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Ketenimine N-fuctionalization of thiazolidine-2,4-diones with acetylenes and isocyanides

Issa Yavari,* Tayebeh Sanaeishoar, Leila Azad and Maryam Ghazvini

Experimental

Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid Analyzer. The results agreed favorably with the calculated values. The IR spectra were measured on a Shimadzu IR-460 instrument at 400–4000 cm^{-1} (in a KBr tablet). ^1H and ^{13}C NMR spectra ($CDCl_3$) were measured with a Bruker Avance DRX-300 spectrometer at 300 and 75 MHz, respectively. Mass spectra were recorded on a FINNIGAN-MAT 8430 spectrometer operating at an ionization potential of 70 eV.

For **4b**: Pale yellow oil, yield: 0.35 g (88%). IR (ν_{max}/cm^{-1}): 2082 (C=C=N), 1734 and 1705 (C=O). ^1H NMR, δ: 1.26 (3 H, t, ^3J 7.2 Hz, Me), 1.29 (3 H, t, ^3J 7.2 Hz, Me), 1.33-1.99 (10 H, m, 5 CH_2), 3.99 (2 H, s, CH_2S), 4.14 (1 H, m, CHN), 4.18 (2 H, q, ^3J 7.2 Hz, CH_2O), 4.25 (2 H, q, ^3J 7.2 Hz, CH_2O), 5.98 (1 H, s, CH). ^{13}C NMR, δ: 14.5 (Me), 14.8 (Me), 24.1 (CH_2), 24.2 (CH_2), 25.7 (CH_2), 24.2 (CH_2), 33.3 (CH_2), 33.4 (CH_2), 34.3 (CH_2S), 53.3 (CHN), 58.2 (CH_2O), 60.8 (CH_2O), 60.9 (CH), 62.9 (C=C=N), 160.4, 166.5, 170.0, 170.3 and 171.0 (C=*C*=N and 4 C=O). Found (%): C, 54.8; H, 6.2; N, 7.2. Calc. for $C_{18}H_{24}N_2O_6S$ (%): C, 54.53; H, 6.10; N, 7.07.

For **4c**: Pale yellow oil, yield: 0.36 g (90%). IR (ν_{max}/cm^{-1}): 2081 (C=C=N), 1747 and 1702 (C=O). ^1H NMR, δ: 1.06 (9 H, s, 3 Me), 1.55 (3 H, s, Me), 1.57 (3 H, s, Me), 1.67 (2 H, s, CH_2), 3.71 (3 H, s, MeO), 3.76 (3 H, s, MeO), 4.00 (2 H, s, CH_2S), 5.99 (1 H, s, CH). ^{13}C NMR, δ: 30.1 (C*Me*$_2$), 32.1 (C*Me*$_3$), 34.1 (*C*Me$_3$), 35.9 (CH_2S), 52.0 (*C*Me$_2$), 53.2 (MeO), 53.7 (MeO), 54.7 (CH_2), 58.3 (CH), 65.6 (C=C=N), 160.1, 167.5, 170.1, 170.5 and 171.0 (C=*C*=N and 4 C=O). Anal. Calcd for $C_{18}H_{26}N_2O_6S$ (398.4): C, 54.26; H, 6.58; N, 7.03%; found: C, 54.5; H, 6.4; N, 7.1%.

For **4d**: Pale yellow oil, yield: 0.36 g (88%). IR (ν_{max}/cm^{-1}): 2080 (C=C=N), 1730 and 1700 (C=O). ^{1}H NMR, δ: 1.07 (9 H, s, 3 Me), 1.25 (3 H, t, ^3J 7.2 Hz, Me), 1.27 (3 H, t, ^3J 7.2 Hz, Me), 1.56 (3 H, s, Me), 1.57 (3 H, s, Me), 1.67 (2 H, s, CH_2), 4.00 (2 H , s, CH_2S), 4.18 (2 H, q, ^3J 7.2 Hz, CH_2O), 4.24 (2 H, q, ^3J 7.2 Hz, CH_2O), 5.97 (1 H, s, CH). ^{13}C NMR, δ: 14.5 (Me), 14.8 (Me), 31.4 (C*Me*$_2$), 31.5 (C*Me*$_3$), 32.1 (*C*Me$_3$), 34.0 (CH_2S), 53.4 (*C*Me$_2$), 54.8 (CH_2), 58.8 (CH), 60.7 (CH_2O), 62.9 (CH_2O), 65.5 (C=C=N), 160.3, 163.9, 170.1, 170.4 and 171.0 (C=*C*=N and 4 C=O). Found (%): C, 56.0; H, 7.2; N, 6.5. Calc. for $C_{20}H_{30}N_2O_6S$ (%): C, 56.32; H, 7.09; N, 6.57.

