

Quiz B in discussion (1st 5 min)

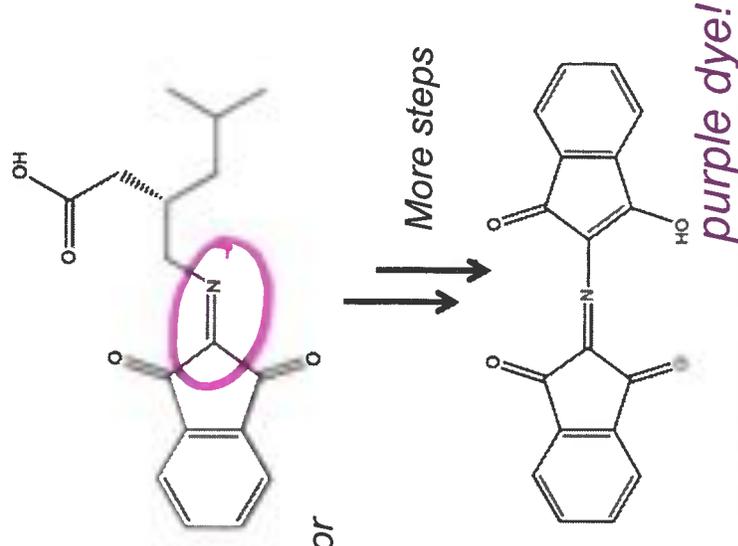
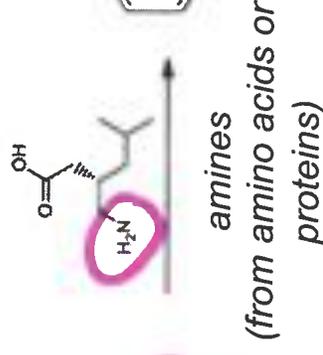
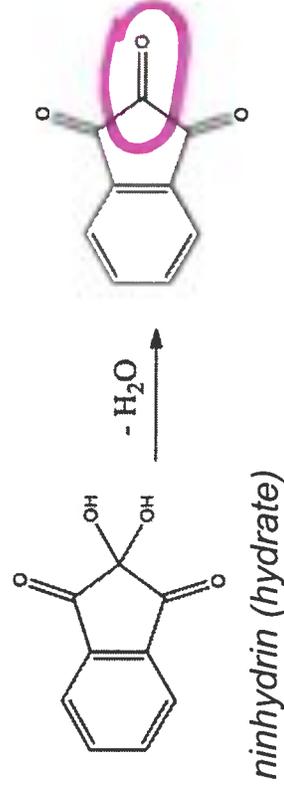
WS 2 and WS 3 are on the website

Midterm 1 is two weeks from today (on May 3)!!

Old midterms are on website so you can see the format.

Show your Caper card (or app) to Kirsten for extra credit. She is sitting in the back row.

Lecture 9: Imines; Acetals

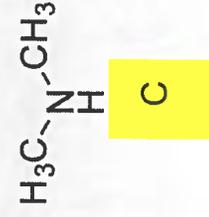
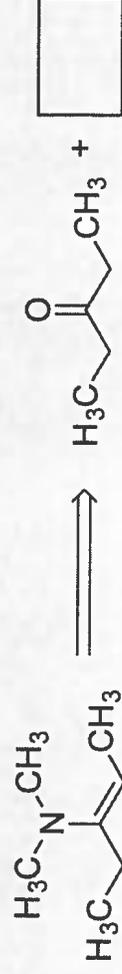


♫ I fought the law (... and the law won) The Clash

Staining for fingerprints involves imine formation. Your fingertips are covered in amines (e.g, amino acids and proteins) and they react with the ninhydrin stain.

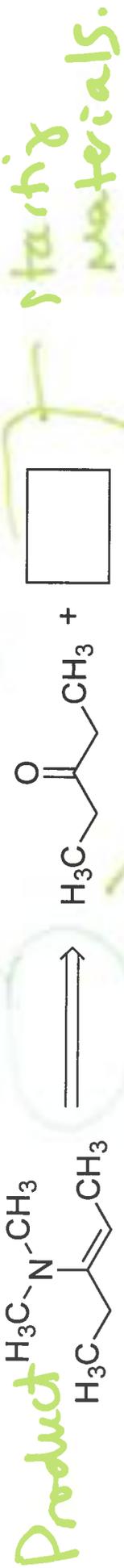
It's hard to argue with an imine.

