

Chapters 17 and 18

- Ketones, aldehydes and reactions
- Will choose order different from textbook
- Problems
 - 16.23, 16.25, 16.26, 16,27, 16,28, 16.31, 16.33, 16.35
 - 17.20, 17.23, 17.25, 17.26, 17.27, 17.28, 17.29, 17.32, 17.34, 17.36, 17.39, 17.43
 - 18.23, 18.25, 18.31, 18.32, 18.35, 18.37, 18.39

Next Weeks

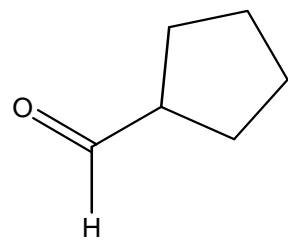
- Lecture today – 11:00 – 11:45 and 1:00 – 1:45
- During interim times – exams returned
- Full meetings this and next Thursday – no Tuesday (M/T exchange)
- Well into Chapter 18 by next Thursday
- By then will be ready to define coverage for exam – March 6

Exam

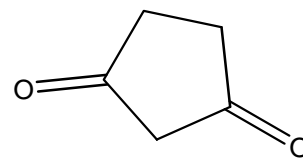
- Average 25 correct – about 75%
- Scale remains intact – estimate
- Next two exams typically lower average, final usually higher
- Maintaining grade realistic – need care if near border
- Improving grade major effort
- Last ‘W’ Day coming up – decide soon

Nomenclature

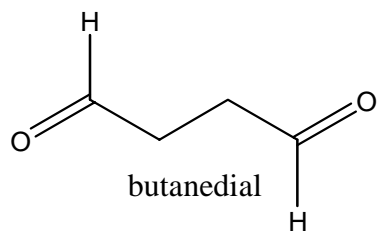
- Aldehyde – al ending (always number 1)
- Ketone – one ending (lowest number possible)
- All lower priority groups (except –en and –yne) named as prefix (hydroxy, amino, etc)
- Many trivial names – not tested



