Supplementary data

Highly Regioselective Cleavages and Iodinations of Cyclic Ethers Utilizing SmI_2

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Typical procedure for the synthesis of oxetanes 4¹: A mixture of KO^iBu - t (1.12 g, 10 mmol) and trimethyloxosulphonium iodide (2.2 g, 10 mmol) in dry t -BuOH (13 mL) was stirred magnetically at 50 °C for 1 h. A solution of styrene epoxide (0.6 g, 5 mmol) in dry t -BuOH (10 mL) was then added dropwise and stirred for 3 days. The solvent was carefully evaporated under reduced pressure and water (30 mL) was added to the residual suspension. The mixture was extracted with n -hexane, dried over anhydrous MgSO_4 and concentrated to give the crude product 4 which was purified by silica-gel column chromatography to afford 4 as a colorless oil (0.47 g, 3.5 mmol, 70%). Isomer could not be detected by ^1H NMR.

5 : The same procedure described for compound 4 was carried out to give 5 (60%) as a

colorless oil. Isomer could not be detected by ^1H NMR.

^1H NMR (CDCl_3) δ 7.30 (m, 5H), 4.83 (m, 1H), 4.68 (m, 1H), 4.52 (m, 1H), 2.64 (m, 3H), 2.35 (m, 1H), 2.15 (m, 1H), 1.98 (m, 1H); ^{13}C NMR δ 141.5, 128.5, 128.3, 125.7, 81.9, 68.1, 39.5, 30.3, 27.4; HREIMS $[\text{M}^+]$ Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}$ 162.1044; found: 162.1049.

6 : The same procedure described for compound 4 was carried out to give 6 (65%) as a colorless oil. Isomer could not be detected by ^1H NMR.

^1H NMR (CDCl_3) δ 7.32 (m, 5H), 4.96 (m, 1H), 4.63 (m, 4H), 3.66 (m, 2H), 2.63 (m, 2H); ^{13}C NMR δ 137.7, 128.3, 127.6, 127.5, 81.2, 73.49, 73.44, 68.9, 23.8; HREIMS $[\text{M}^+]$ Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_2$ 178.09938; found: 178.0991.

7 : The same procedure described for compound 4 was carried out to give 7 (63%) as a colorless oil. Isomer could not be detected by ^1H NMR.

^1H NMR (CDCl_3) δ 7.32 (m, 5H), 4.98 (m, 1H), 4.64 (m, 1H), 4.52 (m, 1H), 4.46 (s, 2H), 3.52 (m, 2H), 2.65 (m, 1H), 2.41 (m, 1H), 2.09 (m, 2H); ^{13}C NMR δ 138.3, 128.3, 127.5, 127.4, 80.2, 73.0, 68.3, 65.9, 38.0, 27.5; HREIMS [M^+] Calcd. for $\text{C}_{12}\text{H}_{16}\text{O}_2$. 192.11503; found: 192.1151.

Typical reaction for the cleavages of cyclic ethers 1a: To a solution of SmI_2 (1.0 mmol) in THP (10 mL) was added cyclic ether 1 (55 mg, 0.55 mmol) and acetyl chloride (39 mg, 0.5 mmol) in one portion. The mixture was stirred for 1 h under argon at room temperature. The reaction mixture was quenched with saturated aqueous NH_4Cl (5 mL). The reaction mixture was diluted with Et_2O (5 mL) and the organic layer was washed with water. The aqueous phase was extracted with Et_2O (10 mL x 2) and the combined organic layers were washed with brine, dried over anhydrous MgSO_4 and concentrated to give the crude product which was purified by silica-gel column chromatography (230-400 mesh, 2 cm x 25 cm, eluent : Et_2O : n-hexane = 1: 1) afforded 1a (117 mg, 87%) as a yellow oil. ^1H NMR (CDCl_3) δ 4.9 (m, 1H), 4.14 (m, 1H), 2.0 (s, 3H), 1.89 (d, J = 6.4, 3H), 1.7 (m, 4H), 1.47 (d, J = 6.3, 3H); ^{13}C NMR δ 170.7, 70.2, 69.7, 38.7, 38.3, 36.1, 35.8, 29.4, 28.8, 21.3, 20.0; HREIMS [M^+] Calcd. for $\text{C}_8\text{H}_{15}\text{IO}_2$.

270.0116; found: 270.0124.