Capcard question: Complete the retrosynthesis

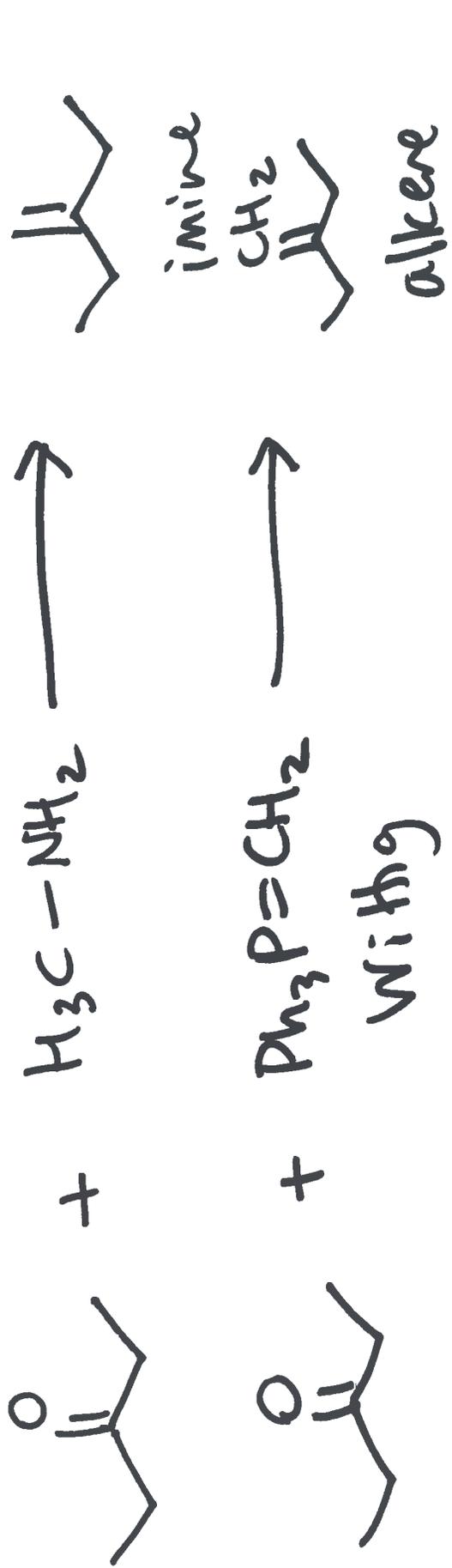
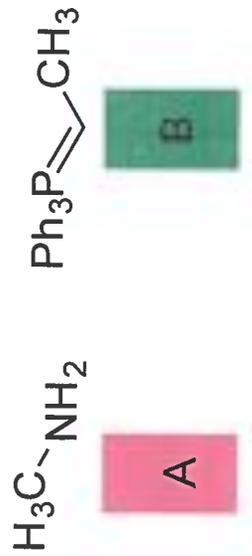
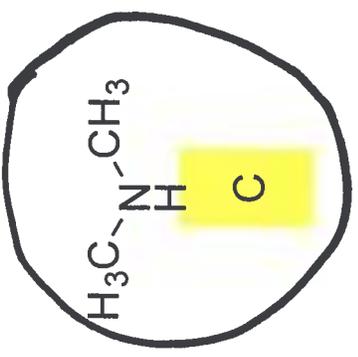


