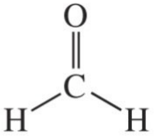
Chapter 16
Aldehydes and Ketones I
Nucleophilic Addition to the Carbonyl Group

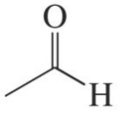
♦ Nomenclature of Aldehydes and Ketones

➔ **Aldehydes are named by replacing the -e of the corresponding parent alkane with -al**

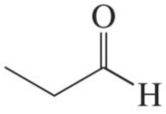
- **The aldehyde functional group is always carbon 1 and need not be numbered**
- **Some of the common names of aldehydes are shown in parenthesis**



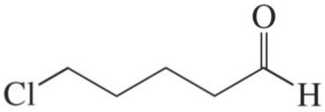
Methanal
(formaldehyde)



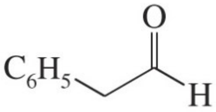
Ethanal
(acetaldehyde)



Propanal
(propionaldehyde)



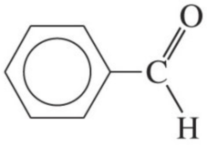
5-Chloropentanal



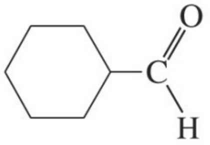
Phenylethanal
(phenylacetaldehyde)

➔ **Aldehyde functional groups bonded to a ring are named using the suffix carbaldehyde**

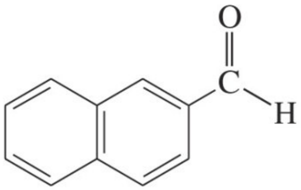
- **Benzaldehyde is used more commonly than the name benzenecarbaldehyde**



Benzenecarbaldehyde
(benzaldehyde)



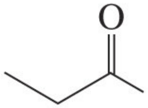
Cyclohexanecarbaldehyde



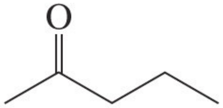
2-Naphthalenecarbaldehyde

➔ **Ketones are named by replacing the -e of the corresponding parent alkane with -one**

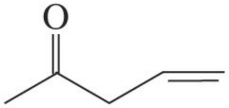
- **The parent chain is numbered to give the ketone carbonyl the lowest possible number**
- **In common nomenclature simple ketones are named by preceding the word ketone with the names of both groups attached to the ketone carbonyl**



Butanone
(ethyl methyl ketone)

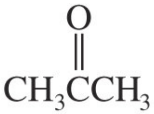


2-Pentanone
(methyl propyl ketone)



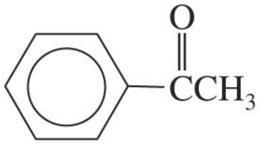
Pent-4-en-2-one
(*not* 1-penten-4-one)
(allyl methyl ketone)

➔ **Common names of ketones that are also IUPAC names are shown below**

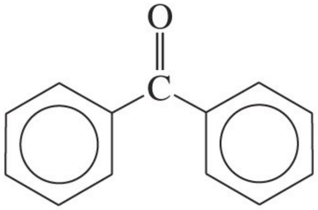


$$CH_3\overset{\overset{O}{\|}}{C}CH_3$$

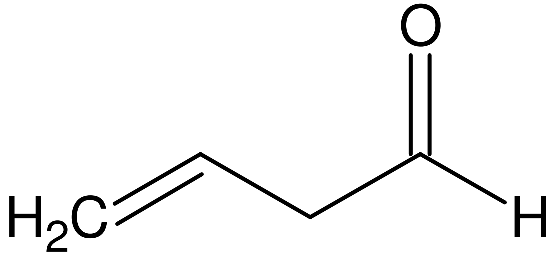
Acetone
(propanone)



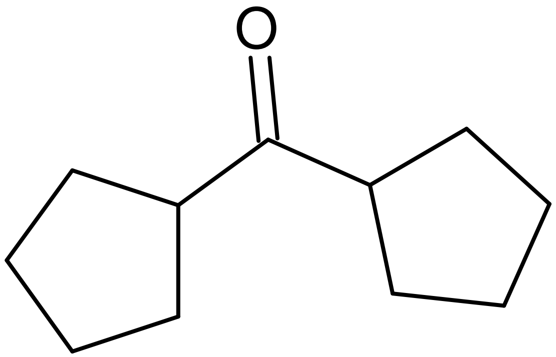
Acetophenone
(1-phenylethanone or methyl phenyl ketone)



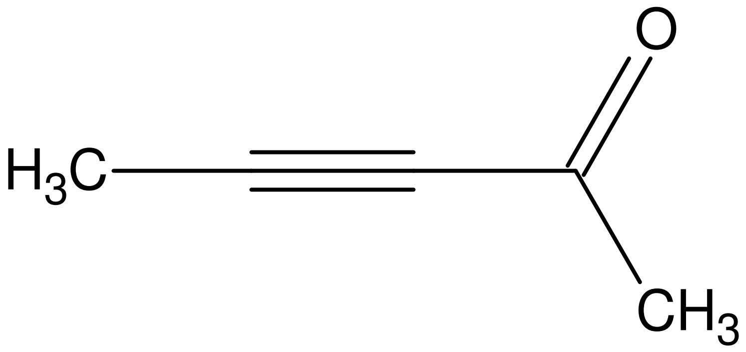
Benzophenone
(diphenylmethanone or diphenyl ketone)



