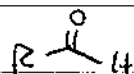


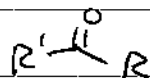
Wade

Ch 18: Ketones & Aldehydes

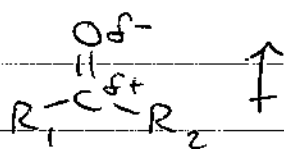
Aldehyde



ketone

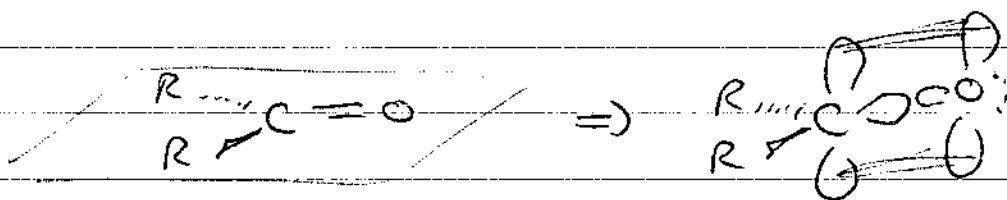


$R, R' = Ar, Alkyl$

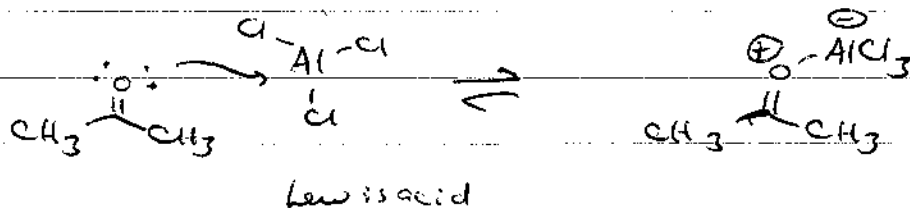
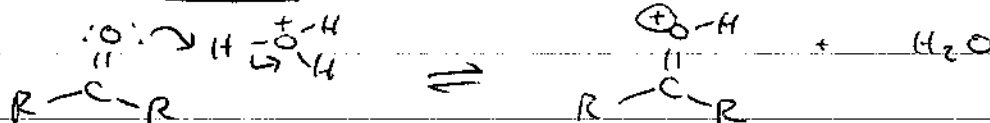


\uparrow
 $\mu = 2.88D$ when $R_1 = R_2 = CH_3$

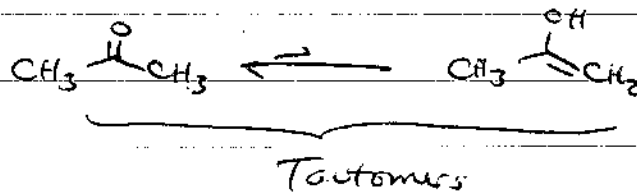
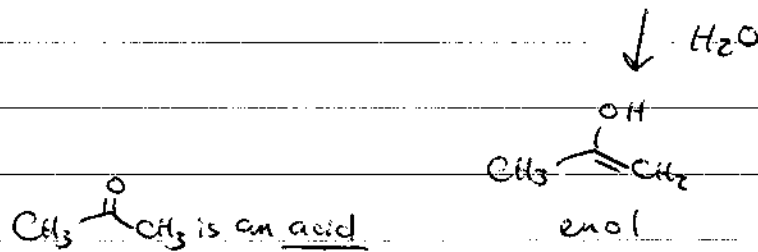
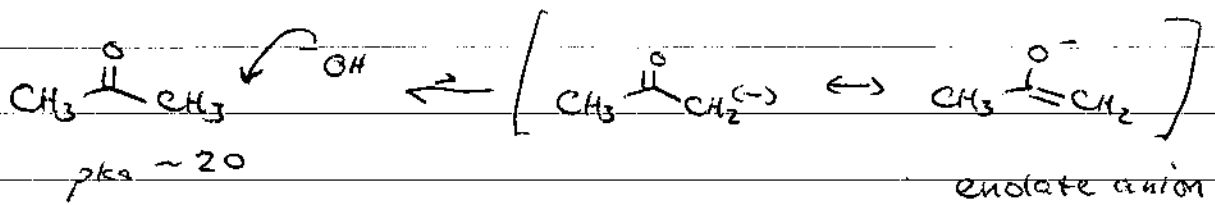
Planar molecule



Acid or Base



Base

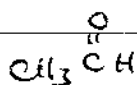


Kemari

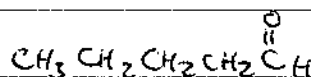
Nomenclature of Aldehydes & Ketones

Aldehydes: -ane \rightarrow -al

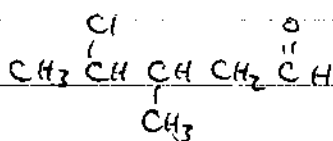
Simple alkanals



Ethane \rightarrow Ethanal
Acetaldehyde



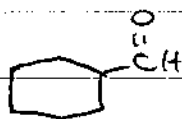
pentanal



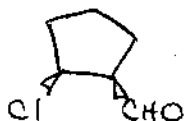
4-chloro-3-methylpentanal

Ring substituted Aldehydes: -ane \rightarrow -ane carbaldehyde

\therefore treats the aldehyde as a subst.

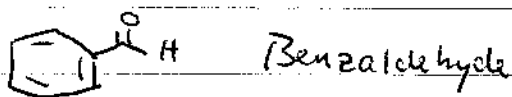


cyclohexane carbaldehyde



cis-2-chlorocyclopentane carbaldehyde

Aryl subst



p-tert-butyl benzaldehyde

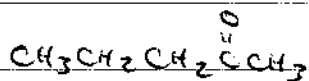
or

4-tert-butyl benzaldehyde

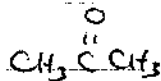
ketones

alkane \rightarrow alkanone

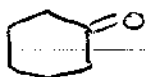
Simple



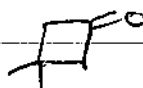
2-pentanone



propanone or acetone



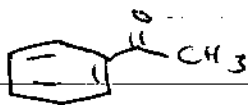
cyclohexanone



3,3-dimethyl

cyclobutanone

Aromatic



1-phenyl-1-ethanone

methyl phenyl ketone

Acetophenone

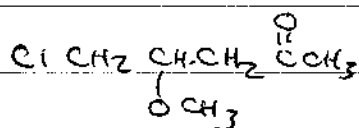


Benzophenone
(diphenyl ketone)

