

Supplementary Information

An efficient synthesis of 1, 8-dioxo-octahydroxanthenes using tetrabutylammonium hydrogen sulfate

Hitendra N. Karade, Manisha Sathe, and M. P. Kaushik*

Process Technology Development Division, Defence R & D Establishment, Jhansi Road,
Gwalior-474002 (MP), India

E-mail: mpkaushik@rediffmail.com

3,3,6,6-Tetramethyl-9-(phenyl)-1,8-dioxo-octahydroxanthene (3a).

mp 204-205°C; IR (KBr, cm^{-1}) ν_{max} 3030, 2950, 1669, 1470, 1363, 1200, 1170, 740, 700; ^1H NMR (400MHz, $\text{DMSO}-d_6$) δ 0.98 (6H, s, $2 \times \text{CH}_3$), 1.12 (6H, s, $2 \times \text{CH}_3$), 2.20 (4H, dd, $J = 1.6 \text{ Hz}$, $J = 2.4 \text{ Hz}$, $2 \times \text{CH}_2$, H-4, H-5), 2.45 (4H, s, $2 \times \text{CH}_2$, H-2, H-7) 4.66 (s, 1H, H-9), 7.21 (5H, m, Ar-H); Anal. Calcd for $\text{C}_{23}\text{H}_{26}\text{O}_3$: C, 78.83; H, 7.47. Found: C, 78.95; H, 7.42.

3,3,6,6-Tetramethyl-9- (4-methoxyphenyl) -1,8-dioxo-octahydroxanthene (3b).

mp 241-243°C; IR (KBr, cm^{-1}) ν_{max} 3031, 2959, 1665, 1460, 1361, 1200, 1170, 855; ^1H NMR (400MHz, $\text{DMSO}-d_6$) δ 1.01 (6H, s, $2 \times \text{CH}_3$), 1.09 (6H, s, $2 \times \text{CH}_3$), 2.20 (6H, dd, 6H, $J = 1.6 \text{ Hz}$, $J = 2.0 \text{ Hz}$, $2 \times \text{CH}_2$, H-4, H-5), 2.46 (4H, s, $2 \times \text{CH}_2$, H-2, H-7), 3.73(3H, s, CH_3O), 4.70 (1H, s, H-9), 6.67-7.28 (4H, m, ArH); Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{O}_4$: C, 75.76; H, 7.41 Found: C, 75.85; H, 7.31.

3,3,6,6-Tetramethyl-9- (4-dimethylamino-phenyl)-1,8-dioxo-octahydroxanthene (3c).

mp 220-222°C; IR (KBr, cm^{-1}) ν_{max} 3025, 2955, 1670, 1465, 1365, 1200, 1165, 851; ^1H NMR (400MHz, $\text{DMSO}-d_6$) δ 1.02 (6H, s, $2 \times \text{CH}_3$), 1.11 (6H, s, $2 \times \text{CH}_3$), 2.21 (4H, dd, $J = 1.6 \text{ Hz}$, $J = 2.4 \text{ Hz}$, $2 \times \text{CH}_2$, H-4, H-5), 2.46 (4H, s, $2 \times \text{CH}_2$, H-2, H-7), 2.88(6H, s, $\text{N}(\text{CH}_3)_2$), 4.67 (1H, s, H-9), 6.62 (2H, s, ArH), 7.15 (2H, s, ArH); Anal. Calcd for $\text{C}_{25}\text{H}_{31}\text{NO}_3$: C, 76.34; H, 7.89; N, 3.56. Found: C, 76.48; H, 7.86; N, 3.43.

3,3,6,6-Tetramethyl-9- (4-chlorophenyl)-1,8-dioxo-octahydroxanthene (3d).

mp 230-231°C; IR (KBr, cm^{-1}) ν_{max} 3021, 2981, 1672, 1471, 1375, 1200, 1162, 852; ^1H NMR (400MHz, $\text{DMSO}-d_6$) δ 0.98 (6H, s, $2 \times \text{CH}_3$), 1.10 (6H, s, $2 \times \text{CH}_3$), 2.23 (4H, dd, $J = 1.6 \text{ Hz}$, $J = 3.6 \text{ Hz}$, $2 \times \text{CH}_2$, H-4, H-5), 2.50 (4H, s, $2 \times \text{CH}_2$, H-2, H-7), 4.64 (1H, s, H-9), 7.26-7.43 (m, 4H, ArH); Anal. Calcd for $\text{C}_{23}\text{H}_{25}\text{ClO}_3$: C, 71.77; H, 6.54. Found: C, 71.89; H, 6.45.

