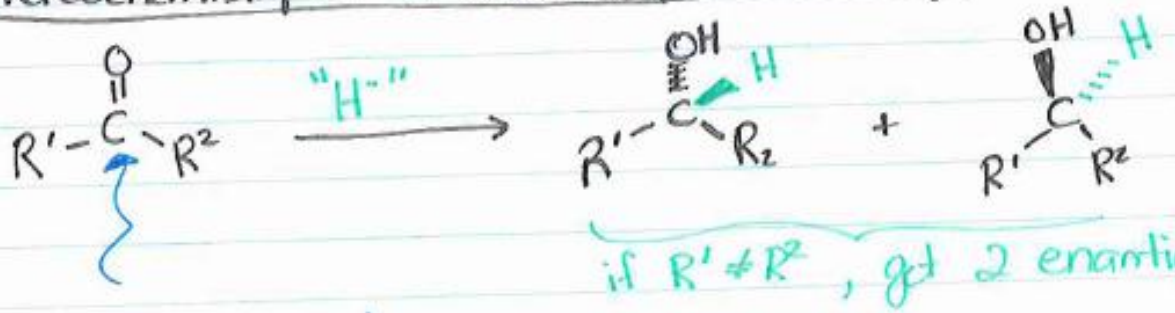
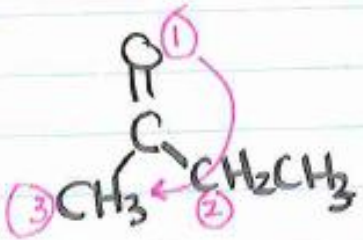
Stereochemistry of H^- addition to carbonyl



if $R' \neq R^2$, get 2 enantiomers

C=O is prochiral
→ if extra group is added, get chiral center
→ chirality of product depends on which face H^- adds to

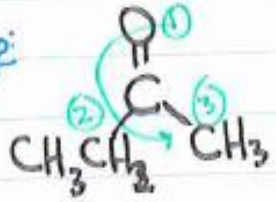
Define "face" = side of planar compound
→ similar to R/S for tetrahedral



≈ R ⇒ "Re" face = side facing us

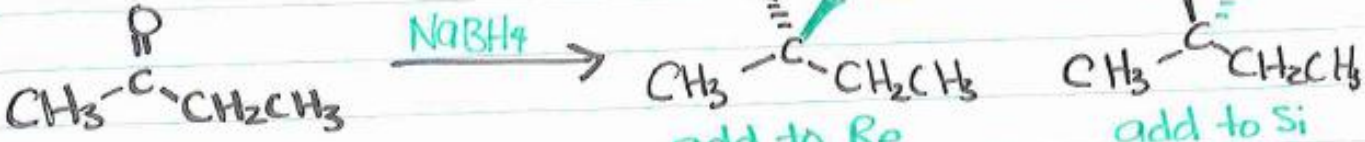
"ray"

flip:



≈ S ⇒ "Si" face = back of Re face
(sigh)

→ we say the Nu adds to the Re or Si face
⇒ Does not necessarily correspond to R/S product
↳ Depends on priority of Nu

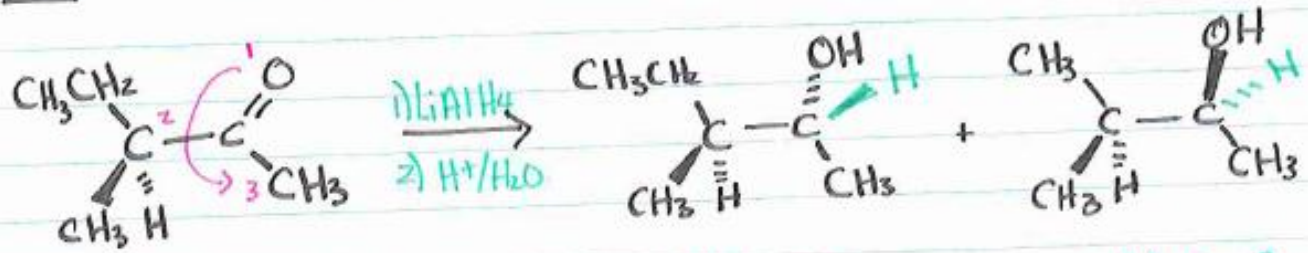


add to Re (front) = S enantiomer

add to Si (back) = R

front (Re) & back (Si) same (sterically) ⟶ ∴ 50 : 50 (racemic)

But - if ketone has chiral center - get 2 possible diastereomers

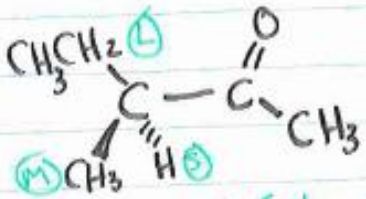


front + back different → can get more of one

To determine which is major:

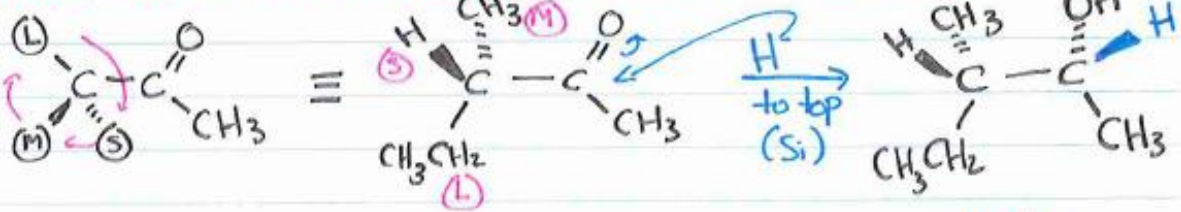
→ consider steric effect of groups on chiral center

Cram's rule:



① Label 3 groups on α-C (the chiral center) as Small (S), Medium (M) + Large (L) → according to physical size (sterics)

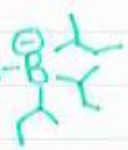
② Line up (L) in plane with other α-C (other side of ketone) so C=O is between (S) + (M) (avoid L!)



③ Add H⁻ from side of smallest group

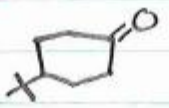
major product

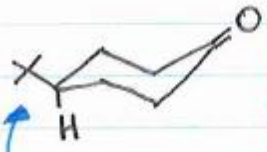
* Works best for bulky H⁻ donors (more steric hinderance)

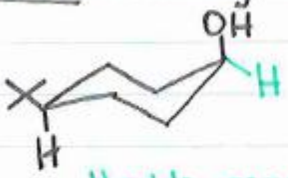
eg  = Lithium tris(sec-butyl) borohydride
aka L-selectride (TM)

K⊕ salt = K-selectride

Addition of H^- to cyclic ketones

e.g. 





or 

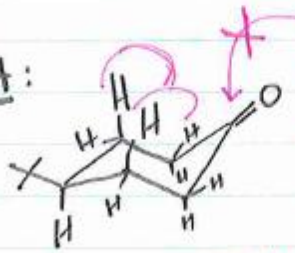
bulky t-butyl must go equatorial

H adds equat. → OH axial

H adds axial → OH eq = more stable

LiAlHy: 8% 92%

But:



93% 7%

axial attack too hindered for bulky H^-

∴ equatorial major!

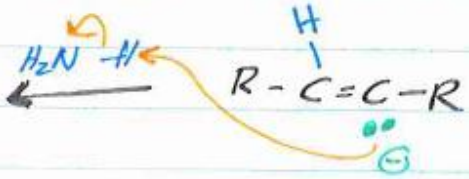
Last type of reduction = dissolving metal red'n

$M \rightarrow M^+ + e^-$

Chem 241:

get trans because more stable

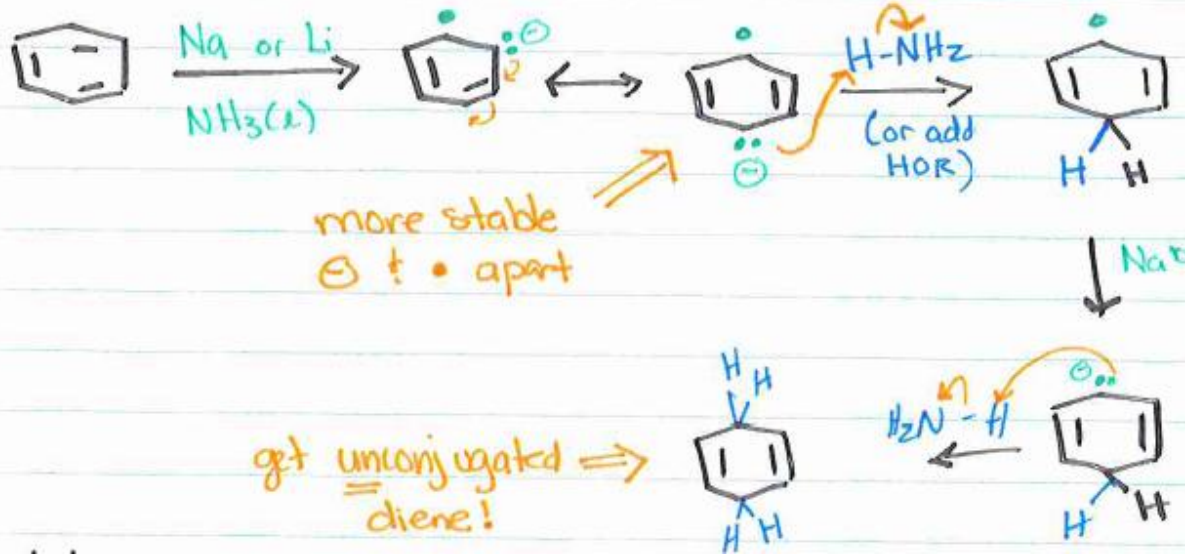
(Lindlar = cis)



From Seminar:!

