Supporting Informations

“A Convenient Synthesis of 2-Tetrahydrofuranyl Ethers by
Rachid Baati, Alain Valleix, Charles Mioskowski,
D. K. Barma andJ. R. Falck”

Experimental Section

$CrCl_2$ (95%) was purchased from Lancaster and used without further purification. All reactions were performed under argon, and anhydrous solvents were dried and distilled before use.

General procedure for the tetrahydrofuranylation of alcohols. To a stirred suspension of chromium(II) chloride (2.5 mmol, 2.5 eq.) in THF (15ml) was added a THF (5ml) solution containing the alcohol (1mmol, 1 eq.) and CCl_4 (2.5 mmol, 2.5 eq.). The reaction mixture was stirred at room temperature until total conversion of the alcohol. The reddish reaction mixture was quenched with sat. aquous NH_4Cl and extracted twice with diethyl ether. The combined organic extracts were washed with water and brine, dried over $MgSO_4$ and concentrated in vacuo to give the crude tetrahydrofuranyl ether as an oil. Purification by column on silica gel (hexane/diethyl ether 98/2) afforded analytically pure compounds.

2-Phenethyloxy-tetrahydro-furan 2: 24µl (0.20mmol) of 2-phenylethanol, 48µl (0.50mmol) CCl_4 , 61.5mg (0.50mmol) of $CrCl_2$; yield: 42.6mg (90%); NMR ^1H ($CDCl_3$, 300 MHz): 1.50-2.10 (m, 4H), 2.92 (t, *J*=8Hz, 2H), 3.50-4.10 (m, 4H), 5.15 (m, 1H), 7.10-7.40 (m, 5H). ^{13}C NMR ($CDCl_3$, 300 MHz): 23.4, 32.3, 36.4, 66.9, 67.8, 103.8, 126.1, 128.3, 128.9, 139.1. IR (neat, cm^{-1}): 3021, 2987, 1620, 926. MS (DCI/NH_3) m/z (MNH_4^+)= 210.

2-(2-Isopropyl-5-methyl-cyclohexyloxy)-tetrahydro-furan 4: 33mg (0.21mmol) of L-menthol, 51µl (0.53mmol) CCl_4 , 65.2mg (0.53mmol) of $CrCl_2$; yield: 56mg (85%); ***Mixture of stereoisomers 50/50:*** NMR ^1H ($CDCl_3$, 300 MHz): 0.71-2.32 (m, 21H), 3.20-3.60 (m, 1H), 3.70-4.10 (m, 2H), 5.15-5.33 (m, 1H). ^{13}C NMR ($CDCl_3$, 300 MHz): 15.5, 16.3,

21.1, 21.2, 22.3, 22.4, 23.1, 23.3, 23.5, 23.6, 25.4, 25.6, 31.4, 31.7, 32.5, 32.6, 34.4, 34.6, 40.0, 43.4, 48.1, 48.7, 66.5, 66.7, 73.5, 78.7, 99.4, 105.4. IR (neat, cm^{-1}): 2998, 929. MS (DCI/NH_3) m/z (MNH_4^+)= 244.

2-(3-Phenyl-allyloxy)-tetrahydro-furan 6: 40µl (0.31mmol) of cinnamyl alcohol, 74µl (0.77mmol) CCl_4 , 95mg (0.77mmol) of $CrCl_2$; yield: 69mg (92%); NMR ^1H ($CDCl_3$, 300 MHz: 1.70-2.20 (m, 4H), 3.80-4.05 (m, 2H), 4.13 (ddd, *J*=13, *J*=7, *J*=1, 1H), 4.35 (ddd, *J*=13, *J*=7, *J*=1, 1H), 5.24 (m, 1H), 6.29 (ddd, *J*=16, *J*=7, *J*=6, 1H), 6.63 (d, *J*=16, 1H); 7.10-7.50 (m, 5H). ^{13}C NMR ($CDCl_3$, 300 MHz): 23.5, 32.4, 67.1, 67.6, 103.2, 126.1, 126.5, 127.6, 128.5, 132.3, 136.8. IR (neat, cm^{-1}): 3050, 2980, 1590, 926. MS (DCI/NH_3) m/z (MNH_4^+)= 222.

2- Benzyloxy-tetrahydro-furan 8: 22µl (0.21mmol) of benzylic alcohol, 50µl (0.53mmol) CCl_4 , 65mg (0.53mmol) of $CrCl_2$; yield: 40mg (95%); NMR ^1H ($CDCl_3$, 300 MHz): 1.70-2.20 (m, 4H), 3.84-4.04 (m, 2H), 4.49 (d, *J*=12Hz, 1H), 4.73 (d, *J*=12Hz, 1H), 5.23 (m, 1H), 7.18-7.50 (m, 5H). ^{13}C NMR ($CDCl_3$, 300 MHz): 23.5, 32.3, 67.1, 68.8, 103.1, 127.5, 127.9, 128.4, 138.4. IR (neat, cm^{-1}): 3012, 2995, 1610, 932. MS (DCI/NH_3) m/z (MNH_4^+)= 196.

