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Ring opening in 1,2,3,4-tetrahydrochromeno[3,2-*c*]pyridines under the action of electron-deficient alkynes

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IR spectra were recorded using an Infralum FT-801 FT-IR spectrometer in KBr pellets. ^{1}H and ^{13}C NMR spectra were acquired on a JEOL JNM-ENM 600 instrument (600 and 150 MHz, respectively) in $CDCl_3$. Residual solvent signals were used as an internal standard ($CDCl_3$: 7.26 ppm for ^{1}H , 77.2 ppm for ^{13}C).

Mass spectra were recorded on an Agilent Technologies LCMS VL Sedex 75 mass spectrometer equipped with Agilent 1100 Series HPLC system (electrospray ionization, ELSD detector). Elemental analysis was performed on a Euro Vector EA-3000 instrument. Melting points were determined in open capillaries on an SMP 10 apparatus. Sorbfil PTKh-AF-A-UF plates were used for TLC, visualization with iodine vapor. Column chromatography was performed with silica gel (40–60 μm, 60 Å).

All solvents were purified by distillation prior to use. Acetylacetylene, methylpropiolate, and DMAD were purchased from Acros Organics and used without additional purification

2-Benzyl-8-bromo-1,2,3,4-tetrahydro-10*H*-chromeno[3,2-*c*]pyridin-10-one (1b). Yield 41%, light-yellow crystals, mp 172-173 °C (EtOAc-hexane, 1:2). IR , ν, cm^{-1}: 1632 (C=O). ^{1}H NMR, δ, ppm (*J*, Hz): 2.78 (4H, s, 4,5-CH_2); 3.54 (2H, s, 1-CH_2); 3.73 (2H, s, $C\underline{H}_2C_6H_5$); 7.26–7.29 (2H, m, H-6, $CH_2C_6\underline{H}_5$); 7.31–7.36 (4H, m, $CH_2C_6\underline{H}_5$); 7.68 (1H, dd, H-7, *J* = 2.5, *J* = 8.9); 8.29 (1H, d, H-9, *J* = 2.5). ^{13}C NMR, δ, ppm : 28.9; 48.5; 48.9; 62.2; 117.4; 118.1; 119.8; 124.6; 127.5; 128.4; 128.5 (2C); 129.2 (2C); 136.2; 137.8; 154.8; 162.7; 175.0. Mass spectrum, m/z: 370, 372 $[M+H]^+$. Found, %: C 61.64; H 4.36; Br 21.58; N 3.78; O 8.64. $C_{19}H_{16}BrNO_2$. Calculated, %: C 61.53; H 4.26; N 3.80.

2-Benzyl-6-ethoxy-1,2,3,4-tetrahydro-10*H*-chromeno[3,2-*c*]pyridin-10-one (1c). Yield 37%, colorless crystals, mp 154-155 ºC (EtOAc- hexane, 1:2). IR, ν, cm^{-1}: 1649 (C=O). ^{1}H NMR, δ, ppm (*J*, Hz): 1.49 (3H, t, *J* = 6.8, $OCH_2\underline{Me}$); 2.77 (2H, m, 4-CH_2); 2.85 (2H, m, 3-CH_2); 3.56 (2H, s, 1-CH_2); 3.74 (2H, s, $C\underline{H}_2C_6H_5$); 4.18 (2H, c, *J* = 6.8, $O\underline{CH}_2Me$); 7.11(1H, dd, *J* = 1.4, *J* = 8.1, H-7); 7.25–7.28 (1H, m, H-8); 7.31–7.34 (3H, m, $CH_2C_6\underline{H}_5$); 7.35–7.38 (2H, m, $CH_2C_6\underline{H}_5$); 7.72 (1H, dd, H-9, *J* = 1.4, *J* = 8.1). ^{13}C NMR, δ, ppm: 14.8; 28.9; 48.6; 48.9; 62.2; 65.1; 115.2; 116.7; 117.0; 124.3; 124.4; 127.4; 128.5 (2C); 129.2 (2C); 137.9; 146.8; 147.9; 162.2; 176.3. Mass spectrum, m/z: 336 $[M+H]^+$. Found, %: C 75.20; H 6.31; N 4.18; O 14.31. $C_{21}H_{21}NO_3$. Calculated, %: C 75.53; H 6.26; N 3.98.

