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Unexpected formation of polycyclic oxygen-containing spiro-heterocycles in the reactions of 2,4-dihydro-3*H*-pyrrol-3-one 1-oxides with benzaldehyde

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Characteristics for compounds **2a**,**b**, **4a**,**b** *and* **5**–**8**.

1-Hydroxy-4-[(1-hydroxy-2,2-dimethyl-5-phenyl-3-oxo-1,2-dihydro-3*H*-pyrrol-4-yl)(phenyl)methyl]-2,2-dimethyl-5-phenyl-1,2-dihydro-3*H*-pyrrol-3-one 2a: yield 35 %, m.p. 141 °C (decomposes). IR (KBr), ν/cm^{-1}: 3200, 2520 (OH), 1680 (C=O), 1618 (C=C). UV (MeOH), λ_{max}/nm (lg ε): 247 (4.25), 352 (4.06). Found (%): C, 71.54; H, 5.75; N, 5.00; Cl, 1.74. $C_{31}H_{30}N_2O_4 \cdot H_2O \cdot 1/12\ CHCl_3$. Calcd. (%): C, 71.46; H, 6.14; N, 5.36; Cl, 1.70. NMR ^{1}H ($(CD_3)_3CO$, 300.13 MHz, δ, ppm): 1.21 (s, 6 H, $C^2(CH_3)_2$), 1.26 (s, 6 H, $C^2(CH_3)_2$), 4.77 (s, 1 H, CH), 6.85–7.4 (m, 15 H, 3 Ph), 8.02 (s, $CHCl_3$), 8.30 (br. s, 2 H, 2 OH). NMR ^{13}C: ($(CD_3)_2CO$, 62.90 MHz, δ, ppm): 21.9 (2×$\underline{C}H_3$), 22.5 (2×$\underline{C}H_3$), 37.5 (CH), 70.8 (2×$\underline{C}^2(CH_3)_2$), 79.2 ($CHCl_3$), 115.1 (2×C^4), 126.1 ((*p*-Ph)CH), 128.1, 129.7 ((*o,m*-Ph)CH), 128.1, 129.8 (2×(*o,m*-Ph)C^5), 129.2 (2×(*p*-Ph)C^5), 132.4 (2×(*i*-Ph)C^5), 141.7 ((*i*-Ph)CH), 174.8 (2×C^5), 201.8 (2×C^3=O).

1-Hydroxy-4-[(1-hydroxy-2,2-dimethyl-5-trifluoromethyl-3-oxo-1,2-dihydro-3*H*-pyrrol-4-yl)(phenyl)methyl]-2,2-dimethyl-5-trifluoromethyl-1,2-dihydro-3*H*-pyrrol-3-one 2b: yield 50 %, m.p. 162 °C (decomposes). IR (KBr), ν/cm^{-1}: 3251 (OH), 1670 (C=O), 1212, 1182, 1159 (CF_3). UV (EtOH), λ_{max}/nm (lg ε): 323 (4.08). Found: *m/z* 478.13271 $[M]^+$. $C_{21}H_{20}F_6N_2O_4$. Calcd.: M = 478.13273. NMR ^{1}H: ($(CD_3)_2CO$, 400.14 MHz, δ, ppm): 1.22 (s, 6 H, $C(CH_3)_2$), 1.26 (s, 6 H, $C(CH_3)_2$), 5.31 (s, 1 H, CH), 7.1–7.3 (m, 5 H, Ph), 8.96 (s, 2 H, OH). NMR ^{13}C: ($(CD_3)_2CO$, 100.61 MHz, δ, ppm): 21.9 (4×$\underline{C}H_3$), 35.8 (CH), 72.5 (2×$\underline{C}^2(CH_3)_2$), 119.8 (*i*-Ph), 121.3 (q, $J_{C,F}$ = 274.7 Hz, 2×CF_3), 127.3, 128.7, 128.8 (*o,m,p*-Ph), 140.7 (C^4), 158.2 (q, $J^2_{C,F}$ = 34.2 Hz, 2×C^5), 201.5 (2×C^3=O).

