

Ionic-liquids-assisted reaction of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes with β -nitrostyrenes

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Experimental

1-(4-Methylphenyl)-2-nitro-3-(3-nitrophenyl)tetrahydro-1H,5H-pyrazolo[1,2-a]pyrazole 7b: R_f 0.57, mp 105 °C (decomp.). ^1H NMR (CDCl_3) δ : 2.18, 2.42 (2m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.34 (s, 3H, ArMe), 3.10, 3.28 (td, m, 2H, MeArCNCH_2 , 2J 9.8 Hz, 3J 4.7 Hz), 3.29, 3.41 (m, td, 2H, $\text{NO}_2\text{ArCNCH}_2$, 2J 9.9 Hz, 3J 4.8 Hz), 4.70 (d, 1H, MeArCH , 3J 6.7 Hz), 4.91 (d, 1H, NO_2ArCH , 3J 5.0 Hz), 5.00 (t, 1H, NO_2CH , 3J 5.8 Hz), 7.17, 7.29 (2d, 4H, H in MeAr, 3J 7.8 Hz), 7.55 [t, 1H, C(5)H in NO_2Ar , 3J 8.0 Hz], 7.84 [d, 1H, C(4)H in NO_2Ar , 3J 8.0 Hz], 8.18 [d, 1H, C(6)H in NO_2Ar , 3J 8.0 Hz], 8.46 [s, 1H, C(2)H in NO_2Ar]. ^{13}C NMR (CDCl_3) δ : 20.95 (MeAr), 23.96 (NCH_2CH_2), 50.36 (MeArCNCH_2), 51.27 ($\text{NO}_2\text{ArCNCH}_2$), 70.60 ($\text{NO}_2\text{ArC}_{\text{ring}}$), 71.75 ($\text{MeArC}_{\text{ring}}$), 102.86 ($\text{NO}_2\text{C}_{\text{ring}}$), 127.27, 129.68, 134.78, 138.42 (MeAr), 122.28, 123.02, 129.86, 133.12, 142.56, 148.63 (NO_2Ar). ^{15}N NMR (CDCl_3) δ : +6.1 ($\text{NO}_2\text{C}_{\text{ring}}\text{H}$), -10.6 (NO_2Ar), -247.9 (MeArCN), -249.7 (NO_2ArCN). IR (ν/cm^{-1}): 646, 688, 745, 830, 914, 1040, 1182, 1253, 1348, 1486, 1524, 1606, 1680, 2862, 2934, 2978, 3074.

1-(4-Methoxyphenyl)-2-nitro-3-(3-nitrophenyl)tetrahydro-1H,5H-pyrazolo[1,2-a]pyrazole 7c: R_f 0.58, mp 110 °C (decomp.). ^1H NMR (CDCl_3) δ : 2.13, 2.41 (2m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.08, 3.27 (2m, 2H, MeOArCNCH_2 , 2J 10.0 Hz, 3J 4.8 Hz), 3.28, 3.40 (m, td, 2H, $\text{NO}_2\text{ArCNCH}_2$, 2J 10.1 Hz, 3J 4.8 Hz), 3.78 (s, 3H, ArOMe), 4.67 (d, 1H, MeOArCH , 3J 6.8 Hz), 4.92 (d, 1H, NO_2ArCH , 3J 5.2 Hz), 4.98 (t, 1H, NO_2CH , 3J 5.8 Hz), 6.87, 7.33 (2d, 4H, H in MeOAr, 3J 8.4 Hz), 7.55 [t, 1H, C(5)H in NO_2Ar , 3J 8.0 Hz], 7.83 [d, 1H, C(4)H in NO_2Ar , 3J 8.0 Hz], 8.16 [d, 1H, C(6)H in NO_2Ar , 3J 8.0 Hz], 8.45 [s, 1H, C(2)H in NO_2Ar]. ^{13}C NMR (CDCl_3) δ : 23.90 (NCH_2CH_2), 50.23 (MeOArCNCH_2), 51.26 ($\text{NO}_2\text{ArCNCH}_2$), 55.22 (MeOAr), 70.43 ($\text{NO}_2\text{ArC}_{\text{ring}}$), 71.53

(MeOArC_{ring}), 102.79 (NO₂C_{ring}), 114.36, 128.57, 129.70, 159.82 (MeOAr), 122.21, 122.95, 129.84, 133.10, 142.72, 148.65 (NO₂Ar). ¹⁵N NMR (CDCl₃) δ: +5.6 (NO₂C_{ring}H), -10.4 (NO₂Ar), -247.3 (MeOArCN), -250.1 (NO₂ArCN). MS, *m/z* (%): 384 (M, 7), 308 (M - NO₂ - Me, 38), 277 (M - MeOC₆H₄, 12), 190 [MeO-C₆H₄CHN₂(CH₂)₃, 40], 194 [NO₂C₆H₄(CH)₂NO₂, 24], 88 (C₆H₄C, 100), 76 (C₆H₄, 54).

