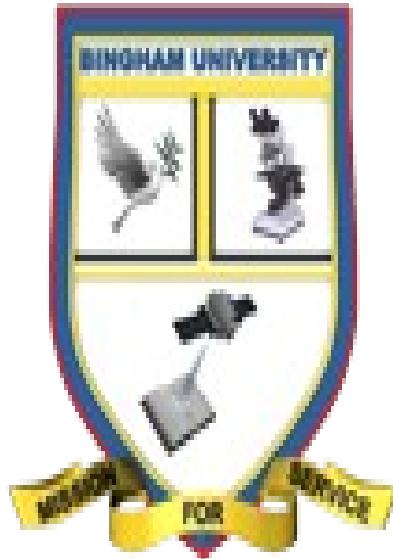




CHM 103: Organic Chemistry I

Presented by:

Assoc Prof Okoli BJ MRSC, MACS



Bingham University



The University with the difference

Department of Chemical Science,
Faculty of Science & Technology

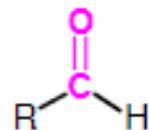


Bingham University

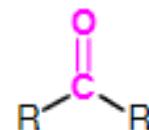
Carbonyl Chemistry

- We begin our study of carbonyl compounds with the study of **aldehydes** and **ketones** (the aldehyde/ketone oxidation level).
 - Carbonyl compounds are molecules containing the carbonyl group, **C=O**. These include:

- Aldehydes**

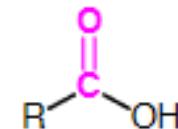


- Ketones**



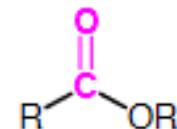
Note: two bonds to heteroatoms

- Carboxylic acids**

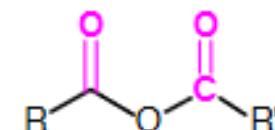


Carboxylic acid derivatives:

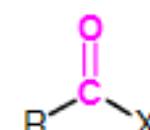
- Esters**



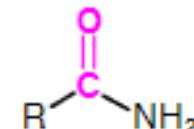
- Anhydrides**



- Acid halides**

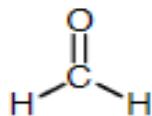


- Amides**

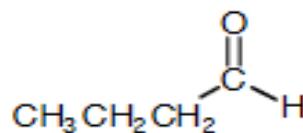


Nomenclature of Aldehydes and Ketones

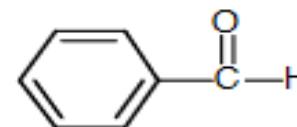
- Common names are used for the simplest aldehydes and ketones:



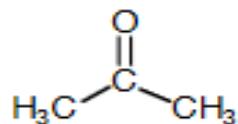
formaldehyde



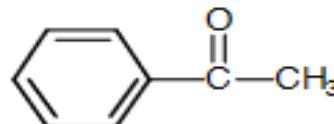
butyraldehyde



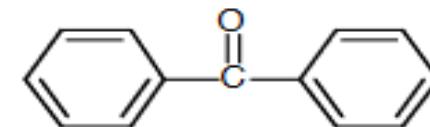
benzaldehyde



acetone

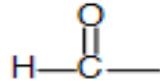


acetophenone

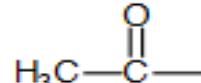


benzophenone

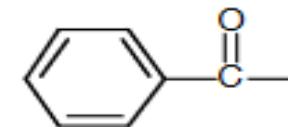
- Common names are also used for carbonyl-containing substituent groups, which are known collectively as *acyl* groups:



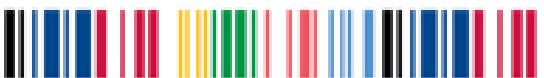
formyl



acetyl

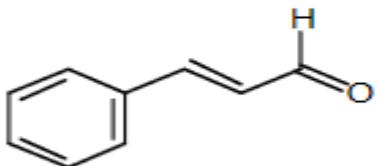


benzoyl

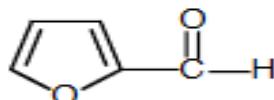


Nomenclature of Aldehydes and Ketones continue

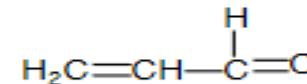
- Traditional names are used for a great many aldehydes and ketones which were recognized as substances long before systems of nomenclature were developed:



cinnamaldehyde

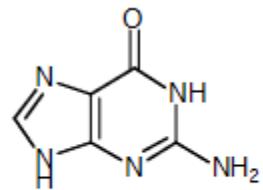


furfural

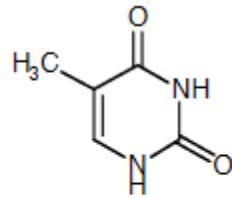


acrolein

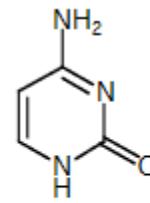
- Three of the four bases which comprise DNA contain carbonyl groups



