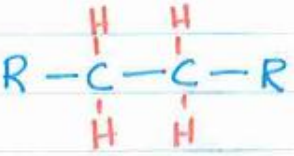
Recap Tuesday: Catalytic Hydrogenation

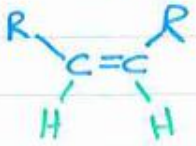
- catalyst usually finely dispersed metal
  → adds H's to same side of molecules (diastereospecific)

- chiral catalysts (soluble transition metal complexes)
  → add preferentially to one side (enantioselective)

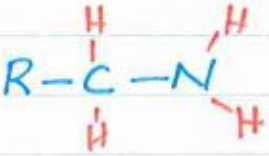
Other groups can be hydrogenated

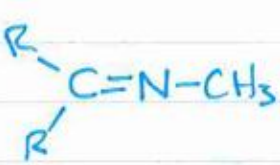
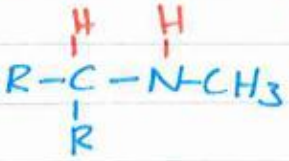
Alkynes: $R-C\equiv C-R \xrightarrow{H_2/Pd}$ 

↓ Chem 241

$\xrightarrow[\text{Lindlar}]{H_2}$  "poisoned" catalyst stops at alkene

Nitro: $R-NO_2 \xrightarrow[Pd/C]{H_2} R-NH_2$

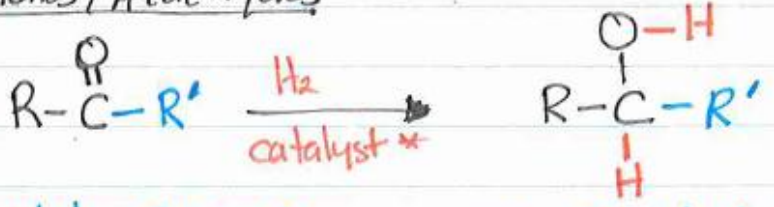
Nitrile: $R-C\equiv N \xrightarrow{"}$ 

Imine:  $\xrightarrow{"}$ 

Chem 242!