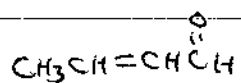


1-phenyl-2-pentanone
Benzyl propyl ketone

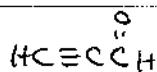
Poly functional compounds



5-chloro-4-methoxy
~~4-methoxy-5-chloro-2-pentanone~~

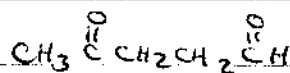


(2-butene + butanal ⇒) 2-butenal



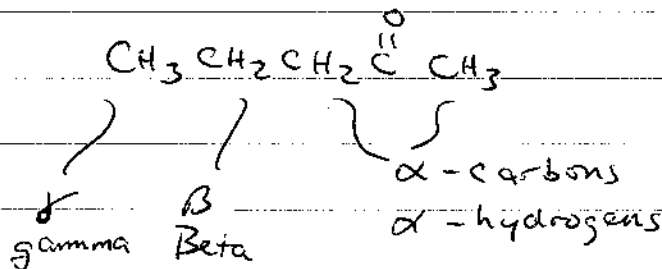
2-propynal

Naming $\text{C}=\text{O}$ as a subst - use "oxo"



4-oxopentanal

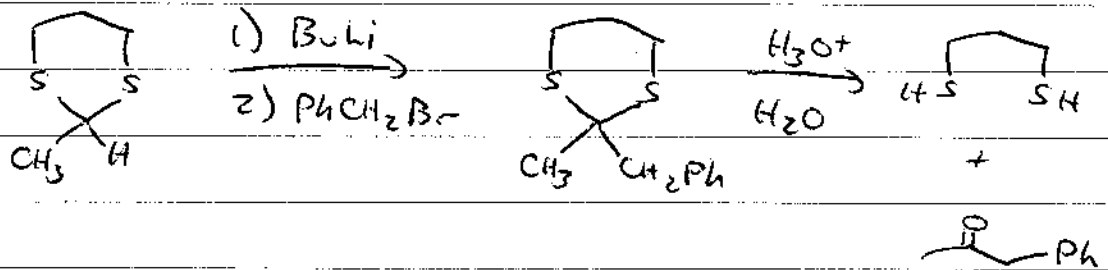
Naming adjacent carbons



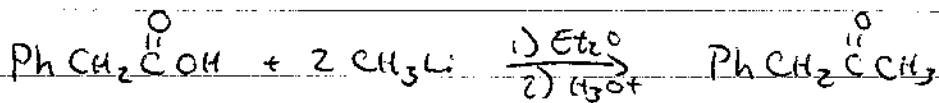
Skip 18-5 for class (go over for lab!)

" 18-6

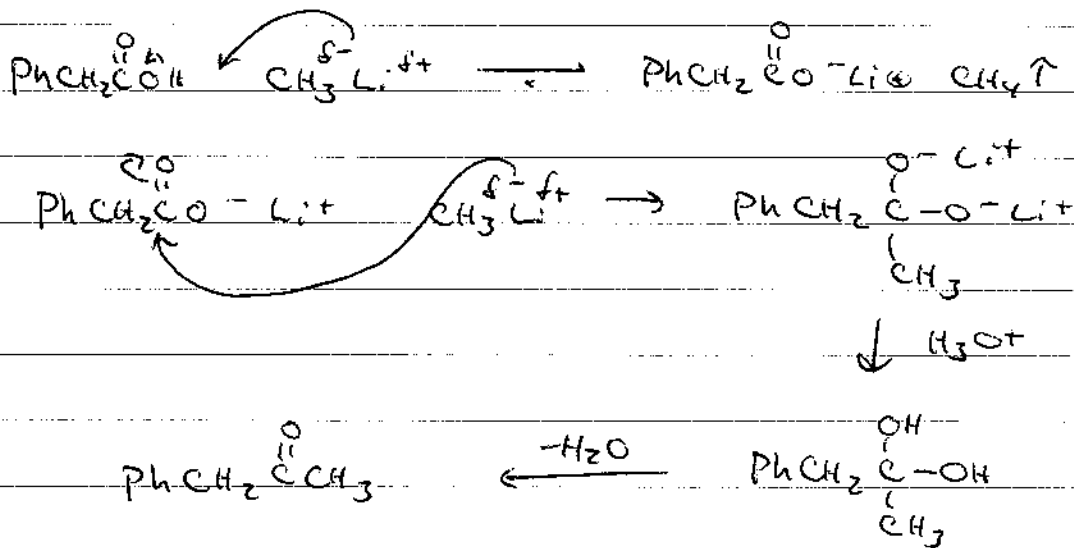
To make a ketone:



Ketones from Carboxylic acids

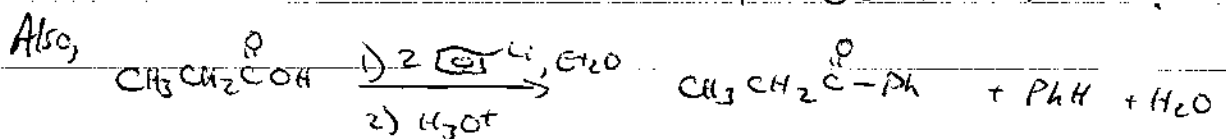


Mechanism



How does CH_3Li attack a negatively charged molecule?

↳ IS A VERY GOOD NU^- !



Synth. of ketones from Nitriles 18-10

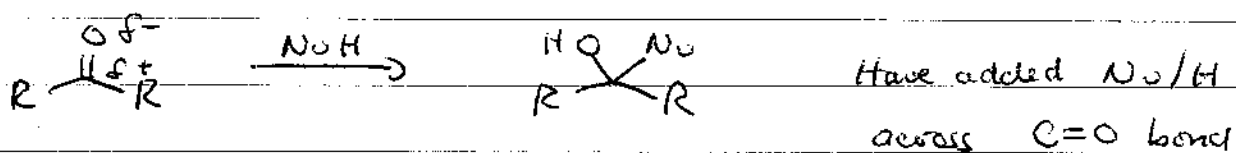
Synth of Aldehydes / ketones from acid chlorides 18-11

We have not seen RCN or $\text{R}\overset{\text{O}}{\parallel}\text{CCl}$ yet!