3,3,6,6-Tetramethyl-9- (2-chlorophenyl)-1,8-dioxo-octahydroxanthene (3e).

mp 224-226°C; IR (KBr, cm^{-1}) ν_{max} 3017, 2970, 1660, 1465, 1371, 1200, 1161, 755; ^1H NMR (400MHz, $\text{DMSO}-d_6$) δ 0.98 (6H, s, $2 \times \text{CH}_3$), 1.10 (6H, s, $2 \times \text{CH}_3$), 2.06 (4H, dd, $J = 1.6 \text{ Hz}$, $J = 3.0 \text{ Hz}$, $2 \times \text{CH}_2$, H-4, H-5), 2.49 (4H, s, $2 \times \text{CH}_2$, H-2, H-7), 4.64(1H, s, H-9), 7.26-7.35 (4H, m, ArH); Anal. Calcd for $\text{C}_{23}\text{H}_{25}\text{ClO}_3$: C, 71.77; H, 6.54. Found: C, 71.88; H, 6.35.

3,3,6,6-Tetramethyl-9-(3-chlorophenyl)-1,8-dioxo-octahydroxanthene (3f).

mp 183-184°C; IR (KBr, cm^{-1}) ν_{max} 3015, 2960, 1662, 1464, 1375, 1204, 1165, 795; ^1H NMR (400MHz, $\text{DMSO}-d_6$) δ 1.02 (6H, s, $2 \times \text{CH}_3$), 1.12 (6H, s, $2 \times \text{CH}_3$), 2.30 (4H, dd, $J = 1.6$ Hz, $J = 3.6$ Hz, $2 \times \text{CH}_2$, H-4, H-5), 2.49 (4H, s, $2 \times \text{CH}_2$, H-2, H-7), 4.74 (1H, s, H-9), 7.11-7.25 (4H, m, ArH); Anal. Calcd for $\text{C}_{23}\text{H}_{25}\text{ClO}_3$: C, 71.77; H, 6.54. Found: C, 71.92; H, 6.41.

3,3,6,6-Tetramethyl-9-(2,4-dichlorophenyl)-1,8-dioxo-octahydroxanthene (3g).

mp 253-254°C; IR (KBr, cm^{-1}) ν_{max} 3021, 2962, 1655, 1465, 1370, 1211, 1161, 790; ^1H NMR (400MHz, $\text{DMSO}-d_6$) δ 1.03 (6H, s, $2 \times \text{CH}_3$), 1.12 (6H, s, $2 \times \text{CH}_3$), 2.21 (4H, dd, $J = 1.6$ Hz, $J = 3.1$ Hz, $2 \times \text{CH}_2$, H-4, H-5), 2.46 (4H, s, $2 \times \text{CH}_2$, H-2, H-7), 4.96 (1H, s, H-9), 7.18-7.93 (3H, m, ArH); Anal. Calcd for $\text{C}_{23}\text{H}_{24}\text{Cl}_2\text{O}_3$: C, 65.87; H, 5.73. Found: C, 65.96; H, 5.59.

3,3,6,6-Tetramethyl-9-(4-nitrophenyl)-1,8-dioxo-octahydroxanthene (3h).

mp 222°C; IR (KBr, cm^{-1}) ν_{max} 3031, 2959, 1665, 1460, 1361, 1200, 1170, 855; ^1H NMR (400MHz, $\text{DMSO}-d_6$) δ 1.00 (6H, s, $2 \times \text{CH}_3$), 1.12 (6H, s, $2 \times \text{CH}_3$), 2.16 (4H, dd, $J = 1.6$ Hz, $J = 3.6$ Hz, $2 \times \text{CH}_2$, H-4, H-5), 2.41 (4H, s, $2 \times \text{CH}_2$, H-2, H-7), 4.46 (1H, s, H-9), 7.50-7.63 (2H, m, ArH), 8.06-8.16 (2H, m, ArH); Anal. Calcd for $\text{C}_{23}\text{H}_{25}\text{NO}_5$: C, 69.85; H, 6.37; N, 3.54 Found: C, 69.89; H, 6.46; N, 3.40.

