Selectivity : Reductions and oxidations

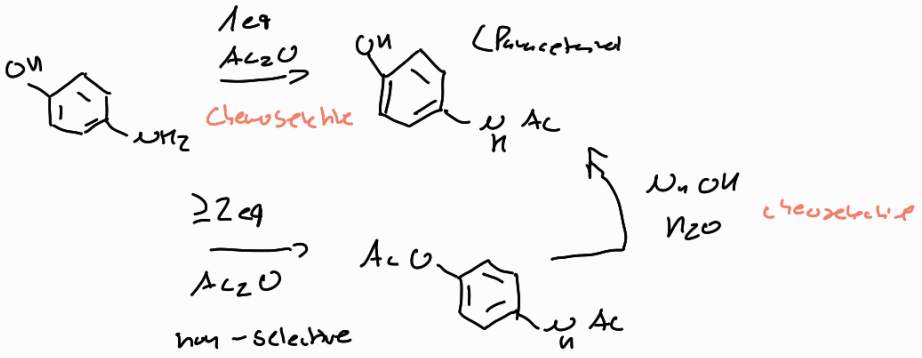
1) Chemo selectivity => which will react?

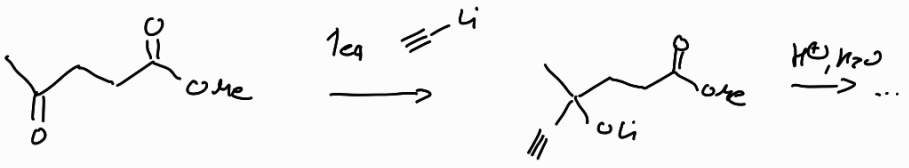
2) Regio selectivity => where react?

3) Steveo selectivity

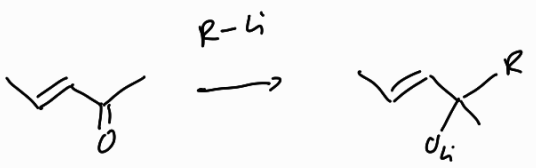
---

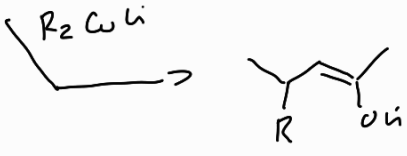
ex Paracetamol





ex





=> since  consided one groupe (michal acceptor)