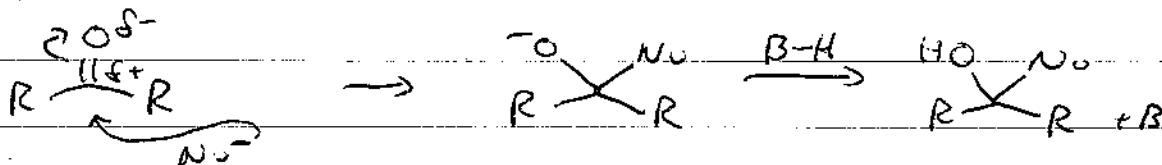
We'll go over this material when we cover these types of molecules

so wait until Ch 21 & skip 18-10, 18-11

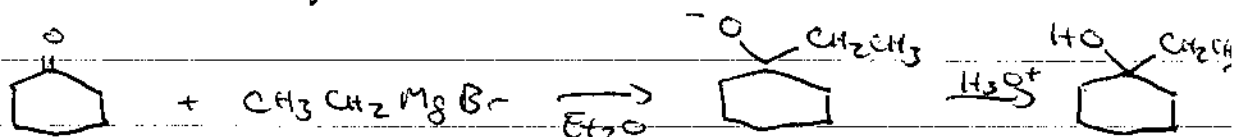
Reactions of ketones & Aldehydes: Nucleophilic Additions



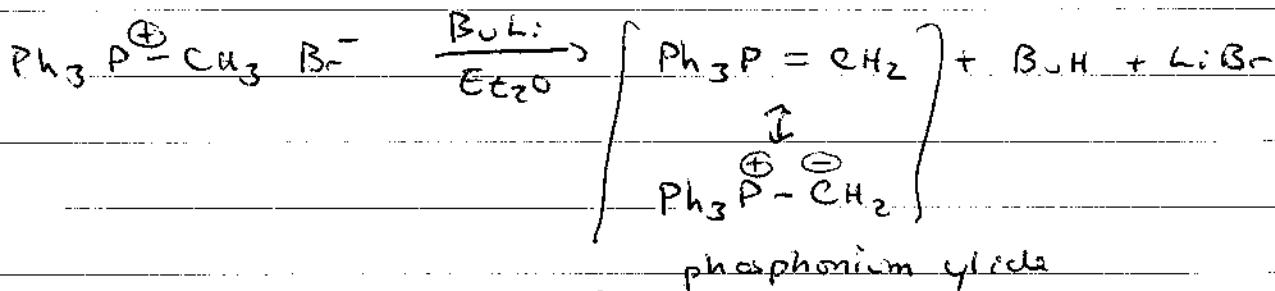
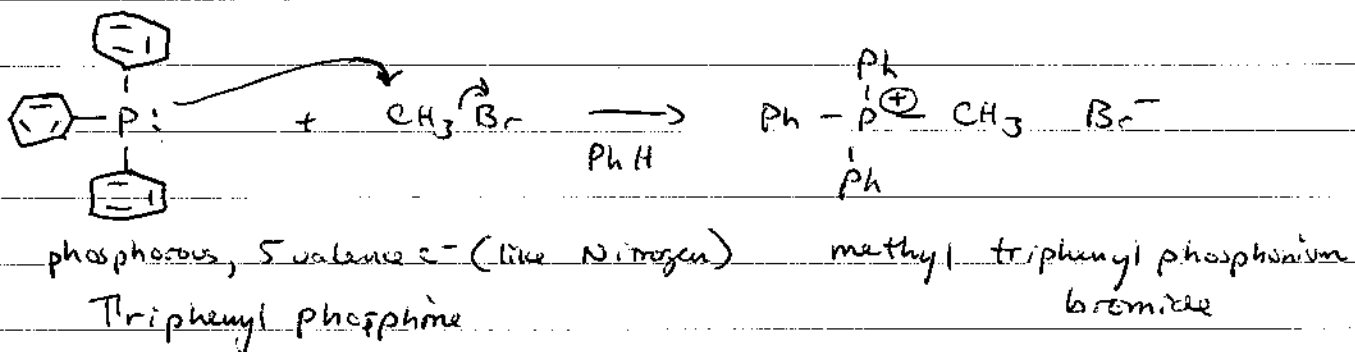
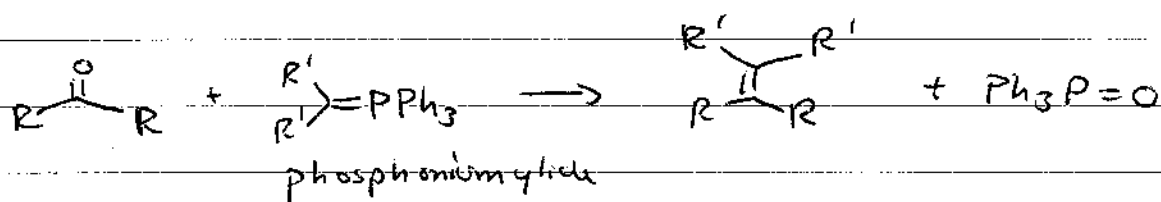
Mech



We've seen for Grignards...