3,3,6,6-Tetramethyl-9-(3-nitrophenyl)-1,8-dioxo-octahydroxanthene (3i).

mp 171.5-172.5°C; IR (KBr, cm^{-1}) ν_{max} 3020, 2961, 1661, 1465, 1364, 1205, 1175, 795; ^1H NMR (400MHz, $\text{DMSO}-d_6$) δ 1.02 (6H, s, $2 \times \text{CH}_3$), 1.13 (6H, s, $2 \times \text{CH}_3$), 2.22 (4H, dd, $J = 1.6$ Hz, $J = 3.6$ Hz, $2 \times \text{CH}_2$, H-4, H-5), 2.53 (4H, s, $2 \times \text{CH}_2$, H-2, H-7), 4.85 (1H, s, H-9), 7.43 (s, 1H, ArH), 7.88-7.95 (3H, m, ArH); Anal. Calcd for $\text{C}_{23}\text{H}_{25}\text{NO}_5$: C, 69.85; H, 6.37; N, 3.54 Found: C, 69.90; H, 6.50; N, 3.42.

3,3,6,6-Tetramethyl-9-(2-nitrophenyl)-1,8-dioxo-octahydroxanthene (3j).

mp 246-248°C; IR (KBr, cm^{-1}) ν_{max} 3025, 2965, 1664, 1470, 1360, 1200, 1170, 755; ^1H NMR (400MHz, $\text{DMSO}-d_6$) δ 0.99 (6H, s, $2 \times \text{CH}_3$), 1.12 (6H, s, $2 \times \text{CH}_3$), 2.16 (4H, dd, $J = 1.6$ Hz, $J = 3.6$ Hz, $2 \times \text{CH}_2$, H-4, H-5), 2.41 (4H, s, $2 \times \text{CH}_2$, H-2, H-7), 5.61 (1H, s, H-9), 7.36-7.45 (4H, m, ArH); Anal. Calcd for $\text{C}_{23}\text{H}_{25}\text{NO}_5$: C, 69.85; H, 6.37; N, 3.54 Found: C, 69.93; H, 6.54; N, 3.36.

3,3,6,6-Tetramethyl-9-(4-hydroxyphenyl)-1,8-dioxo-octahydroxanthene (3k).

mp 246-247°C; IR (KBr, cm^{-1}) ν_{max} 3431, 3031, 2959, 1665, 1460, 1361, 1200, 1170, 850; ^1H NMR (400MHz, $\text{DMSO}-d_6$) δ 0.99 (6H, s, $2 \times \text{CH}_3$), 1.10 (6H, s, $2 \times \text{CH}_3$), 2.30 (4H, dd, $J = 1.6$ Hz, $J = 4.0$ Hz, $2 \times \text{CH}_2$, H-4, H-5), 2.47 (4H, s, $2 \times \text{CH}_2$, H-2, H-7), 4.62 (1H, s, H-9), 6.53-6.55 (2H, d, $J = 8.0$ Hz, ArH), 6.71 (1H, s, OH), 7.06-7.08 (2H, d, $J = 8.0$ Hz, ArH); Anal. Calcd for $\text{C}_{23}\text{H}_{26}\text{NO}_4$: C, 75.38; H, 7.15; Found: C, 75.26; H, 7.09.

3,3,6,6-Tetramethyl-9-(4-methylphenyl)-1,8-dioxo-octahydroxanthene (3l).

mp 217-218°C; IR (KBr, cm^{-1}) ν_{max} 3020, 2960, 1661, 1465, 1365, 1205, 1175, 853; ^1H NMR (400MHz, $\text{DMSO}-d_6$) δ 1.03 (6H, s, $2 \times \text{CH}_3$), 1.12 (6H, s, $2 \times \text{CH}_3$), 2.07 (4H, dd, $J = 1.6$ Hz, $J = 2.4$ Hz, $2 \times \text{CH}_2$, H-4, H-5), 2.40 (4H, s, $2 \times \text{CH}_2$, H-2, H-7), 2.43 (3H, s, CH_3Ar), 4.69 (1H, s, H-9), 6.80-7.28 (4H, m, ArH); Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{O}_3$: C, 79.08; H, 7.74; Found: C, 79.25; H, 7.59.