Capercard question: Complete the retrosynthesis

Retrosynthesis

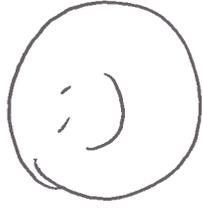


enamine



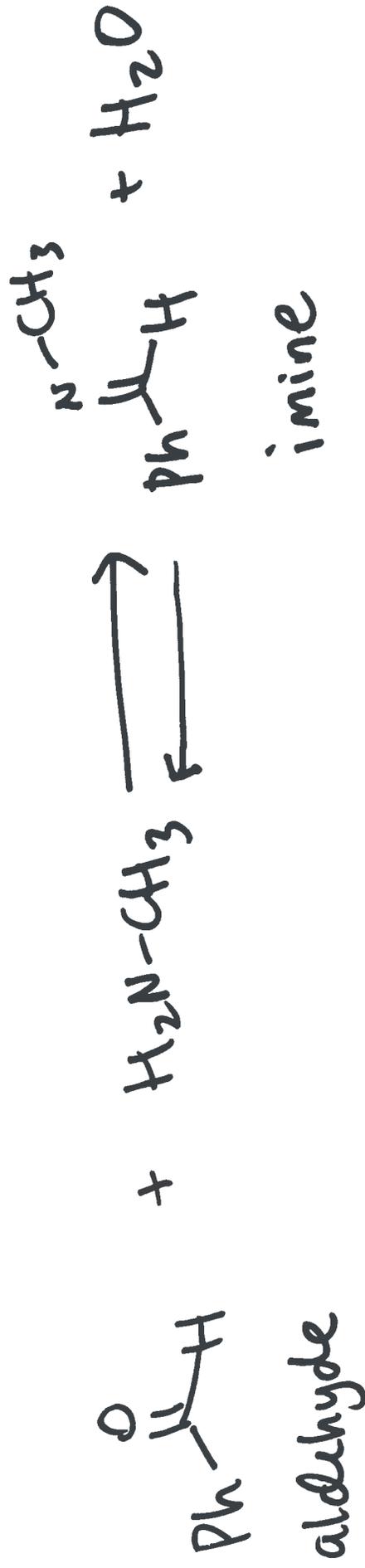
②

Finger print demo in class!



④
Imines + Enamines.

- fast
- reversible
- mild acid



Equilibrium!
Position of equilibrium (SM vs Products)
influenced using Le Chatelier's Principle.
of equivalents, reaction conditions can favor

SM or products.

5



Add
extra
equivalent
equivalents

WANT

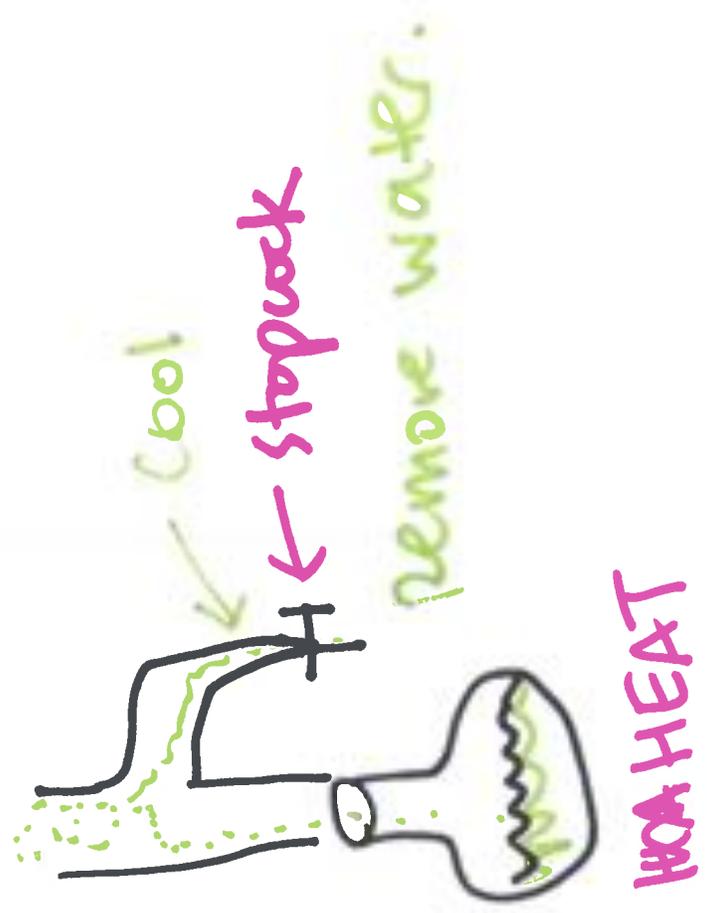
Remove
byproducts

push equilibrium
to the
right

$$K_{eq} = \frac{[\text{imine}][\text{H}_2\text{O}]}{[\text{aldehyde}][\text{amine}]}$$