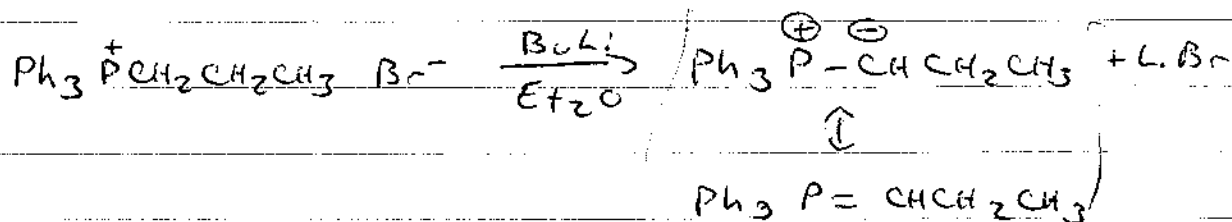
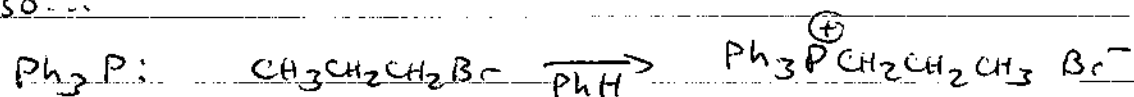


The Wittig Rxn

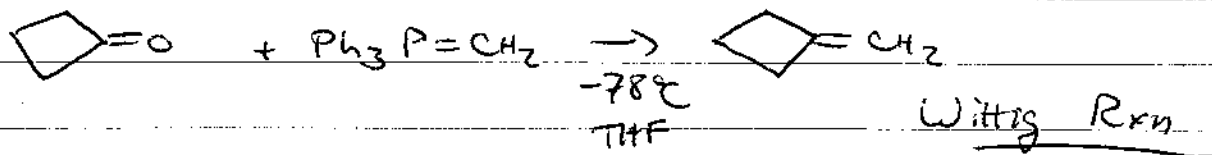


↙ π bond → formed by donation of e⁻ pair on CH₂ into empty 3d orbital on P

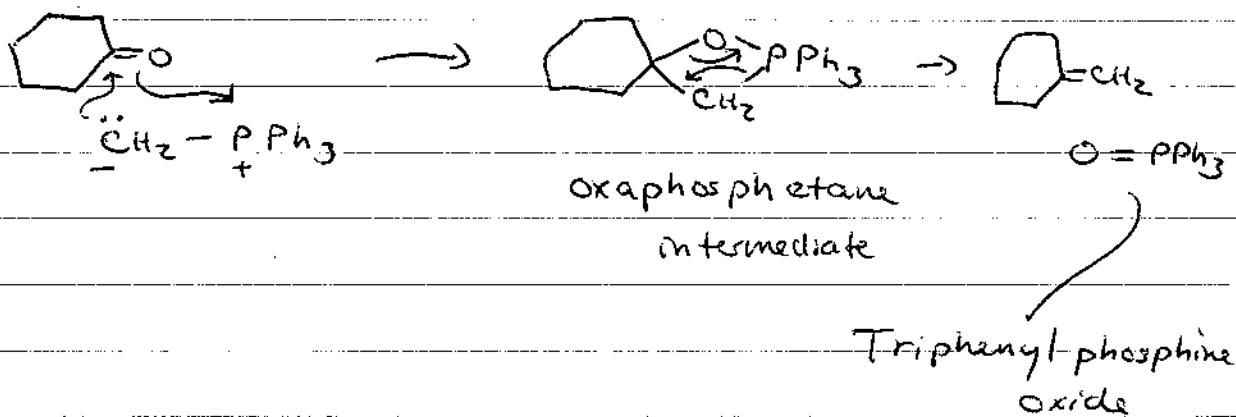
Also...



Called Wittig Reagents



Mechanism

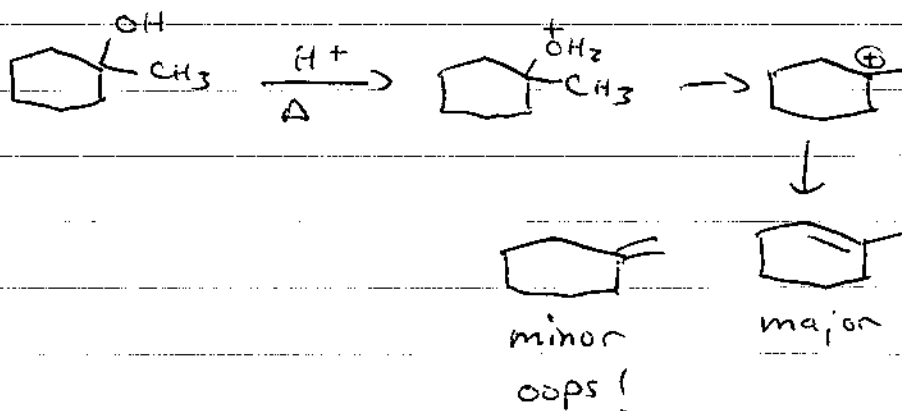


Formation of P=O bond is part of the driving force of this rxn

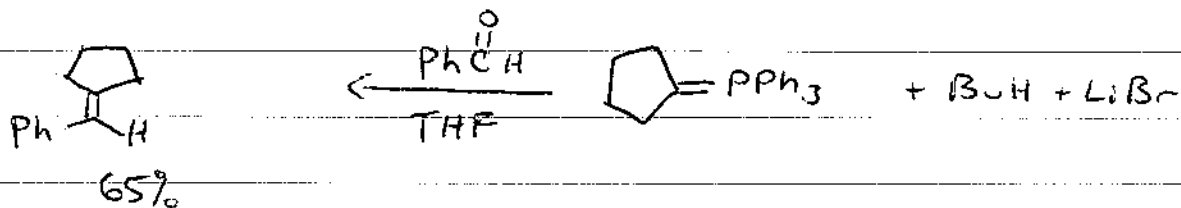
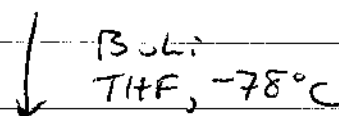
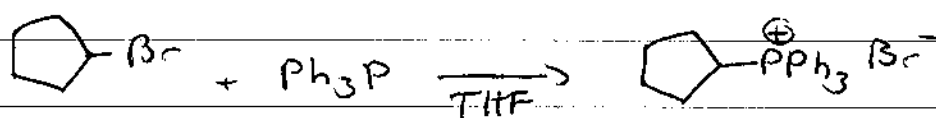
Wittig Rxn is an Imp't Synthetic tool!

- 1) Requires Basic conditions
- 2) Low temps

i.e., to make an exocyclic double bond...

