**Supplement 7: Summary of Reactions To And From ROH (Alcohols) (no phenols here)**

*Chemistry 4524 Organic Chemistry II SEE CHAPTER 17*

**Reactions to ROH: the baker’s dozen (pp. 502-512)**

***a) Organolithium & Grignard rxns to bigger alcohols***

R’ R’

**aldehyde ketone** then H2O/H+ | |

**1)R**MgX/ether + R’ ***CHO*** or R’ R“***C=O*** ------🡪 **R-*CH-O***H or **R**-***C-O***H

**2o** |  **3o**

R”

**R ester** then H2O/H+ |

**2)** 2**R**MgX + R’***CH=O*** --------🡪 **R’**-***C -O***H + R”OH

| | **3o**

OR”  **R** R’ R’

ether then H2O/H+ | |

**3)** **R**Li + R’ ***CHO*** or R’ R“***C=O*** ---------------🡪 **R-*CH-O***H or **R**-***C-O***H

|

R”

O ether, then H2O/H+

**4**)RMgX + CH2-CH2 --------------🡪 RCH2CH2 OH (1o increase by 2C)

**b)** ***Reductions of carbonyls*** **R’**

**aldehyde or ketone** *Pt, Pd,Ru or Ni* |

**5)** (**R**CHO or **RR’** CO) + H2 (gas) ------------------------🡪 **R-**CH2**OH** or **R** -CH-**OH**

**1o 2o**

*in ether, then H2O*

**6)** (**R**CHO or **RR’**CO) + LiAlH4 --------------------------🡪 same as above

*in water or methanol*

**7)** (**R**CHO or **RR’** CO) + NaBH4 ---------------------------🡪same as above

**carboxylic acid** *in ether, then H2O*

**8**) **R**COOH + LiAlH4 ---------------------------🡪 **R**CH2**OH**

**1o**

**ester** *in ether, then H2O*

**9**) R-C=**O** + LiAlH4  --------------------------🡪 RCH2**OH** + ***R’O***H

| **1o**

***OR’***

***c) Additions across alkenes***

***H20****/H2SO4*

**10)** RR’C=CHR-------------------🡪 RR’C-CHR” markovnikoff

| |**(carbocations/Hydrolysis) *HO H***

***1,2 or 3o***

*Hg(OAc)2*/THF N*aBH4*/**OH-**

**11)** RR’C=CHR”----------------🡪 ------------🡪 same as above markovnikoff

**(H.C.Brown/mercuration-demercuration)**

B2H6/diglyme H2O2/**OH-**

**12)** RR’C=CHR”---------------🡪 ------------🡪 RR’C-CHR” anti-markovnikoff

| | **(H.C. Brown/hydroboration-oxidation*)***  ***H OH***

**d) hydrolysis of RX**:

in acetone/H2O & heat

**13)** ex. t-butyl chloride -------- --------------🡪 t-butanol (easy with 3o)..

needs KHCO3 base and heat if 1o RX)

**Reactions from ROH: the dirty dozen (pp 512-524)**

**a)**R**-OH**

aq or non-aq

**1)** Classical **Halogenation** R-**OH** + H**X** R**-X** + H2O

loss or inversion of stereochemistry

loss via SN1 if R=2,3o

inversion via SN2 if R=1o w/5-coordinate transition for 1o

in ether or freon

**2)** Modern’ **Halgenation**  R-**OH** + SO**X**2 R**-X** + S**O**2 + HX neat

**3)** More Modern **Halogenation** 3R**-OH** + P**X**3 3R**-X** + H3P**O**3

retention of stereochemistry for both

H2SO4/reflux

4) Dehydration 1 & 2o ROH alkenes

**b) RO-H cleavages**

H2SO4/heat

**4) Ether** synthesis by dehydration RO-**H** +R-**OH** RO-R+**H2O**

acid-catalyzed condensation...a non-Williamson method

H2SO4/heat

**5)** **Ester** synthesis by dehydration RO-**H** + **HO-**C=O RO**-C=O** + **H2**O

| |

R’ R’

acid-catalyzed cross-condensation...acid+ alcohol=ester

**6)** **Ester** synthesis by acylation RO-**H** + **Cl-**C=O pyridine RO-C=O + HCl

| |

R’ R’

base-catalyzed cross-condensation...acid chloride+alcohol=ester

conc H2SO4

**7)** inorganic OXY ester syntheses RO-H + Ho-(oxy) RO-OXY + H2O

ex. CH3O-H + HO-NO2 CH3O-NO2 +H2O

neat

**8) metal (M) alkoxide** synthesis RO-**H** + **M**(= Li,Na, K,Al,,Zn) RO**-M+** + **H**2

route to reactive alkoxide anion, RO-, which leads to soaps, perfumes, food products

heat, KHSO4(weak base)

**9)** **alkyl sulfonate** synthesis RO-**H** + R’SO2-**Cl** RO-SO2R’ + **HC**l

general way to make a good leaving group for further substitution



(sulfonate ester)

*example* C2H5 O\_ M+ (Can be any Y-)

CH3OC2H5

**c)oxidative cleavages:** R***H***CHO**-H** ***hydroxy and α-H eliminations***

K2Cr2O7 /H2 SO4

**10)** oxidation of 1o alcohol to **acids** R***H***CH-O-**H** RC**OOH ONE** **O** added

loss of hydroxyl H, cleavage of α-H by O  pcc

**11)** oxidation of 1o alcohol to **aldehydes** R***H***CH-O-**H** RCH**=**O **ZERO** **O** added

loss of both hydroxyl and α-H

K2Cr2O7/H2SO4

**12)** oxidation of 2o alcohols to **ketones** RR’***H***C-O-**H** RR**’**C=O **ZERO O** added

loss of both hydroxyl and α-H