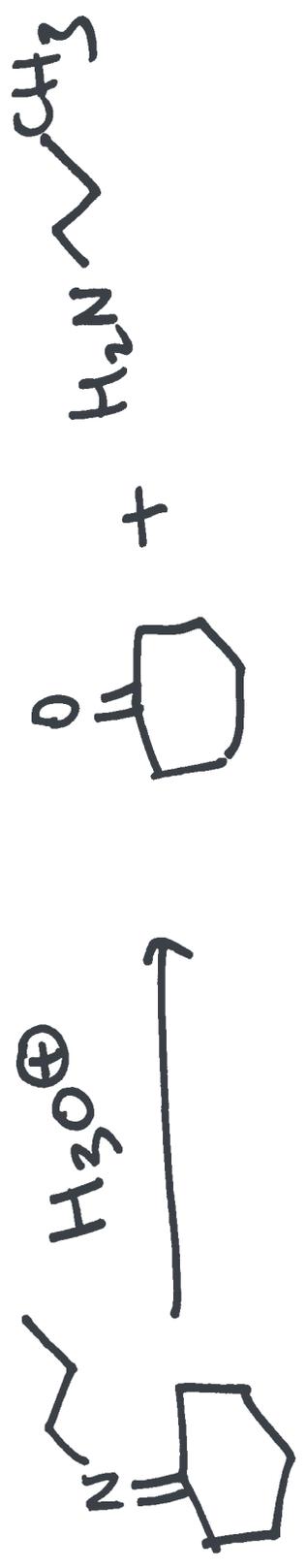
6

to remove water: Dean Stark trap.



①

Take home problem:



Draw mechanism for imine hydrolysis.

for formation of imine from ketone.

21.13: Addition of oxygen based nucleophiles.

up until now: added " H^{\ominus} "

" RC^{\ominus} " Grignard
 RLi

$NaCN$

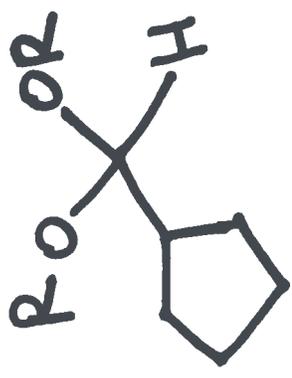
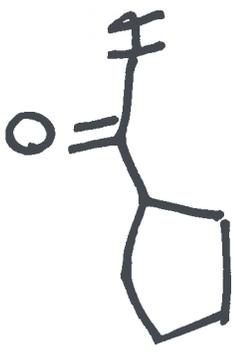
Wittig.

" HNR_2 "

Today: Hof (alcohols)

Adding to aldehydes + ketones

9



aldehyde

IR

ketones.

H-OH

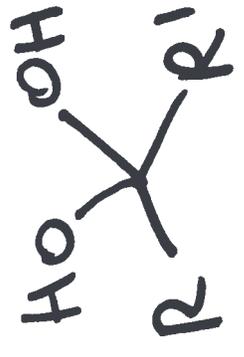
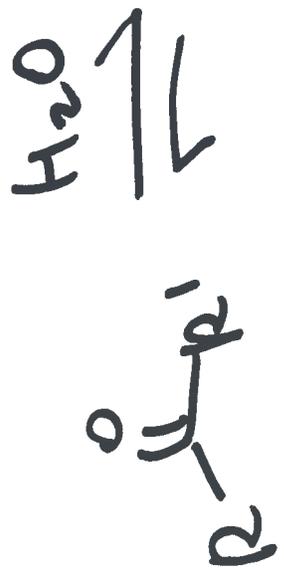
H-OCH₃