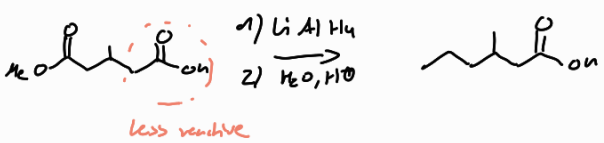
Reductions

Rule of Thumb : use mildest agent possible !! => gives Chemoselectivity

Aldehydes & ketones

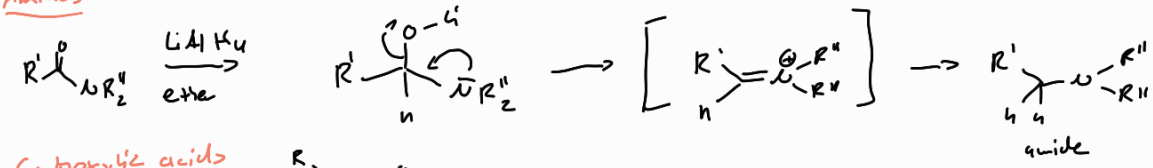
$NaBH_4$ - Stable, easy to handle, safe

Esters

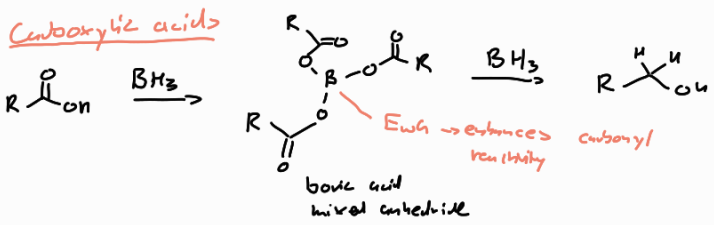


=> Alternatively $LiBH_4$ = less reactive

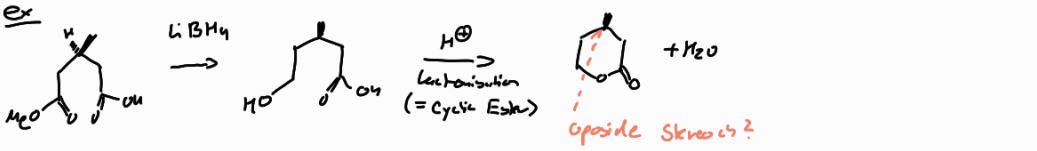
Amides

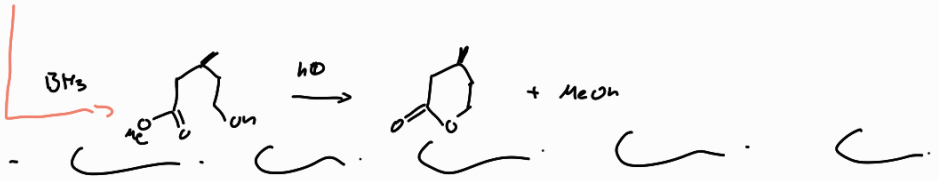


Carboxylic acids



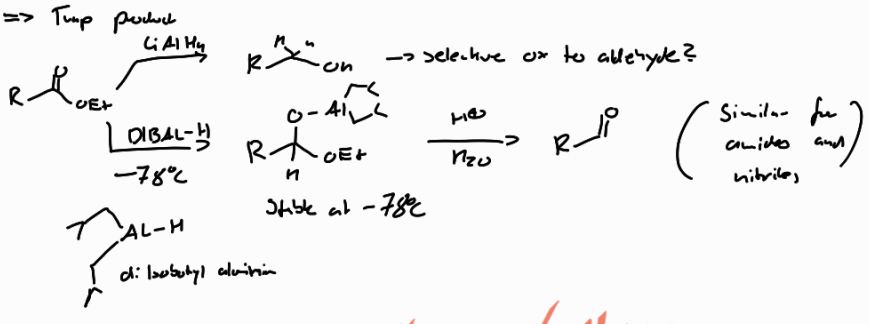
ex





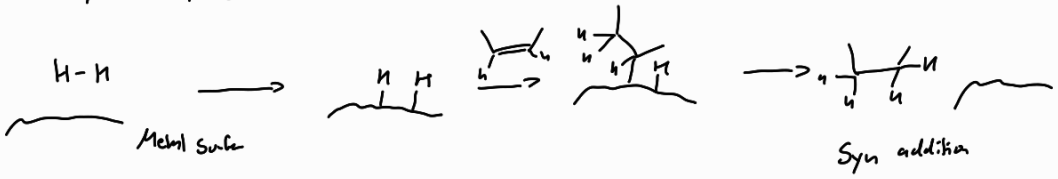
Reduce ester / Amide to aldehyde ?

Problem: aldehyde is more reactive
=> Trap product



Reduction of alkenes / alkynes

=> Catalytic hydrogen "molecular" hydrogen

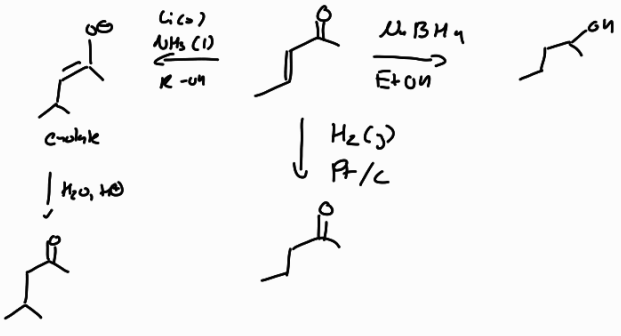


ex Pd, Pt, Ru, Rh, Ni

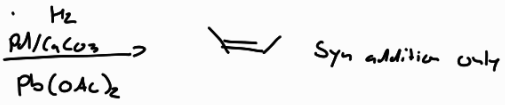
alkene → alkane

=> Also Reduction of Michael acceptors

Early lecture (3)