4-Benzylidene-2,2-dimethyl-5-phenyl-2,4-dihydro-3*H*-pyrrol-3-one 1-oxide 4a, isomer ***E*:** m.p. 130.5-133.5 °C (hexane–ethyl acetate). IR (KBr), ν/cm^{-1}: 1730 (C=O), 1586,1568, 1511 (C=C, C=N). UV (EtOH), λ_{max}/nm (lg ε): 234 (4.14), 315 (4.18), 382 (4.09). Found (%): C, 78.51; H, 5.96; N, 4.92. $C_{19}H_{17}NO_2$. Calcd. (%): C, 78.33; H, 5.88; N, 4.81. NMR ^{1}H: ($CDCl_3$, 200.13 MHz, δ, ppm): 1.57 (s, 6 H, $C(CH_3)_2$), 6.93 (s, 1 H, CH), 7.3–7.4 (m, 3 H), 7.45–7.6 (m, 3 H), 7.7–7.8 (m, 2 H),7.9–8.0 (m, 2 H, 2 Ph). NMR ^{13}C: ($CDCl_3$, 100.61 MHz, δ, ppm): 21.3 ($C^2(\underline{C}H_3)_2$), 74.4 ($\underline{C}^2(CH_3)_2$), 126.4 (*i*-Ph), 127.3 (C^4), 128.1, 128.5, 129.4, 130.0, 130.7, 131.2 (*o,m,p*-Ph), 133.6 (*i*-Ph), 135.4 (CH), 145.2 (C^5=N), 198.0 (dm, $J^3_{C,H}$ = 10.7 Hz, C^3=O). **4a,** isomer ***Z*:** Yellow oil. NMR ^{1}H: (CCl_4, 200.13 MHz, δ, ppm): 1.52 (s, 6 H, $C(C\underline{H}_3)_2$), 6.79–7.3 (m, 11 H, 2 Ph, CH). NMR ^{13}C: ($CDCl_3$, 75.48 MHz, δ, ppm): 21.3 ($C^2(\underline{C}H_3)_2$), 74.3 ($\underline{C}^2(CH_3)_2$), 125.8 (*i*-Ph), 127.1 (C^4), 127.4, 127.7, 129.2, 129.2, 129.5, 130.3 (*o,m,p*-Ph), 131.3 (CH), 132.8 (*i*-Ph), 142.2 (C^5=N), 199.6 (C^3=O). Yield of an isomers mixture: 25%.

(4*Z*)-4-Benzylidene-2,2-dimethyl-5-trifluoromethyl-2,4-dihydro-3*H*-pyrrol-3-one 1-oxide 4b: yield 30 %, m.p. 95.5–96.5 °C (hexane–ethyl acetate). IR (KBr), ν/cm^{-1}: 1732 (C=O), 1583, 1562, 1528 (C=C, C=N), 1196, 1172, 1129 (CF_3). UV (EtOH), λ_{max}/nm (lg ε): 241 (3.68), 340 (4.28). Found: *m/z* 283.08220 $[M]^+$. $C_{14}H_{12}F_3NO_2$. Calcd.: M = 283.08200. NMR ^{1}H: (CCl_4, 200.13 MHz, δ, ppm): 1.48 (s, 6 H, $C^2(C\underline{H}_3)_2$), 7.12 (s, 1 H, C^4=C–$\underline{H}$), 7.31–7.39 (m, 3 H), 7.85–7.90 (m, 2 H, Ph). NMR ^{13}C: ($CDCl_3$, 100.63 MHz, δ, ppm): 21.5 ($C^2(\underline{C}H_3)_2$), 77.5 ($\underline{C}^2(CH_3)_2$), 119.8 (q, $J_{C,F}$ = 274.7 Hz, CF_3), 123.5 (C^4), 128.5, 131.6, 131.7 (*o,m,p*-Ph), 133.3 (*i*-Ph), 134.8 (q, $J^2_{C,F}$ = 34 Hz, C^5), 136.6 (q, $J^4_{C,F}$ = 3.3 Hz, CH), 195.7 (C^3=O).

4-Benzyl-1-hydroxy-2,2-dimethyl-5-phenyl-1,2-dihydro-3*H*-pyrrol-3-one 5: yield 35 %, m.p. 131-137 °C (decomposes above 45 °C). IR ($CHCl_3$), ν/cm^{-1}: 3559, 3292 (OH), 1769, 1675 (C=O, C=C). UV (EtOH), λ_{max}/nm (lg ε): 252 (4.02), 309 (3.72), 353 (3.80). Found: *m/z* 293.14151 $[M]^+$. $C_{19}H_{19}NO_2$. Calcd.: M = 293.14158. NMR ^{1}H: ($CDCl_3$, 300.13 MHz, δ, ppm): 1.38 (s, 6 H, $C(C\underline{H}_3)_2$), 3.52 (s, 2 H, CH_2), 5.61 (broad s, 1 H, OH), 7.1–7.25 (m, 5 H, Ph), 7.35–7.5 (m, 5 H, Ph).