Acetic acid 4-iodo-1-methylbutyl ester (2a). The ratio of **2a** and **2b** was determined by

^1H NMR analysis of the mixture of **2a** and **2b**. The **2a** and **2b** were separated by column

chromatography (2 cm x 30 cm, eluent: ethyl acetate : n-hexane = 1: 20). **2a**: yellow oil;

^1H NMR (CDCl_3) δ 4.91 (m, 1H), 3.15 (t, $J=6.8$, 2H), 1.99 (s, 3H), 1.88-1.55 (m, 4H),

1.21 (d, $J=6.3$, 3H); ^{13}C NMR δ 170.5, 69.7, 36.6, 29.3, 21.2, 19.9, 6.1; HREIMS [M^+]

Calcd. for $\text{C}_7\text{H}_{13}\text{IO}_2$. 255.9960; found: 255.9968, **2b**: yellow oil; ^1H NMR (CDCl_3)

δ 4.12 (m, 1H), 4.05 (t, $J=6.1$, 2H), 2.02 (s, 3H), 1.92 (d, $J=6.9$, 3H), 1.88-1.55 (m,

4H); ^{13}C NMR δ 171.0, 63.4, 39.1, 29.0, 28.95, 28.90, 20.9; HREIMS [M^+] Calcd. for

$\text{C}_7\text{H}_{13}\text{IO}_2$. 255.9960; found: 255.9960.

3a : The same procedure described for compound **1a** was carried out to give **3a** (70%)

as the major product. Yellow oil; ^1H NMR (CDCl_3) δ 5.07 (m, 1H), 4.22 (dd, $J=11.9$,

3.5, 1H), 4.04 (dd, $J=11.9$, 6.3, 1H), 3.16 (t, $J=6.7$, 2H), 2.05 (s, 3H), 1.82-1.65 (m,

4H); ^{13}C NMR δ 170.7, 70.3, 64.8, 31.6, 28.9, 21.0, 20.7, 5.6; HREIMS [M^+] Calcd. for

$\text{C}_7\text{H}_{13}\text{IO}_3$. 271.9909; found: 271.9892.

Benzoic acid 3-phenylpropyl ester (4b). The same procedure described for compound **1a** was carried out to give deiodinated product **4b** (89%) as a sole product. **4b**: yellow oil; ^1H NMR (CDCl_3) δ 8.0-7.1 (m, 10H), 4.35 (t, $J = 6.5$, 2H), 2.8 (t, $J = 7.6$, 2H), 2.1 (m, 2H); ^{13}C NMR δ 166, 141, 132, 130, 129, 128.5, 128.4, 128.3, 126, 64.2, 32, 30; HREIMS [M^+] Calcd. for $\text{C}_{16}\text{H}_{16}\text{IO}_2$ 240.1150; found: 240.1150.

5a : The reaction gave a mixture **5a** and **5b** in the ratio 5 : 4 as indicated by ^1H NMR. The same procedure for compound **1a** was carried out to give **5a** (46%) and **5b** (36%). **5a**: yellow oil; ^1H NMR (CDCl_3) δ 7.28 (m, 5H), 4.95 (m, 1H), 3.12 (m, 2H), 2.61 (m, 2H), 2.15 (m, 2H), 2.04 (s, 3H), 1.83 (m, 2H); ^{13}C NMR δ 170.6, 141.1, 128.4, 128.2, 126.0, 73.8, 38.5, 35.3, 31.5, 21.0, -0.25; HREIMS [M^+] Calcd. for $\text{C}_{13}\text{H}_{17}\text{IO}_2$ 332.0273; found: 332.0242.

5b : yellow oil (36%); ^1H NMR (CDCl_3) δ 7.28 (m, 5H), 4.27 (m, 1H), 4.11 (m, 2H), 2.88 (m, 1H), 2.71 (m, 1H), 2.19-2.02 (m, 4H), 1.99 (s, 3H); ^{13}C NMR δ 170.8, 140.4, 128.4, 128.2, 126.0, 63.9, 42.1, 39.1, 35.4, 32.6, 20.8; HREIMS [M^+] Calcd. for $\text{C}_{13}\text{H}_{17}\text{IO}_2$ 332.0273; found: 332.0207.

6a : The same procedure described for compound **1a** was carried out to give **6a** as a sole product (81%). The **6b** could not be detected by ^1H NMR. Yellow oil; ^1H NMR (CDCl_3) δ 7.32 (m, 5H), 5.05 (m, 1H), 4.53 (d, $J = 11.8$, 1H), 4.49 (d, $J = 12.1$, 1H), 3.52 (d, $J = 4.6$, 2H), 3.11 (m, 2H), 2.20 (m, 2H), 2.05 (s, 3H); ^{13}C NMR δ 170.4, 137.7, 128.4, 127.7, 127.6, 73.2, 72.7, 70.1, 35.0, 21.0, 0.037; HREIMS [M^+] Calcd. for $\text{C}_{10}\text{H}_{17}\text{IO}_3$. 348.0222; found: 348.0221.