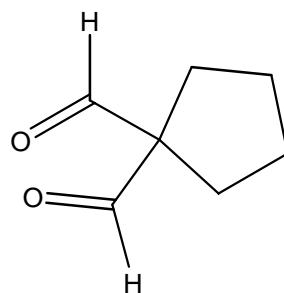
cyclopentanecarboxaldehyde



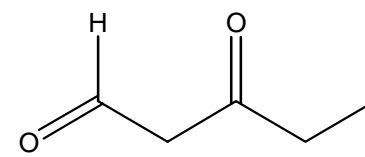
1,3-cyclopentanedione



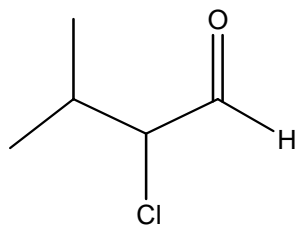
butanedial



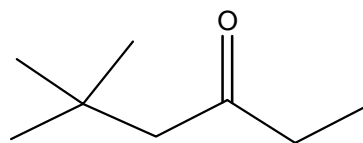
1,1-cyclopentanedicarboxaldehyde



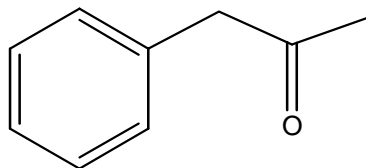
3-oxopentanal



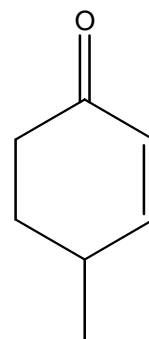
2-chloro-3-methylbutanal



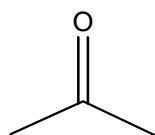
5,5-dimethyl-3-hexanone



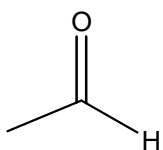
1-phenyl-2-propanone



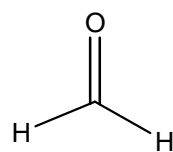
4-methyl-2-cyclohexenone



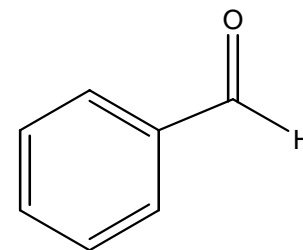
acetone



acetaldehyde



formaldehyde



benzaldehyde

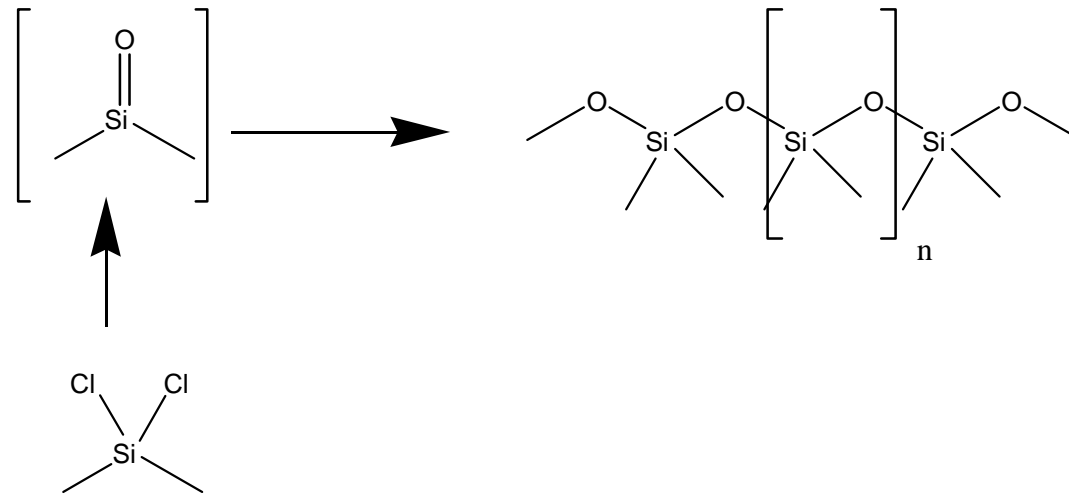
Preparation

- Hydration of alkynes
 - Enol formation – will need to remember
- Friedel-Crafts acylation – aryl ketones
- Oxidation of alcohols – PCC of primary alcohols, CrO_3/H^+ or PCC of secondary alcohols
- Ozonolysis – fragments
- Summary = Table 17.1

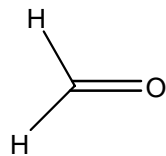
Consider double bond species

- Alkenes – Lewis bases, weak π bonds
 - Electrophilic additions, not reversible
- Arenes – Lewis bases, aromaticity
 - Electrophilic substitution, restore aromaticity
- Carbonyls – Lewis acids, strong π bonds
 - Nucleophilic additions, can be reversible
- Some contrasts

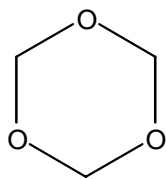
Silicones



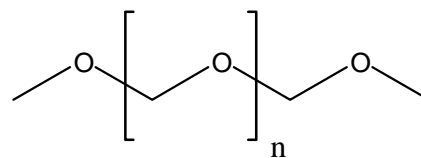
Formaldehyde



formaldehyde



trioxane

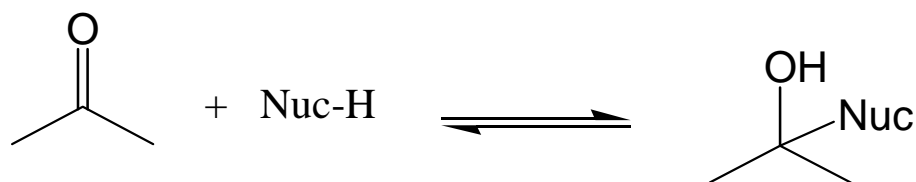


paraformaldehyde

Aldehyde and ketone reactions

- Table 17.2
- Wolff-Kishner and Clemmensen reductions
- Reduction to alcohol – NaBH_4 , LiAlH_4
- These reactions are not generally reversible

General Scheme

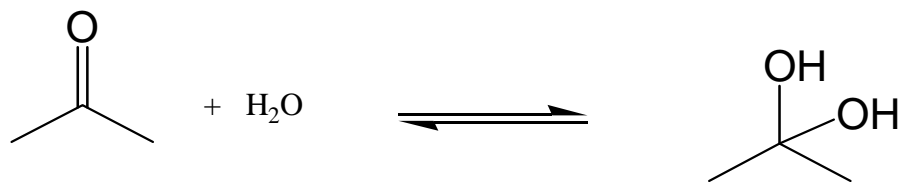


While C=O is a strong bond, the reaction only goes back to starting material when Nuc is a decent leaving group