1-(4-Ethoxyphenyl)-2-nitro-3-(3-nitrophenyl)tetrahydro-1H,5H-pyrazolo[1,2-a]pyrazole 7d: *R*_f 0.60, mp 140 °C (decomp.). ¹H NMR (CDCl₃) δ: 1.40 (t, 3H, MeCH₂O), 2.17, 2.41 (2m, 2H, CH₂CH₂CH₂), 3.07, 3.28 (td, m, 2H, EtOArCNCH₂, ²*J* 9.6 Hz, ³*J* 4.6 Hz), 3.28, 3.40 (m, td, 2H, NO₂ArCNCH₂, ²*J* 9.8 Hz, ³*J* 4.7 Hz), 4.02 (q, 2H, MeCH₂O), 4.66 (d, 1H, EtOArCH, ³*J* 6.8 Hz), 4.91 (d, 1H, NO₂ArCH, ³*J* 5.0 Hz), 4.98 (t, 1H, NO₂CH, ³*J* 5.7 Hz), 6.87, 7.31 (2d, 4H, H in EtOAr, ³*J* 8.5 Hz), 7.56 [t, 1H, C(5)H in NO₂Ar, ³*J* 8.0 Hz], 7.84 [d, 1H, C(4)H in NO₂Ar, ³*J* 8.0 Hz], 8.17 [d, 1H, C(6)H in NO₂Ar, ³*J* 8.0 Hz], 8.45 [s, 1H, C(2)H in NO₂Ar]. ¹³C NMR (CDCl₃) δ: 22.10 (CH₃CH₂OAr), 23.93 (NCH₂CH₂), 50.23 (EtOArCNCH₂), 51.28 (NO₂ArCNCH₂), 63.47 (MeCH₂OAr), 70.48 (NO₂ArC_{ring}), 71.58 (EtOArC_{ring}), 102.85 (NO₂C_{ring}), 114.70, 128.36, 129.53, 159.21 (EtOAr), 122.23, 122.95, 129.84, 133.09, 142.78, 148.69 (NO₂Ar). ¹⁵N NMR (CDCl₃) δ: +6.8 (NO₂C_{ring}H), -9.7 (NO₂Ar), -249.29 (MeOArCN), -251.55 (NO₂ArCN). IR (ν/cm⁻¹): 644, 688, 740, 808, 828, 916, 1036, 1180, 1252, 1344, 1456, 1488, 1524, 1608, 1652, 1684, 2856, 2924, 2980, 3080. MS, *m/z* (%): 398 (M, 4), 322 (M - C₆H₄, M - NO₂ - Et, 45), 264 (M - 2NO₂ - EtO, 7), 231 (M - EtO - C₆H₄ - NO₂, 10), 204 [EtOC₆H₄CHN₂(CH₂)₃, 45], 194 [NO₂C₆H₄(CH)₂NO₂, 38], 89 (C₆H₄CH, 100), 76 (C₆H₄, 67).

1-(4-Methylphenyl)-2-nitro-3-phenyltetrahydro-1H,5H-pyrazolo[1,2-a]pyrazole 7e: nondistilled oil, *R*_f 0.54. ¹H NMR (CDCl₃) δ: 2.16, 2.38 (2m, 2H, CH₂CH₂CH₂, Δν 41.42 Hz), 2.36 (s, 3H, ArMe), 3.24, 3.34 (2m, 4H, NCH₂, ³*J* 5.38 Hz, Δν 20.02 Hz), 4.71 (d, 1H, MeArCH, ³*J* 6.35 Hz), 4.77 (d, 1H, ArCH, ³*J* 5.86 Hz), 5.08 (t, 1H, NO₂CH, ³*J* 5.86 Hz), 7.19, 7.37 (2d, 4H, H in MeAr, ³*J* 7.81 Hz), 7.37, 7.50 (2m, 5H, H in Ph). ¹³C NMR (CDCl₃) δ: 21.19 (MeAr), 23.97 (NCH₂CH₂), 50.84 (MeArCNCH₂), 51.10 (ArCNCH₂), 71.94 (MeArC_{ring} and ArC_{ring}), 103.44 (NO₂C_{ring}), 127.25, 129.64, 136.13, 138.14 (MeAr), 127.25, 128.26, 128.97, 139.66 (Ph). MS, *m/z* (%): 174

[MeC₆H₄CHN₂(CH₂)₃, 25], 160 (M – MeC₆H₄CH – – NO₂CH, 6), 149 [Ph(CH)₂NO₂, 5], 111 (M – C₆H₄Me – NO₂ – Ph, 7), 105 (MeC₆H₄CH, 100), 91 (MeC₆H₄, 45), 77 (Ph, 40), 69 [N₂(CH₂)₃ + H, 45], 43 [(CH₂)₃ – H, 60]. IR (ν/cm⁻¹): 668, 700, 812, 840, 1044, 1160, 1232, 1288, 1356, 1456, 1552, 1616, 1684, 1740, 2852, 2924, 2960, 3028.