H-OEt

hydrate; R=H

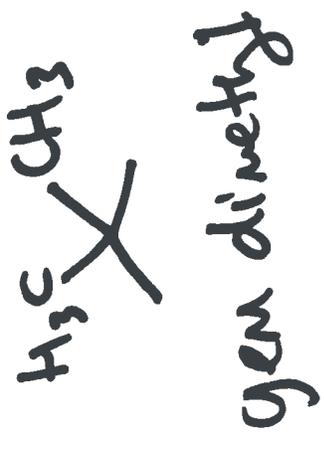
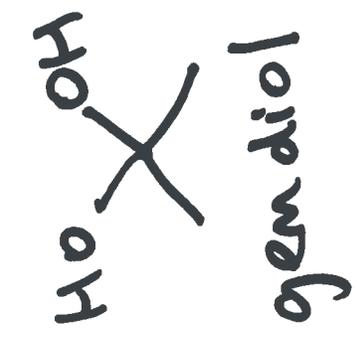
acetal; R=alkyl
(or ketal)

Hydration : addition of water.

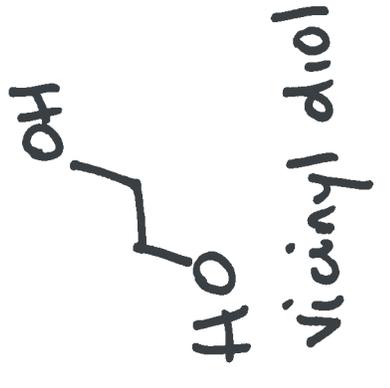


hydrate
gem-diol
geminal diol

geminal = attached to same carbon
(twins)



vicinal = attached to adjacent carbons
vicinity, neighbors



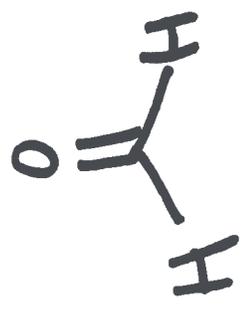
to decide where equilibrium lies...

look at stability of carbonyl.

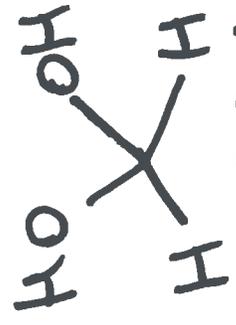
less stable = more reactive = more hydrate formed.