Rule of thumb, when Nuc-H can be deprotonated by a base, reversibility can occur

Thus Grignard and hydride are not reversible

Hydration



Fast at low pH - protonation of C=O activates it

Fast at high pH - hydroxide ion activates

Slow at neutral pH

Keq usually well to the left - table 17.3

formaldehyde 2300

acetaldehyde 1

2-methylpropanal 0.2

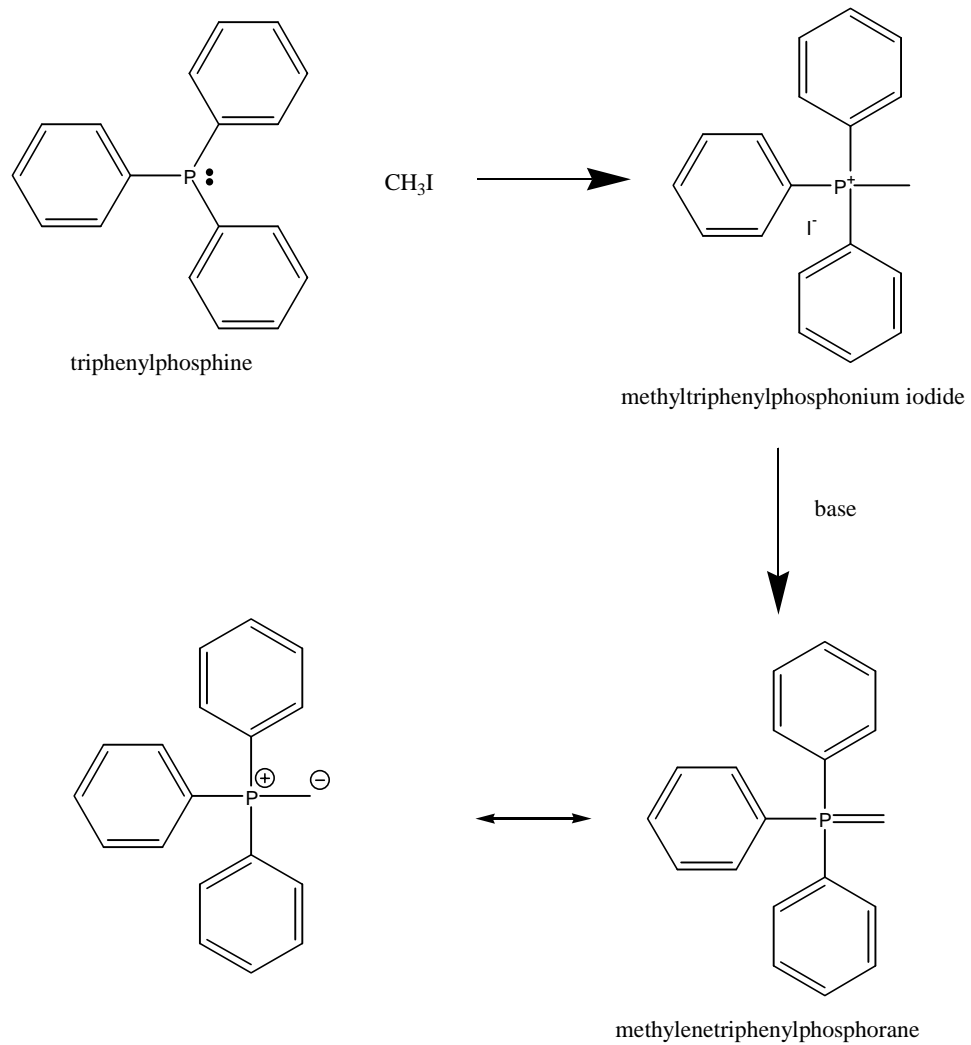
acetone .0014

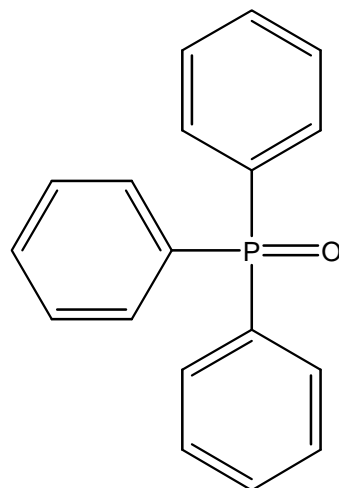
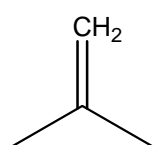
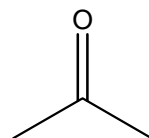
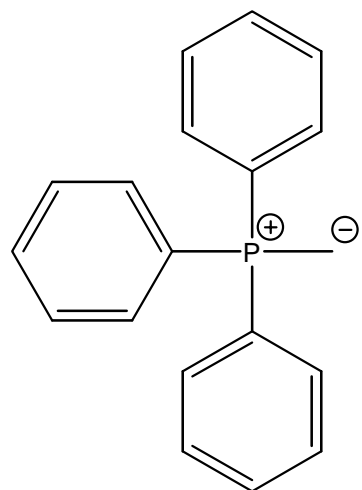