7a : The reaction gave mixed **7a** and **7b** in the ratio 4 : 1 as indicated by ^1H NMR. The same procedure described for compound **1a** was carried out to give **7a** (67%) and **7b** (16%). Yellow oil; ^1H NMR (CDCl_3) δ 7.30 (m, 5H), 5.04 (m, 1H), 4.45 (s, 2H), 3.47 (m, 2H), 3.09 (m, 2H), 2.11 (m, 2H), 2.00 (s, 3H), 1.89 (m, 2H); ^{13}C NMR δ 170.5, 138.1, 128.3, 127.7, 127.6, 73.1, 72.1, 66.3, 38.7, 33.8, 21.0, -0.255; HREIMS [M^+] Calcd. for $\text{C}_{14}\text{H}_{19}\text{IO}_3$. 362.0378; found: 362.0396.

7b (16%). ^1H NMR (CDCl_3) δ 7.29 (m, 5H), 4.50 (s, 2H), 4.48-4.16 (m, 3H), 3.62 (m,

2H), 2.12-2.01 (m, 4H), 2.03 (s, 3H); ^{13}C NMR δ 170.8, 138.1, 128.3, 127.7, 127.6, 73.2, 69.4, 64.1, 40.5, 39.2, 29.9, 20.8; HREIMS $[\text{M}^+]$ Calcd. for $\text{C}_{14}\text{H}_{19}\text{IO}_3$, 362.0378; found: 362.0356.

Acetic acid 1-benzyloxymethyl-2-iodo-ethyl ester (8a). The same procedure described for compound **1a** was carried out to give **8a** (91%) as a sole product. The **8b** could not be detected by ^1H NMR. Yellow oil; ^1H NMR (CDCl_3) δ 7.29 (m, 5H), 4.90 (m, 1H), 4.54 (q, $J=3.4$, 2H), 3.67 (dd, $J=10.3$, 4.9, 1H), 3.56 (dd, $J=10.3$, 5.1, 1H), 3.43 (dd, $J=10.4$, 5.6, 1H), 3.33 (dd, $J=10.4$, 5.6, 1H), 2.07 (s, 3H); ^{13}C NMR δ 170.01, 137.55, 128.41, 127.82, 127.68, 73.39, 71.30, 70.02, 20.96, 3.92 ; HREIMS $[\text{M}^+]$ Calcd. for $\text{C}_{12}\text{H}_{15}\text{IO}_3$, 334.0065; found: 334.0059.

Acetic acid 3-benzyloxy-1-iodomethylpropyl ester (9a). The same procedure described for compound **1a** was carried out to give **9a** (92%) as a sole product. The **9b** could not be detected by ^1H NMR. Yellow oil; ^1H NMR (CDCl_3) δ 7.31 (m, 5H), 4.84 (m, 1H), 4.46 (q, $J=4.3$, 2H), 3.48 (m, 2H), 3.44 (dd, $J=10.6$, 4.7, 1H), 3.27 (dd, $J=$

10.7, 5.0, 1H), 2.02 (s, 3H), 1.96 (m, 2H); ^{13}C NMR δ 170.15, 137.99, 128.35, 127.64, 127.62, 73.02, 69.87, 65.79, 34.39, 20.98, 8.83; HREIMS $[\text{M}^+]$ Calcd. for $\text{C}_{13}\text{H}_{17}\text{IO}_3$, 348.022; found: 348.023.

Acetic acid 1-iodomethyl-3-phenylpropyl ester (10a). The same procedure described for compound **1a** was carried out to give **10a** (91%) as a sole product. The **10b** could not be detected by ^1H NMR. Yellow oil; ^1H NMR (CDCl_3) δ 7.23 (m, 5H), 4.71 (m, 1H), 3.36 (dd, $J = 10.8, 5.2$, 1H), 3.26 (dd, $J = 10.7, 5.2$, 1H), 2.63 (m, 2H), 2.07 (s, 3H), 1.99 (m, 2H); ^{13}C NMR δ 170.32, 140.73, 128.50, 128.28, 126.16, 71.72, 35.77, 31.39, 21.04, 8.14; HREIMS $[\text{M}^+]$ Calcd. for $\text{C}_{12}\text{H}_{15}\text{IO}_2$, 318.0116; found: 318.0110.

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