%); mp 171-172°C (literature^[15] 172-173°C); IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3084, 1594, 1571, 1512, 1340, 1052, 1008, 837, 734; ^1H NMR (400 MHz, CDCl_3): δ 8.08 (d, $J = 7.2$ Hz, 2H), 7.98 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 104.96, 125.44, 139.20, 147.81.

3-Chloriodobenzene (2c):

Yield 15%; mp 56-57°C (literature^[14] 57°C); IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3050, 1590, 1562, 1451, 1325, 1059, 1005, 874, 745, 670; ^1H NMR (300 MHz, DMSO- d_6): δ 7.91 (s, 1 H), 7.80 (d, $J = 7.7$ Hz, 1H), 7.49 (d, $J = 7.5$ Hz, 1H), 7.17 (t, $J = 7.7$ Hz, 1H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 103.3, 116.1, 133.3, 133.5, 138.4, 141.1.

4-Cyanoiodobenzene (2e):

Yield 78%; mp 126-127°C (literature^[16] 124-128°C); IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 2962, 2220, 1720, 1581, 812, 705; ^1H NMR (300 MHz, CDCl_3): δ 7.80 (d, $J = 8.51$ Hz, 2H), 7.32 (d, $J = 8.51$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 109.5, 116.1, 122.5, 132.1, 134.7.

4-Iodoacetophenone (2f):

Yield 80%; mp 83-84°C (literature^[15] 84-85°C); IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 2931, 1673, 1580, 1391, 1064, 824, 616; ^1H NMR (300 MHz, CDCl_3): δ 7.82 (d, $J = 8.5$ Hz, 2H), 7.69 (d, $J = 8.5$ Hz, 2H), 2.59 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 26.1, 107.1, 129.0, 134.6, 139.1, 191.9.

4-Iodobenzophenone (2g):

Yield 82%; mp 100-102°C (literature^[14] 101-102°C); IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3041, 2919, 1609, 1583, 1280, 1014, 739, 652; ^1H NMR (300 MHz, CDCl_3): δ 7.85 (d, $J = 8.5$ Hz, 2H), 7.88 (d, $J = 8.2$ Hz, 2H), 7.68 (m, 1H), 7.52 (d, $J = 8.4$ Hz, 2H), 7.50 (t, $J = 7.8$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 105.8, 126.1, 129.1, 132.8, 133.6, 135.8, 136.1, 140.3, 200.5.

4-Iodobenzoic acid (2h):

Yield 84%; mp 267-269°C (literature^[14] 269-270°C); IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 2551-3663, 1741, 1609, 1571, 1280, 1100, 741, 670; ^1H NMR (300 MHz, DMSO- d_6): δ 7.92 (d, J = 7.7 Hz, 2H), 7.84 (d, J = 7.7 Hz, 2H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 101.4, 130.3, 132.5, 167.8.

2-Iodobenzoic acid (2k):

Yield 81%; mp 161-163°C (literature^[15] 161-162°C); IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3082, 3068, 3011, 1688, 1583, 1467, 1430, 1304, 1295, 1271, 1016, 738, 680; ^1H NMR (400 MHz, CDCl_3): δ 11 (s, 1H), 8.06-7.98 (m, 3H), 7.65 (1H); ^{13}C NMR (25 MHz, CDCl_3): δ 94.7, 128, 132.1, 133.2, 133.5, 142, 171.1.

2,4,6-trichloriodobenze (2l):

Yield 35%; mp 52-53°C (literature^[15] 53-54°C); IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3100, 1608; ^1H NMR (300 MHz, DMSO- d_6): δ 8.99 (s, 2 H); ^{13}C NMR (75 MHz, DMSO- d_6): δ 99, 125.3, 125.3, 138, 150.2, 150.2.

2-Chloro-3-iodopyridine (2n):

White solid (yield 79%); mp 90-92°C (literature^[17] 91-93°C); IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3052, 1557, 1389, 1137, 797, 722, 640; ^1H NMR (400 MHz, CDCl_3): δ 8.38 (dd, J = 4.6, 1.7 Hz, 1H), 8.16 (dd, J = 7.9, 1.6 Hz, 1H), 6.96 (dd, J = 7.9, 4.7 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 94.9, 123.2, 148.8, 148.9, 154.5.

3-Iodopyridine (2o):

Light beige solid (yield 75%); mp 52-53°C (literature^[14] 53.5°C); IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3100, 1604; ^1H NMR (400 MHz, CDCl_3): δ 8.6 (s, 1H), 8.12 (dd, J = 4.3 and 1.4 Hz, 1H), 7.95

(dd, $J = 8.1$ and 1.3 Hz, 1H), 6.44 (dd, $J = 8.1$ and 4.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 85.4, 118.8, 139.1, 139.9, 149.1.

2,4-Dinitroiodobenzene (2q):

Yellow solid (yield 86%); mp $87\text{-}89^\circ\text{C}$ (literature^[15] $88.5\text{-}89^\circ\text{C}$); IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3097, 1596, 1585, 1531, 1349, 1026, 834, 730; ^1H NMR (400 MHz, CDCl_3): δ 8.68 (d, $J = 2.6$ Hz, 1H), 8.32 (d, $J = 8.1$ Hz, 1H), 8.12 (dd, $J = 8.1$ and 2.6 Hz, 1H); ^{13}C NMR (22.5 MHz, CDCl_3): δ 94.5, 120.33, 126.90, 143.43, 148.18, 152.58.

1,2,3,5-Tetraiodobenzene (2r):

Yellow crystale (yield 38%); mp $161\text{-}163^\circ\text{C}$ (literature^[18] $162\text{-}165^\circ\text{C}$); IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3090, 1595; ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ 8.19 (s, 2 H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$): δ 97.0, 110.5, 122.2, 145.4.