Carbonyls - can also be reduced by H_2/catalyst

(A) Ketones/Aldehydes

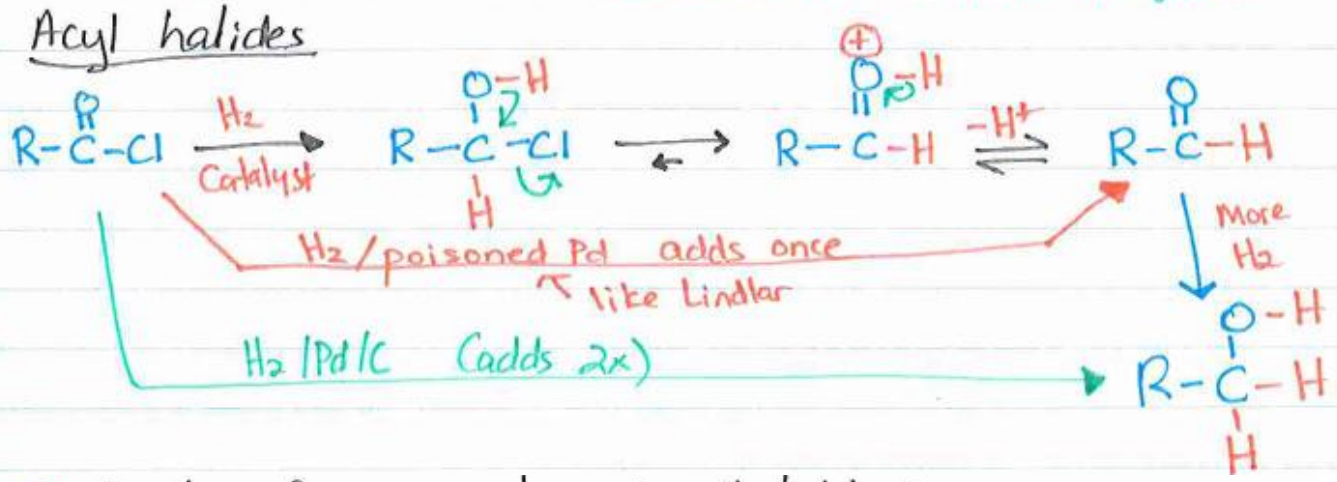


$R' = \overset{|}{C}-$ (ketone) ⟶ 2° alcohol

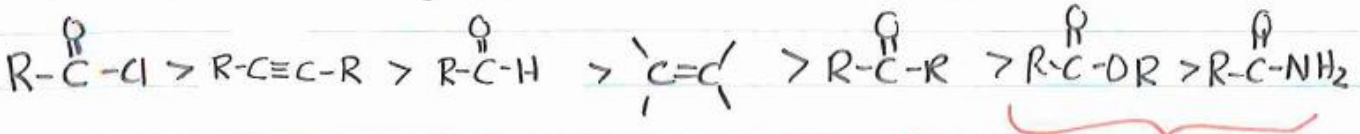
$R' = H$ (aldehyde) ⟶ 1° alcohol

* catalyst : Raney Nickel = Finely dispersed Ni powder with H_2 absorbed in it
→ don't need to add H_2 (gas)!

