

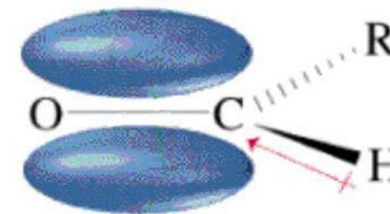
# **DAMIETTA UNIVERSITY**

## **CHEM-103: BASIC ORGANIC CHEMISTRY**

### **LECTURE 8**

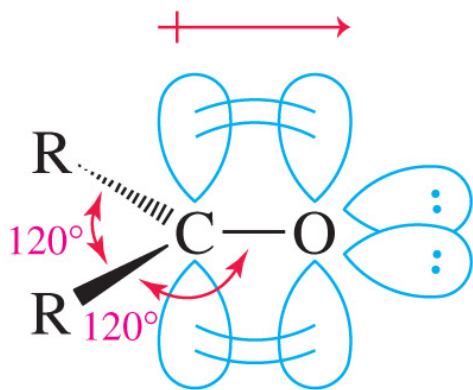
**Dr Ali El-Agamey**

*Organic Chemistry*, 7<sup>th</sup> Edition  
L. G. Wade, Jr.



# Ketones and Aldehydes

# Carbonyl Structure

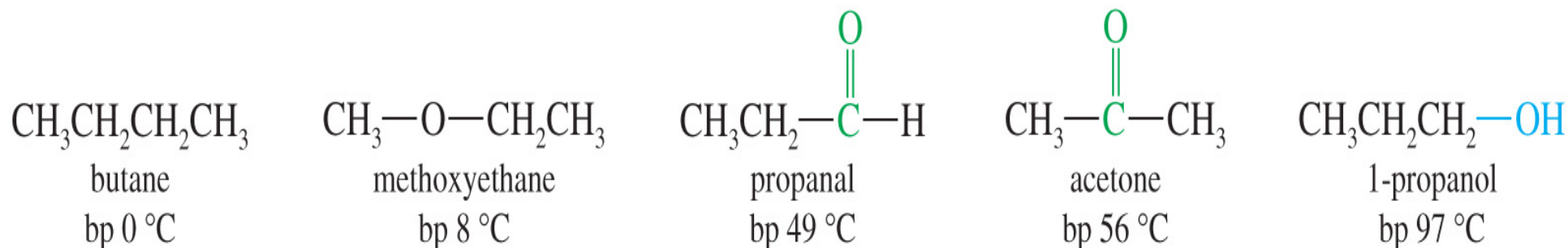


	<i>length</i>	<i>energy</i>
ketone $\text{C}=\text{O}$ bond	1.23 Å	745 kJ/mol (178 kcal/mol)
alkene $\text{C}=\text{C}$ bond	1.34 Å	611 kJ/mol (146 kcal/mol)

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- Carbon is  $sp^2$  hybridized.
- $\text{C}=\text{O}$  bond is shorter, **stronger**, and **more polar** than  $\text{C}=\text{C}$  bond in alkenes.

# Boiling Points<sup>1</sup>



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- Ketones and aldehydes are more polar, so they have a higher boiling point than **comparable** alkanes or ethers.
- They cannot hydrogen-bond to each other, so their boiling point is lower than comparable alcohol.

# Bond Dipole Moments for Some Common Covalent Bonds

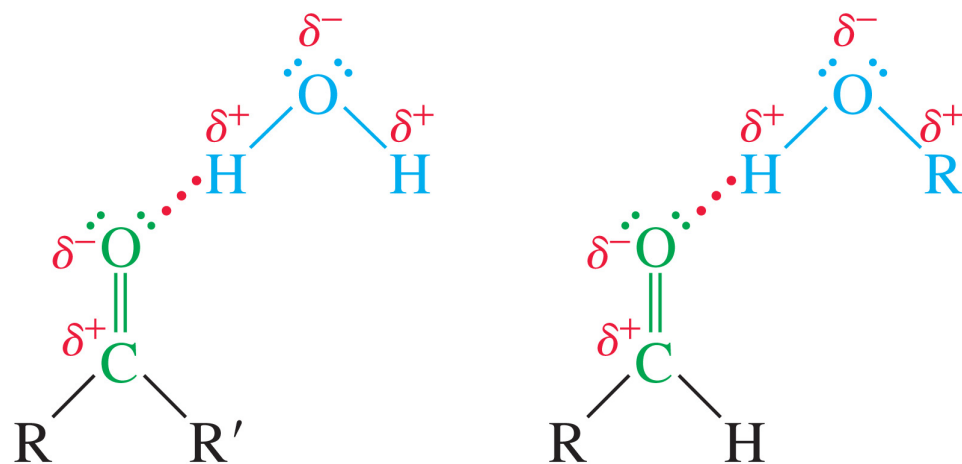
**TABLE 2-1**

Bond Dipole Moments (Debye) for Some Common Covalent Bonds

Bond	Dipole Moment, $\mu$	Bond	Dipole Moment, $\mu$
$\overset{+}{\text{C}}-\overset{\rightarrow}{\text{N}}$	0.22 D	$\overset{+}{\text{H}}-\overset{\rightarrow}{\text{C}}$	0.3 D
* $\overset{+}{\text{C}}-\overset{\rightarrow}{\text{O}}$	0.86 D	$\overset{+}{\text{H}}-\overset{\rightarrow}{\text{N}}$	1.31 D
$\overset{+}{\text{C}}-\overset{\rightarrow}{\text{F}}$	1.51 D	$\overset{+}{\text{H}}-\overset{\rightarrow}{\text{O}}$	1.53 D
$\overset{+}{\text{C}}-\overset{\rightarrow}{\text{Cl}}$	1.56 D	$\overset{+}{\text{C}}=\overset{\rightarrow}{\text{O}}$	2.4 D *
$\overset{+}{\text{C}}-\overset{\rightarrow}{\text{Br}}$	1.48 D	$\overset{+}{\text{C}}\equiv\overset{\rightarrow}{\text{N}}$	3.6 D
$\overset{+}{\text{C}}-\overset{\rightarrow}{\text{I}}$	1.29 D		