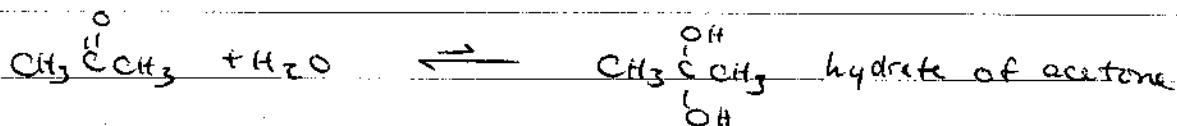
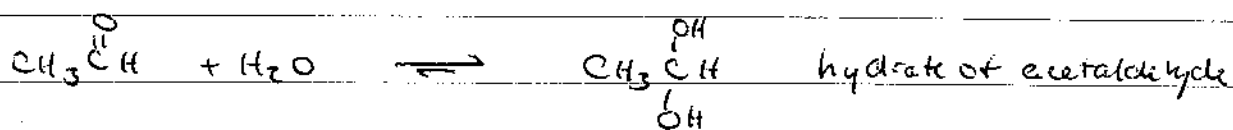


Another Example



How can we make C1CCC(C1)=C ?

Reactions of Water w/ Aldehydes & Ketones (18-14)



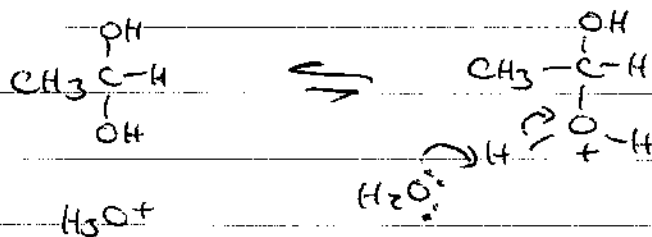
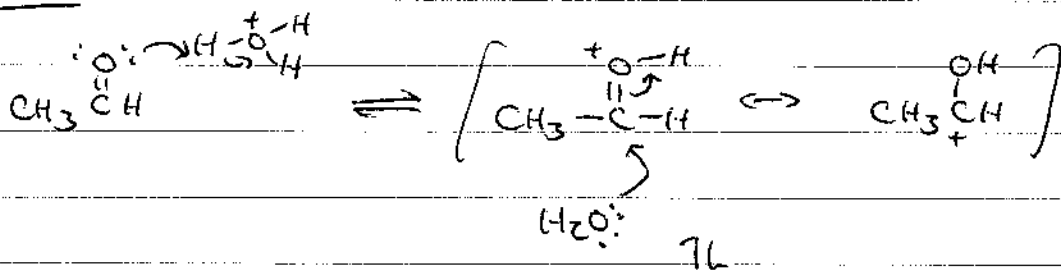
aldehydes form hydrates faster than ketones

→ $\text{R}\overset{\text{O}}{\parallel}\text{CH}$ is more electrophilic due to

- less EDG's at "C"
- less sterically hindered

Generally formed under mildly acidic conditions

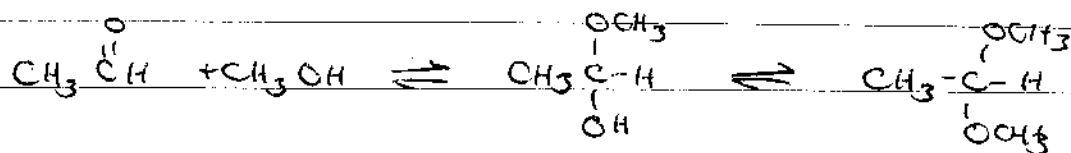
Mech



Can also be base-catalyzed

NOTE: Ch 18-18

Acetal formation / ketal formation



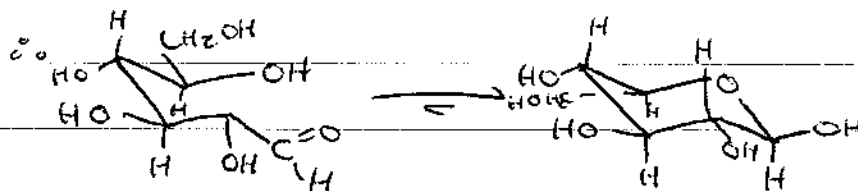
1-methoxy ethanal
a hemiacetal

1,1-dimethoxy
ethane

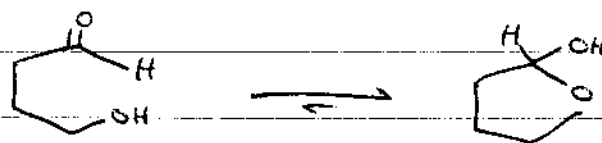
an acetal

Generally formed under mildly acidic conditions!

hemiketals & hemiacetals are generally unstable, except
when part of same molecule (i.e., intramolecular
formation)