Dimethyl (2*E*)-2-{*N*-benzyl-*N*-[(2-ethenyl-4-oxo-4*H*-chromen-3-yl)methyl]amino}but-2-endioate (2b). Yield 72%, pink crystals, mp 189 ºC (with decomposition). IR, ν, cm^{-1}: 1637 (CO), 1697 (CO_2Me), 1743 (CO_2Me). ^{1}H NMR, δ, ppm (*J*, Hz): 3.61 (3H, s, CO_2Me); 3.93 (3H, s, CO_2Me); 4.35 (2H, s, N-CH_2); 4.43 (2H, s, $C\underline{H}_2C_6H_5$); 4.85 (1H, s, C=C$\underline{H}$-CO_2Me); 5.80 (1H, d, *J*=11.0, CH=C$\underline{H}_2$); 6.36 (1H, d, *J*=16.5, CH=C$\underline{H}_2$); 6.85 (1H, dd, *J*=11.0, *J*=16.5, C$\underline{H}$=CH_2); 7.09-7.20 (5H, m, $CH_2C_6\underline{H}_5$); 7.40-7.45 (2H, ,m H-7,8); 7.60 (1H, t, *J*=7.6, H-6); 8.10 (1H, t, *J*=7.6, H-5). ^{13}C NMR, δ, ppm: 43.6; 50.9; 53.2 (2C); 87.2; 114.9; 117.8; 122.7; 125.3; 125.4; 126.1; 126.7; 126.9; 127.3; 128.6 (3C); 134.1; 136.3; 154.8; 155.3; 160.3; 166.5; 168.2; 177.9. Mass spectrum, m/z: 434 $[M+H]^+$. Found (%): C 69.35; H 5.46; N 3.18. $C_{25}H_{23}NO_6$. Calculated (%): C 69.27; H 5.35; N 3.23; O 22.15.

3-({*N*-benzyl-*N*-[(1*E*)-3-oxobut-1-en-1-yl]amino}methyl)-2-ethenyl-4*H*-chromen-4-one (2c). Yield 68%, yellow crystals, mp 100-102 ºC. IR, ν, cm^{-1}: 1628 (CO), 1643 (COMe). ^{1}H NMR, δ, ppm (*J*, Hz): 2.04 (3H, s, COMe); 4.33 (2H, s, N-CH_2); 4.37 (2H, s, $C\underline{H}_2C_6H_5$); 5.22 (1H, d, *J*=13.1, CH=C$\underline{H}$-COMe); 5.73 (1H, d, *J*=11.2, CH=C$\underline{H}_2$); 6.34 (1H, d, *J*=16.8, $CH=CH_2$); 6.62 (1H, dd, *J*=11.2, *J*=16.8, CH=CH2); 7.07-7.18 (5H, m, $CH_2C_6\underline{H}_5$); 7.29-7.60 (3H, m, H-6,7, 8); 7.61 (1H, d, *J*=13.1, C$\underline{H}$=CH-COMe); 8.10 (1H, dd, *J*=1.9, *J*=8.1, H-5). ^{13}C NMR, δ, ppm: 29.1; 44.3; 50.9; 117.9; 122.9; 124.2; 125.3 (2C); 125.5; 126.0 (2C); 126.3; 127.1; 127.6; 128.8 (3C); 134.3; 155.4; 159.5; 178.0. Mass spectrum, m/z: 360 $[M+H]^+$. Found (%): C 76.75; H 5.96; N 3.88; O 13.40. $C_{23}H_{21}NO_3$. Calculated (%): C 76.86; H 5.89; N 3.90; O 13.35.

Methyl (2*E*)-3-{*N*-benzyl-*N*-[(2-ethenyl-8-ethoxy-4-oxo-4*H*-chromen-3-yl)methyl]amino}-prop-2-enoate (2d). Yield 74 %, light-yellow crystals, mp 122-124 ºC. IR, ν, cm^{-1}: 1638 (CO), 1690(CO_2Me). ^{1}H NMR, δ, ppm (*J*, Hz): 1.50 (3H, t, *J*=7.0, $OCH_2C\underline{H}_3$); 3.63 (3H, s, OMe); 4.17 (2H, c, *J*=7.0, $OC\underline{H}_2Me$); 4.35 (2H, s, N-CH_2); 4.39 (2H, s, $C\underline{H}_2C_6H_5$); 4.74 (1H, d, *J*=12.8, CH=C$\underline{H}$-CO_2Me); 5.79 (1H, d, *J*=11.0, CH=C$\underline{H}_2$); 6.49 (1H, d, *J*=16.5, CH=C$\underline{H}_2$); 6.69 (1H, dd, *J*=11.0, *J*=16.5, C$\underline{H}$=CH_2); 7.10-7.30 (7H, m, H-6,7+ $CH_2C_6\underline{H}_5$); 8.16 (1H, d, *J*=7.8, H-5); 7.77

(1H, d, *J*=12.8, C<u>H</u>=CH-CO_2Me). Mass spectrum, m/z: 420 $[M+H]^+$. Found (%): C 71.41; H 6.12; N 3.55. $C_{25}H_{25}NO_5$. Calculated (%): C 71.58; H 6.01; N 3.34; O 19.07.