3,3,6,6-Tetramethyl-9-(benzo(3,4)dioxol-5-yl)-1,8-dioxo-octahydroxanthene (3m).

mp 218.5-220°C; IR (KBr, cm^{-1}) ν_{max} 3025, 2962, 1664, 1460, 1363, 1200, 1170, 945, 790; ^1H NMR (400MHz, DMSO- d_6) δ 1.00 (6H, s, $2 \times \text{CH}_3$), 1.13 (6H, s, $2 \times \text{CH}_3$), 2.16 (4H, dd, $J = 1.6$ Hz, $J = 2.8$ Hz, $2 \times \text{CH}_2$, H-4, H-5), 2.41 (4H, s, $2 \times \text{CH}_2$, H-2, H-7), 4.46 (1H, s, H-9), 5.90 (2H, s, OCH_2O), 6.75-6.86 (3H, m, ArH); Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{O}_5$: C, 73.07; H, 6.64. Found: C, 73.16; H, 6.68.

3,3,6,6-Tetramethyl-9-styryl-1,8-dioxo-octahydroxanthene (3n).

mp 175-177°C; IR (KBr, cm^{-1}) ν_{max} 3025, 2962, 1664, 1460, 1363, 1200, 1170, 1040, 970, 740, 700; ^1H NMR (400MHz, DMSO- d_6) δ 1.14 (12H, s, $4 \times \text{CH}_3$), 2.32 (4H, s, $4 \times \text{CH}_2$), 2.46 (4H, s, $4 \times \text{CH}_2$), 4.42 (1H, s, H-9), 6.25-6.33 (2H, m, $-\text{CH}=\text{CH}-$), 7.18-7.28 (5H, m, ArH); Anal. Calcd for $\text{C}_{25}\text{H}_{28}\text{O}_3$: C, 79.79; H, 7.45. Found: C, 79.91; H, 7.30.

3,3,6,6-Tetramethyl-9-(3-ethoxy-4-hydroxyphenyl)-1,8-dioxo-octahydroxanthene (3o).

mp 194-196°C; IR (KBr, cm^{-1}) ν_{max} 3431, 2950, 1669, 1515, 1441, 1363, 1278, 1194; ^1H NMR (400 MHz, DMSO- d_6) δ 0.90 (6H, s, $2 \times \text{CH}_3$), 1.02 (6H, s, $2 \times \text{CH}_3$), 1.28 (3H, t, $J = 6.9$ Hz, $-\text{OCH}_2\text{CH}_3$), 2.05-2.09 and 2.23-2.27 (4H, 2 $\times$ d, $J = 16.00$ Hz, 16.00 Hz, $2 \times \text{CH}_2$, H-4, H-5), 2.50-2.53 (4H, d, 12.00 Hz, $2 \times \text{CH}_2$, H-2, H-7), 3.90 (2H, q, $J = 6.9$ Hz, $-\text{OCH}_2\text{CH}_3$), 4.40 (1H, s, H-9), 6.59-6.66 (3H, m, Ar-H), 8.69 (1H, s, $-\text{OH}$); ^{13}C NMR (100 MHz, DMSO- d_6): δ 14.70 (CH_3 , $-\text{CH}_2\text{CH}_3$), 26.31 ($2 \times \text{CH}_3$), 28.69 ($2 \times \text{CH}_3$), 30.33 (C-3, C-6), 31.80 (C-9), 38.87 (C-4, C-5), 50.05 (C-2, C-7), 63.84 (CH_2 , $-\text{CH}_2\text{CH}_3$), 114.00 (Ar-C), 114.68 (Ar-C), 115.01 (2C, C=C), 120.32 (Ar-C), 135.28 (Ar-C), 145.22 (C-OH), 145.87 (C-OEt), 162.55 (2C, C=C), 196.05 ($2 \times \text{C}=\text{O}$); ESI-MS m/z : 433 (M+Na, 5%), 273 ($\text{M}^+-\text{C}_8\text{H}_9\text{O}_2$, 100%), 843 (2M+23).

3,3,6,6-Tetramethyl-9-(2-methoxy-5-bromophenyl)-1,8-dioxo-octahydroxanthene (3p).