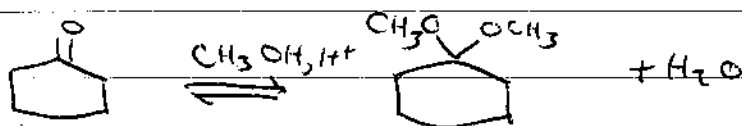
glucose



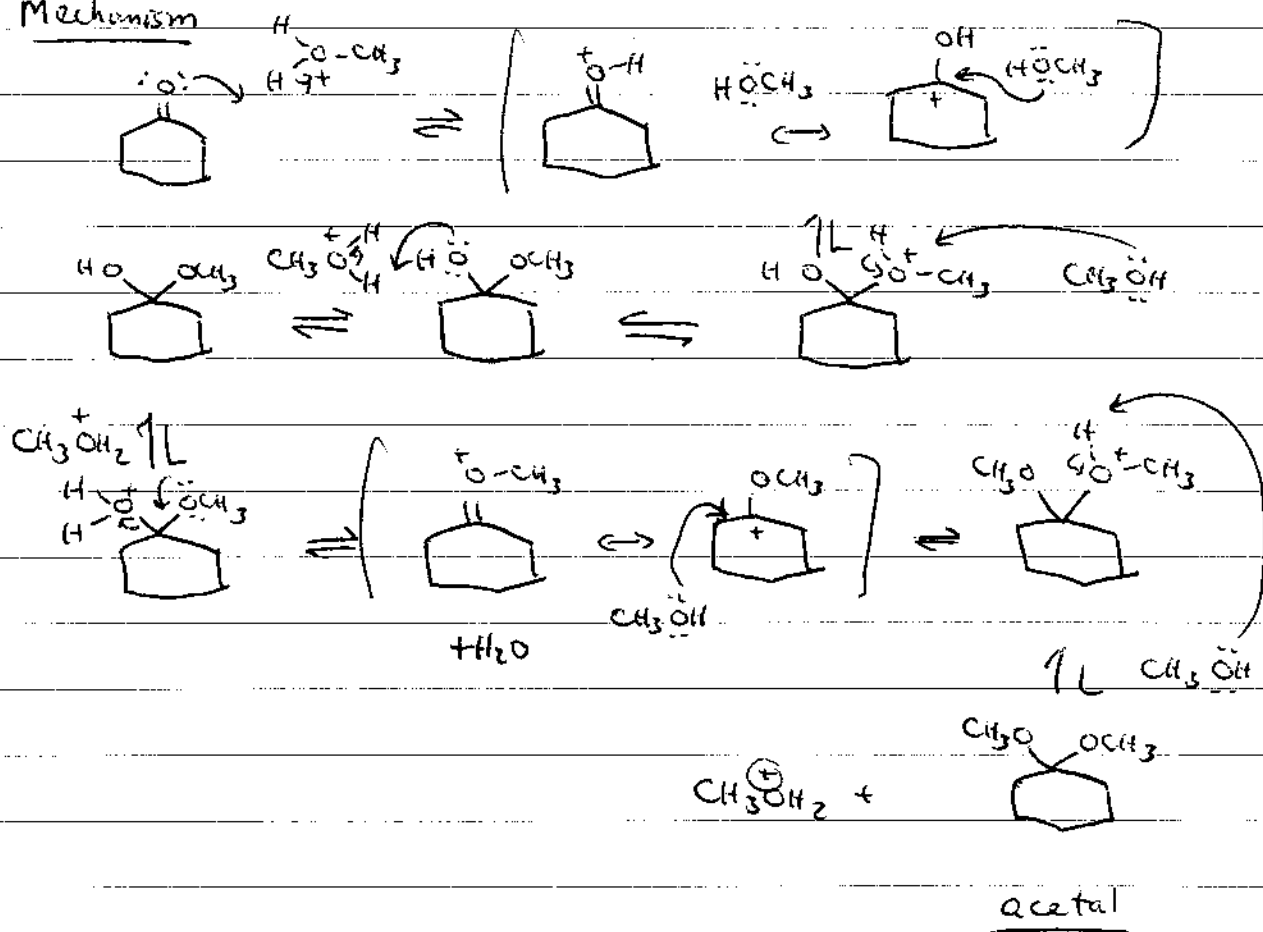
4-hydroxybutanal

H&

ketals (formed from ketones)