hexafluoroacetone 22000

To isolate a product

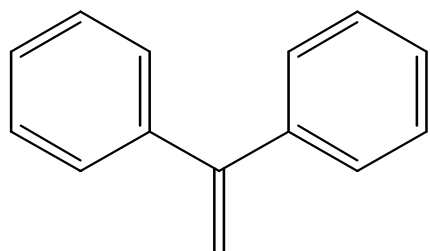
- Need to make reaction irreversible
- Loss of a small molecule
- Often water – not always
- Can't make hydration irreversible – can go to enol, but not more stable
- This will be recurring theme of chapter 17

Wittig Reaction

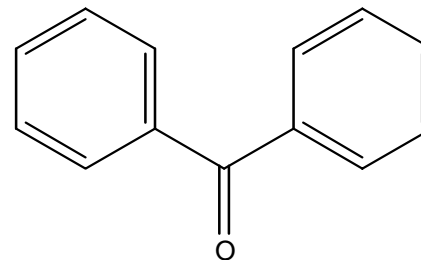
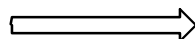




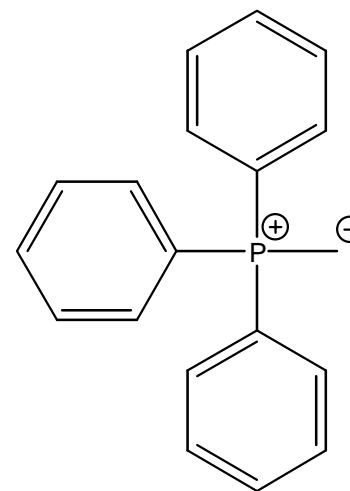
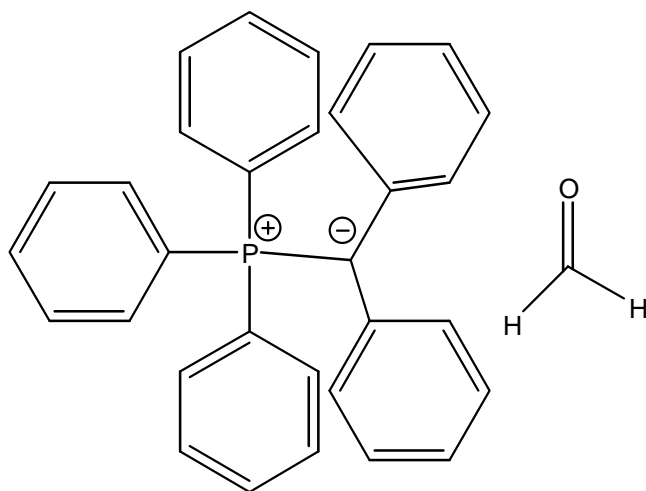
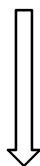
Retrosynthesis