(B) Acyl halides



Selectivity of groups towards H_2/catalyst

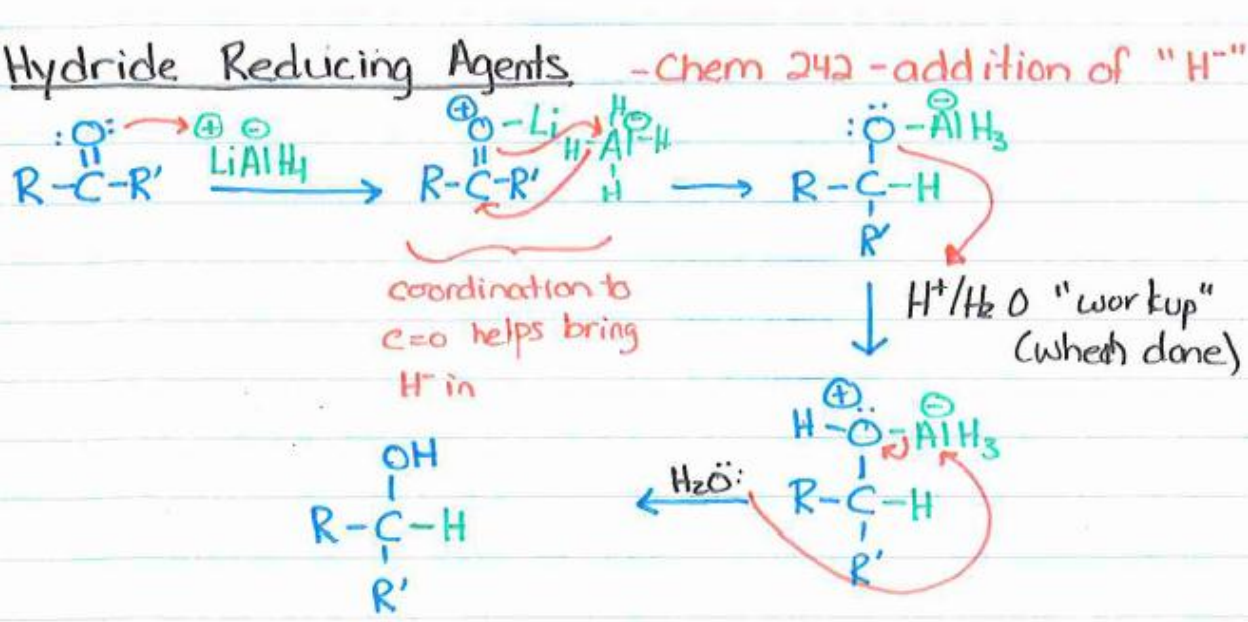


need better catalyst / higher pressure H_2

very hard to reduce

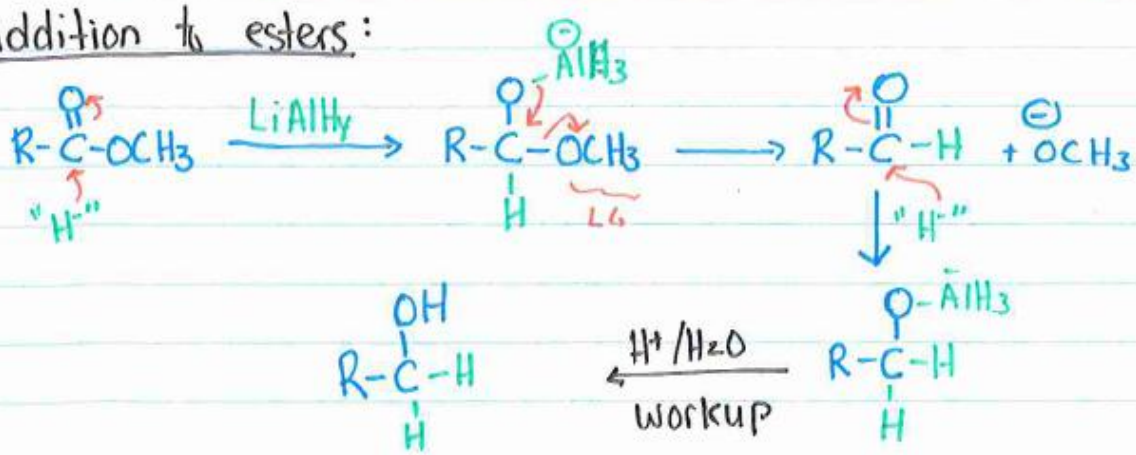
→ Can selectively reduce only most reactive by choosing appropriate catalyst + conditions
↓
pressure H_2 / temp.

Hydride Reducing Agents - Chem 242 - addition of "H^-" to C=O

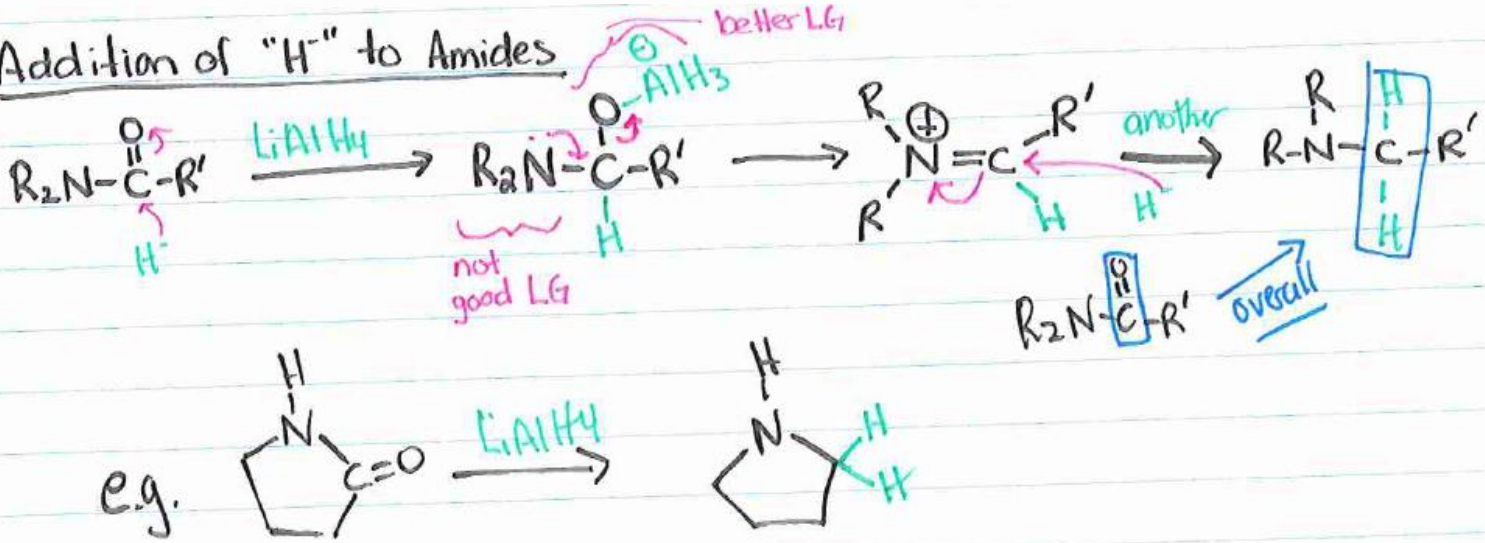


⇒ Each $LiAlH_4$ can donate 4 H's

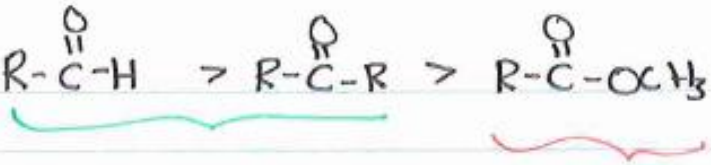
Addition to esters:



Addition of "H^-" to Amides



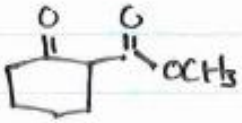
Selectivity



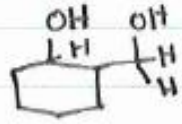
can use $NaBH_4$
- milder, safer
- ↓ more selective

needs $LiAlH_4$
- reduces "everything"
- reacts violently with H_2O!

e.g.

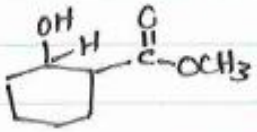


1) $LiAlH_4$
2) H^+/H_2O



- both reduced

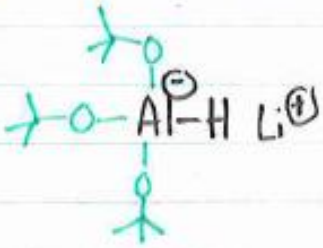
1) $NaBH_4$
2) H^+/H_2O



- only ketone reduced

Other hydride donors

① replace one or more H's with other groups

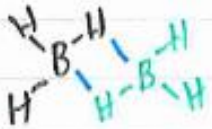


- Lithium tris(t-butoxy) aluminum hydride
- much more bulky ∴ reacts slower (more selective)

$Et_3\overset{\ominus}{B}H\ Li^{\oplus}$ "Superhydride"
- advantage → soluble in THF ($NaBH_4$/$LiAlH_4$ insoluble)

② Derivatives of Borane (BH_3) and Alane (AlH_3)

- B_2H_6 =



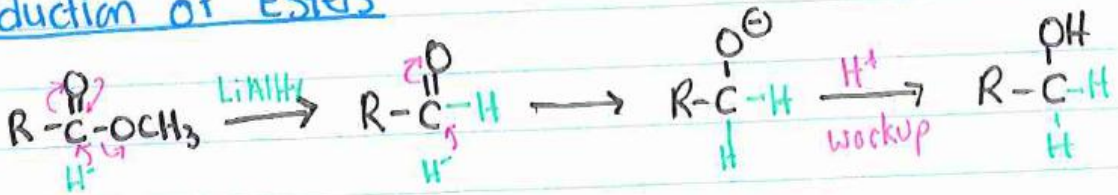
= diborane (hydroboration!)

- $BH_3 \cdot THF$ =

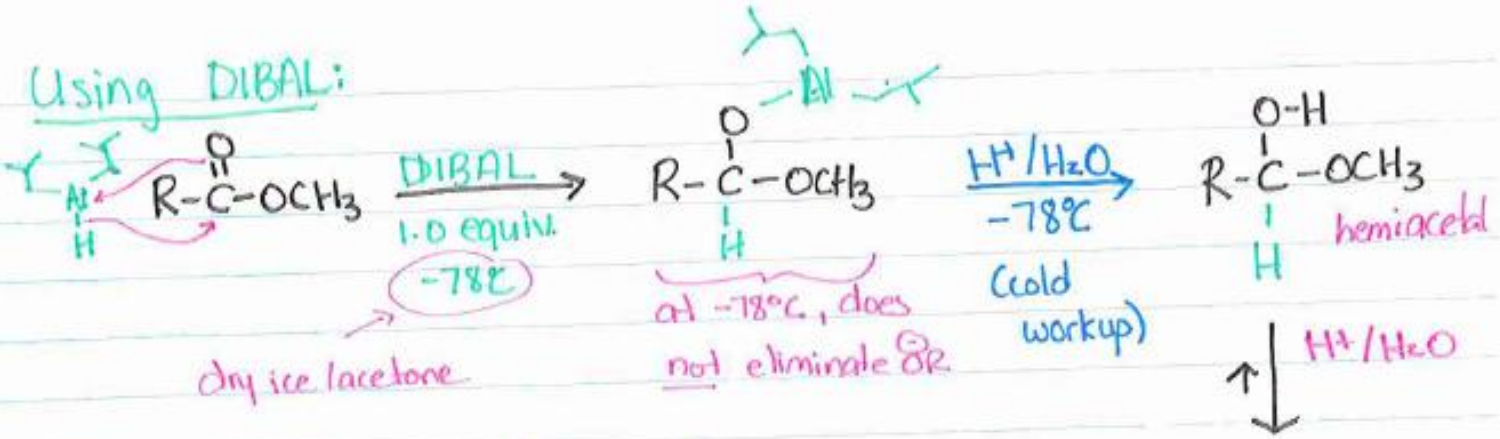
= di-isobutyl aluminum hydride = DIBAL or DIBAL-H