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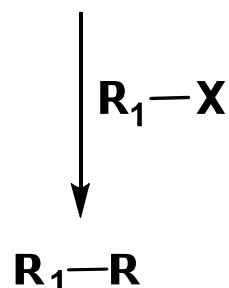
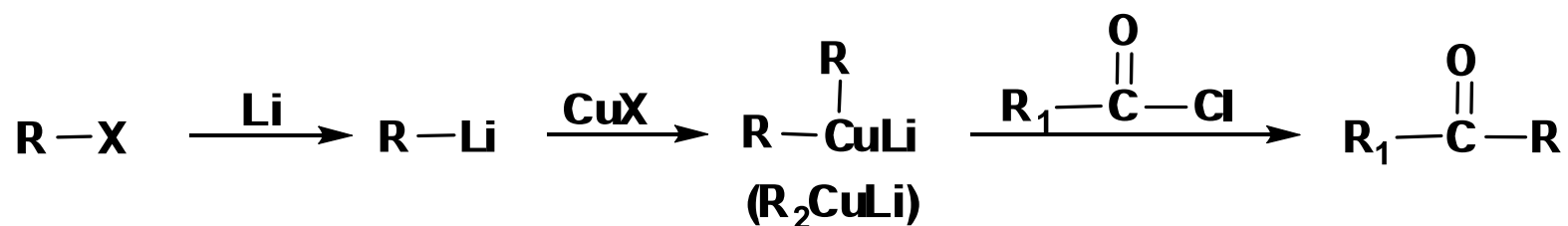
# Solubility of Ketones and Aldehydes



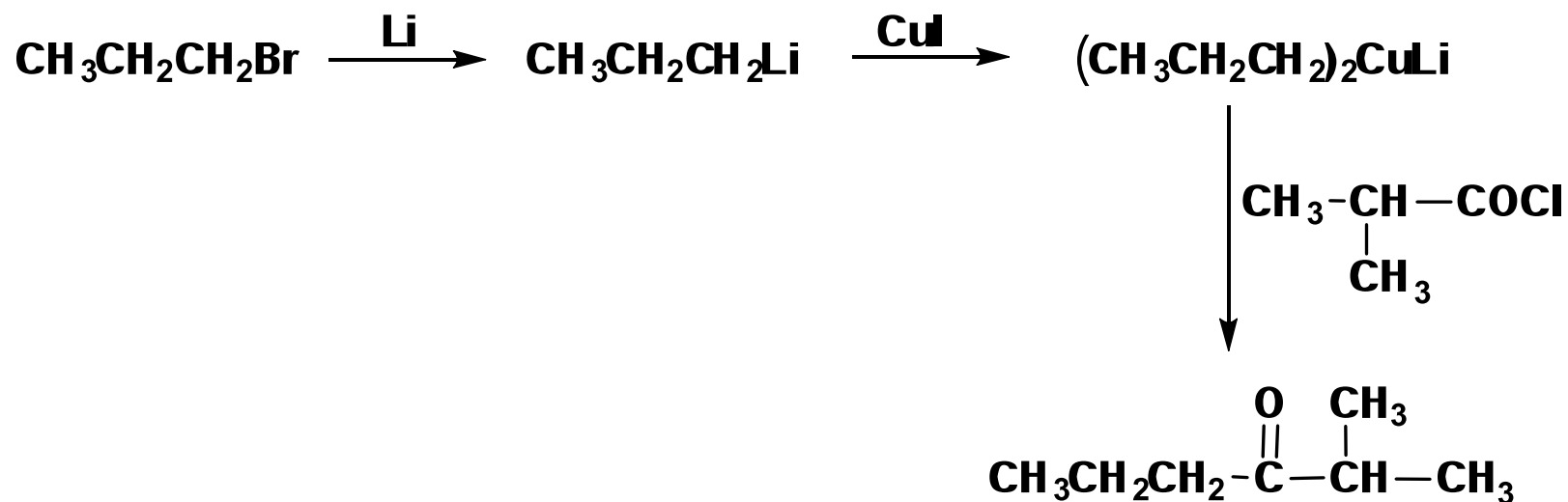
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- Good solvent for alcohols.
- Lone pair of electrons on oxygen of carbonyl can accept a hydrogen bond from O—H or N—H.
- Acetone and acetaldehyde are **miscible** in water.