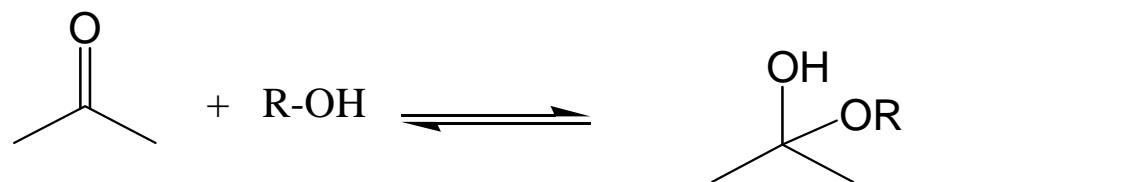
diphenylethylene



benzophenone

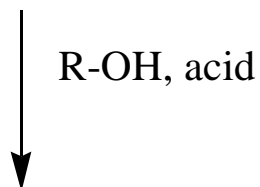


Reactions with alcohols

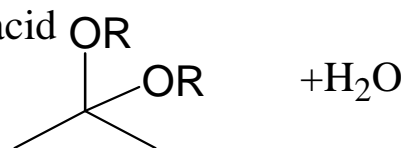


hemiacetal or hemiketal

first step catalyzed by acid or base
but easily reversible, difficult to isolate

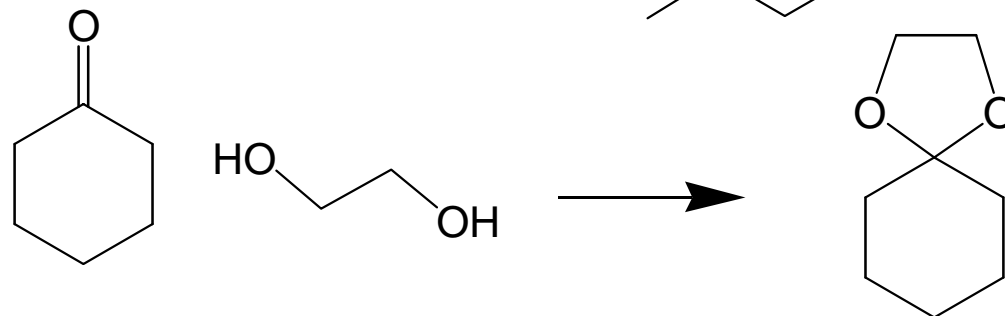
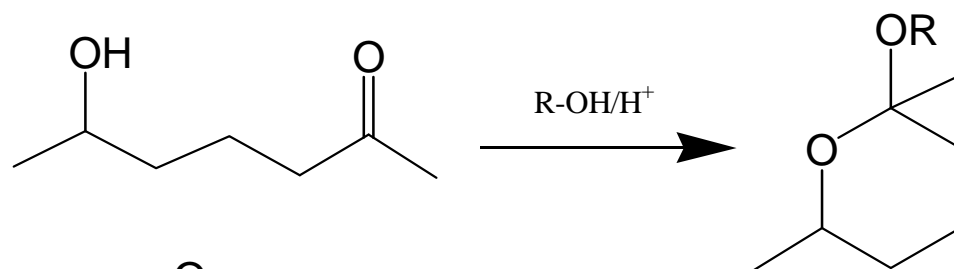
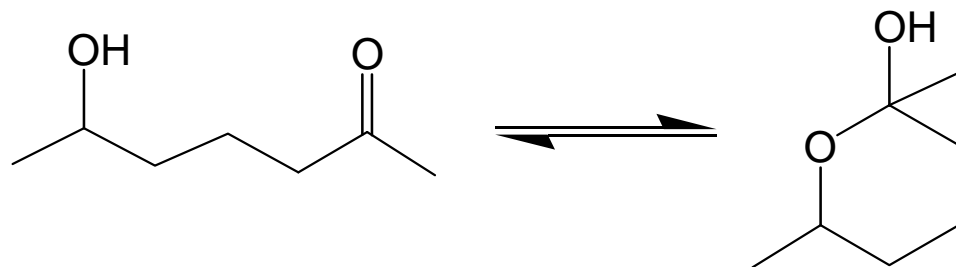


if run in acid and remove water, dehydration
product can be isolated until add water and acid
to reverse