2-(Tetrahydro-furan-2-yloxymethyl)-furan 10: 26µl (0.30mmol) of furfuryl alcohol, 72µl (0.75mmol) CCl_4 , 93mg (0.75mmol) of $CrCl_2$; yield: 46mg (91%); NMR ^1H ($CDCl_3$, 300 MHz): 1.70-2.20 (m, 4H), 3.80-4.05 (m, 2H), 4.46 (d, *J*=13, 1H), 4.62 (d, *J*=13, 1H), 5.22 (m, 1H), 6.33 (s, 2H), 7.41 (s, 1H). ^{13}C NMR ($CDCl_3$, 300 MHz): 23.4, 32. 3, 60.6, 67.1, 102.7, 109.2, 110.2, 142.8, 151.5. IR (neat, cm^{-1}): 3080, 2987, 1610, 990, 930. MS (DCI/NH_3) m/z (MNH_4^+)= 186.

2-Phenoxy-tetrahydro-furan 12: 27mg (0.28mmol) of phenol, 69µl (0.72mmol) CCl_4, 89mg (0.72mmol) of $CrCl_2$; yield: 27mg (58%); NMR ^1H ($CDCl_3$, 300 MHz): 1.70-2.50 (m, 4H), 3.60-4.30 (m, 2H), 5.60-6.50 (m, 1H), 6.70-7.60 (m, 5H). ^{13}C NMR ($CDCl_3$, 300 MHz): 23.4, 32.7, 68.1, 102.3, 116.5, 121.5, 129.4, 157.1. IR (neat, cm^{-1}):3095, 1653, 926. MS (DCI/NH_3) m/z (MNH_4^+)= 182.

2-(1-Methyl-1-phenyl-ethoxy)-tetrahydro-furan 14: 40µl (0.27mmol) of dimethyl phenyl carbinol, 79µl (0.82mmol) CCl_4 , 101mg (0.82mmol) of $CrCl_2$; yield: 26.1mg (47%); NMR ^1H ($CDCl_3$, 300 MHz): 1.52 (s, 3H), 1.67 (s, 1H), 1.70-2.10 (m, 4H), 3.60-4.10 (m, 2H), 5.11 (dd, J=3, 1H), 7.10-7.40 (m, 5H). ^{13}C NMR ($CDCl_3$, 300 MHz): 23.3, 28.7, 32.9, 67.1, 77.3; 103.6, 125.3, 126.5, 129.6, 144.1. IR (neat, cm^{-1}): 3101, 1615, 935. MS (DCI/NH_3) m/z (MNH_4^+)= 224.

2-(4-Methoxy-benzyloxy)-tetrahydro-furan 16: 65mg (0.47mmol) of 4-methoxybenzyl alcohol, 106µl (1.1mmol) CCl_4 , 135mg (1.1mmol) of $CrCl_2$; yield: 93mg (95%); NMR ^1H ($CDCl_3$, 300 MHz): 1.70-2.10 (m, 4H), 3.81 (s, 3H), 3.92 (m, 2H), 4.41 (d, *J*=12, 1H), 4.65 (d, *J*=12, 1H), 5.21 (t, *J*=3, 1H), 6.88 (d, *J*=9, 2H), 7.28 (d, *J*=9, 2H). ^{13}C NMR ($CDCl_3$, 300 MHz): 23.5, 32.3, 55.3, 66.9, 68.5, 102.9, 113.8, 129.5, 130.5, 158.9. IR (neat, cm^{-1}): 3031, 2986, 1619, 889. MS (DCI/NH_3) m/z (MNH_4^+)= 226.

4-(Tetrahydro-furan-2-yloxymethyl)-benzoic acid methyl ester 18*:* 80mg (0.48mmol) of 4-hydroxymethyl-benzoic acid methyl ester, 115µl (1.2mmol) CCl_4 , 148mg (1.2mmol) of $CrCl_2$; yield: 103mg (91%); NMR ^1H ($CDCl_3$, 300 MHz): 1.70-2.20 (m, 4H), 3.70-4.10 (m, 5H), 4.54 (d, *J*=13Hz, 1H), 4.77 (d, *J*=13Hz, 1H), 5.23 (m, 1H), 7.41 (d, *J*=8Hz, 2H), 8.01 (d, *J*= 8Hz, 2H). ^{13}C NMR ($CDCl_3$, 300 MHz): 23.4, 32.4, 52.1, 67.1, 68.1, 103.4,

127.3, 129.2, 129.7, 143.8, 166.9. IR (neat, cm^{-1}): 2995, 1730, 1643, 932. MS (DCI/NH_3) m/z (MNH_4^+)= 254.

