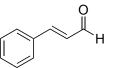
19.1 Intro to Aldehydes & Ketones	19.2 Nomenclature	19.3 Making Aldehydes & Ketones
19.4 Intro to Nucleophilic Addition	19.5 Oxygen Nucleophiles:	19.6 Nitrogen Nucleophilies: Imines
Reactions	Acetals & Hemiacetals	and Enamines
19.7 Hydrolysis of Acetals, Imines,	19.9 Hydrogen Nucleophiles:	19.10 Carbon Nucleophiles:
& Enamines	Reduction Reactions	Grignards, Cyanide, and Wittigs
19.12 Synthesis Strategies		

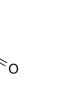
[19.1] Introduction to some Cool Aldehydes & Ketones





Cinnamaldehyde (cinnamon fragrance)

Benzaldehyde (almond extract)



I-Menthone

(peppermint

component)

Thujone

0

(absinthe component)

[19.2] Nomenclature

Aldehyde parent	Ketone parent	Aldehyde or ketone substituent on parent chain	Single C aldehyde substituent
-anal	-one	-0X0	-carbaldehyde

Draw structures from names...

Butanal 3-oxobutanal 4-hydroxy-2-pentanone cyclohexanecarbaldehyde

Reaction Review – what have we learned about aldehydes & ketones so far?

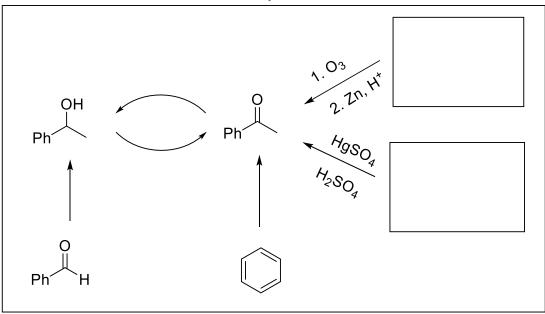
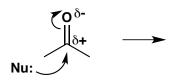


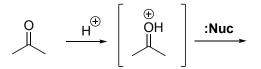
TABLE 19.1				
		Oxidation of Secondary Alcohols	12.10	
A SUMMARY OF ALDEHYDE PREPARATION METHODS COVERED IN PREVIOUS CHAPTERS				
REACTION	SECTION	R H ₂ SO ₄ , H ₂ O R R		
Oxidation of Primary Alcohols	12.10	A variety of strong or mild oxidizing agents can be used to oxidize secondary alcohols. The resulting ketone does not undergo further oxidation.		
OH PCC, CH ₂ Cl ₂ O or DMP, CH ₂ Cl ₂		Ozonolysis of Alkenes	8.13	
R or 1) DMSO, (COCI) ₂ R H 2) Et ₃ N		$ \begin{array}{c} R \\ \xrightarrow{R} \\ \xrightarrow{1} \\ \xrightarrow{2} \\ \xrightarrow{1} \\ \xrightarrow$		
When treated with a strong oxidizing agent, primary alcohols are oxidized to carboxylic acids. Formation of an aldehyde requires a mild oxidizing agent, such as the oxidizing agents shown above, that will not further oxidize the resulting aldehyde.		R R Tetrasubstituted alkenes are cleaved to form ketones.		
Ozonolysis of Alkenes	8.13	Acid-Catalyzed Hydration of Terminal Alkynes	9.7	
$ \begin{array}{c} H \\ H \\ R \\$		$R \xrightarrow{H_2SO_4, H_2O} R \xrightarrow{O} CH_3$		
Ozonolysis will cleave a C=C double bond. If either carbon atom bears a hydrogen atom, an aldehyde will be formed.		This procedure results in a Markovnikov addition of water across the π bond, followed by tautomerization to form a methyl ketone.		
		Friedel–Crafts Acylation	18.6	
Hydroboration-Oxidation of Terminal Alkynes	9.7		10.0	
$R \xrightarrow{1) R_2 B - H} R \xrightarrow{H} O$	211			
Hydroboration-oxidation results in an <i>anti</i> -Markovnikov addition of water across a π bond, followed by tautomerization of the resulting enol to form an aldehyde.		Aromatic rings that are not too strongly deactivated will react with an acyl halide in the presence of a Lewis acid to produce an aryl ketone.		