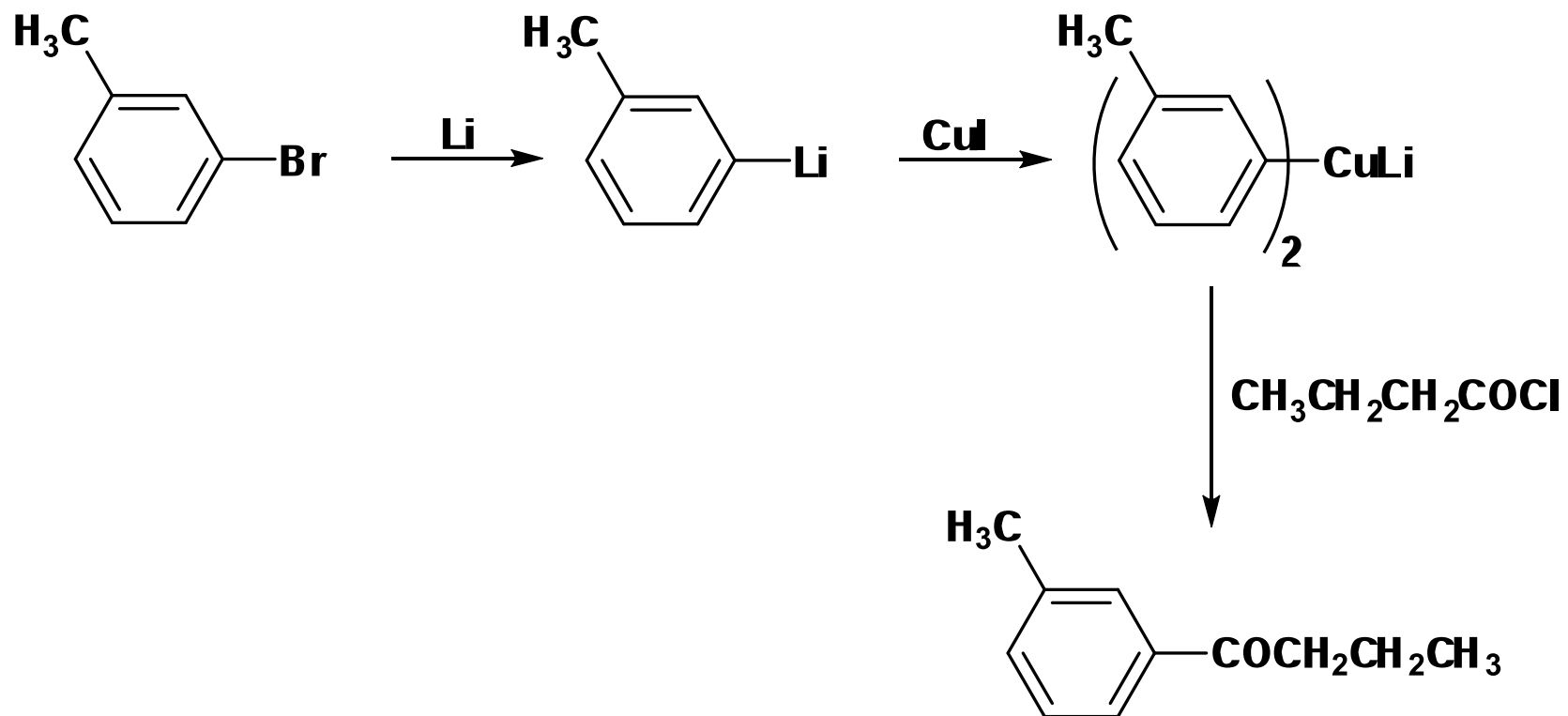
# Preparation of ketones



R and R<sub>1</sub> may be alkyl or aryl

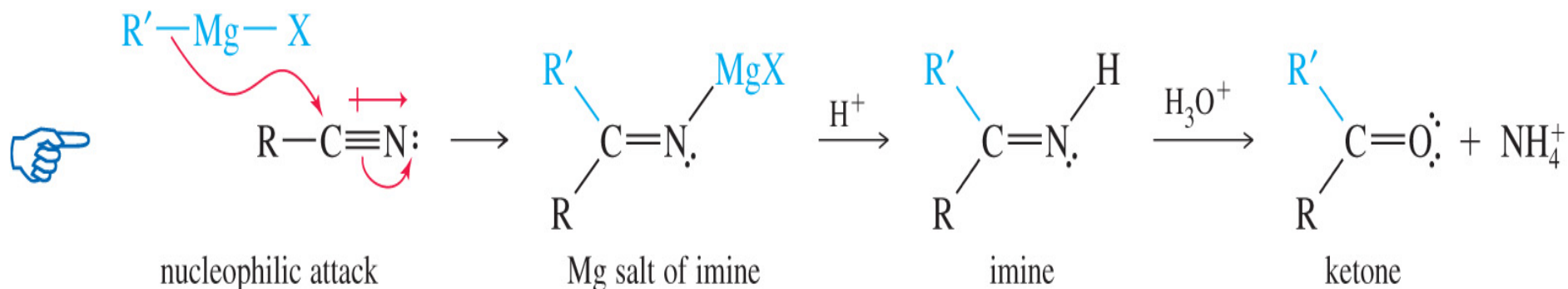


# Preparation of ketones





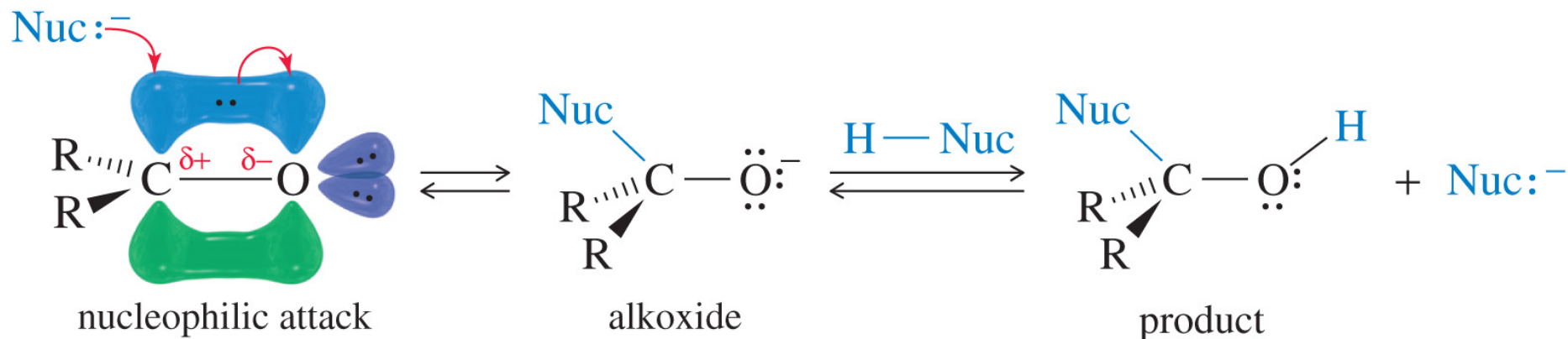
# Preparation of ketones



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- A Grignard or organolithium reagent can attack the carbon of the nitrile.
- The imine is then **hydrolyzed** to form a ketone.

