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Diaziridine ring expansion in 6-aryl-1,5-diazabicylo[3.1.0]hexanes on treatment with nitriles assisted by ionic liquids

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Experimental data

*Ethyl 1-(4-ethoxyphenyl)-6,7-dihydro-1*H,5H*-pyrazolo[1,2-*a*][1,2,4]triazole-3-carboxylate* **5a**: nondistilled oil, R_f 0.43. ^{1}H NMR ($CDCl_3$) δ: 1.24 (t, 3H, C*H*$_3$CH$_2$OAr, ^3J 7.12 Hz); 1.34 (t, 3H, C*H*$_3$CH$_2$OCO, ^3J 7.02 Hz); 1.93, 2.30 (2m, 2H, C*H*$_2$CH$_2$N=N, ^2J 10.50 Hz, Δν 181.97 Hz); 2.93, 3.05 (2m, 2H, C*H*$_2$NC=N, ^2J 13.60, Δν 60 Hz); 3.66, 3.71 (2m, 2H, C*H*$_2$N–N, ^2J 12.10 Hz, Δν 25 Hz); 3.97 (q, 2H, CH$_3$C*H*$_2$OAr, ^3J 7.12 Hz); 4.14 (q, 2H, CH$_3$C*H*$_2$OCO, ^3J 7.02 Hz); 5.24 (s, 1H, ArC*H*N); 6.84, 7.42 (2d, 4H in Ar, ^3J 8.70 Hz). ^{13}C NMR ($CDCl_3$) δ: 15.00 (*C*H$_3$CH$_2$OAr); 15.11 (*C*H$_3$CH$_2$OCO); 25.37 (CH$_2$*C*H$_2$CH$_2$); 46.63 (*C*H$_2$N–N); 49.94 (*C*H$_2$NC=N); 60.84 (Ar*C*HN); 62.44 (ArO*C*H$_2$); 63.96 (COO*C*H$_2$); 114.76, 118.67, 129.62, 146.57 (Ar); 156.22 (NC=N); 159.72 (OC=O). MS, m/z (I%): 204 (M - EtOCOC≡N, 5), 134 (M - EtOCOC≡N – pyrazolidine, 30), 99 (EtOCOC≡N, 10), 76 (C_6H_4, 15), 71 (pyrazolidine, 100).

*Ethyl 1-(4-isopropoxyphenyl)-6,7-dihydro-1*H,5H*-pyrazolo[1,2-*a*][1,2,4]triazole-3-carboxylate* **5b**: nondistilled oil, R_f 0.51. ^{1}H NMR ($CDCl_3$) δ: 1.31 (d, 6H, *Me*$_2$CHOAr, ^3J 7.41 Hz), 2.57 (m, 1H, NCH$_2$C*H*, ^2J 11.11 Hz), 3.05 (m, 3H, NCH$_2$C*H*, ^2J 11.11 Hz, CH$_2$NC=N, ^2J 14.06 Hz, Δν 88.89 Hz), 4.53 (m, 3H, C*H*$_2$N–N, ^2J 8.88 Hz, Me$_2$C*H*OAr, ^3J 7.41 Hz), 5.62 (s, 1H, ArC*H*N), 6.89, 7.48 (2d, 4H in Ar, ^3J 8.16 Hz). ^{13}C NMR ($CDCl_3$) δ: 22.03 (*Me*$_2$CHOAr), 22.12 (Me*C*H$_2$OCO), 34.68 (CH$_2$*C*H$_2$CH$_2$), 36.17 (CH$_2$N–N), 49.71 (br., *C*H$_2$NC=N), 49.78 (COO*C*H$_2$), 60.18 (Ar*C*HN), 61.87 (ArO*C*HMe$_2$), 116.02, 124.26, 129.93, 135.50 (Ar), 157.10 (NC=N), 158.73 (OC=O).

*Ethyl 1-(4-methylphenyl)-6,7-dihydro-1*H,5H*-pyrazolo[1,2-*a*][1,2,4]triazole-3-carboxylate* **5d**: nondistilled oil, R_f 0.38. ^{1}H NMR ($CDCl_3$) δ: 1.23 (t, 3H, COOCH$_2$C*H*$_3$, ^3J 7.14 Hz), 2.02, 2.29 (2m, 2H, NCH$_2$C*H*$_2$, Δν 73.37 Hz), 2.38 (s, 3H, C*H*$_3$Ar), 3.02 (m, 2H, C*H*$_2$NC=N, ^2J 8.04 Hz), 3.73 (m, 2H, C*H*$_2$N–N, ^2J 7.34 Hz), 4.05 (q, 2H, COOC*H*$_2$CH$_3$, ^3J 7.14 Hz), 5.28 (s, 1H, ArC*H*N), 7.13, 7.41 (2d, 4H in Ar, ^3J 8.69 Hz). ^{13}C NMR ($CDCl_3$) δ: 14.25 (*C*H$_3$CH$_2$OCO); 20.96 (*C*H$_3$Ar); 25.04 (CH$_2$*C*H$_2$CH$_2$); 46.22 (*C*H$_2$N–N); 49.50 (*C*H$_2$NC=N); 60.74 (Ar*C*HN); 61.93 (CH$_3$*C*H$_2$OCO); 118.34, 128.19, 129.50, 146.18 (Ar); 155.96 (NC=N); 158.50 (OC=O).