For **4e**: Pale yellow oil, yield: 0.40 g (88%). IR (KBr) (ν_{max}/cm^{-1}): 2082 (C=C=N), 1747 and 1969 (C=O). ^{1}H NMR: δ_H = 1.20-2.06 (10 H, m, 5 CH_2), 3.72 (3 H, s, MeO), 3.78 (3 H, s, MeO), 3.98 (1 H, m, CHN), 6.14 (1 H, s, CH), 7.30-7.51 (5 H, m, 5 CH), 7.90 (1 H, s, CH). ^{13}C NMR: δ_C = 22.0 (CH_2), 24.3 (CH_2), 25.6 (CH_2), 33.4 (CH_2), 33.5 (CH_2), 52.2 (CHN), 53.1 (MeO), 53.7 (MeO), 58.3 (CH), 60.9 (C=C=N), 120.2 (C), 130.4 (2 CH), 130.7 (2 CH), 130.8 (CH), 134.9 (C), 141.7 (CH), 165.6, 167.4, 167.6, 169.7 and 170.0 (C=*C*=N and 4 C=O). Found (%): C, 60.3; H, 5.4; N, 6.2. Calc. for $C_{23}H_{24}N_2O_6S$ (%): C, 60.51; H, 5.30; N, 6.14.

For **4f**: Pale yellow oil, yield: 0.40 g (85%). IR (ν_{max}/cm^{-1}): 2081 (C=C=N), 1745 and 1710 (C=O). ^{1}H NMR, δ: 1.20-2.04 (10 H, m, 5 CH_2), 2.37 (3 H, s, Me), 3.69 (3 H, s, MeO), 3.78 (3 H, s, MeO), 4.00 (1 H, m, CHN), 6.14 (1 H, s, CH), 7.29-7.42 (4 H, m, 4 CH), 7.98 (1 H, s, CH). ^{13}C NMR, δ: 21.8 (Me), 25.7 (CH_2), 25.9 (CH_2), 27.1 (CH_2), 33.2 (CH_2), 34.4 (CH_2), 51.6 (CHN), 52.2 (MeO), 57.0 (MeO), 59.4 (CH), 60.8 (C=C=N), 120.4 (C), 128.0 (CH), 129.6 (CH), 131.6 (CH), 133.3 (CH), 135.9 (C), 139.5 (C), 145.1 (CH), 159.9, 163.4, 166.0, 166.5 and 170.1 (C=*C*=N and 4 C=O). Found (%): C, 61.5; H, 5.5; N, 5.9. Calc. for $C_{24}H_{26}N_2O_6S$ (%): C, 61.26; H, 5.57; N, 5.95.

For **4g**: Pale yellow oil, yield: 0.41 g (87%). IR (ν_{max}/cm^{-1}): 2077 (C=C=N), 1740 and 1797 (C=O). ^{1}H NMR, δ: 1.22-2.06 (10 H, m, 5 CH_2), 2.44 (3 H, s, Me), 3.65 (3 H, s, MeO), 3.81 (3 H, s, MeO), 4.00 (1 H, m, CHN), 6.14 (1 H, s, CH), 7.29 (2 H, d, ^3J 7.5 Hz, 2 CH), 7.41 (2 H, d, ^3J 7.5 Hz, 2 CH), 7.90 (1 H, s, CH). ^{13}C NMR, δ: 22.0 (Me), 24.3 (CH_2), 25.6 (CH_2), 33.5 (CH_2), 33.6 (CH_2), 34.1 (CH_2), 52.1 (CHN), 53.1 (MeO), 53.7 (MeO), 58.3 (CH), 60.9 (C=C=N), 120.2 (C), 130.4 (2 CH), 130.7 (2 CH), 131.1 (C), 134.9 (C), 141.7 (CH), 161.8, 165.7, 166.1, 167.6 and 170.0 (C=*C*=N and 4 C=O). Found (%): C, 60.0; H, 5.5; N, 5.9. Calc. for $C_{24}H_{26}N_2O_6S$ (%): C, 61.26; H, 5.57; N, 5.95.

For **4h**: Yellow oil, yield: 0.37 g (75%). IR (ν_{max}/cm^{-1}): 2077 (C=C=N), 1744 and 1713 (C=O). ^{1}H NMR, δ: 1.27-2.05 (10 H, m, 5 CH_2), 3.72 (3 H, s, MeO), 3.80 (3 H, s, MeO), 4.00 (1 H, m, CHN), 6.15 (1 H, s, CH), 7.70 (2 H, d, ^3J 8.5 Hz, 2 CH), 8.01 (1 H, s, CH), 8.35 (2 H, d, ^3J 8.5 Hz, 2 CH). ^{13}C NMR, δ: 24.3 (CH_2), 25.6 (CH_2), 25.8 (CH_2), 33.4 (CH_2), 33.5 (CH_2), 52.2 (CHN), 53.5 (MeO), 53.9 (MeO), 57.8 (CH), 60.8 (C=C=N), 117.6 (C), 124.8 (2 CH), 126.2 (C), 131.0 (2 CH), 131.4 (C), 139.8 (CH), 163.6, 165.0, 168.1, 169.5 and 174.1 (C=*C*=N and 4 C=O). Found (%): C, 55.36; H, 4.5; N, 8.3. Calc. for $C_{23}H_{23}N_3O_8S$ (%): C, 55.08; H, 4.62; N, 8.38.