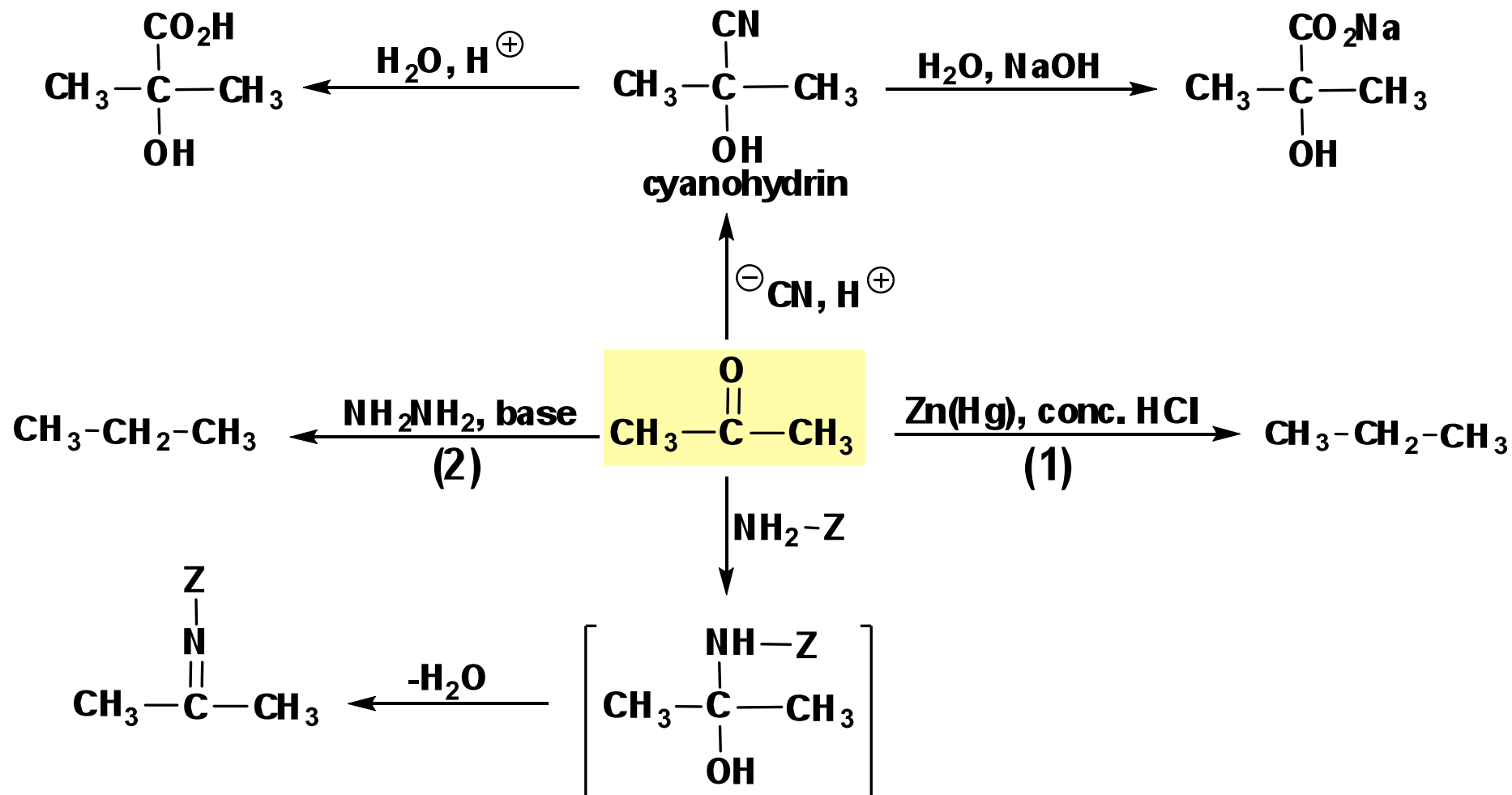
# Nucleophilic Addition



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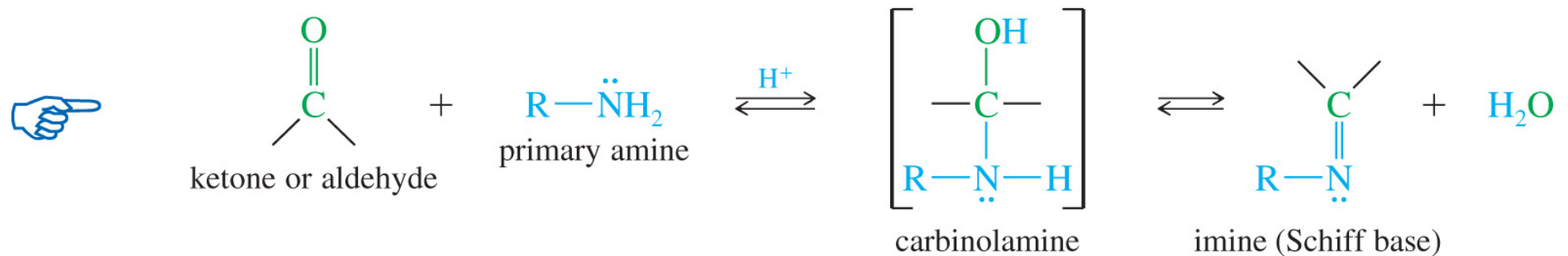
- A strong nucleophile attacks the carbonyl carbon, forming an alkoxide ion that is then protonated.
- **Aldehydes are more reactive than ketones.**