Special Selectivities

(A) Reduction of Esters

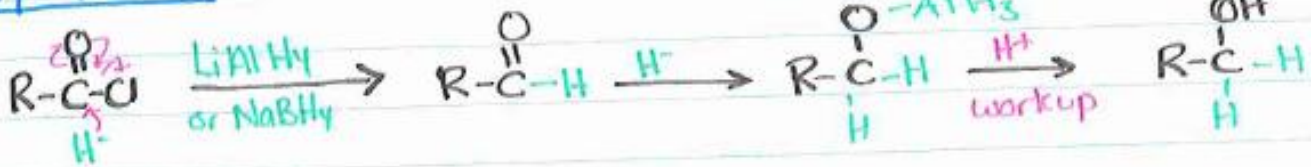
Saw: 

Using DIBAL:

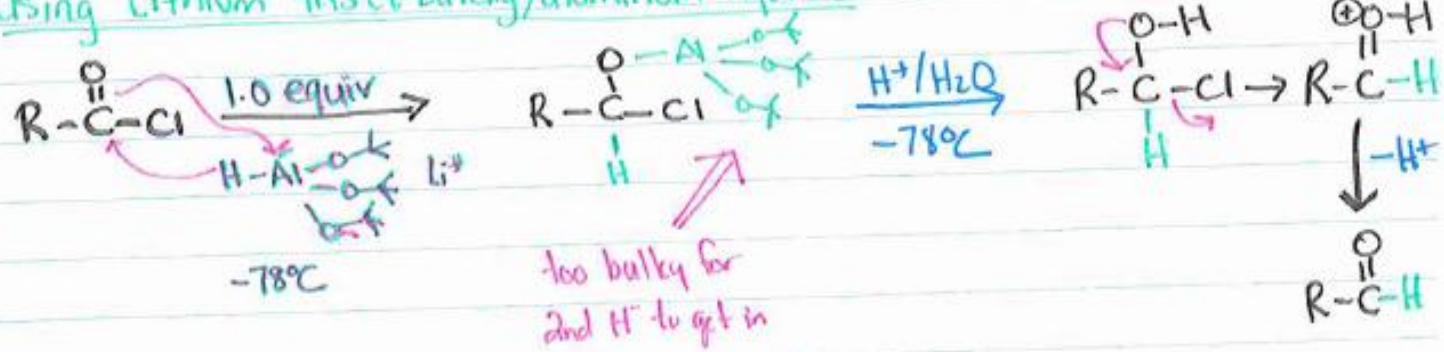


→ as long as keep cold, and no excess DIBAL → get aldehyde!

(B) Acyl Halides

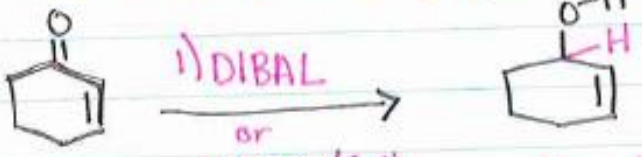
Seen: 

Using Lithium tris(t-butoxy)aluminum hydride:

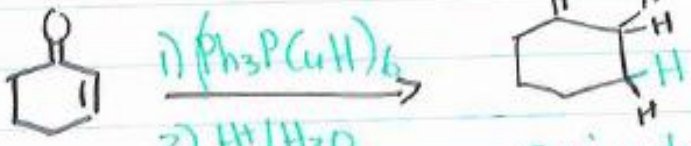


Addition to α,β-unsaturated ketones

-direct vs conjugate!



direct



conjugate (like cuprate)

→ $NaBH_4$ without $CeCl_3$ gives mixture of direct + conjugate