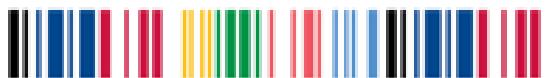
guanine (G)



thymine (T)

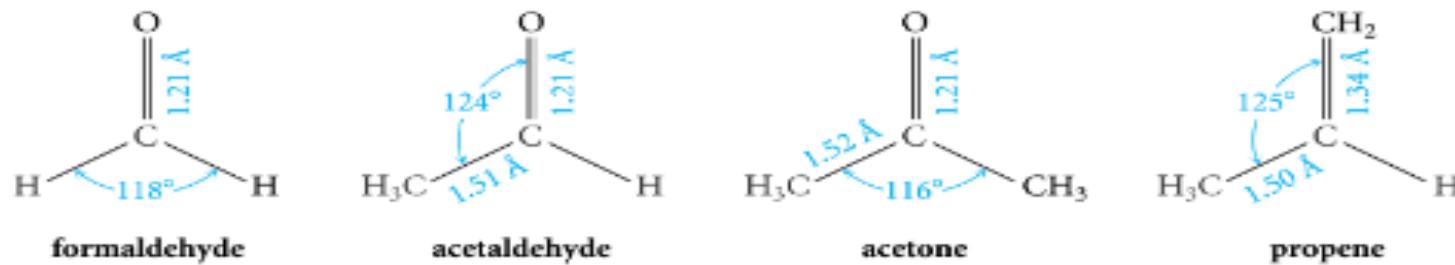


cytosine (C)

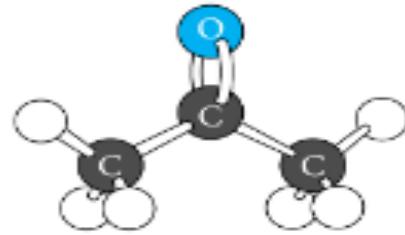


Structure of Aldehydes and Ketones

- The carbonyl carbon of an aldehyde or ketone is sp^2 -hybridized.
 - The bond angle is close to 120° (trigonal planar).
 - The carbon-oxygen double bond consists of:
 - A σ C-O bond
 - A π C=O bond
- We can compare the C=O bond length to those of C=C double bonds*



(a)



(b)

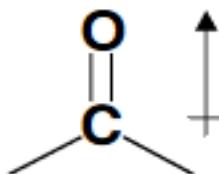


(c)



Properties of Aldehydes and Ketones

- Aldehydes and ketones are polar molecules because the C=O bond has a dipole moment:



For acetone:

dipole moment = 2.7 D

boiling point = 56.5 °C

dipole moment = 0.4 D

boiling point = -47.4 °C

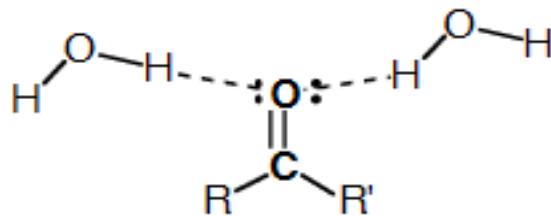
dipole moment = 1.7 D

boiling point = 82.3 °C

For propene:

For i-propanol:

- Their polarity makes aldehydes and ketones have higher boiling points than alkenes of similar molecular weight.
- Aldehydes and ketones are not hydrogen bond donors (they can't donate a proton); therefore, they have lower boiling points than alcohols of similar molecular weight.
- Aldehydes and ketones are hydrogen bond acceptors; this makes them have considerable solubilities in water.



Ketones such as acetone are good solvents because they dissolve both aqueous and organic compounds
Recall that acetone is a *polar, aprotic* solvent.



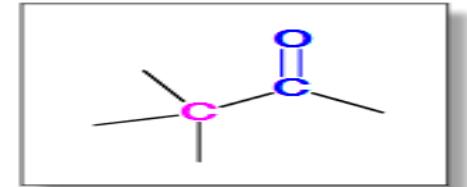
Reactions of Aldehydes and Ketones

- The reactions of aldehydes and ketones can be divided into two main categories:

- Reactions of the **carbonyl group**



- Reactions involving the **α -carbon**



- Carbonyl group** reactions fall into three main groups:

- Reactions with acids

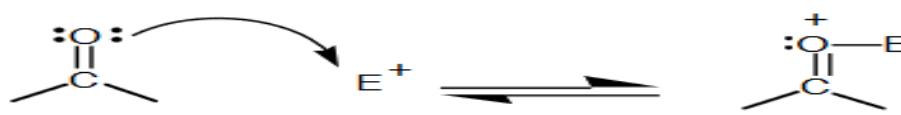
- Addition reactions

- Oxidation

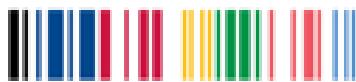
- Reactions with acids:

- The carbonyl oxygen is weakly basic.