mp 204-206°C; IR (KBr, cm^{-1}) ν_{max} 2947, 2875, 1663, 1483, 1359, 1248, 1198, 883; ^1H NMR (400 MHz, DMSO- d_6) δ 0.85 (6H, s, $2 \times \text{CH}_3$), 1.02 (6H, s, $2 \times \text{CH}_3$), 1.997-2.037 and 2.268-2.228 (4H, 2 $\times$ d, $J = 16.00$ Hz, 16.00 Hz, $2 \times \text{CH}_2$, H-4, H-5), 2.54 (4H, s, H-2, H-7), 3.67 (s, 3H, $-\text{OCH}_3$), 4.49 (1H, s, H-9), 6.83-7.31 (3H, m, Ar-H); ^{13}C NMR (100 MHz, DMSO- d_6): δ 25.67 ($2 \times \text{CH}_3$), 29.03 ($2 \times \text{CH}_3$), 29.84 (2C, C-3, C-6), 31.90 (OCH_3), 38.87 (C-9), 50.03 (2C, C-4, C-5), 55.52 (2C, C-2, C-7), 111.27 (Ar-C), 111.52 (Ar-C), 113.39 (2C, C=C), 130.25 (Ar-C), 132.29 (Ar-C), 134.10 (Ar-C), 156.94 (Ar-C), 163.91 (2C, C=C), 196.24 (2C, C=O); ESI-MS m/z : 459 (M+H, 68%), 273 ($\text{M}^+-\text{C}_7\text{H}_6\text{BrO}$, 100%).

Bis (1,8-dioxo-octahydroxanthene) (3q).

mp 236-238°C; IR (KBr, cm^{-1}) ν_{max} 2957, 2879, 1664, 1457, 1368, 1203, 1158, 779; ^1H NMR (400 MHz, CDCl_3) δ 1.00 (12H, s, $4 \times \text{CH}_3$), 1.08 (12H, s, $4 \times \text{CH}_3$), 2.10-2.14 and 2.16-2.20 (8H, 2 $\times$ d, $J = 16.00$ Hz, 16.00 Hz, $4 \times \text{CH}_2$), 2.398-2.442 and 2.511-2.555 (8H, 2 $\times$ d, $J = 17.6$ Hz, 17.6 Hz, $4 \times \text{CH}_2$), 4.68 (2H, s,), 7.04-7.26 (4H, m, Ar-H); ^{13}C NMR (100 MHz, CDCl_3): δ 27.68 ($4 \times \text{CH}_3$), 29.35 ($4 \times \text{CH}_3$), 31.42 ($2 \times \text{C}-3$, $2 \times \text{C}-6$), 32.32 ($2 \times \text{C}-9$), 40.92 ($4 \times \text{C}-4$, C-5), 50.91 ($4 \times \text{C}-2$, C-7), 115.66 ($4 \times \text{C}=\text{C}$), 126.55 (Ar-C), 127.95 (Ar-C), 128.39 (Ar-C), 143.74 ($2 \times \text{Ar}-\text{C}$), 162.53 (C=C), 196.60 ($4 \times \text{C}=\text{O}$); ESI-MS m/z : 623 (M+H, 100%), 645 (M+Na, 40%), 661 (M+K, 20%), 273 ($\text{M}^+-\text{C}_{23}\text{H}_{25}\text{O}_3$, 100%).

3,3,6,6-Tetramethyl-9-(pyridin-2-yl)-1,8-dioxo-octahydroxanthene (3r).

mp 188-190°C; IR (KBr, cm^{-1}) ν_{max} 3053, 3007, 2957, 1656, 1467, 1364, 1199, 1156, 820; ^1H NMR (400 MHz, CDCl_3) δ 1.00 (6H, s, $2 \times \text{CH}_3$), 1.10 (6H, s, $2 \times \text{CH}_3$), 2.13-2.17 and 2.22-2.26 (4H, $2 \times \text{d}$, $J = 16.00$ Hz, 16.00 Hz, $2 \times \text{CH}_2$, H-4, H-5), 2.435-2.479 and 2.508-2.552 (4H, $2 \times \text{d}$, $J = 17.6$ Hz, 17.6 Hz, $2 \times \text{CH}_2$, H-2, H-7), 4.86 (1H, s, H-9), 6.99 (1H, t, $J = 5.3$ Hz, Ar-H), 7.54 (1H, t, $J = 6.1$ Hz Ar-H), 7.60 (1H, d, $J = 7.6$ Hz), 8.38 (1H, d, $J = 4.52$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 27.26 (2C, CH_3), 29.47 (2C, CH_3), 32.42 (2C C-3, C-6), 34.57 (C-9), 41.00 (2C, C-4, C-5), 50.90 (2C, C-2, C-7), 114.47 (2C, C=C), 121.49 (Ar-C), 125.04 (Ar-C), 135.78 (Ar-C), 149.03 (Ar-C), 161.88 (2C, C=C), 163.47 (C=C), 197.05 (2C, C=O); ESI-MS m/z : 352 (M+H, 100%), 374 (M+23), 725 (2M+23).