Iodoacetoxylation of Glycals Using Cerium(IV) Ammonium Nitrate, Sodium Iodide and Acetic Acid: Stereoselective Synthesis of 2-Deoxy-2-Iodo-α-Mannopyranosyl Acetates

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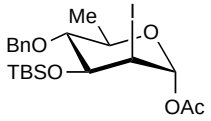
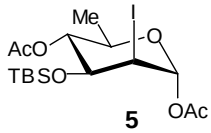
SUPPORTING INFORMATION

Tabulated spectroscopic data for iodo acetates **2**, **5**, **7**, **9**, and **15** (4 pages). See any current masthead page for ordering information.



2

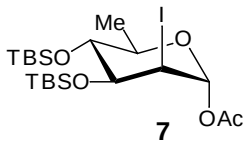
Data for Iodoacetate **2**: mp 62–65 °C; $[\alpha]_D^{23}$ +27.9° (c 1.05, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 5 H), 6.32 (d, *J* = 1.7 Hz, 1 H), 4.90, 4.62 (AB system, *J* = 11.0 Hz, 2 H), 4.28 (dd, *J* = 4.2, 1.7 Hz, 1 H), 3.92 – 3.87 (m, 1 H), 3.45 (apparent t, *J* = 8.8 Hz, 1 H), 3.26 (dd, *J* = 8.6, 4.2 Hz, 1 H), 2.09 (s, 3 H), 1.29 (d, *J* = 6.1 Hz, 3 H), 0.99 (s, 9 H), 0.13 (s, 3 H), 0.12 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 137.9, 128.4, 127.9, 127.7, 95.3, 82.5, 75.5, 71.0, 69.9, 36.6, 25.9, 20.8, 18.0, 17.9, –4.4, –4.6; IR (thin film) 2955, 2930, 2857, 1750, 1498, 1472, 1463, 1454, 1373, 1293, 1252, 1219, 1188, 1147, 1119, 1060, 1011, 936, 904, 861, 838, 778, 737, 698, 676 cm^{-1}; high resolution FAB MS calcd for $C_{21}H_{33}IO_5Si$ ($M+Na^+$) 543.1042, found 543.1058. *Anal*. Calcd for $C_{21}H_{33}IO_5Si$: C, 48.46; H, 6.39; Found C 49.14; H, 6.42.



5

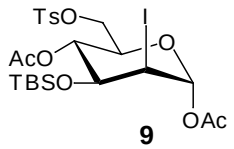
Data for Iodoacetate **5**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.33 (d, *J* = 1.7 Hz, 1 H), 5.02 (apparent t, *J* = 9.2 Hz, 1 H), 4.24 (dd, *J* = 5.4, 2.0 Hz, 1 H), 3.92 – 3.89 (m, 1 H), 3.25 (dd, *J* = 8.8, 4.4 Hz, 1 H), 2.12 (s, 3 H), 2.07 (s, 3 H), 1.20 (d, *J* = 6.4 Hz, 3 H), 0.89 (s, 9 H), 0.08 (s, 3 H), 0.06 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 168.5, 95.2, 75.1, 69.7, 67.5, 34.8, 25.5, 21.0, 20.9, 17.8, 17.6, –4.6, –4.7; IR (thin film) 2957, 2931, 2896, 2858, 1751, 1473, 1464, 1372, 1298, 1225, 1183, 1150, 1103, 1048, 1006, 935, 888, 862, 839, 779, 753, 680, 627 cm^{-1}; high resolution FAB MS calcd for $C_{16}H_{29}IO_6Si$ ($M+Na^+$) calcd 495.0678, found 495.0665. Isomerically pure **5** was obtained in 48% yield by recrystallization

of the reaction mixture. In several experiments (performed under slightly different conditions which resulted in a lower manno to gluco product ratio) where the products were isolated by chromatography, the mixture of α-manno and β-gluco iodoacetate isomers was obtained in up to 65% yield.



7

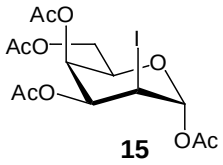
Data for Iodoacetate **7**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.27 (d, *J* = 3.4 Hz, 1 H), 4.34 (s, 1 H), 3.87 – 3.81 (m, 1 H), 3.65 (apparent t, *J* = 7.3 Hz, 1 H), 3.25 (broad s, 1 H), 2.11 (s, 3 H), 1.31 (d, *J* = 6.6 Hz, 3 H), 0.96 (s, 9 H), 0.91 (s, 9 H), 0.15 (s, 3 H), 0.12 (s, 6 H), 0.11 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 92.0, 80.2, 75.7, 73.7, 26.3, 26.0, 20.9, 18.3, 18.0, –3.2, –3.3, –4.1, –4.9; IR (thin film) 2956, 2930, 2897, 2858, 1756, 1473, 1371, 1293, 1252, 1221, 1188, 1153, 1119, 1105, 1055, 1007, 927, 904, 874, 858, 838, 777, 735, 668 cm^{-1}; high resolution FAB MS calcd. for $C_{20}H_{41}IO_5Si_2$ ($M+Na^+$) 567.1437, found 567.1447.



9

Data for Iodoacetate **9** : ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2 H), 7.36 (d, *J* = 8.6 Hz, 2 H), 6.30 (d, *J* = 1.7 Hz, 1 H), 5.07 (apparent t, *J* = 9.2 Hz, 1 H), 4.21 (dd, *J* = 4.4, 2.0 Hz, 1 H), 4.13 – 4.09 (m, 2 H), 3.32 (dd, *J* = 8.8, 4.4 Hz, 1 H), 2.46 (s, 3 H), 2.15 (s, 3 H), 2.09 (s, 3 H), 0.90 (s, 9 H), 0.10 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 168.1, 144.9, 132.3, 129.7, 128.0, 94.5, 71.5, 70.5, 68.4, 67.4, 33.6, 25.4, 21.6, 20.8, 17.8, –4.7, –4.8; IR (thin film) 2930, 2858, 1752, 1598, 1472, 1370, 1295, 1217,

1190, 1177, 1146, 1097, 1046, 1008, 949, 839, 779, 667 cm^{-1}; high resolution FAB MS calcd for $C_{23}H_{35}IO_9SSi$ ($M+Na^+$) 665.0715, found 665.0730.



15

Data for Iodoacetate **15** : ^1H NMR (500 MHz, $CDCl_3$) δ 6.43 (s, 1 H), 5.36 (broad s, 1 H), 4.83 (apparent t, *J* = 4.2 Hz, 1 H), 4.34 (ddd, *J* = 6.8, 6.4, 2.0 Hz, 1 H), 4.23 (dd, *J* = 4.2, 0.7 Hz, 1 H), 4.18 (d, *J* = 6.8 Hz, 2 H), 2.12 (s, 3 H), 2.08 (s, 3 H), 2.02 (s, 3 H), 1.98 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 169.8, 169.3, 168.0, 95.8, 68.8, 64.6, 61.3, 20.8, 20.7, 20.5, 18.8; IR (thin film) 1749, 1434, 1372, 1218, 1133, 1073, 1051, 994, 939 cm^{-1}; high resolution FAB MS calcd for $C_{14}H_{19}IO_9$ ($M+Na^+$) 480.9973, found 480.9969.