- Both Bronsted and Lewis acids can interact with a lone pair of electrons on the carbonyl oxygen.

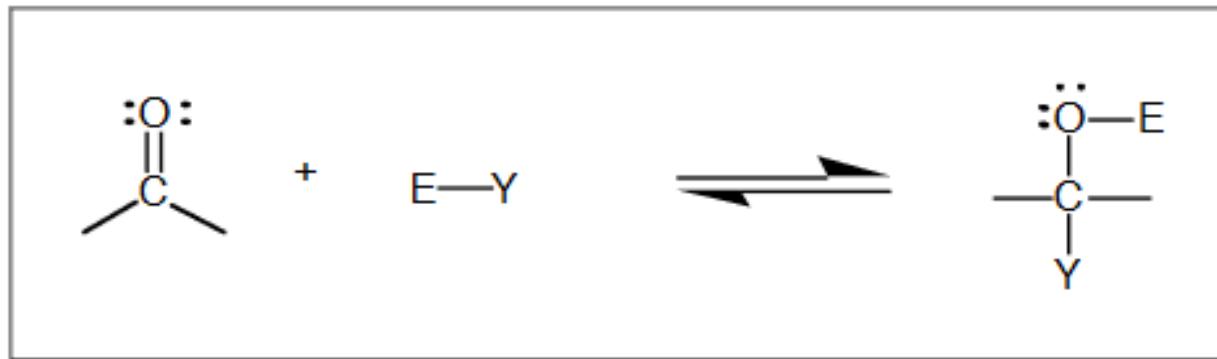


- For example, when the Bronsted acid H_3O^+ is used:



Reactions of Aldehydes and Ketones

- Addition Reactions
 - Carbonyl groups in aldehydes and ketones undergo addition reactions.
 - This is one of the most important reactions of the carbonyl group.

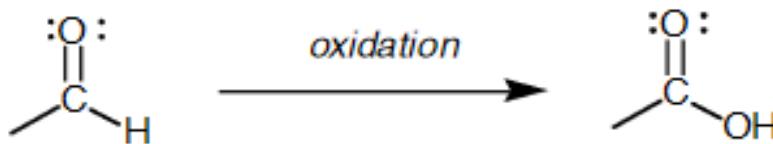


- Addition reactions occur by two different mechanisms:
 - Base-catalyzed addition (under basic or neutral conditions)
 - Acid-catalyzed addition (under acidic conditions)
- In some cases, we can carry out the same overall reaction using either set of conditions (acidic or basic).

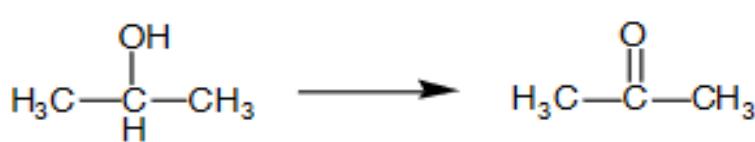


Reactions of Aldehydes and Ketones

- Carbonyl groups in aldehydes and ketones may be oxidized to form compounds at the next “oxidation level”, that of carboxylic acids.



- Alcohols are oxidized to aldehydes and ketones
(example: biological oxidation of ethanol to acetaldehyde)
- The carbonyl group may be further oxidized to carboxylic acids