# Reactions of aldehydes and ketones



(1) Clemmensen reduction (2) Wolff-Kishner reduction

# Formation of Imines



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- **Ammonia or a primary amine** reacts with a ketone or an aldehyde to form an imine.
- Imines are nitrogen analogues of ketones and aldehydes with a C=N bond in place of the carbonyl group.
- Optimum pH is around 4.5

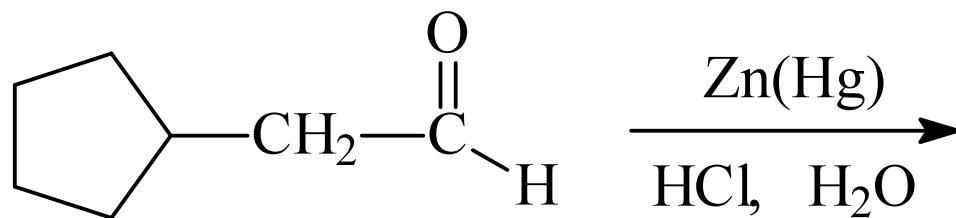
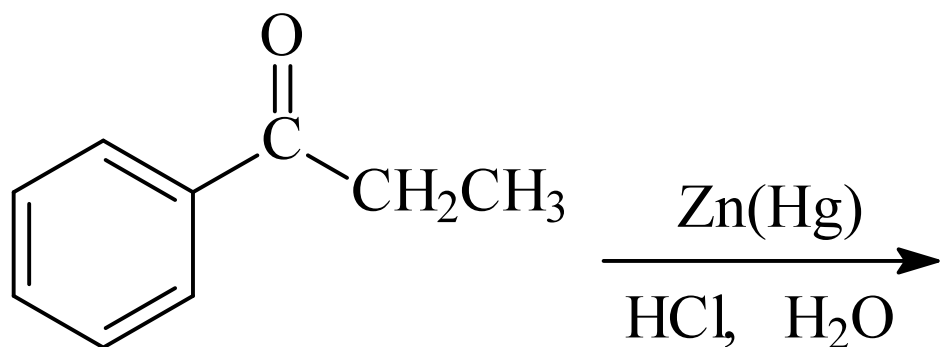
# Other Condensations with Amines



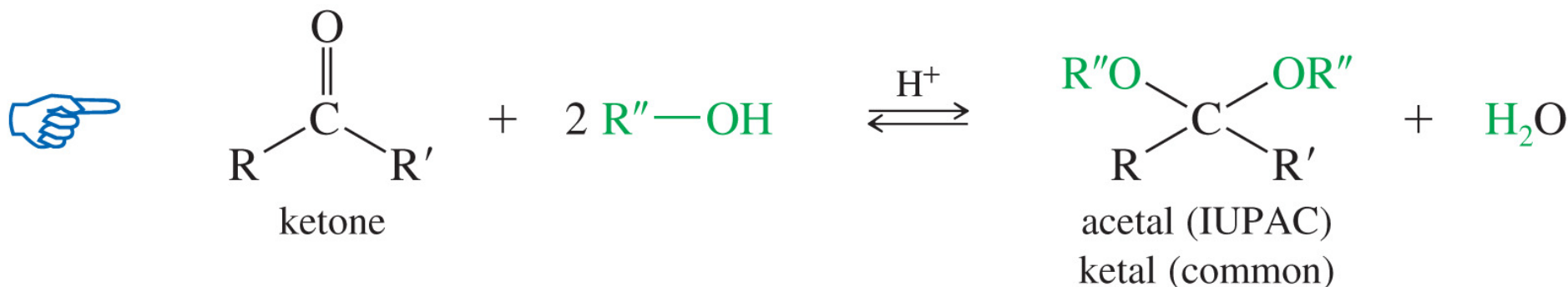
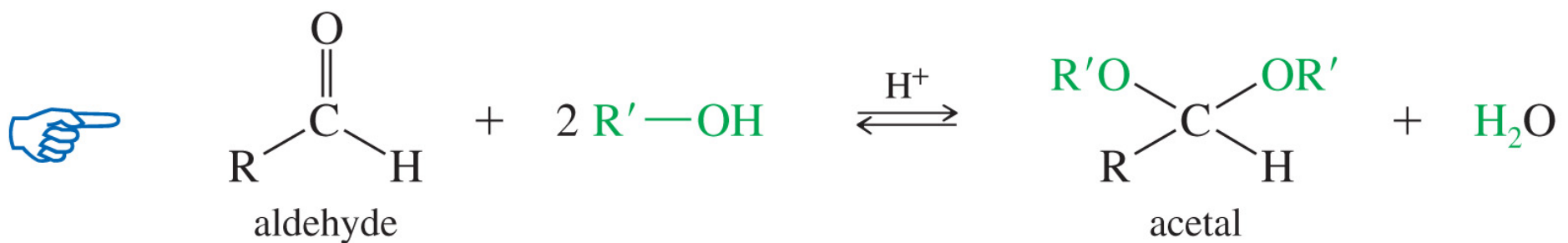
<i>Z in Z—NH<sub>2</sub></i>	<i>Reagent</i>	<i>Product</i>
—H	$\text{H}_2\ddot{\text{N}}-\boxed{\text{H}}$ ammonia	$\text{>C}=\ddot{\text{N}}-\boxed{\text{H}}$ an imine
—R	$\text{H}_2\ddot{\text{N}}-\boxed{\text{R}}$ primary amine	$\text{>C}=\ddot{\text{N}}-\boxed{\text{R}}$ an imine (Schiff base)
—OH	$\text{H}_2\ddot{\text{N}}-\boxed{\text{OH}}$ hydroxylamine	$\text{>C}=\ddot{\text{N}}-\boxed{\text{OH}}$ an oxime
—NH <sub>2</sub>	$\text{H}_2\ddot{\text{N}}-\boxed{\text{NH}_2}$ hydrazine	$\text{>C}=\ddot{\text{N}}-\boxed{\text{NH}_2}$ a hydrazone
—NHPh	$\text{H}_2\ddot{\text{N}}-\boxed{\text{NHPh}}$ phenylhydrazine	$\text{>C}=\ddot{\text{N}}-\boxed{\text{NHPh}}$ a phenylhydrazone
$\text{—NHCNH}_2$	$\text{H}_2\ddot{\text{N}}-\boxed{\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2}$ semicarbazide	$\text{>C}=\ddot{\text{N}}-\boxed{\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2}$ a semicarbazone