Alkyne Hydration

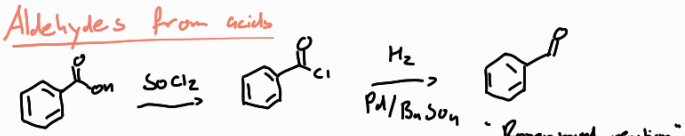


Syn addition only

Pb poison catalyst

Lindlar catalyst

Aldehydes from acids

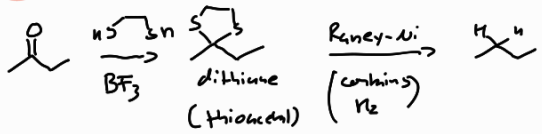


Benzoic acid

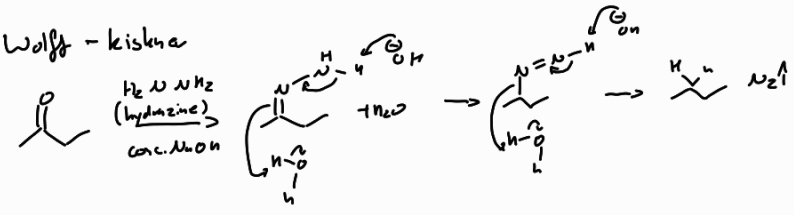
"Rosenmund reaction"

Reduction of aldehydes and Ketones to alkanes

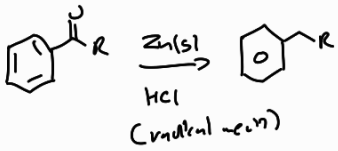
1) Dithianes:



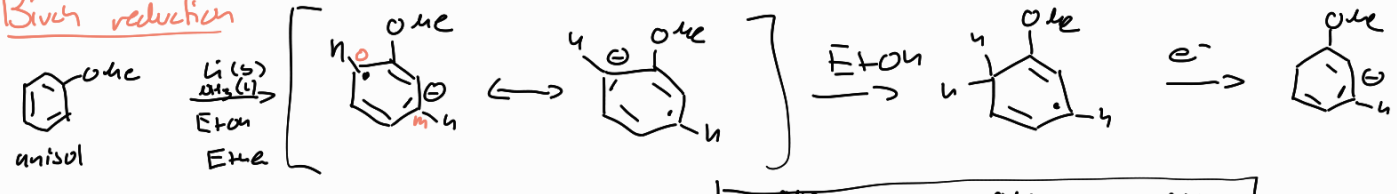
2) Wolff-Kishner

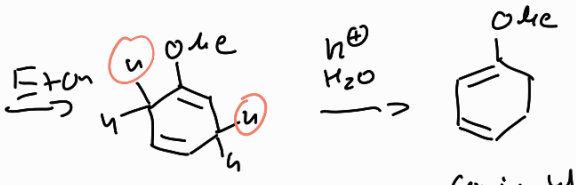


3) Clemmensen



Birch reduction



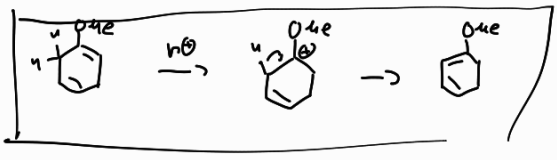


2H added

not aromatic

Conjugated diene

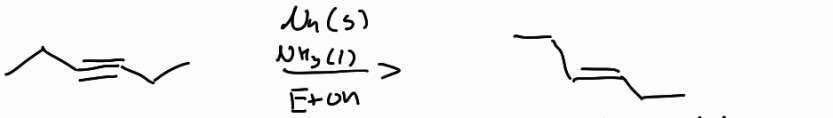
= thermodynamically favoured



=> e⁻ donating group => Ortho and meta radical anion

=> e⁻ withdrawing group => Para radical anion

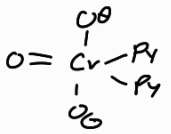
Dissolving metal reduction of alkynes



anti addition

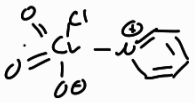
Oxidations and chemoselectivities

Cr-reagents a) $CrO_3 + H_2O \rightarrow H_2CrO_4$ (chromic acid)

b) $Py_2 \cdot CrO_3 \rightarrow$  Py = pyridine = 

Collins reagent

Stable were com with

c) PCL = pyridinium chlorochromate 

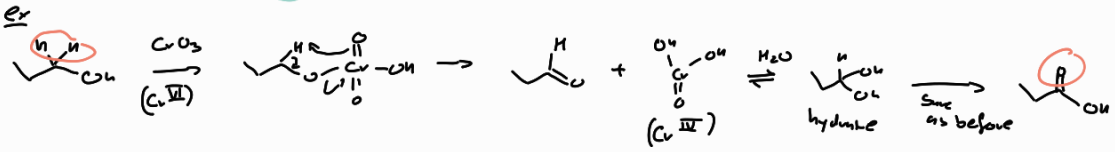
d) PDC =  di chromate

1°  →  (acid)

2°  →  (ketone)

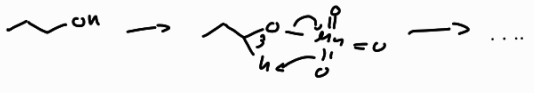
Mech

$H^{\oplus}$ abstraction 

ex 

Other oxidants

Strong

$KMnO_4$ oxidises alkenes: 

Manganate ester

or

$Na_2Cr_2O_7$ + H_2SO_4 $\xrightarrow{H_2O}$ $HCrO_4$  (Jones' reagent)

Mild

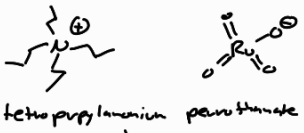
→ Only Aldehyde not acid

1° alkenol → aldehyde

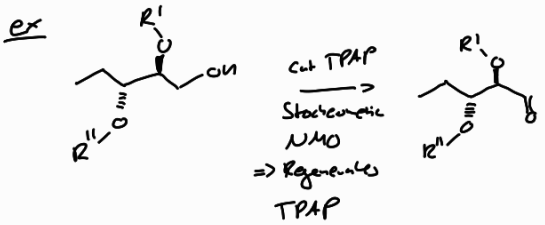
1) PCC can oxidise to aldehyde if careful

Safer alternative

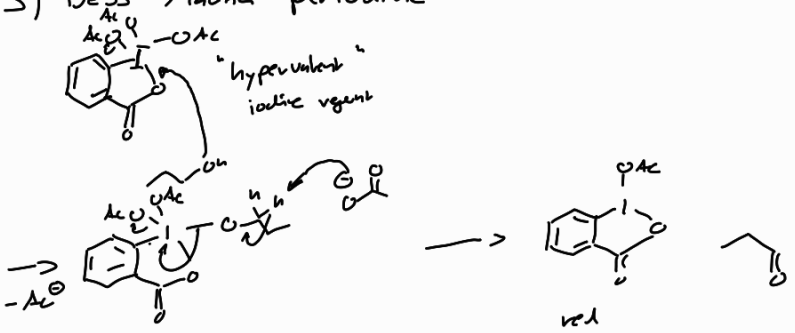
2) NMO + TPAP NMO = 

TPAP = 

tetrapropylammonium (counter ion) perruthenate

ex 

3) Dess - Martin periodine



4) Swern Oxidation

DMSO + Oxalylchloride