

Insertion of carbon disulfide into the diaziridine ring of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes assisted by ionic liquids

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Experimental

3-(4-Ethoxyphenyl)dihydro-5H-pyrazolo[1,2-c][1,3,4]thiadiazole-1-thione 5b: R_f 0.71 [*n*-hexane–ethyl acetate, 2:1 (v/v)], mp 118.0–118.5 °C. $^1\text{H NMR}$ (CDCl_3) δ : 1.42 (t, 3H, Me, 3J 6.7 Hz), 2.55 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$, 2J 9.8 Hz, 3J 4.7 Hz), 2.75, 3.15 (2m, 2H, ArCNCH_2 , 2J 9.9 Hz, 3J 4.7 Hz, $\Delta\nu$ 156.0 Hz), 3.78, 3.93 (2m, 2H, SCNCH_2 , 2J 9.8 Hz, 3J 4.7 Hz, $\Delta\nu$ 60.1 Hz), 4.05 (q, 2H, OCH_2 , 3J 6.7 Hz), 5.75 (s, 1H, ArCH), 6.80, 7.50 (2d, 4H, H in Ar, 3J 10.1 Hz). $^{13}\text{C NMR}$ (CDCl_3) δ : 14.81 (OCC), 27.67 (CCC), 45.82 (SCNCC), 51.34 (ArCNCC), 63.68 (ArOC), 74.82 (ArC_{ring}), 114.88, 125.73, 129.28, 160.13 (Ar), 180.34 (C=S). IR (ν/cm^{-1}): 1052, 1124, 1172, 1336, 1448, 1516, 1612. MS, m/z (%): 280 (M, 29), 203 (M – CS_2 -H, 100), 175 (M – CS_2 - MeH – H, 12), 76 (CS_2 , C_6H_4 , 62).

3-(4-Isopropoxyphenyl)dihydro-5H-pyrazolo[1,2-c][1,3,4]thiadiazole-1-thione 5c: R_f 0.71 [*n*-hexane–ethyl acetate, 2:1 (v/v)], mp 60.0–60.5 °C. $^1\text{H NMR}$ (CDCl_3): 1.35 (d, 6H, OCMe_2 , 3J 6.1 Hz), 2.55 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$, 2J 9.7 Hz), 2.75, 3.15 (2m, 2H, ArCNCH_2 , 2J 9.8 Hz, 3J 4.4 Hz, $\Delta\nu$ 74.7 Hz), 3.78, 3.93 (2m, 2H, SCNCH_2 , 2J 10.6 Hz, 3J 4.4 Hz, $\Delta\nu$ 28.3 Hz), 4.55 (m, 1H, OCHMe_2 , 3J 6.1 Hz), 5.75 (s, 1H, SCH), 6.80, 7.50 (2d, 4H, H in Ar, 3J 8.7 Hz). $^{13}\text{C NMR}$ (CDCl_3) δ : 22.01 (OCMe), 27.68 (CCC), 45.80 (SCNCC), 51.36 (ArCNCC), 70.04 (ArOC), 74.83 (ArC_{ring}), 115.99, 125.49, 129.28, 159.09 (Ar), 180.07 (C=S). IR (ν/cm^{-1}): 1052, 1124, 1180, 1376, 1448, 1508, 1608. MS, m/z (%): 294 (M, 32), 218 (M – CS_2 , 63), 175 (M – CS_2 - Pr^1 , 100), 107 [M – CS_2 - Pr^1 - $\text{N}_2\text{C}_3\text{H}_4$ (ring), 65], 76 (CS_2 , C_6H_4 , 90), 41 (Pr^1 , 70).

