

Nitraminofurazans in aza-Michael reactions

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Experimental

N-(4-Nitrofurazan-3-yl)-*N*-(3-oxopropyl)nitramide **2a**: 73%, viscous oil, R_f 0.6 (CH₂Cl₂–C₅H₁₂, 5:1). IR (NaCl, ν/cm^{-1}): 2980, 2856, 1732, 1700, 1588, 1548, 1436, 1372, 1284, 1216, 1112, 1092, 1032, 828. ¹H NMR (CDCl₃) δ : 3.19 (t, 2H, CH₂CO, J 5.6 Hz), 4.50 (t, 2H, CH₂N, J 5.6 Hz), 9.72 (s, 1H, O=CH). ¹³C NMR (CDCl₃) δ : 40.9 (CH₂CHO), 47.4 (CH₂N), 147.2 (CNNO₂), 155.8 (t, C–NO₂, $^1J_{14\text{N},13\text{C}}$ 19 Hz), 199.2 (C=O). ¹⁴N NMR (CDCl₃) δ : –39.0 (C–NO₂, $\nu_{1/2}$ 16 Hz), –42.9 (N–NO₂, $\nu_{1/2}$ 31 Hz). Found (%): C, 26.06; H, 2.26; N, 30.23. Calc. for C₅H₅N₅O₆ (%): C, 25.98; H, 2.18; N, 30.30.

N-(4-Hydroxy-3-oxobutyl)-*N*-(4-nitrofurazan-3-yl)nitramide **2c**: 64%, mp 79–80 °C (CCl₄), R_f 0.3 (CH₂Cl₂). IR (KBr, ν/cm^{-1}) 3496, 3028, 2912, 1712, 1592, 1568, 1544, 1436, 1376, 1292, 1260, 1092, 1048, 1032, 972, 828. ¹H NMR (CDCl₃) δ : 3.13 (t, 2H, CH₂CH₂CO, J 6.5 Hz), 4.30 (s, 2H, HOCH₂CO), 4.57 (t, 2H, CH₂N, J 6.5 Hz). ¹³C NMR (CDCl₃) δ : 35.7 (CH₂CH₂CO), 48.1 (CH₂N), 68.1 (CH₂OH), 147.2 (CNNO₂), 155.7 (t, C–NO₂, $^1J_{14\text{N},13\text{C}}$ 19.8 Hz), 207.7 (C=O). ¹⁴N NMR (CDCl₃) δ : –39.1 (C–NO₂, $\nu_{1/2}$ 14.4 Hz), –43.2 (N–NO₂, $\nu_{1/2}$ 32.2 Hz). Found (%): C, 27.56; H, 2.74; N, 26.75. Calc. for C₆H₇N₅O₆ (%): C, 27.60; H, 2.70; N, 26.82.

Ethyl 3-[*N*-nitro-*N*-(4-nitrofurazan-3-yl)amino]propanoate **2d**: 12%, viscous oil, R_f 0.25 (CH₂Cl₂–C₅H₁₂, 2:1). ¹H NMR (CDCl₃) δ : 1.23 (t, 3H, Me, J 7.1 Hz), 2.95 (t, 2H, CH₂CH₂CO, J 5.55 Hz), 4.06 (s, 2H, CH₂Me, J 7.1 Hz), 4.51 (t, 2H, CH₂N, J 5.45 Hz). ¹³C NMR (CDCl₃) δ : 14.1 (Me), 31.8 (CH₂C=O), 49.7 (CH₂N), 61.7 (CH₂O), 147.5 (CNNO₂), 156.1 (t, C–NO₂, $^1J_{14\text{N},13\text{C}}$ 19 Hz), 171.2 (C=O). ¹⁴N NMR (CDCl₃) δ : –38.9 (C–NO₂, $\nu_{1/2}$ 26 Hz), –42.8 (N–NO₂, $\nu_{1/2}$ 25 Hz). Found (%): C, 30.64; H, 3.37; N, 25.39. Calc. for C₇H₉N₅O₇ (%): C, 30.55; H, 3.30; N, 25.45.

3-[*N*-Nitro-*N*-(4-nitrofurazan-3-yl)amino]propanoic acid **5**: mp 143–144 °C (PrⁱOH), R_f 0.5 (CCl₄–MeCN, 3:1). IR (KBr, ν/cm^{-1}): 3150–3050, 1708, 1592, 1576, 1548, 1496, 1440, 1400, 1364, 1312, 1284, 1248, 1224, 1108, 1080, 1036, 996, 956. ¹H NMR (DMSO-*d*₆) δ : 2.82 (br., 2H, CH₂CH₂CO), 4.41 (br., 2H, CH₂N). ¹³C NMR

(DMSO- d_6) δ : 31.4 (CH₂C=O), 49.5 (CH₂N), 147.0 (CNNO₂), 156.3 (C–NO₂), 172.2 (C=O). ¹⁴N NMR (DMSO- d_6 -CDCl₃) δ : –37.2 (C–NO₂, $\nu_{1/2}$ 17 Hz), –39.8 (N–NO₂, $\nu_{1/2}$ 24 Hz). MS, m/z (%): 230 (1) [M – OH]⁺, 201 [M – NO₂]⁺, 183 (10), 156 (8), 138 (6), 125 (14), 73 (83), 46 (100). Found (%): C, 24.37; H, 2.06; N, 28.29. Calc. for C₅H₅N₅O₇ (%): C, 24.30; H, 2.04; N, 28.34.

N-[3-(2,4-Dinitrophenylhydrazono)propyl]-N-(4-nitrofurazan-3-yl)nitramide **6a**: mp 92–94 °C (CCl₄), R_f 0.6 (CH₂Cl₂–CCl₄, 1:1). Found (%): C, 32.22; H, 2.30; N, 30.56. Calc. for C₁₁H₉N₉O₉ (%): C, 32.13; H, 2.21; N, 30.65.

N-[3-(2,4-Dinitrophenylhydrazono)butyl]-N-(4-nitrofurazan-3-yl)nitramide **6b**: mp 133–134 °C, R_f 0.7 (CH₂Cl₂). IR (KBr, ν/cm^{-1}): 3316, 3104, 1620, 1592, 1544, 1516, 1504, 1424, 1340, 1312, 1284, 1224, 1140, 1108, 1060, 924. Found (%): C, 33.98; H, 2.57; N, 29.54. Calc. for C₁₂H₁₁N₉O₉ (%): C, 33.89; H, 2.61; N, 29.64.