1-(4-Ethoxyphenyl)-2-nitro-3-phenyltetrahydro-1H,5H-pyrazolo[1,2-a]pyrazole
7g: R_f 0.58, mp 101 °C (decomp.). ¹H NMR (CDCl₃) δ: 1.42 (t, 3H, MeCH₂O, ³J 6.83 Hz), 2.13, 2.37 (2m, 2H, CH₂CH₂CH₂, Δν 48.84 Hz), 3.27 (m, 4H, NCH₂), 4.35 (q, 2H, MeCH₂O, ³J 7.32 Hz), 4.68 (d, 1H, EtOArCH, ³J 6.35 Hz), 4.77 (d, 1H, ArCH, ³J 5.37 Hz), 5.07 (t, 1H, NO₂CH, ³J 6.35 Hz), 6.90, 7.37 (2d, 4H, H in EtOAr, ³J 8.3 Hz), 7.37, 7.52 (2m, 5H, H_{Ph}, ³J 6.35 Hz). ¹³C NMR (CDCl₃) δ: 14.84 (MeCH₂OAr), 23.97 (NCH₂CH₂), 50.71 (MeArCNCH₂), 51.13 (ArCNCH₂), 63.50 (MeCH₂OAr), 71.78 (MeArC_{ring}), 71.86 (ArC_{ring}), 103.53 (NO₂C_{ring}), 114.89, 127.22, 130.94, 158.92 (EtOAr), 128.20, 128.55, 128.97, 139.87 (Ph). IR (ν/cm⁻¹): 668, 772, 1044, 1188, 1248, 1264, 1300, 1396, 1496, 1612, 1652, 1684, 2884, 2932, 2980, 3132.

5-(4-Methylphenyl)-6-(3-nitrophenyl)-2,3-dihydro-1H-pyrazolo[1,2-a]pyrazol-4-ium tetrafluoroborate **8b**: mp 212.5–213.0 °C. ¹H NMR ([²H₆]DMSO) δ: 2.40 (s, 3H, ArMe), 2.92 (m, 2H, CH₂CH₂CH₂), 4.54 (t, 2H, MeAr-CNCH₂, ³J 7.2 Hz), 4.68 (t, 2H, NO₂ArCNCH₂, ³J 7.2 Hz), 7.41, 7.44 (2d, 4H, H in MeAr, ³J 8.0 Hz), 7.68 [d, 1H, C(6)H in NO₂Ar, ³J 8.0 Hz], 7.70 [t, 1H, C(5)H in NO₂Ar, ³J 8.0 Hz], 8.14 [s, 1H, C(2)H in NO₂Ar], 8.22 [d, 1H, C(4)H in NO₂Ar, ³J 8.0 Hz], 9.01 (s, 1H, NO₂ArCH). ¹³C NMR ([²H₆]DMSO) δ: 20.99 (MeAr), 26.25 (NCH₂CH₂), 48.33 (MeArCNCH₂), 49.31 (CHNCH₂), 122.56 (NO₂ArC_{ring}), 130.11 (NC_{ring}), 139.64 (MeArC_{ring}), 121.88, 129.04, 130.14, 141.26 (MeAr), 122.52, 123.09, 130.67, 130.84, 134.31, 148.09 (NO₂Ar). ¹⁵N NMR ([²H₆]DMSO) δ: –11.3 (NO₂Ar), –167.3 (MeArCN), –168.3 (CHN). IR (ν/cm⁻¹): 688, 748, 824, 852, 1052, 1192, 1348, 1524, 1552, 1580, 1616, 2984, 3072, 3092, 3144.

5-(4-Ethoxyphenyl)-6-(3-nitrophenyl)-2,3-dihydro-1H-pyrazolo[1,2-a]pyrazol-4-ium tetrafluoroborate **8d**: mp 194.5–195.0 °C. ¹H NMR ([²H₆]DMSO) δ: 1.46 (t, 3H, ArOCH₂Me) 2.90 (m, 2H, CH₂CH₂CH₂), 4.11 (q, 2H, ArOCH₂Me), 4.53 (t, 2H,

MeArCNCH₂, ³J 7.2 Hz), 4.67 (t, 2H, NO₂ArCNCH₂, ³J 7.2 Hz), 7.12, 7.45 (2d, 4H, H in EtOAr, ³J 8.6 Hz), 7.69 [m, 2H, C(5)H, C(6)H in NO₂Ar], 8.13 [s, 1H, C(2)H in NO₂Ar], 8.22 [d, 1H, C(4)H in NO₂Ar, ³J 7.1 Hz], 9.00 (s, 1H, NO₂ArCH). ¹³C NMR ([²H₆]DMSO) δ: 14.41 (MeCH₂OAr), 26.20 (NCH₂CH₂), 48.18 (MeOArCNCH₂), 49.19 (CHNCH₂), 63.46 (MeCH₂OAr), 122.29 (NO₂ArC_{ring}), 130.05 (NC_{ring}), 139.54 (MeOArC_{ring}), 115.44, 116.40, 130.75, 160.50 (EtOAr), 122.42, 123.01, 130.65, 130.91, 134.24, 148.06 (NO₂Ar). ¹⁵N NMR ([²H₆]DMSO) δ: -8.7 (NO₂Ar), -166.5 (MeArCN), -168.6 (CHN). IR (ν/cm⁻¹): 688, 738, 1076, 1190, 1250, 1305, 1346, 1442, 1522, 1614, 2876, 2964, 3080, 3146.