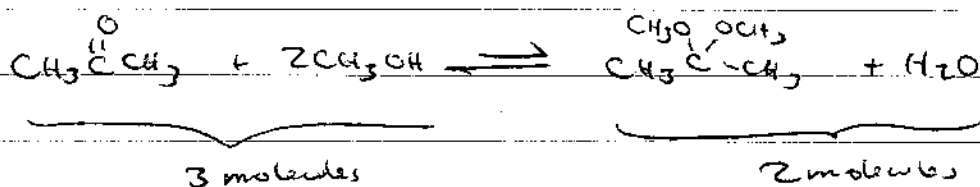
Mechanism



Can make rxn go to completion by removing water
 Dean-Stark apparatus

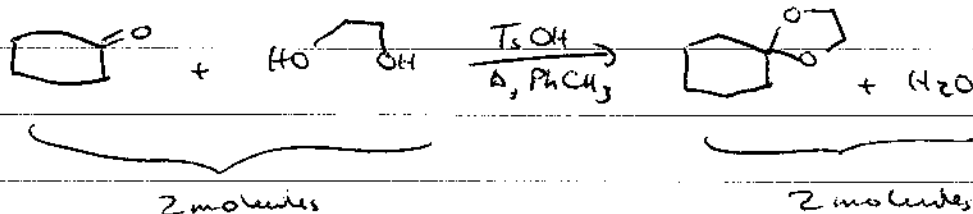
Cyclic Acetals

acetal formation is usually unfavorable due to entropic reasons

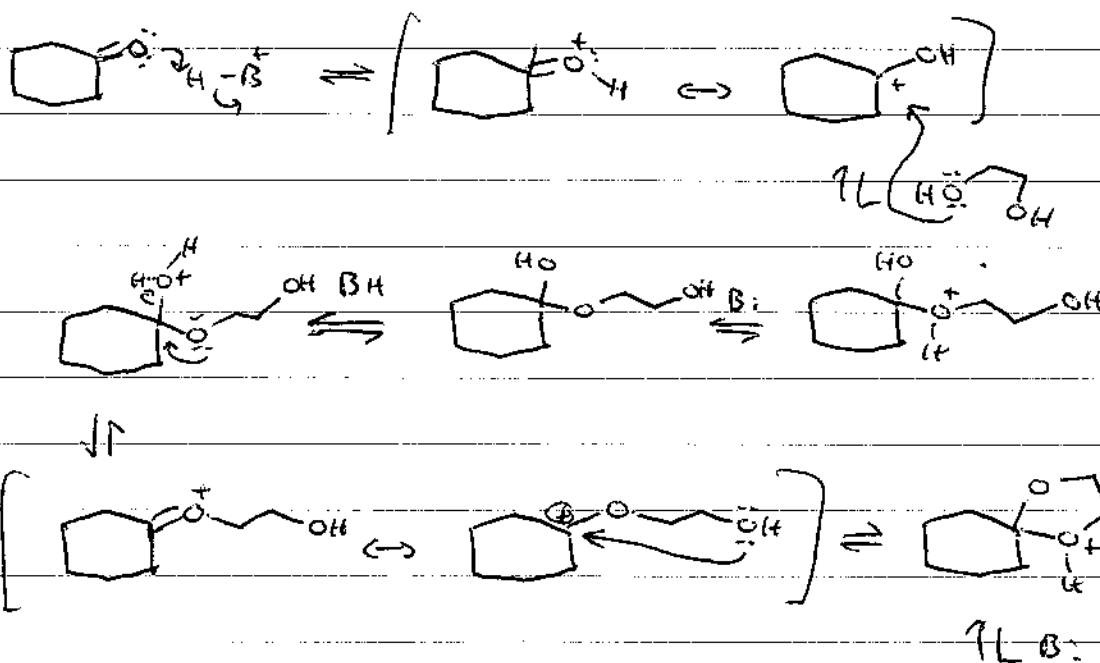


$\Delta S = -$

However,



Mechanism




Intramolecular Rns are always faster than inter-molecular rns

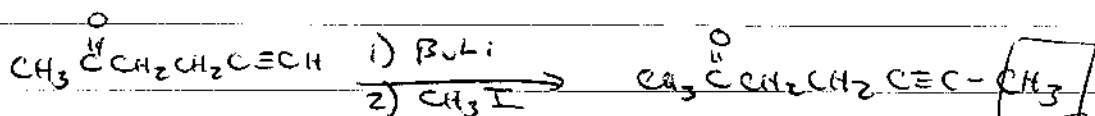
Also, 5+6-membered ring formation is generally good!

Protecting groups

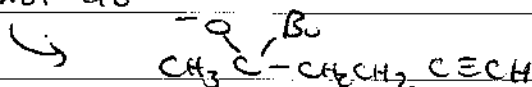
used when you need to do chemistry on one pt of a molecule
but not another.

For  use acetals => are stable to base/nucleophile
attacks & reducing agents

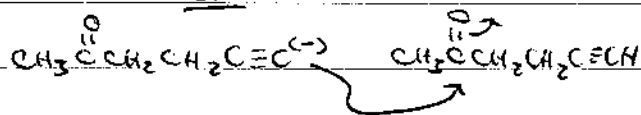
Example



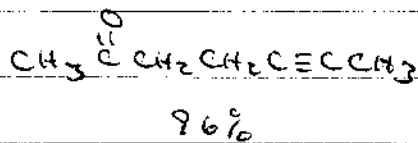
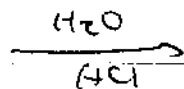
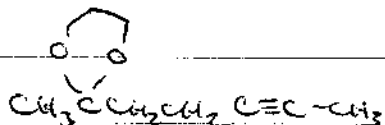
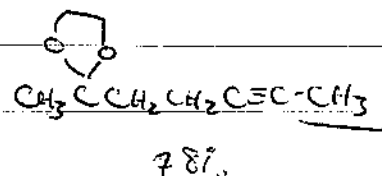
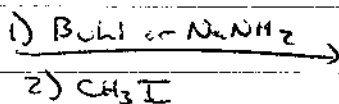
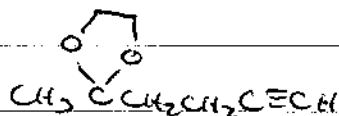
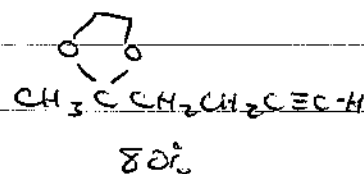
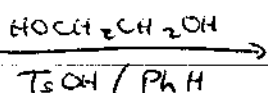
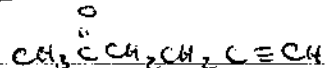
PROBLEM! cannot do



OR



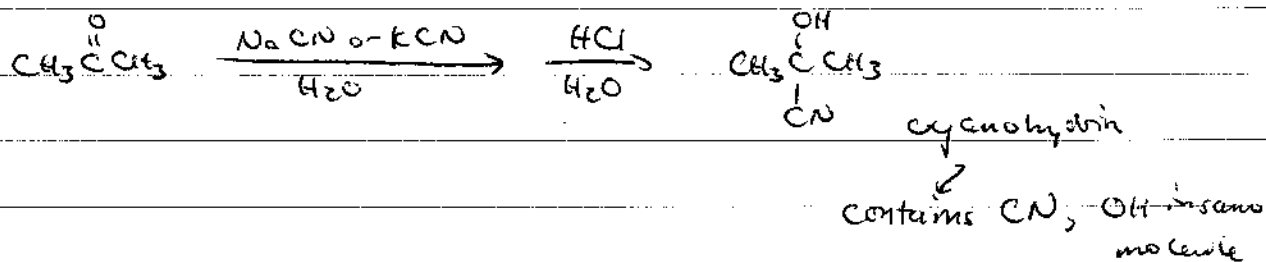
BUT



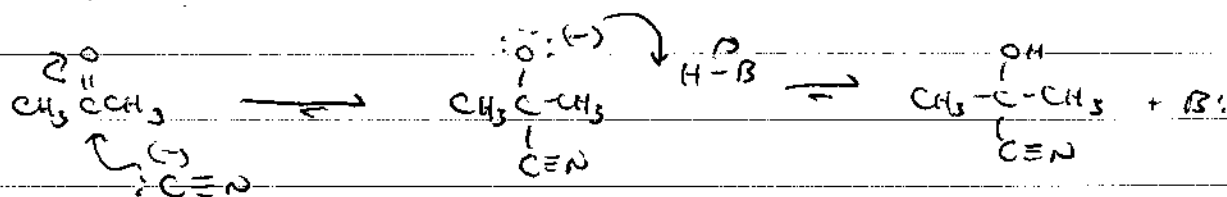
Adds 2 steps but is necessary!