least stable

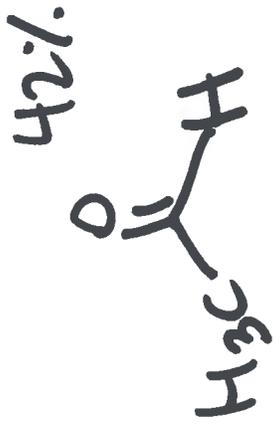
Most stable



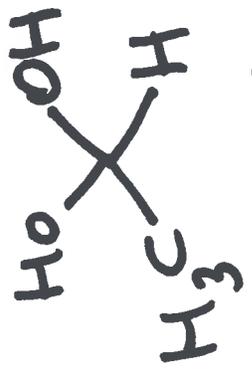
1%



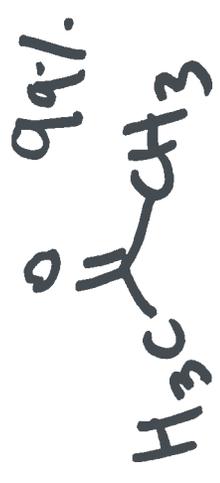
99%



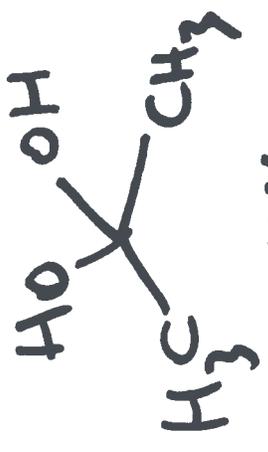
42%



58%

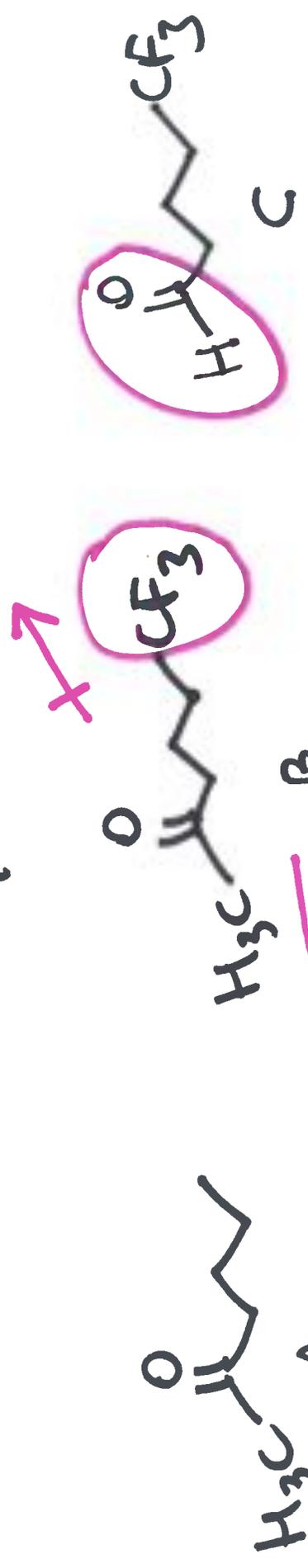


99%



<1%

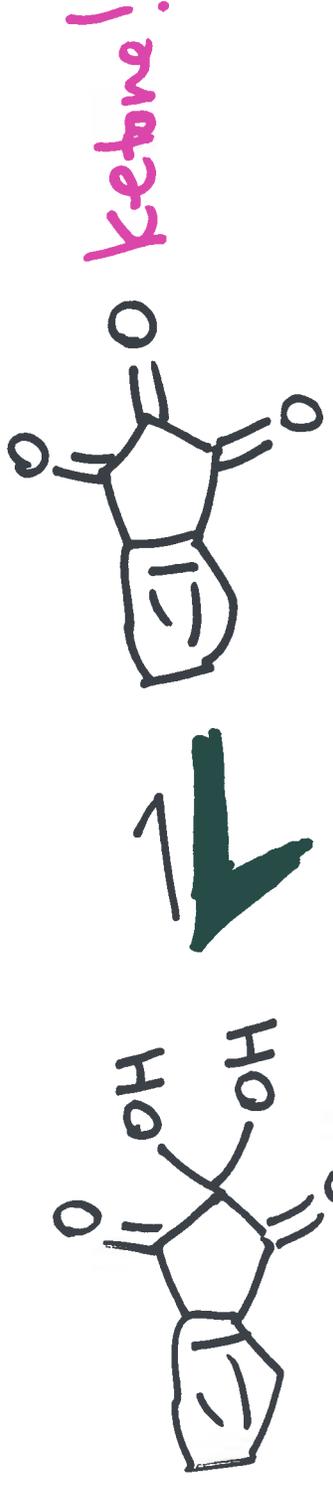
Can fine tune stability with electronics...
EWG's withdraw will favor hydrate



Rank: Most hydrate $C > B > A$
Least hydrate

fastest reaction with NaBH₄
 $C > B > A$

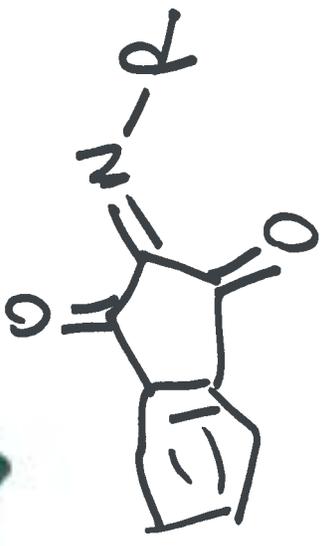
Ninhydrin is a hydrate!!