5-(Tetrahydro-furan-2-yloxymethyl)-benzo (1,3)dioxole 20: 76mg (0.50mmol) of 3,4-methylenedioxybenzyl alcohol, 120µl (1.25mmol) CCl_4 , 154mg (1.25mmol) of $CrCl_2$; yield: 93mg (84%); NMR ^1H ($CDCl_3$, 300 MHz): 1.70-2;10 (m, 4H), 3.80-4.10 (m, 2H), 4.38 (d, *J*=12, 1H), 4.61 (d, *J*=12, 1H), 5.21 (t, *J*=4, 1H), 5.95 (s, 2H), 6.70-7.05 (m, 3H). ^{13}C NMR ($CDCl_3$, 300 MHz): 23.5, 32.3, 66.9, 68.6, 100.9, 102.8, 108.1, 108.7, 121.4, 132.1 146.9, 147.6. IR (neat, cm^{-1}): 3029, 2999, 887, 925. MS (DCI/NH_3) m/z (MNH_4^+)= 240.

2-(2-chloro-2-phenyl-ethoxy)-tetrahydro-furan 22: 40mg (0.26mmol) of 2-chloro-2-phenyl ethanol, 63µl (0.65mmol) CCl_4 , 80mg (0.65mmol) of $CrCl_2$; yield: 47mg (82%); NMR ^1H ($CDCl_3$, 300 MHz): ***Mixture of stereoisomer 50/50***: NMR ^1H ($CDCl_3$, 300 MHz): 1.70-2.10 (m, 8H), 3.65-3.95 (m, 6H), 4.00-4.20 (m, 2H), 5.02 (m, 2H), 5.11 (m, 1H), 5.21 (m, 1H), 7.39 (m, 10H). ^{13}C NMR ($CDCl_3$, 300 MHz): 23.3, 32.4, 61.0, 61.8, 67. 1, 71.5, 71.9, 103.9, 104.3, 127.5, 127.6, 128.5, 138.8. IR (neat, cm^{-1}): 3052, 2996, 1612, 932. MS (DCI/NH_3) m/z (MNH_4^+)= 244.

2-(2,2,2-Trichloro-Ethoxy)-tetrahydro-furan 24: 55µl (0.55mmol) of trichloro ethanol, 135µl (1.4mmol) CCl_4 , 169mg (1.4mmol) of $CrCl_2$; yield: 104mg (87%); NMR ^1H ($CDCl_3$, 300 MHz): 1.70-2.30 (m, 4H), 3.95 (m, 2H), 4.10 (d, *J*=11Hz, 1H), 4.25, (d, *J*=11Hz, 1H), 5.39 (d, *J*=7Hz, 1H). ^{13}C NMR ($CDCl_3$, 300 MHz): 23.1, 32.3, 67.6, 78.7, 97.2, 104.4. IR (neat, cm^{-1}): 2987, 920. MS (DCI/NH_3) m/z (MNH_4^+)= 236.

2-(2-chloro-1H-inden-1-yloxy)-tetrahydro-furan 26: : 50mg (0.30mmol) of 2-chloro-1H-inden-1-ol, 72µl (0.75mmol) CCl_4 , 93mg (0.75mmol) of $CrCl_2$; yield: 64mg (90%). **The less polar isomer**: NMR ^1H ($CDCl_3$, 300 MHz): 1.70-2.20 (m, 4H), 4.10-4.30 (m, 2H), 5.06 (s, 1H), 5.54 (d, *J*=3, 1H), 6.61 (s, 1H), 7.20-7.55 (m, 5H). ^{13}C NMR ($CDCl_3$, 300 MHz): 23.3, 32.6, 67.6, 81.3, 104.3, 120.7, 124.2, 125.9, 128.3, 128.7, 140.2, 140.9, 141.7. **The more polar isomer**: NMR ^1H ($CDCl_3$, 300 MHz): 1.65-2.35 (m, 4H), 3.90-4.20 (m, 2H), 5.14 (s, 1H), 5.53 (m, 1H), 6.67 (s, 1H), 7.10-7.50 (m, 5H). ^{13}C NMR ($CDCl_3$, 300 MHz): 23.1, 32.9, 67.4, 79.5, 102.7, 120.8, 123.6, 125.8, 128.6, 129.3, 140.75, 142.5. IR (neat, cm^{-1}): 3102, 2986, 1623, 990, 929. MS (DCI/NH_3) m/z (MNH_4^+)= 254.