*1-(4-Ethoxyphenyl)-3-(trichloromethyl)-6,7-dihydro-1*H,5H*-pyrazolo[1,2-a][1,2,4]triazole* **5e**: R_f 0.67, mp 100.5-101.0ºC. ^{1}H NMR ($CDCl_3$) δ: 1.38 (t, 3H, C*H*$_3$CH$_2$OAr, ^3J 7.41 Hz), 2.18 (m, 2H, C*H*$_2$CH$_2$N, ^2J 9.16 Hz), 2.69, 3.05 (2m, 2H, C*H*$_2$NC=N, , ^2J 9.97 Hz, Δν 74.97 Hz), 3.73, 4.09 (2m, 2H, C*H*$_2$N–N, Δν 79.31 Hz), 4.06 (q, 2H, CH$_3$C*H*$_2$OAr, ^3J 7.41 Hz), 5.99 (s, 1H, ArC*H*N), 6.91, 7.40 (2d, 4H in Ar, ^3J 8.33 Hz). ^{13}C NMR ($CDCl_3$) δ: 14.86 (*C*H$_3$CH$_2$OAr); 24.86 (CH$_2$*C*H$_2$CH$_2$); 47.23 (*C*H$_2$N–N); 50.08 (br., *C*H$_2$NC=N); 63.52

(CH_3CH_2OAr); 87.46 (Ar*C*HN); 88.82 (CCl_3); 114.58, 121.84, 128.13, 159.04 (Ar); 162.58 (NC=N). MS, m/z (I%): 348 (M, 20), 278 (M – pyrazolidine, 12), 230 (M – CCl_3, 12), 160 (M – (pyrazolidine + CCl_3), 100), 131 (M – (pyrazolidine + CCl_3 + Et), 65), 76 (C_6H_4, 57), 71 (pyrazolidine, 5).

*1-(4-Isopropoxyphenyl)-3-(trichloromethyl)-6,7-dihydro-1*H,*5*H-*pyrazolo[1,2-a][1,2,4]triazole* **5f**: R_f 0.73, m.p. 105.0-105.5ºC. ^{1}H NMR ($CDCl_3$) δ: 1.31 (d, 6H, (CH_3)$_2$CHOAr, ^3J 8.33 Hz), 2.18 (m, 2H, CH_2CH_2N, ^2J 10.00 Hz), 2.69, 3.05 (2br.m, 2H, CH_2NC=N, Δν 81.63 Hz), 3.71, 4.10 (2br.m, 2H, CH_2N–N, Δν 87.46 Hz), 4.56 (m, 1H, (CH_3)$_2$C*H*OAr, ^3J 8.33 Hz), 5.95 (s, 1H, ArC*H*N), 6.89, 7.39 (2d, 4H in Ar, ^3J 8.30 Hz). ^{13}C NMR ($CDCl_3$) δ: 22.03 ((CH_3)$_2$CHOAr); 24.78 ($CH_2CH_2CH_2$); 47.29 (br., CH_2N–N); 49.85 (br., CH_2NC=N); 69.85 (ArO*C*H(CH_3)$_2$); 87.49 (Ar*C*HN); 88.02 (CCl_3); 115.86, 128.13, 157.98 (Ar); 162.96 (NC=N). MS, m/z (I%): 362 (M, 44), 292 (M – pyrazolidine, 10), 249 (M – (pyrazolidine + Pr^i), 47), 227 (M - Pr^{i}OC_6H_4, 50), 135 (Pr^{i}OC_6H_4, 85), 76 (C_6H_4, 30), 71 (pyrazolidine, 10), 43 (Pr^i, 100).

Intermediate **6e**: R_f 0.52. ^{1}H NMR ($CDCl_3$) δ: 7.01, 7.84 (2d, 4H in Ar, ^3J 8.33 Hz); 9.88 (s, 1H, ArC*H*N).

Intermediate **6f**: R_f 0.60 [*n*-hexane-ethyl acetate, 2:1 (v/v)]. ^{1}H NMR ($CDCl_3$) δ: 7.20, 7.83 (2d, 4H in Ar, ^3J 8.33 Hz); 9.88 (s, 1H, ArC*H*N). ^{13}C NMR ($CDCl_3$) δ: 21.88 ((CH_3)$_2$CHOAr), 70.30 (ArO*C*H(CH_3)$_2$), 115.57, 132.04 (Ar), 162.50 (NC=N), 190.87 (Ar*C*HN).