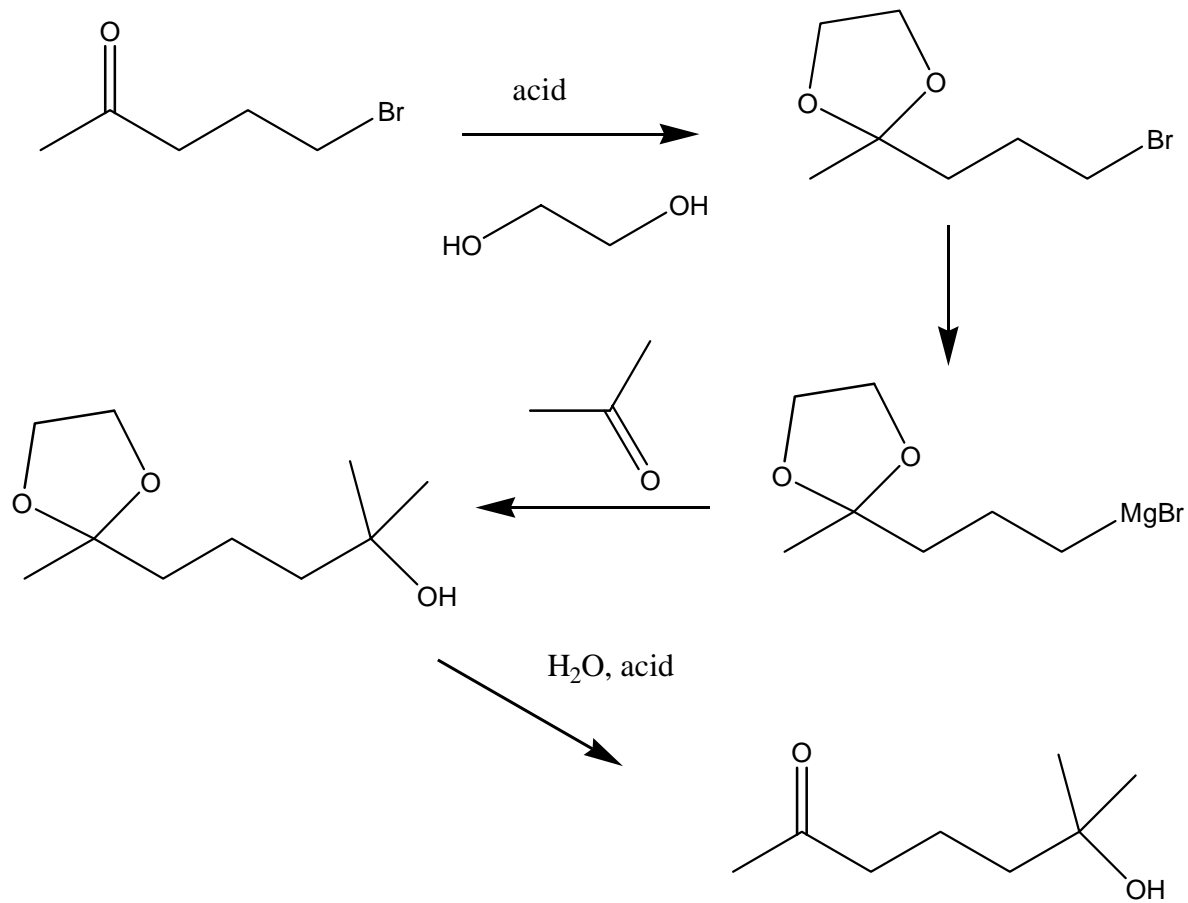


acetal/ketal; now irreversible

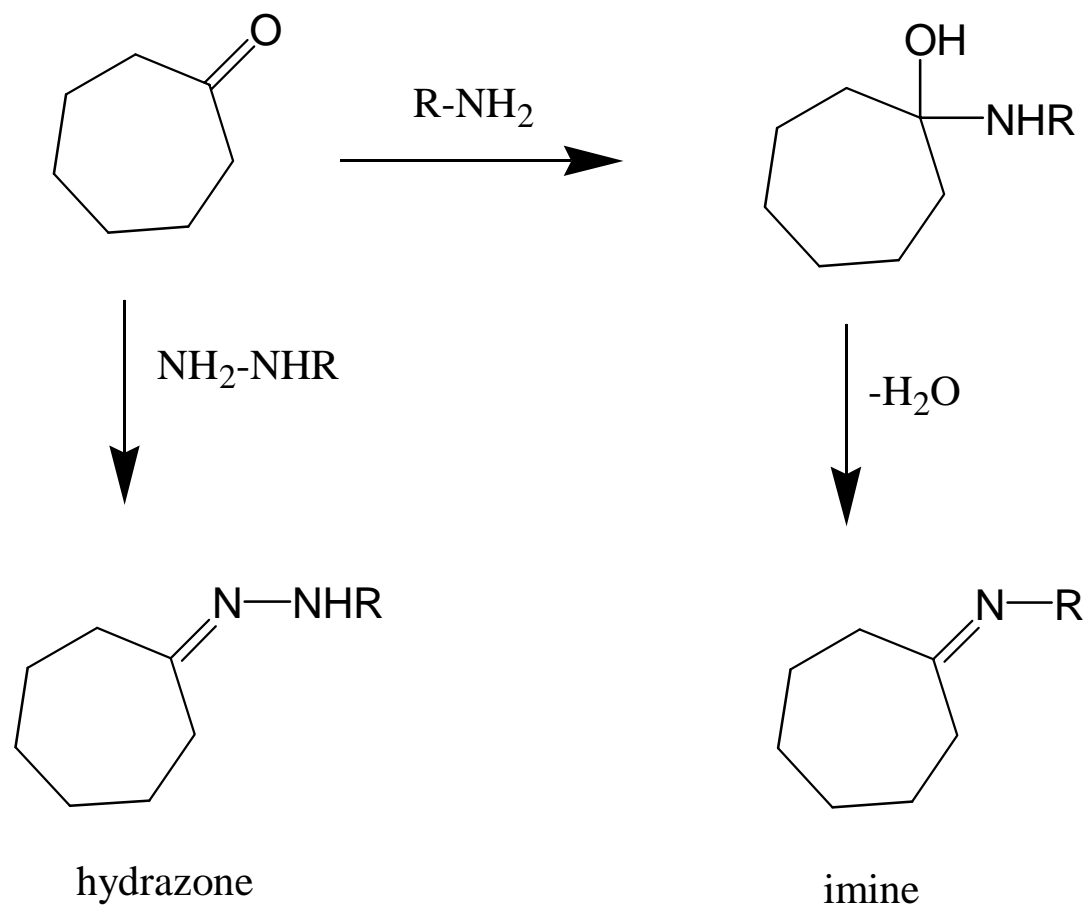
Cyclic variations



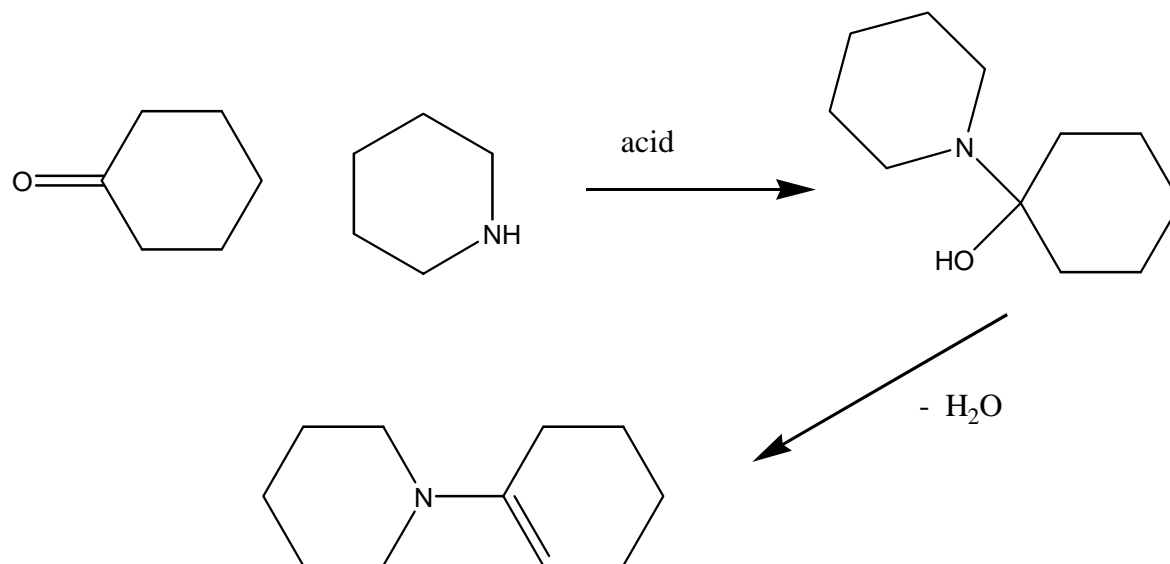
Protecting group



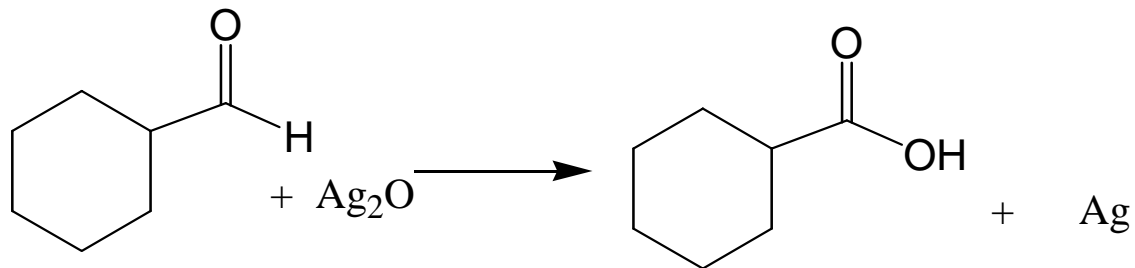