[19.4] Nucleophilic Attack at Carbonyl C

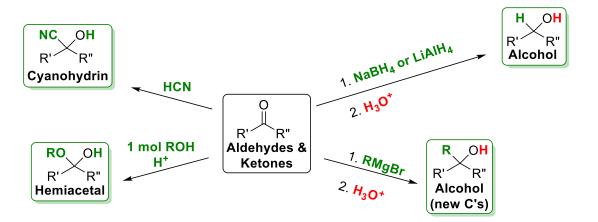
Basic Conditions



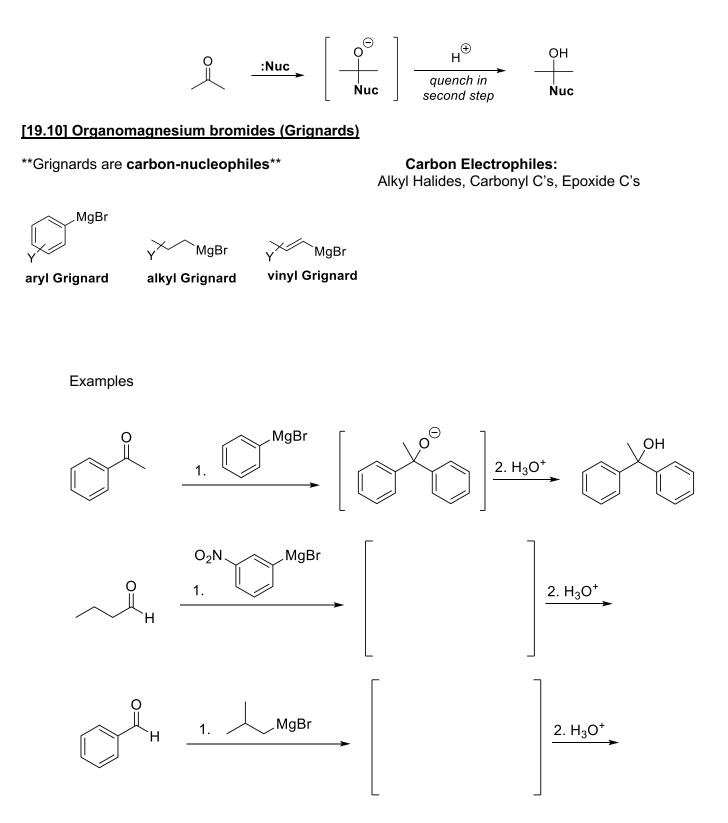
Acidic Conditions



Nucleophilic Addition: A sampler platter of hydrogen, carbon, and oxygen nucleophiles



Basic Nucleophilic Addition Mechanism – Grignard & Hydride Additions



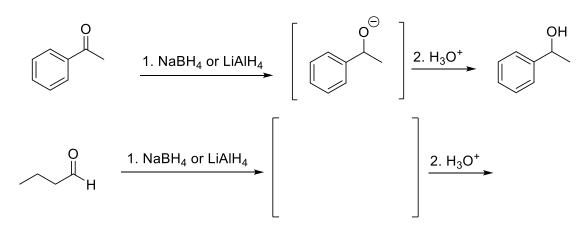
[19.9] Aldehyde & Ketone Reductions – Hydride Additions