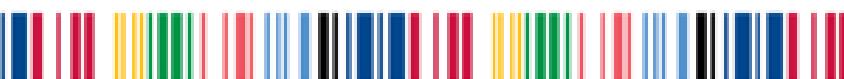


alcohol to **aldehyde**: two electron oxidation



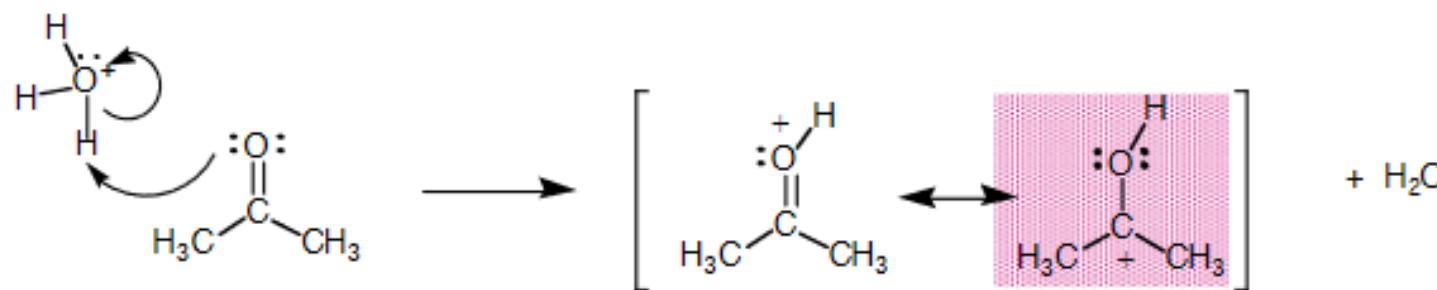
alcohol to **carboxylic acid**: four electron oxidation

aldehyde to carboxylic acid:
two electron oxidation

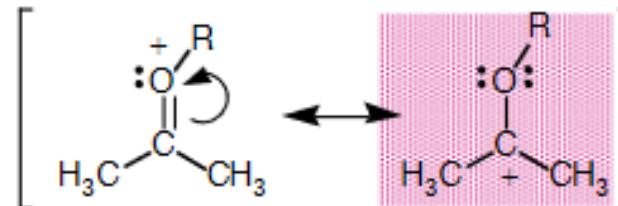


Basicity of Aldehydes and Ketones

- Reactions which occur at the carbonyl oxygen of aldehydes and ketones:
 - The weakly basic carbonyl oxygen reacts with protons or Lewis acids
 - The protonated form of the aldehyde or ketone is resonance-stabilized
 - This gives the aldehyde/ketone conjugate acid carbocation character

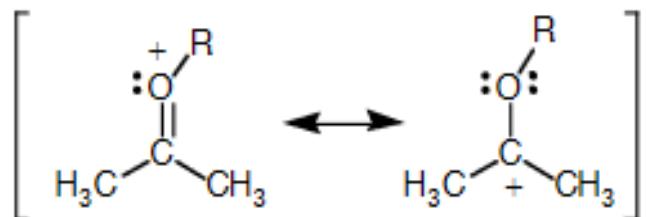


- Protonated aldehydes and ketones can be thought of as **α -hydroxy carbocations**
- When an alkyl group replaces (conceptually) the proton, an **α -alkoxy carbocation** is formed:

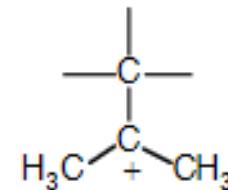
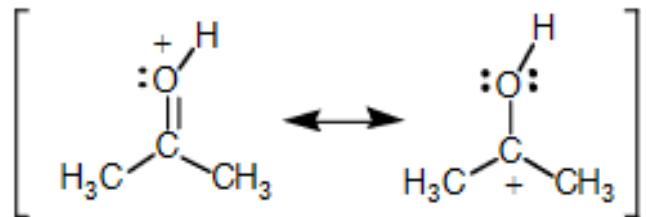


α -Hydroxy (Alkoxy) Carbocations

- α -Hydroxy (Alkoxy) carbocations are more stable than ordinary carbocations



...more stable than:



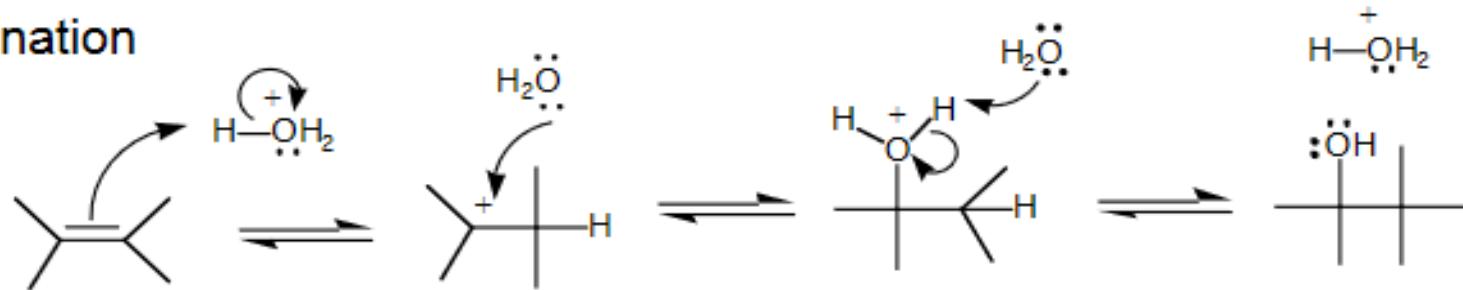
- The polar effect of the oxygen in the carbon-oxygen bond attracts electrons.
- But... electron-attracting groups adjacent to carbocations are destabilizing
- However, the resonance stabilization outweighs this destabilization