3-(4-Chlorophenyl)dihydro-5H-pyrazolo[1,2-c][1,3,4]thiadiazole-1-thione 5e: R_f 0.74 [*n*-hexane–ethyl acetate, 2:1 (v/v)]. $^1\text{H NMR}$ (CDCl_3) δ : 2.55 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$, 2J 9.2 Hz), 2.75, 3.15 (2m, 2H, ArCNCH_2 , 2J 10.3 Hz, 3J 4.2 Hz, $\Delta\nu$ 65.3 Hz), 3.78, 3.93 (2m, 2H, SCNCH_2 , 2J 10.4 Hz, 3J 4.7 Hz, $\Delta\nu$ 53.1 Hz), 5.75 (s, 1H, SCH), 6.80, 7.50 (2d, 4H, H in Ar, 3J 8.1 Hz). $^{13}\text{C NMR}$ (CDCl_3) δ : 27.53 (CCC), 45.79 (SCNCC), 51.24 (ArCNCC), 74.50 (ArC_{ring}), 131.25, 134.80, 135.30, 161.10 (Ar), 181.15 (C=S).

6-Ethoxyphenyl-1,5-diazabicyclo[3.1.0]hexane 8b: yield 86%, R_f 0.47 (5% NH_3 in CHCl_3), mp 105.5–106.0 °C. ^1H NMR (CDCl_3) δ : 1.40 (t, 3H, OCH_2Me , 3J 6.7 Hz), 1.88 (m, 2H, NCH_2CH_2 , 2J 9.9 Hz, 3J 4.2 Hz), 3.05 (s, 1H, ArCH), 3.14, 3.57 (2m, 4H, NCH_2 , 2J 9.9 Hz, 3J 4.3 Hz), 4.03 (q, 2H, OCH_2 , 3J 6.7 Hz), 6.83, 7.23 (2d, 4H, Ar, 3J 7.0 Hz). ^{13}C NMR (CDCl_3) δ : 14.94 (OCH_2Me), 21.90 (NCH_2CH_2), 52.30 (2 NCH_2), 56.56 (ArC_{ring}), 63.51 (OCH_2), 114.42, 128.44, 128.96, 159.35 (C_{Ar}). IR (ν/cm^{-1}): 812, 972, 1048, 1176, 1248, 1312, 1520, 1616, 1920, 2880, 2948, 2976, 3044. MS, m/z (%): 204 (M, 35), 203 (M – H, 100), 175 (M – H – MeCH, 100), 105 [M – H – MeCH – NN(CH_2) $_3$ (ring), 15], 76 (C_6H_4 , 20).

6-Isopropoxyphenyl-1,5-diazabicyclo[3.1.0]hexane 8c: yield 96%, R_f 0.46 (5% NH_3 in CHCl_3), mp 107.0–107.5 °C. ^1H NMR (CDCl_3) δ : 1.32 (d, 6H, OCHMe_2 , 3J 7.8 Hz), 1.87 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$, 2J 8.0 Hz, 3J 4.1 Hz), 3.02 (s, 1H, $\text{ArC}_{\text{ring}}\text{H}$), 3.12, 3.55 (2m, 4H, NCH_2 , 2J 8.0 Hz, 3J 4.2 Hz), 4.51 (m, 1H, OCHMe_2 , 3J 7.8 Hz), 6.81, 7.21 (2d, 4H, Ar, 3J 9.3 Hz). ^{13}C NMR (CDCl_3) δ : 21.82 ($\text{CH}_2\text{CH}_2\text{CH}_2$), 22.10 (2 OCHMe_2), 52.22 (2 NCH_2), 56.45 (OCH), 69.80 (ArC_{ring}), 115.82, 128.45, 128.91, 158.28 (C_{Ar}). IR (ν/cm^{-1}): 812, 956, 976, 1104, 1120, 1172, 1184, 1244, 1252, 1308, 1384, 1516, 1616, 1916, 2876, 2932, 2876, 3048. MS, m/z (%): 218 (M, 20), 175 (M – CHMe_2 , 100), 107 [M – CHMe_2 – NN(CH_2) $_3$ (ring), 25], 76 (C_6H_4 , 20).