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# Homework: Complete the following equations



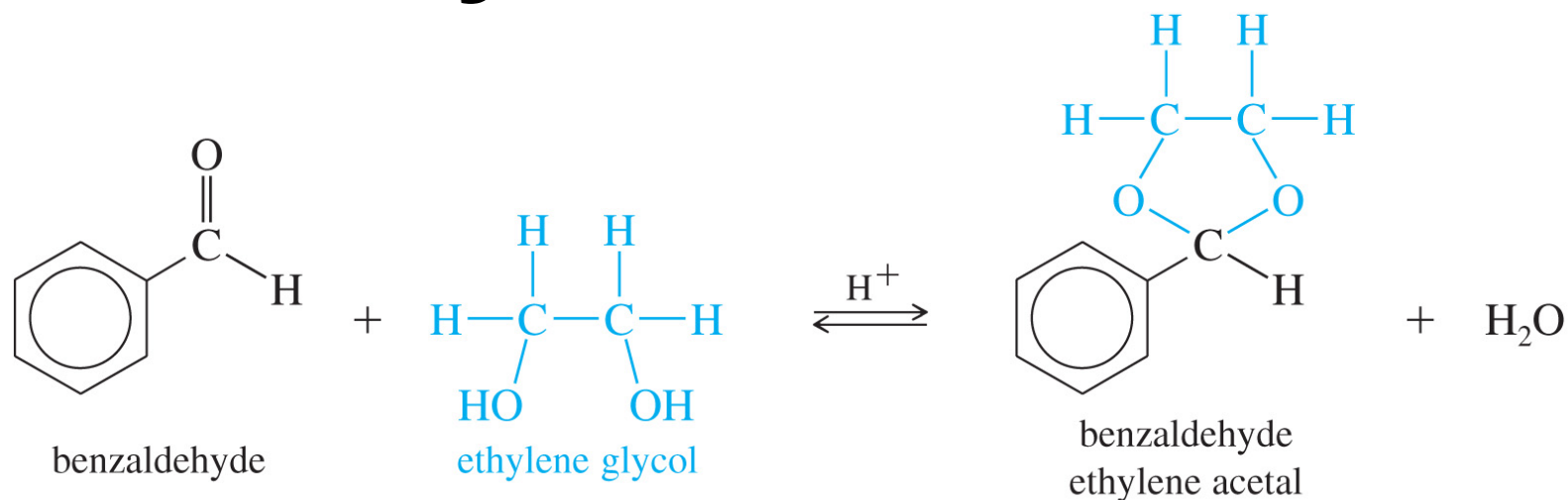
# Formation of Acetals



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- Acetals can easily be converted into carbonyl compounds and alcohol in the presence of **dilute acid** ( $\text{H}_3\text{O}^+$ ) (remember reaction is **reversible**) however, they are **stable** in the presence of **base**.

# Cyclic Acetals

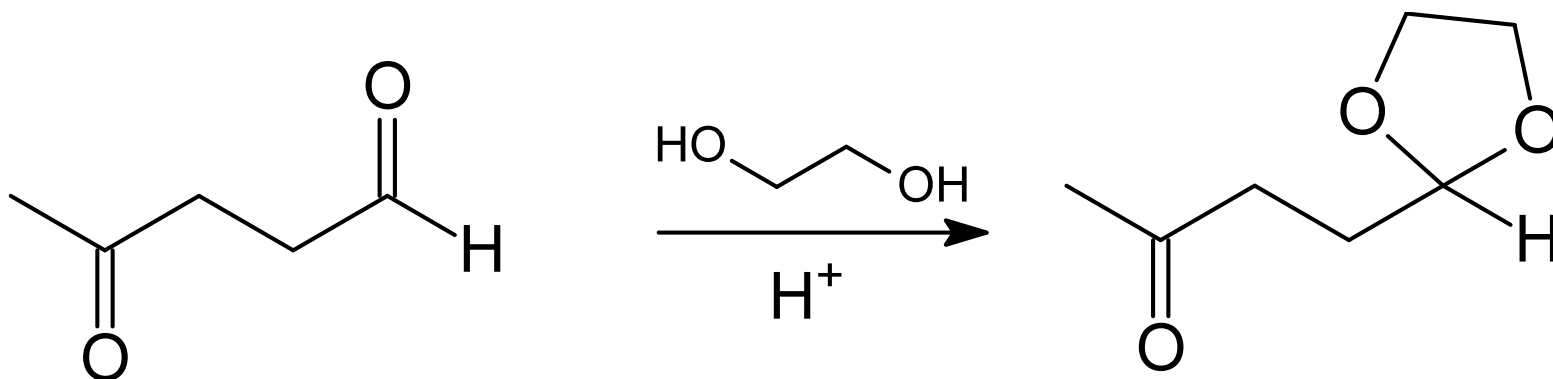


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- Addition of a diol produces a **cyclic acetal**.
- The reaction is **reversible**.
- This reaction is used in synthesis to **protect carbonyls** from reaction.