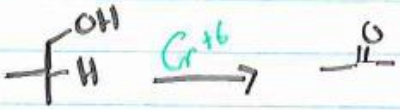
Birch reduction - for benzene rings!

General:

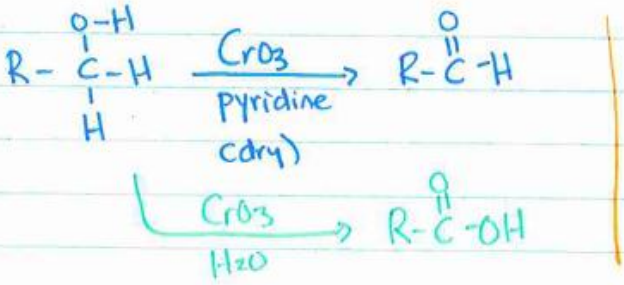


Oxidation

① Alcohols - Chem 242!



1°

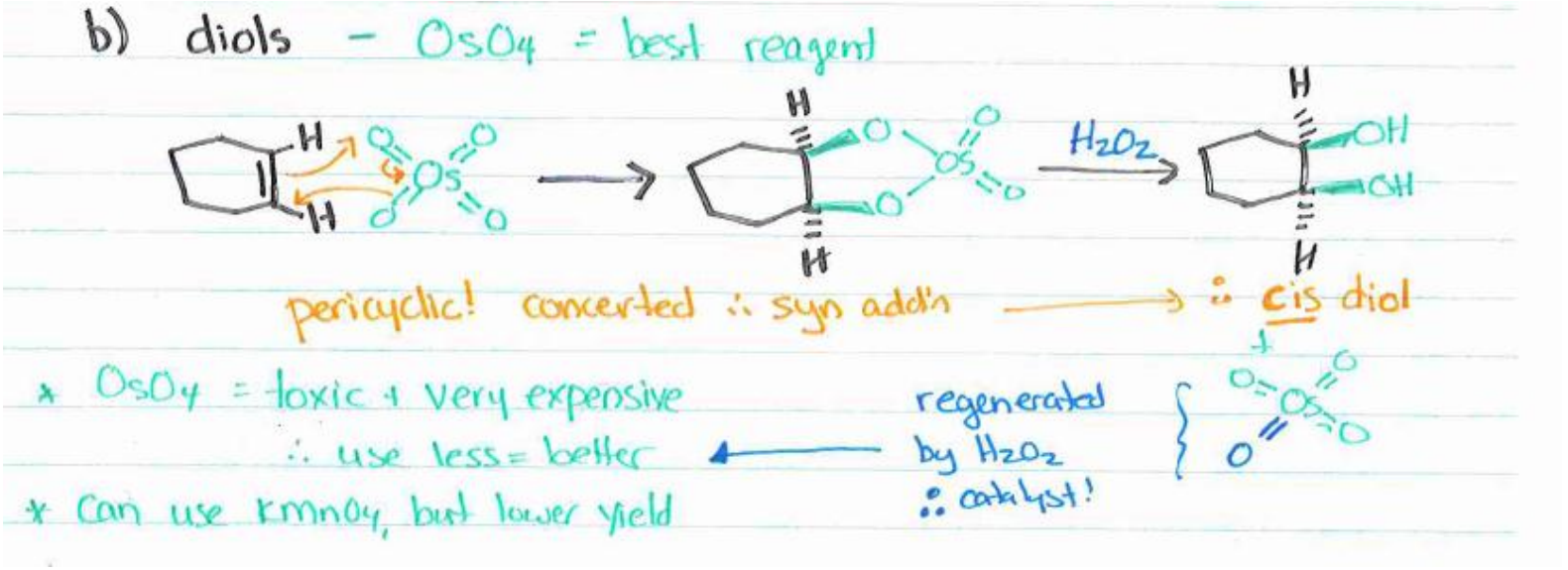


② Ketones - Baeyer- Villiger (seen!)

③ Alkenes - 3 possible products (depending on reagents)

a) epoxides - seen (MCPBA or Sharpless)

From Seminar:!



c) Cleavage of double bond: Ozonolysis