Hydrides are **hydrogen-nucleophiles** NaBH₄ = sodium borohydride LiAl

LiAlH₄ = lithium aluminum hydride

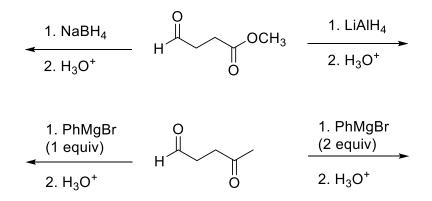
Limitations:

Examples

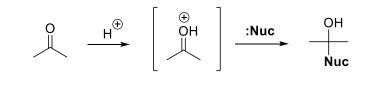


Aldehydes are more reactive than ketones and esters **

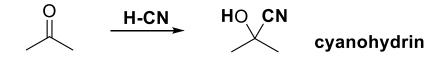
Chemoselective Reactions Examples



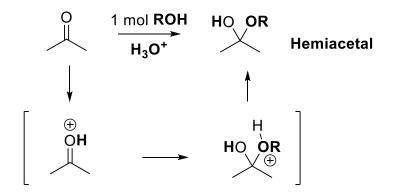
Simple Acidic Nucleophilic Addition Mechanisms - Cyanohydrins & Hemiacetals



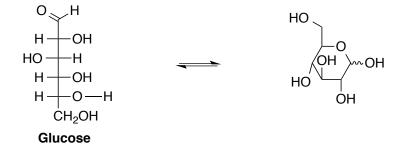
[19.10] Addition of HCN: Cyanohydrin Formation



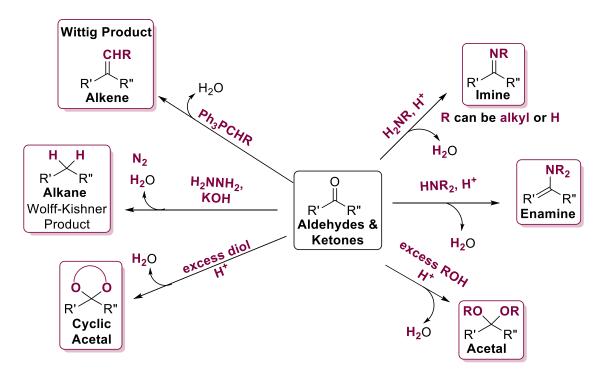
[19.5] Addition of Alcohols: Hemiacetal Formation



Hemiacetals in Nature: Sugars

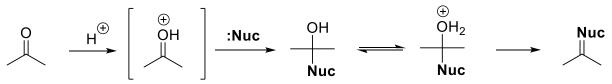


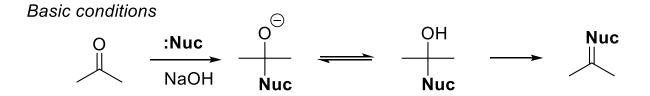
Aldehydes & Ketones gone wild! When they lose their carbonyl oxygen...



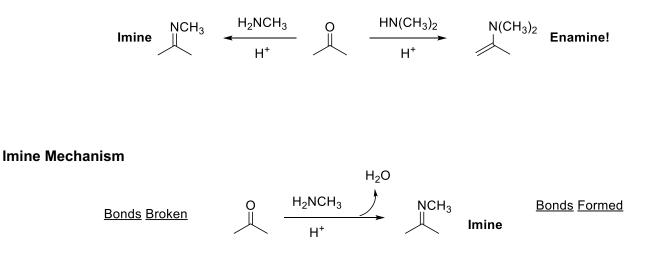
Nucleophilic Additon w/ Dehydration

Acidic conditions

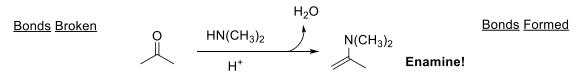




[19.6] IMINES & ENAMINES FROM ALDEHYDES & KETONES

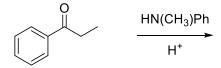


Enamine Mechanism



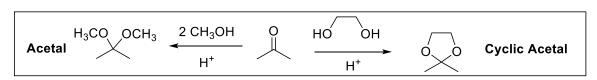
Predict the products:

$$H^{+} \xrightarrow{H^{+}} H^{+}$$

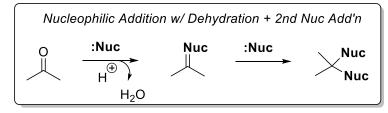


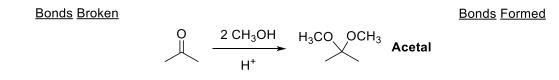
8B, Chapter 19

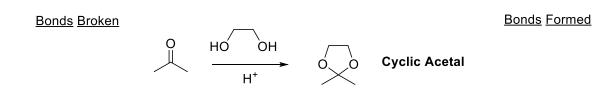
[19.5] ACETALS FROM ALDEHYDES & KETONES



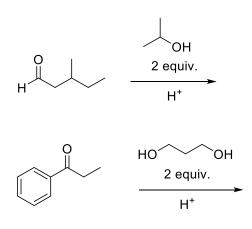
Acetal Mechanism - The Combo!







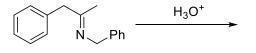
Predict the products:



[19.7] Imine, Enamine, and Acetal Hydrolysis



Carbonyl



$$H_3O^+$$

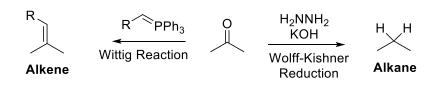
Alcohol

Carbonyl

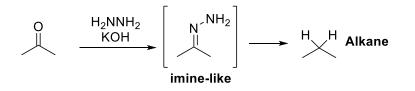
 H_3O^+ ÓÒ-

 H_3O^+

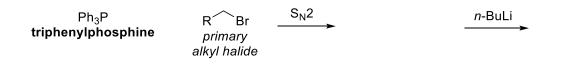
ALKENES & ALKANES FROM ALDEHYDES & KETONES



[19.6] Wolff-Kishner Reduction

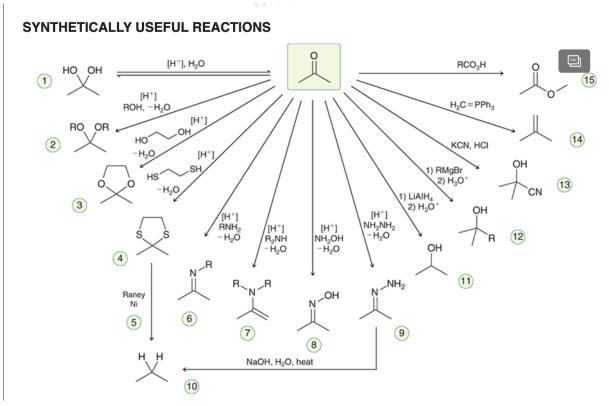


[19.10] Wittig Reagent

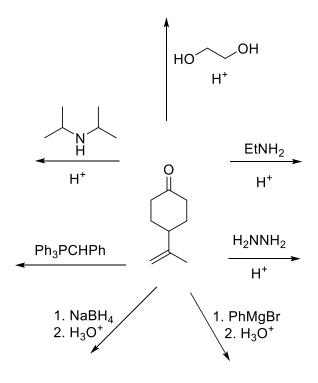


Reaction with ketone

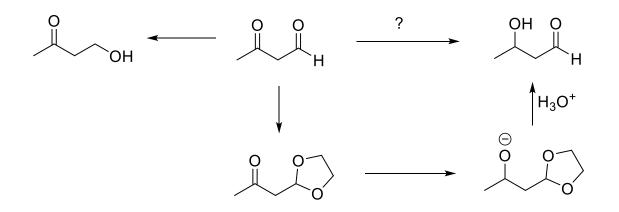
O PPh₃



Ketone Reaction Starburst



[19.5] Acetal Protecting Group - Temporarily mask aldehydes & ketones



Both syntheses below require a protecting group. Outline the steps.