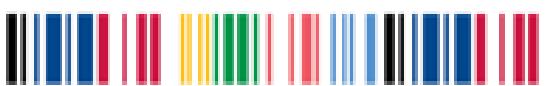
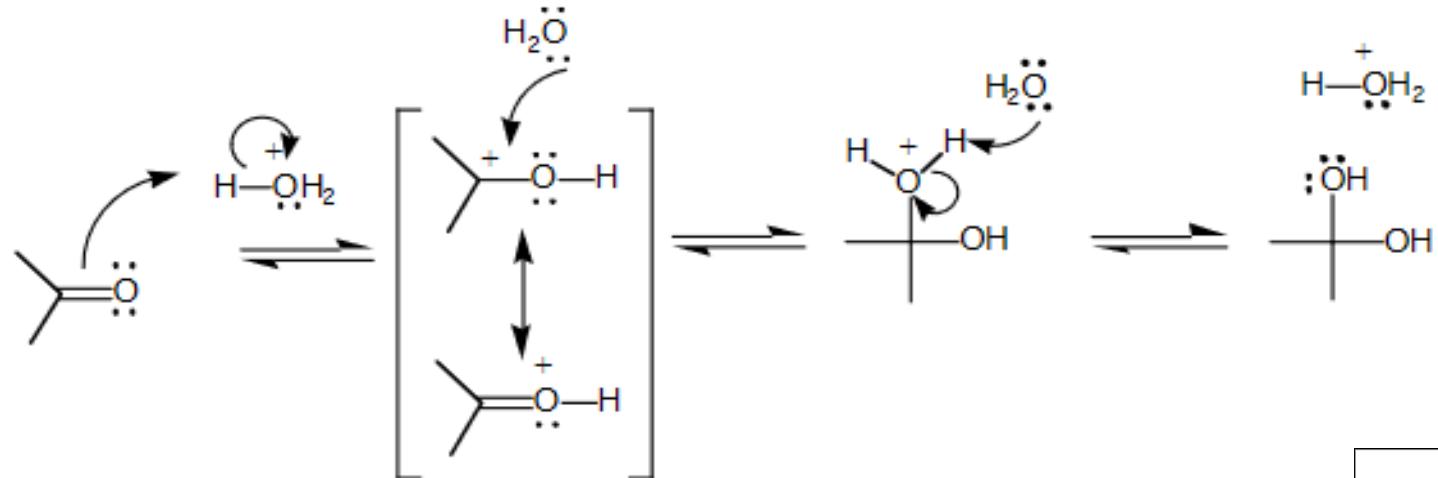
Addition Under Acidic Conditions

- Addition of water to carbonyl compounds under acidic conditions is analogous to addition of water to alkenes
- The reaction occurs in three steps:
 - Protonation
 - Addition
 - Deprotonation

alkene:

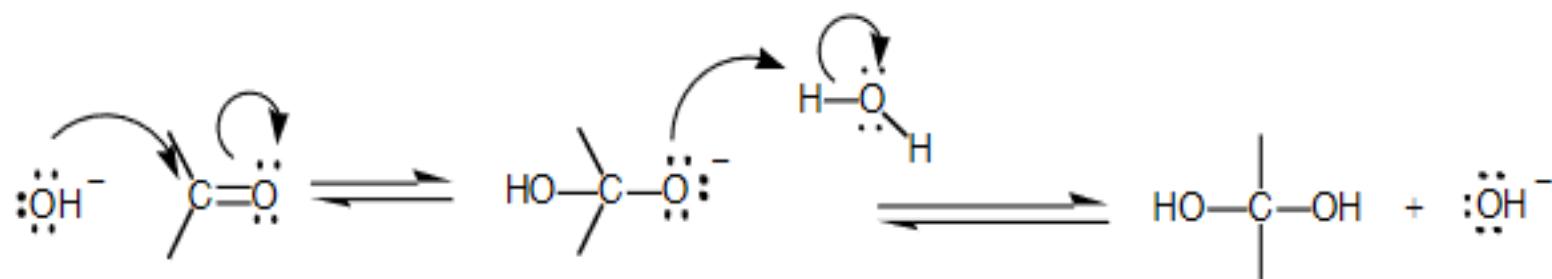


ketone:



Addition Under Basic Conditions

- Addition of water to carbonyl compounds under **basic** conditions has no analogy in reactions of alkenes
- The reaction occurs in two steps:
 - Addition of OH^- to carbonyl carbon
 - Protonation of carbonyl oxygen
- Addition occurs directly because OH^- is a more reactive nucleophile than H_2O

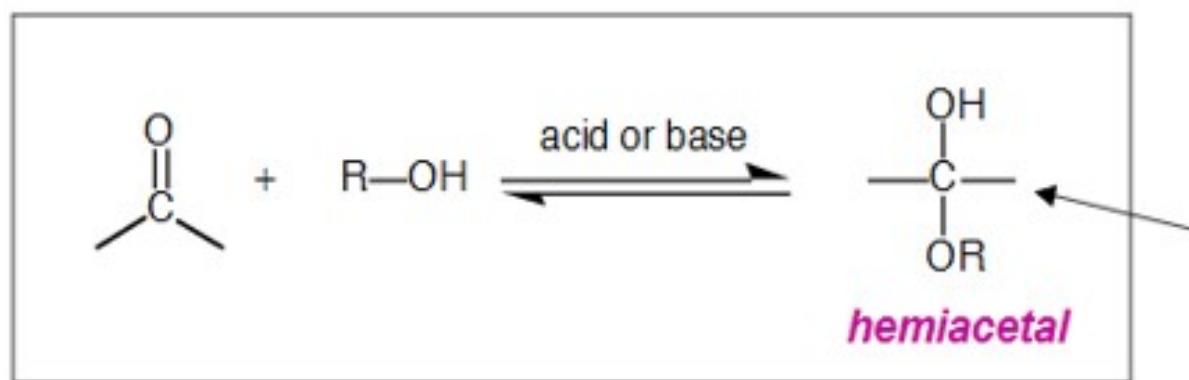


- Note that regioselectivity of addition is the same for acid or base catalyzed nucleophilic addition



Formation of Hemiacetals and Acets

- When an alcohol adds reversibly to an aldehyde or ketone, the product is called a hemiacetal.
- Hemiacetals are formed in both acid- and base-catalyzed reactions.



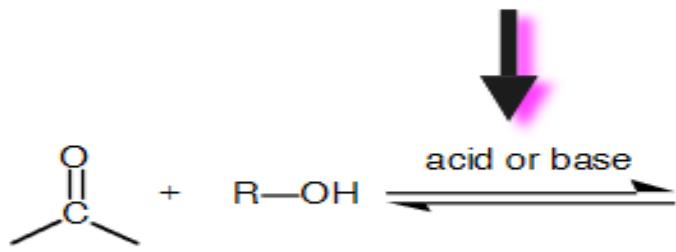
- Hemiacetals are unstable and can't be isolated in most cases.
- Hemiacetals undergo further reversible reactions under acidic conditions only.
 - This reaction involves carbocation chemistry.



Formation of Acetals

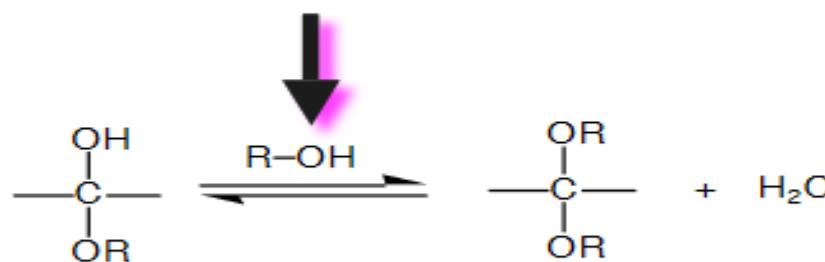
- Hemiacetals react further with alcohols under acidic conditions to form **acetals**.