very electrophilic



Finger print

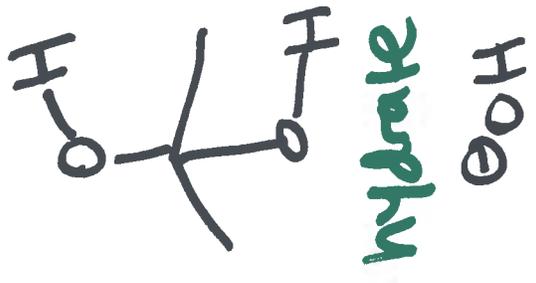
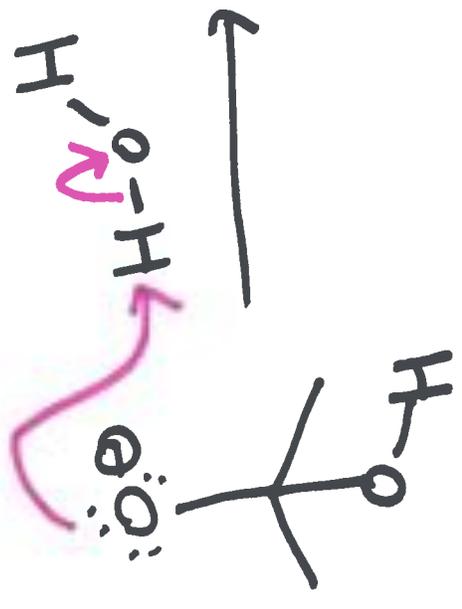
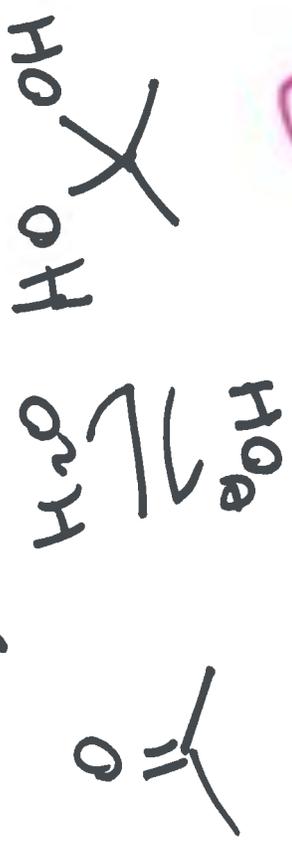


imine

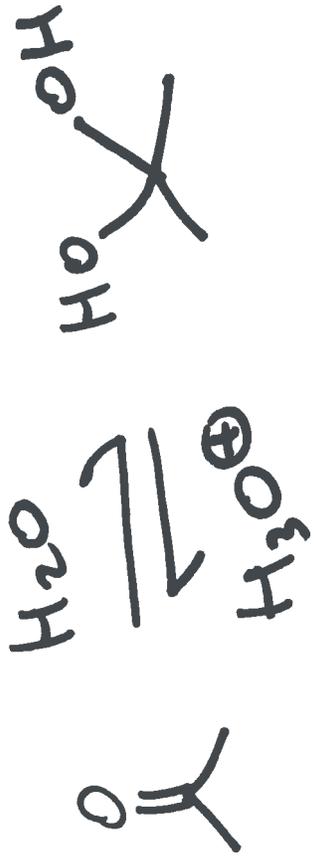
Mechanism of hydrate formation

- acid or base catalyzed!
- All steps are reversible!

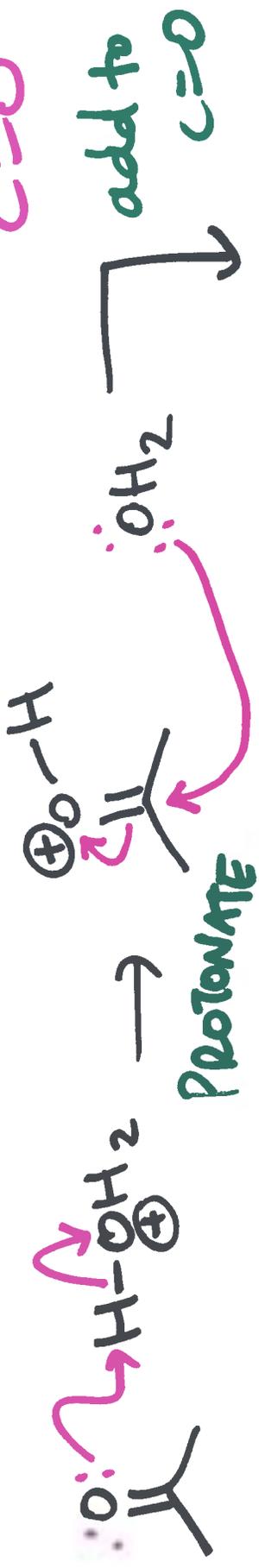
① Base-catalyzed.