4-Benzyl-2,2-dimethyl-5-phenyl-1,2-dihydro-3*H*-pyrrol-3-one 6: yield 30 %, m.p. 140–142.5 °C. IR (KBr), ν/cm^{-1}: 3240 (NH), 1637 (C=O, C=C). UV (EtOH), λ_{max}/nm (lg ε): 240 (4.09), 345 (3.92). Found: *m/z* 277.14662 $[M]^+$. $C_{19}H_{17}NO$. Calcd.: M = 277.14666. NMR ^{1}H: ($CDCl_3$, 200.13 MHz, δ, ppm): 1.37 (s, 6 H, $C(C\underline{H}_3)_2$), 3.63 (s, 2 H, CH_2), 5.00 (broad s, 1 H, NH),7.05–7.30 (m, 5 H, Ph), 7.38–7.54 (m, 5 H, Ph).

3,3,10,10-Tetramethyl-1,8,12-triphenyl-6-oxa-2,9-diazadispiro[4.1.4.1]dodeca-1,8-diene-4,11-dione 2,9-dioxide 7: yield 10 %, m.p. 170–172 °C (hexane–ethyl acetate). IR (KBr), ν/cm^{-1}: 1785 (C=O), 1578, 1489 (C=C, C=N). UV (MeOH), λ_{max}/nm (lg ε): 248 (4.18), 293 (4.26). Found (%): C, 72.63; H, 5.61; N, 5.29. $C_{31}H_{28}N_2O_5$. Calcd. (%): C, 73.21; H, 5.55; N, 5.51. NMR ^{1}H: ($CDCl_3$, 400.13 MHz, δ, ppm): 1.43 (s, 3 H, CH_3), 1.47 (s, 6 H, $2CH_3$), 1.50 (s, 3 H, CH_3), 4.83 (s, 1 H, CH), 6.76–6.89 (m, 1 H), 7.00–7.10 (m, 2 H), 7.12–7.18 (m, 4 H), 7.23–7.33 (m, 4 H), 7.37–7.48 (m, 2 H), 7.60–7.65 (m, 1 H), 7.82–7.86 (m, 1 H, 3 Ph). NMR ^{13}C: ($CDCl_3$, 100.61 MHz, δ, ppm): 20.0, 21.1, 21.4, 21.6 (4 CH_3), 56.8 (CH), 74.0 (2 signals $\underline{C}(CH_3)_2$), 89.7 (2 signals C–O), 125.7, 128.2, 128.6, 128.7, 129.1, 129.2, 129.5, 129.9, 130.6, 131.3, 133.7 (3 Ph), 142.0, 145.3, (2 Ph–$\underline{C}$=N), 203.5 (C=O).

3a,6a-Dihydroxy-5',5',6,6-tetramethyl-2,2',3-triphenyl-3,3a,6,6a-tetrahydrospiro(furo[2,3-c]pyrrole-2,3'-pyrrol)-4'(5'*H*)-one 1',5-dioxide 8: yield 6 %, m.p. 245 °C (decomposes, ethyl acetate–MeOH). IR (KBr), ν/cm^{-1}: 3388 (OH), 1776 (C=O), 1759 (C=N). NMR ^{1}H: ($CDCl_3$, 400.13 MHz, δ, ppm): 0.39 (s, 3 H, CH_3), 1.43 (s, 3 H, CH_3), 1.64 (s, 3 H, CH_3), 1.67 (s, 3 H, CH_3), 3.69 (s, 1 H, OH), 3.85 (s, 1 H, CH), 6.32 (s, 1 H, OH), 6.88–6.93 (m, 2 H), 7.07–7.14 (m, 2 H), 7.15–7.43 (m, 8 H), 7.92–7.99 (m, 3 H, 3 Ph). NMR ^{13}C: ($CDCl_3$, 100.61 MHz, δ, ppm): 18.5, 19.7, 22.1, 24.4 (4 CH_3), 59.9 (CH), 74.8, 78.3 (2 $\underline{C}(CH_3)_2$), 85.2 (C–OH), 95.5 (C–O), 108.9 (O–C–OH), 125.7, 126.6, 127.8, 128.0, 128.8, 128.9, 130.0, 130.7, 131.1, 132.6 (3 Ph), 137.7, 141.2, (2 Ph–$\underline{C}$=N), 214.1 (C=O).