catalyzed by acid or base



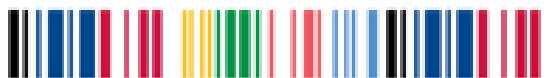
*aldehyde
or ketone*

catalyzed only by acid



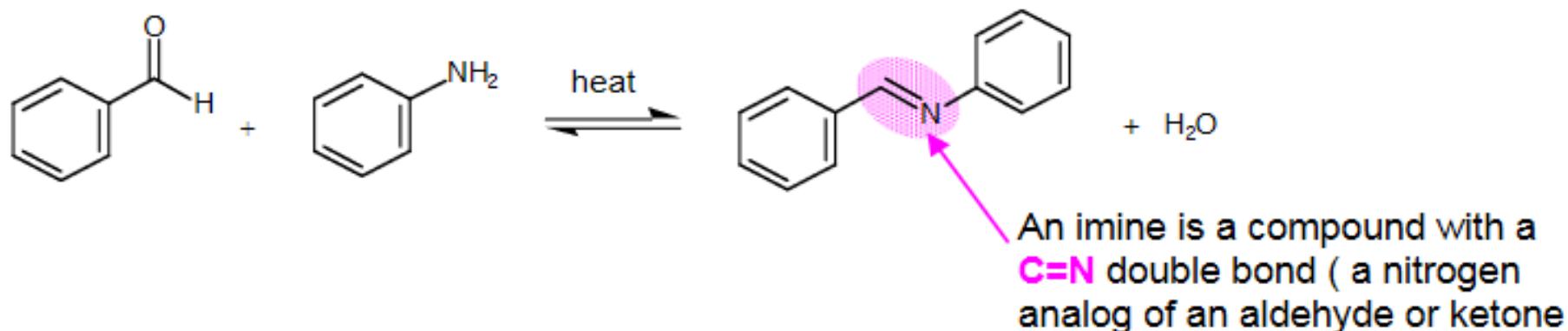
hemiacetal

acetal



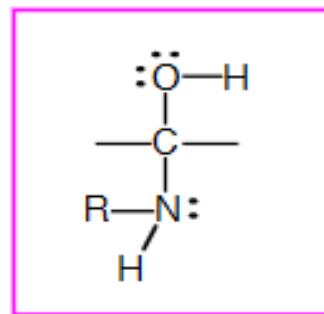
Reactions of Aldehydes and Ketones with Amines

- Aldehydes and ketones react with primary amines to form **imines**, or **Schiff bases**.

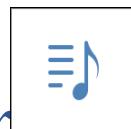


- The mechanism of imine formation involves the nucleophilic addition of the amine to the carbonyl carbon, forming a stable intermediate species called a **carbinolamine**.

Carbinolamines are compounds with an amine group and a hydroxy group attached to the same carbon.

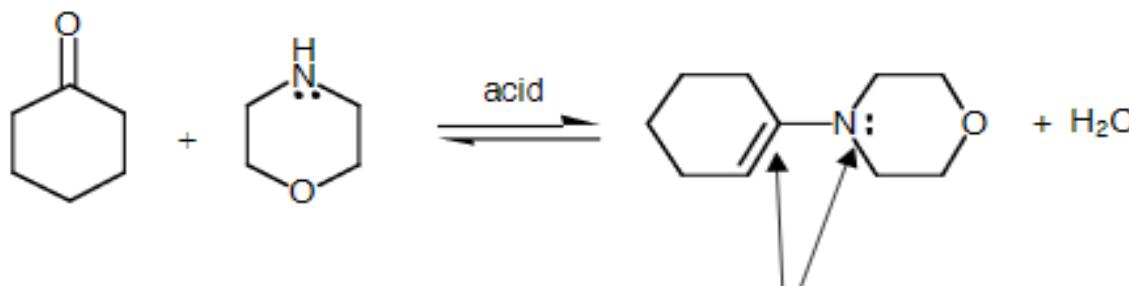


Carbinolamines are analogous to hemiacetals.



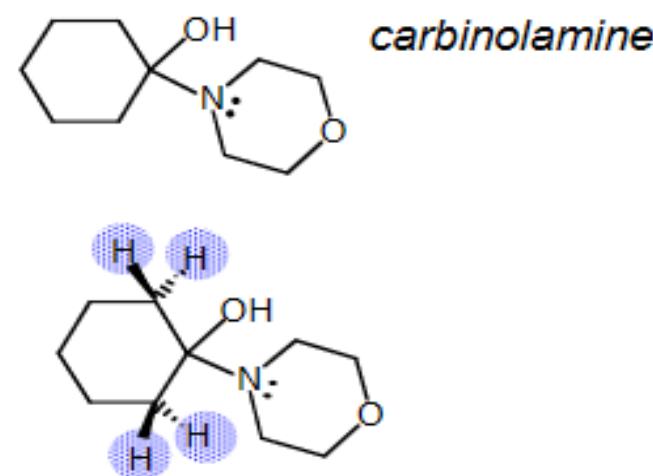
Reaction of Aldehydes/Ketones with 2°Amines

- Aldehydes and ketones react with secondary amines to form **enamines**.



Enamines have a nitrogen bound to a carbon which is part of a C=C double bond.