Addns to $\overset{\text{O}}{\parallel}{\text{C}}$: other nucleophiles

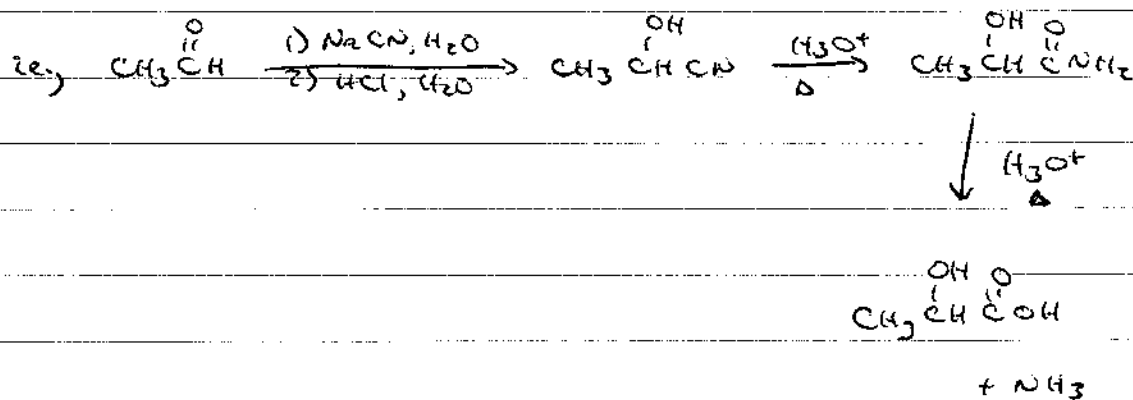
Cyanohydrin formation



Mech

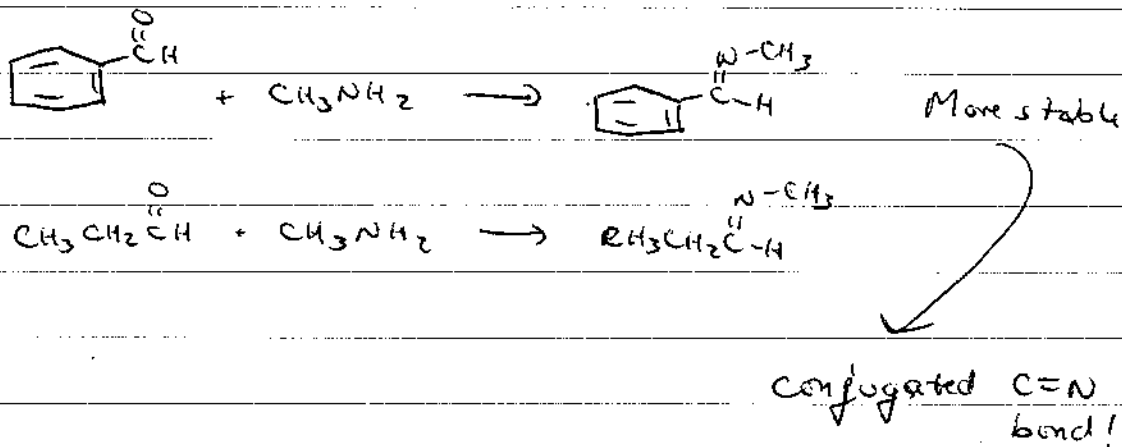


Imp't rxn since have increased the C atoms by one & also introduces 2 new fun'l g groups to the molecule (-OH, -CN) to do rxns on.

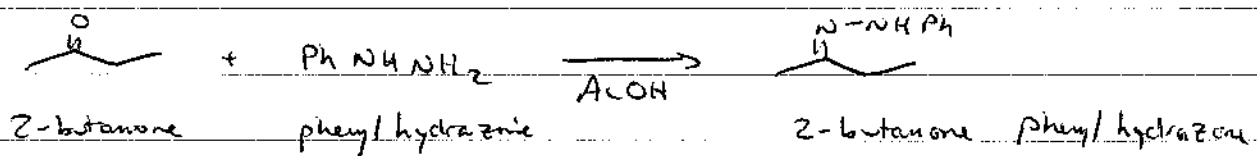
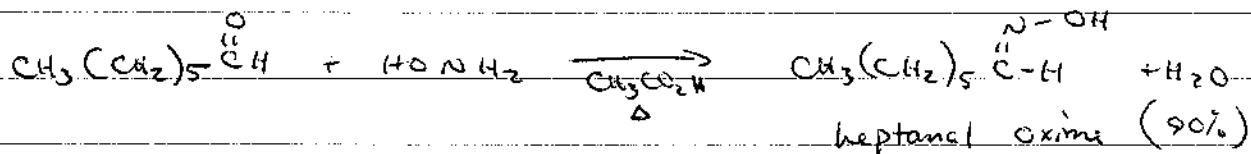


Reactivities

- 1) ketones react slower than aldehydes (more hindered)
- 2) Aromatic imines are more stable than Aliphatic imines



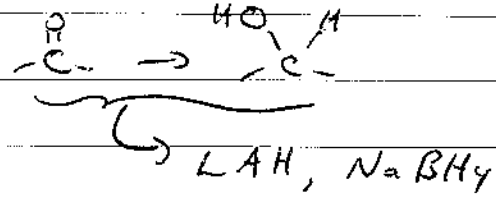
Oximes & Hydrazones



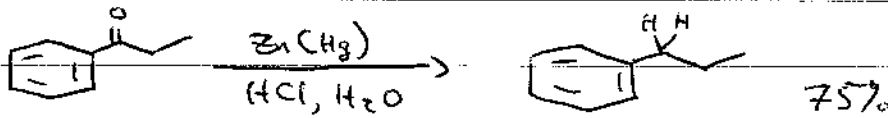
Recall, HONH2 & H2NNHR are stronger nucleophiles ~~are~~ than RNH2 due to presence of 2nd heteroatom

Skip/Read Ch 18-20

Reductions of Ketones/Aldehydes

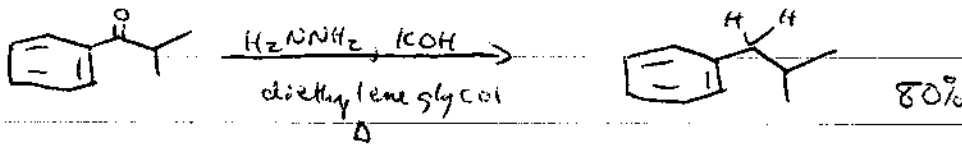


Clemmenson Reduction



Problems: a) uses Hg
b) H⁺ cat. rxn

Wolff-Kishner Reduction



uses basic conditions

Mechanism