Dimethyl (2*E*)-2-{*N*-benzyl-*N*-[(2-ethenyl-8-ethoxy-4-oxo-4*H*-chromen-3-yl)methyl]-amino}but-2-enedioate (2e). Yield 69 %, beige crystals, mp 175-176 ºC. IR, ν, cm^{-1}: 1636 (CO), 1697 (CO_2Me), 1741 (CO_2Me). ^{1}H NMR, δ, ppm (*J*, Hz): 1.50 (3H, t, *J*=6.9, $OCH_2C\underline{H}_3$); 3.60 (3H, s, $CO_2C\underline{H}_3$); 3.93 (3H, s, $CO_2C\underline{H}_3$); 4.16 (2H, c, *J*=6.9, $OC\underline{H}_2$Me); 4.35 (2H, s, N-CH_2); 4.42 (2H, s, $C\underline{H}_2C_6H_5$); 4.82 (1H, s, C=C<u>H</u>-CO_2Me); 5.83 (1H, d, *J*=11.0, CH=C<u>H</u>$_2$); 6.46 (1H, d, *J*=16.9, CH=C<u>H</u>$_2$); 6.86 (1H, dd, *J*=11.0, *J*=16.9, C<u>H</u>=CH_2); 7.10-7.23 (7H, m, H-6,7+$CH_2C_6\underline{H}_5$); 7.65 (1H, d, *J*=7.8, H-5). Mass spectrum, m/z: 478 $[M+H]^+$. Found (%): C 67.35; H 5.46; N 3.10. $C_{27}H_{27}NO_7$. Calculated (%): C 67.91; H 5.70; N 2.93; O 23.45.

Methyl (2*E*)-3-{*N*-benzyl-*N*-[(6-bromo-2-ethenyl-4-oxo-4*H*-chromen-3-yl)methyl]amino}-prop-2-enoate (2f). Yield 73%, colorless crystals, mp 97-99 ºC. IR, ν, cm^{-1}: 1627 (CO), 1667 (CO_2Me). ^{1}H NMR, δ, ppm (*J*, Hz): 3.64 (3H, s, CO_2Me); 4.33 (2H, s, N-CH_2); 4.38 (2H, s, $C\underline{H}_2C_6H_5$); 4.76 (1H, d, *J*=12.8, CH=C<u>H</u>-CO_2Me); 5.81 (1H, d, *J*=11.4, CH=C<u>H</u>$_2$); 6.38 (1H, d, *J*=16.9, CH=C<u>H</u>$_2$); 6.68 (1H, dd, *J*=11.4, *J*=16.9, C<u>H</u>=CH_2); 7.13-7.19 (3H, m, $CH_2C_6\underline{H}_5$); 7.22-7.24 (2H, m, $CH_2C_6\underline{H}_5$); 7.32 (1H, d, *J*=8.7, H-8);7.37 (1H, t, *J*=7.3, H-7); 7.73 (1H, dd, *J*=2.2, *J*=8.7, H-7); 7.76 (1H, d, *J*=12.8, C<u>H</u>=CH-CO_2Me); 8.27 (1H, d, *J*=2.2, H-5). ^{13}C NMR, δ, ppm : 48.5; 50.6; 53.5; 85.9; 116.1; 118.5; 119.7; 124.1; 125.7; 126.1; 127.1 (2C); 127.5; 128.5(2C); 128.7; 136.4; 137.0; 152.3; 154.1; 159.6; 170.0; 176.6. Mass spectrum, m/z: 454, 456 $[M+H]^+$. Found (%): C 60.76; H 4.50; N 3.15; O 14.11. $C_{23}H_{20}BrNO_4$. Calculated (%): C 60.81; H 4.44; Br 17.59; N 3.08; O 14.09.

Dimethyl (2*E*)-2-(8-bromo-10-oxo-4,10-dihydro-10*H*-chromeno[3,2-*c*]pyridin-2(3*H*)-yl)but-2-enedioate (3b). Yield 84 %, colourless crystals, mp 219-220 ºC. IR, ν, cm^{-1}: 1629 (CO), 1692 (CO_2Me), 1731 (CO_2Me). ^{1}H NMR, δ, ppm (*J*, Hz): 2.86 (2H, t, *J*=5.4, 4-CH_2); 3.49 (2H, t, *J*=5.4, 3-CH_2); 3.65 (3H, s, CO_2Me); 3.95 (3H, s, CO_2Me); 4.13 (2H, s, N-CH_2); 5.00 (1H, s, C=C<u>H</u>-CO_2Me); 7.32 (1H, d, *J*=9.2, H-9); 7.74 (1H, dd, *J*=9.1, *J*=2.4, H-7); 8.31 (1H, d, *J*=2.4, H-6). ^{13}C NMR, δ, ppm: 28.0; 42.9; 44.1; 51.2; 53.4; 88.4; 114.9; 118.0; 119.8; 124.3; 128.4; 129.2; 137.8; 153.7; 154.8; 162.7; 167.9; 175.0. Mass spectrum, m/z: 422, 424 $[M+H]^+$. Found (%): C 51.25; H 3.82; N 3.28; O 27.86. $C_{18}H_{16}BrNO_6$. Calculated (%): C 51.16; H 3.78; Br 18.95; N 3.31; O 27.74.