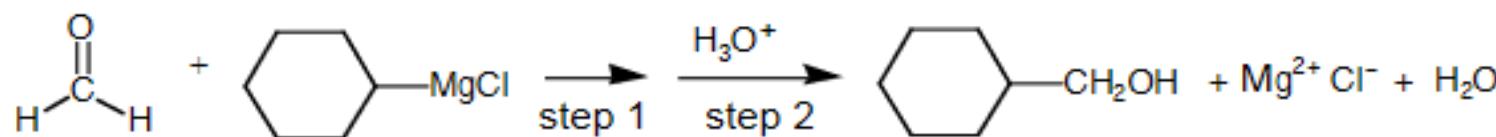
- The mechanism involves nucleophilic addition of the amine to the carbonyl to form a carbinolamine.
- Enamines form only if the carbonyl compound has at least one hydrogen on a carbon adjacent to the carbonyl carbon.
- Formation of the alkene may be recognized as an elimination reaction.



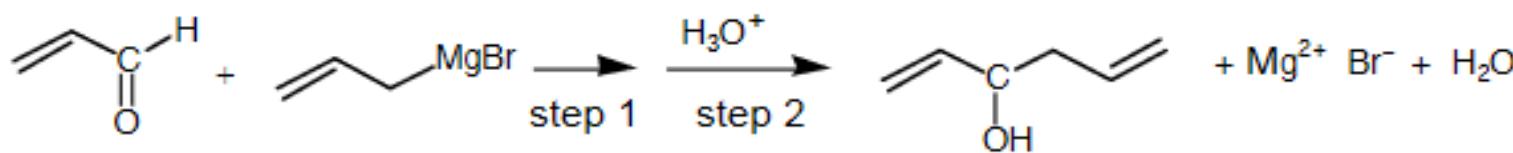
Addition Using Grignard Reagents

- Primary, secondary and tertiary alcohols may be formed in the reactions of aldehydes or ketones with Grignard reagents.

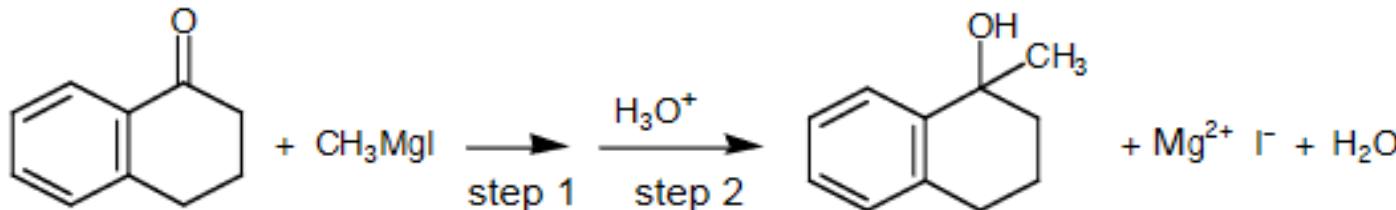
primary alcohols from formaldehyde



secondary alcohols from aldehydes

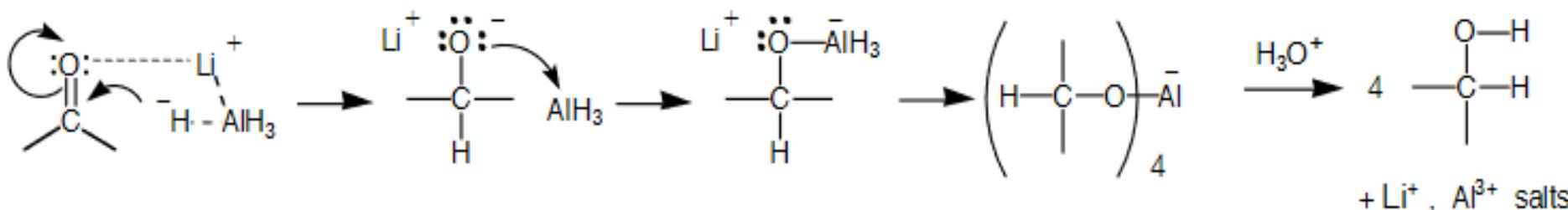


tertiary alcohols from ketones



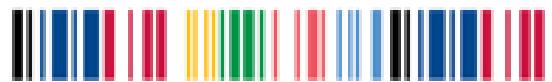
Metal Hydrides

- LiAlH₄ and NaBH₄ act in a fashion similar to Grignard reagents.
- The hydride ion H⁻ acts as the nucleophilic reagent adding to the carbonyl carbon atom of an aldehyde or a ketone.



- The hydride ion in LiAlH₄ is more basic than the hydride ion in NaBH₄, and therefore it is more reactive.
- Some functional groups which may be reduced by LiAlH₄ are unreactive with NaBH₄ (e.g., alkyl halides R-X, nitro groups -NO₂)
 - Therefore NaBH₄ may be used to reduce C=O bonds in the presence of such groups.





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Thanks for Listening...



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