Primary Amines



Secondary Amines - enamines

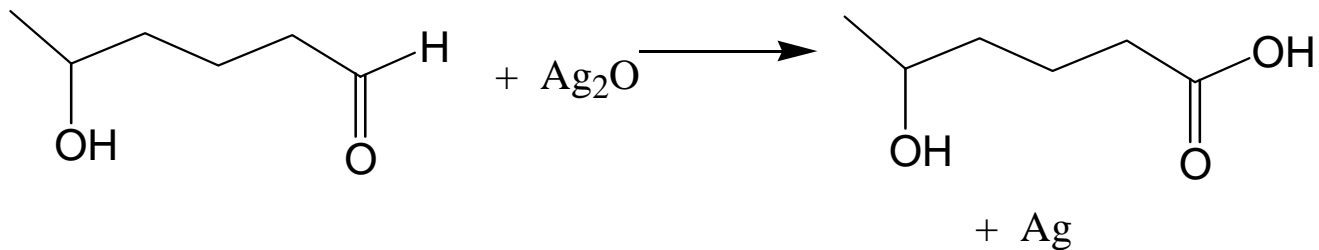


Tollen's Test

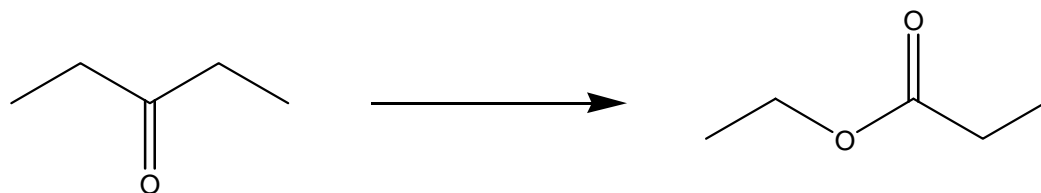
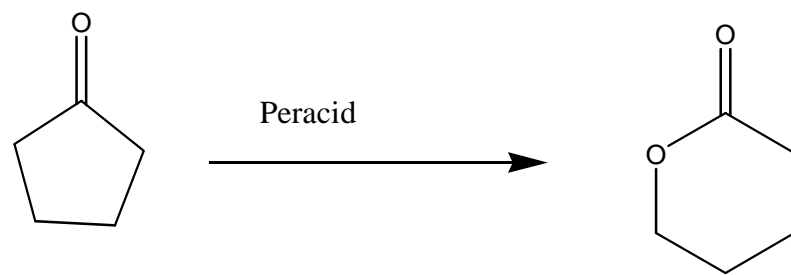


Formation of silver mirror is test for aldehydes (not ketones)

Does not react with alcohols



Baeyer-Villiger Reaction



Stereochemical Considerations

- Addition to C=O gives an sp³ carbon
- Potentially a new chiral center
- Diastereoselectivity
- enantioselectivity