② Acidic conditions

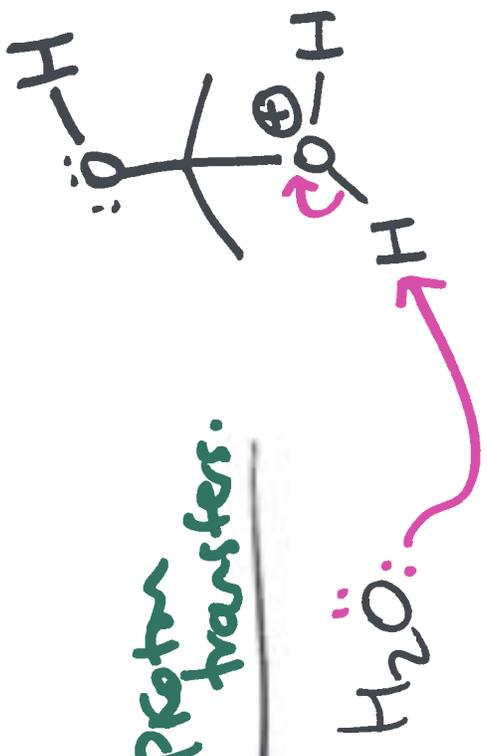
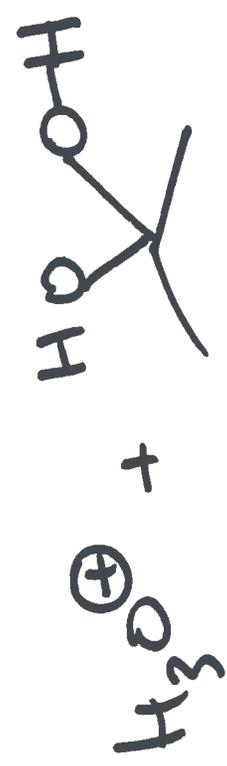


Acidic
condition:
PROTONATE
your
C=O



add to
C=O

Proton
transfer.



Under acidic conditions

ALL organic intermediates are neutral or \oplus ve charge.

For example H_2O ok

H_3O^+ ok

$\oplus O-H$
 \parallel ok

FIX your PROTON TRANSFERS

$\ominus OH$	ok	Avoid these
$\ominus O-X$	<u>Not</u> ok	even

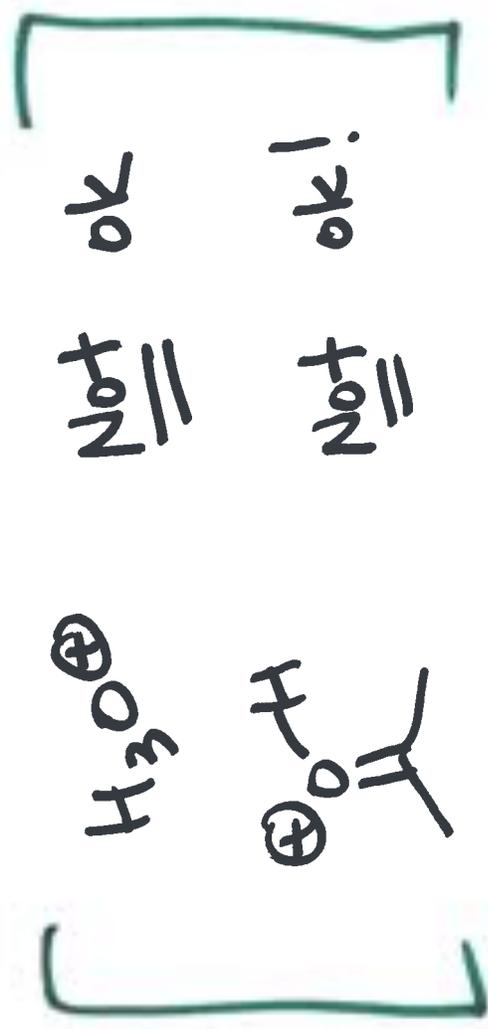
Under basic conditions:

All intermediates neutral or e^-

For example: H_2O ok

e^-OH ok

e^-O^- ok



Fix

Proton transfers!