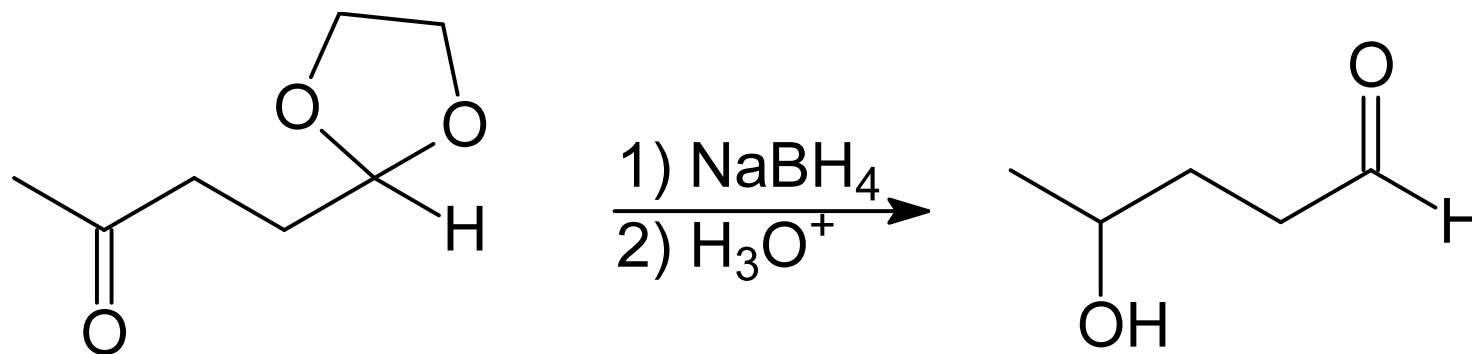


# Acetals as Protecting Groups



- **Aldehydes are more reactive than ketones.**

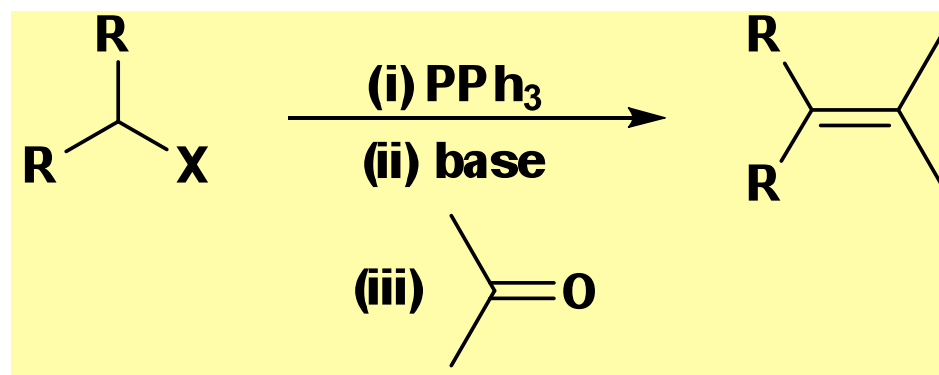
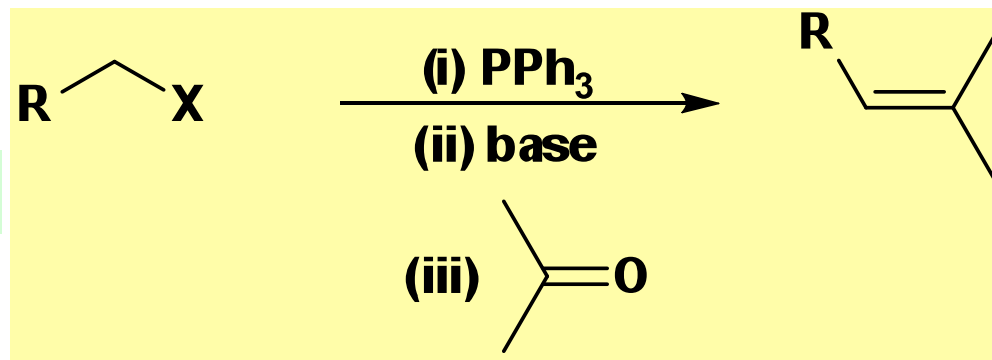
# Reaction and Deprotection



- The acetal will not react with NaBH<sub>4</sub>, so only the ketone will get reduced.
- Hydrolysis conditions will remove the acetal to restore the aldehyde.

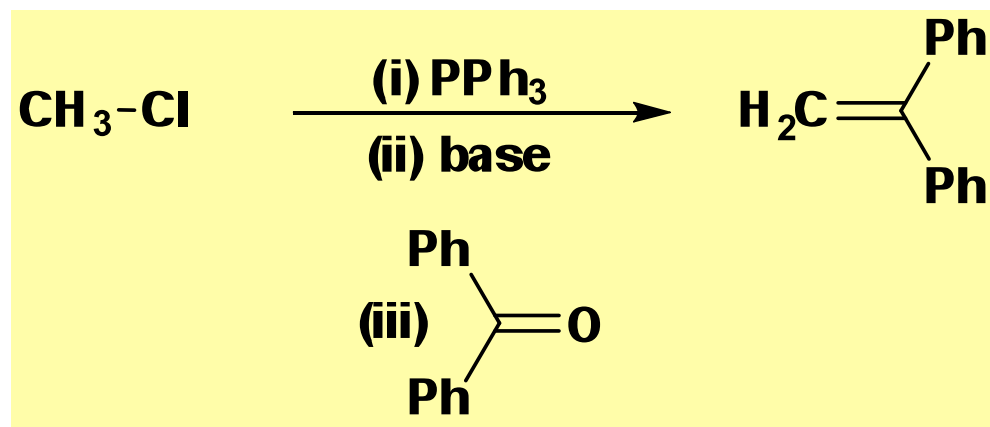
# The Wittig Reaction

$\text{PPh}_3$ : triphenylphosphine



- The Wittig reaction converts the carbonyl group into a new  $\text{C}=\text{C}$  double bond.