For **4i**: Pale yellow oil, yield: 0.38 g (80%). IR (ν_{max}/cm^{-1}): 2074 (C=C=N), 1740 and 1700 (C=O). ^{1}H NMR, δ: 1.21-2.06 (10 H, m, 5 CH_2), 3.76 (3 H, s, MeO), 3.78 (3 H, s, MeO), 3.99 (1 H, m, CHN), 6.14 (1 H, s, CH), 7.18-7.25 (2 H, m, 2 CH), 7.48-7.57 (2 H, m, 2 CH), 7.88 (1 H, s, CH). ^{13}C NMR, δ: 24.3 (CH_2), 25.7 (CH_2), 31.4 (CH_2), 33.5 (CH_2), 34.3 (CH_2), 52.2 (CHN), 53.2 (MeO), 53.8 (MeO), 58.1 (CH), 60.9 (C=C=N), 115.1 (C), 117.0 (d, $^2J_{CF}$ 21.7 Hz , 2 CH), 121.1 (d, $^4J_{CF}$ 4.5 Hz , C),132.2 (d, $^1J_{CF}$ 330.0 Hz, C-F), 132.7 (d, $^3J_{CF}$ 8.2 Hz , 2 CH), 143.4 (CH), 165.5, 165.9, 167.0, 167.5 and 170.0 (C=*C*=N and 4 C=O). Found (%): C, 58.0; H, 4.8; N, 5.8. Calc. for $C_{23}H_{23}FN_2O_6S$ (%): C, 58.22; H, 4.89; N, 5.90.

For **4j**: Pale yellow oil, yield: 0.39 g (85%). IR (ν_{max}/cm^{-1}): 2080 (C=C=N), 1741 and 1705 (C=O). ^{1}H NMR, δ: 1.22-2.06 (10 H, m, 5 CH_2), 3.72 (3 H, s, MeO), 3.78 (3 H, s, MeO), 3.99 (1 H, m, CHN), 6.12 (1 H, s, CH), 7.20 (H, dd, ^3J 4.8 Hz, ^3J 3.6 Hz, CH), 7.41 (H, d, ^3J 3.6 Hz, CH), 7.67 (H, d, ^3J 4.8 Hz, CH), 8.01 (1 H, s, CH). ^{13}C NMR, δ: 24.3 (CH_2), 25.6 (CH_2), 25.7 (CH_2), 32.8 (CH_2), 33.5 (CH_2), 52.1 (CHN), 53.2 (MeO), 53.7 (MeO), 58.2 (CH), 60.9 (C=C=N), 119.4 (C), 127.3 (C), 129.0 (CH), 132.5 (CH), 133.8 (CH), 138.0 (CH), 163.4, 165.3, 166.7, 167.5 and 170.0 (C=*C*=N and 4 C=O). Found (%): C, 54.3; H, 4.7; N, 6.2. Calc. for $C_{21}H_{22}N_2O_6S_2$ (%): C, 54.53; H, 4.79; N, 6.06.

For **4k**: Pale yellow oil, yield: 0.43 g (87%). IR (ν_{max}/cm^{-1}): 2077 (C=C=N), 1747 and 1700 (C=O). ^{1}H NMR, δ: 1.07 (9 H, s, 3 Me), 1.57 (3 H, s, Me), 1.60 (3 H, s, Me), 1.69 (2 H, s, CH_2), 2.41 (3 H, s, Me), 3.71 (3 H, s, MeO), 3.77 (3 H, s, MeO), 6.13 (1 H, s, CH), 7.29 (2 H, d, ^3J 7.2 Hz, 2 CH), 7.40 (2 H, d, ^3J 7.2 Hz, 2 CH), 7.89 (1 H, s, CH). ^{13}C NMR, δ: 22.0 (Me), 31.4 (C*Me*$_3$), 32.1 (C*Me*$_2$), 32.8 (*C*Me$_3$), 51.8 (*C*Me$_2$), 53.0 (MeO), 53.7 (MeO), 54.8 (CH_2), 58.8 (CH), 65.6 (C=C=N), 120.2 (C), 130.4 (2 CH), 130.7 (2 CH), 130.9 (C), 134.8 (C), 141.8 (CH), 165.6, 166.2, 167.1, 167.6 and 170.1 (C=*C*=N and 4 C=O). Found (%): C, 62.2; H, 6.5; N, 5.7. Calc. for $C_{26}H_{32}N_2O_6S$ (%): C, 62.38; H, 6.44; N, 5.60.