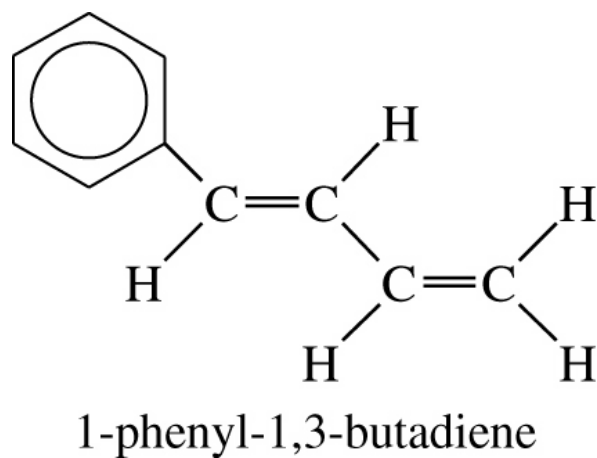
# The Wittig Reaction



- In 1979, the **Nobel Prize** was awarded to Georg Wittig and to H.C. Brown in recognition of their remarkable contributions to synthetic organic chemistry.<sup>1</sup>

# Solved Problem

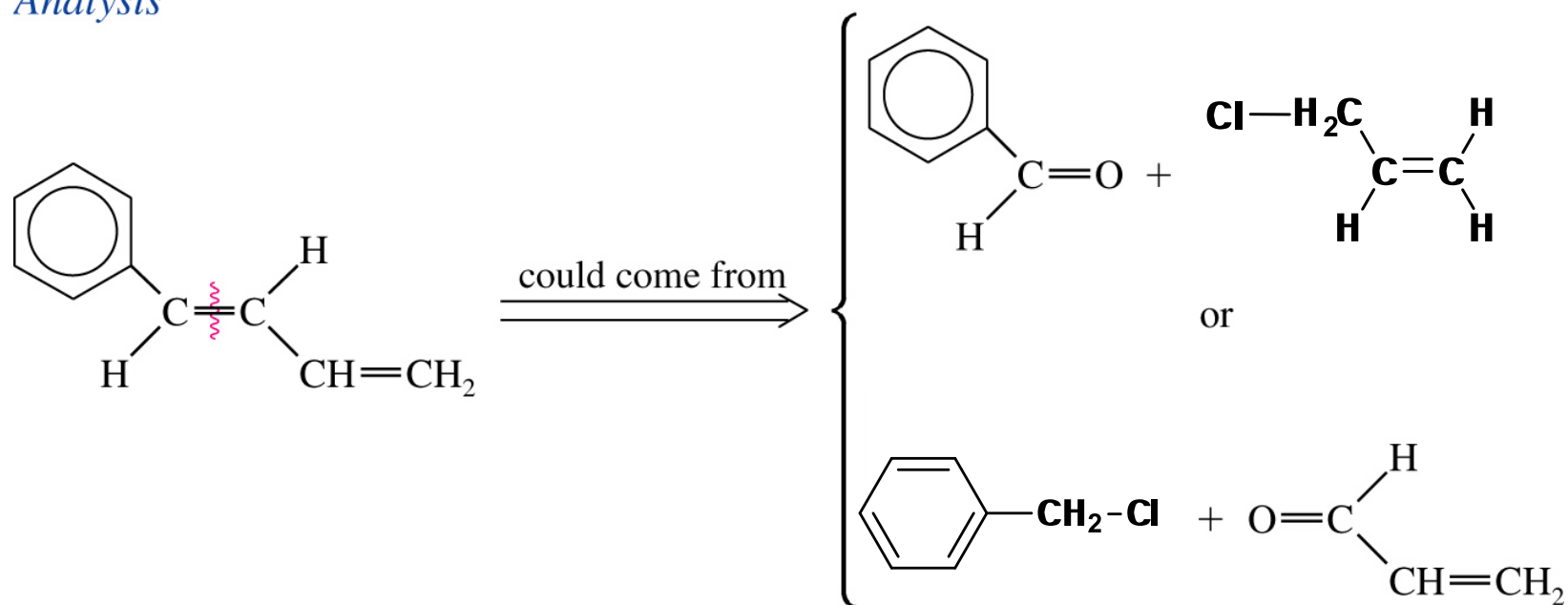
Show how you would use a Wittig reaction to synthesize 1-phenyl-1,3-butadiene.



## Solution

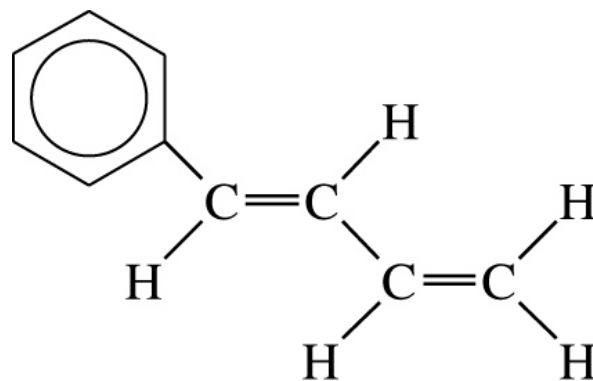
This molecule has two double bonds that might be formed by Wittig reactions. **The central double bond** could be formed in either of two ways. Both of these syntheses will probably work, and both will produce a **mixture of cis and trans** isomers.

### Analysis



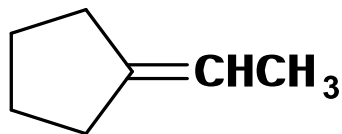
# Homework

**Show** how you would synthesize 1-phenyl-1,3-butadiene by forming the **terminal double bond** using Wittig reaction.



1-phenyl-1,3-butadiene

**Show** how you would synthesize the following compound using Wittig reaction.<sup>1</sup>



# Homework

**Show how** you would synthesize the following compound from starting materials containing **no more than six carbon atoms**.