3-butenal



dicyclopentylmethanone
or dicyclopentyl ketone



pent-3-yn-2-one
or 3-pentyn-2-one

♦ Physical Properties

- ➔ **Molecules of aldehyde (or ketone) cannot hydrogen bond to each other**
  - **They rely only on intermolecular dipole-dipole interactions and therefore have lower boiling points than the corresponding alcohols**

Butane
bp −0.5°C
(MW = 58)

Propanal
bp 49°C
(MW = 58)

Acetone
bp 56.1°C
(MW = 58)

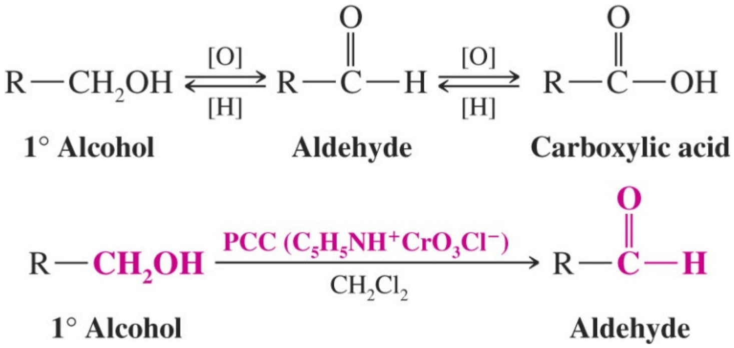
1-Propanol
bp 97.2°C
(MW = 60)

- ➔ **Aldehydes and ketones can form hydrogen bonds with water and therefore low molecular weight aldehydes and ketones have appreciable water solubility**

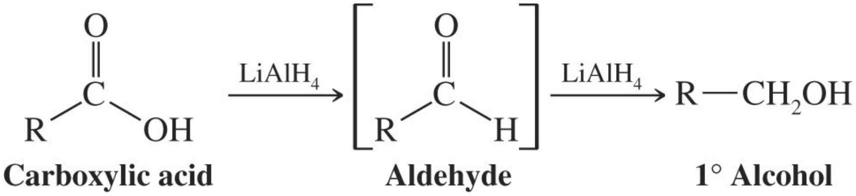
Formula	Name	mp (°C)	bp (°C)	Solubility in Water
HCHO	Formaldehyde	−92	−21	Very soluble
CH_3CHO	Acetaldehyde	−125	21	∞
CH_3CH_2CHO	Propanal	−81	49	Very soluble
$CH_3(CH_2)_2CHO$	Butanal	−99	76	Soluble
$CH_3(CH_2)_3CHO$	Pentanal	−91.5	102	Slightly soluble
$CH_3(CH_2)_4CHO$	Hexanal	−51	131	Slightly soluble
C_6H_5CHO	Benzaldehyde	−26	178	Slightly soluble
$C_6H_5CH_2CHO$	Phenylacetaldehyde	33	193	Slightly soluble
CH_3COCH_3	Acetone	−95	56.1	∞
$CH_3COCH_2CH_3$	Butanone	−86	79.6	Very soluble
$CH_3COCH_2CH_2CH_3$	2-Pentanone	−78	102	Soluble
$CH_3CH_2COCH_2CH_3$	3-Pentanone	−39	102	Soluble
$C_6H_5COCH_3$	Acetophenone	21	202	Insoluble
$C_6H_5COC_6H_5$	Benzophenone	48	306	Insoluble

♦ Synthesis of Aldehydes

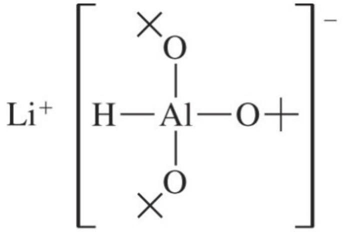
- **Aldehydes by Oxidation of 1º Alcohols**
  - ➔ **Primary alcohols are oxidized to aldehydes by PCC**



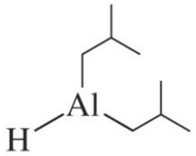
- **Aldehydes by Reduction of Acyl Chlorides, Esters and Nitriles**
  - ➔ **Reduction of carboxylic acid to aldehyde is impossible to stop at the aldehyde stage**
    - **Aldehydes are much more easily reduced than carboxylic acids**



- ➔ **Reduction to an aldehyde can be accomplished by using a more reactive carboxylic acid derivatives such as an acyl chloride, ester or nitrile and a less reactive hydride source**
  - **The use of a sterically hindered and therefore less reactive aluminum hydride reagent is important**

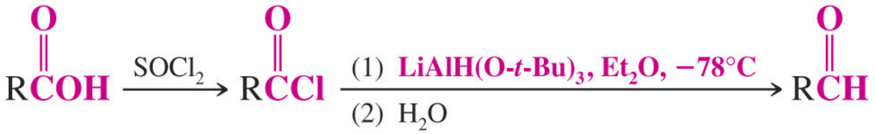


Lithium tri-*tert*-butoxy-aluminum hydride

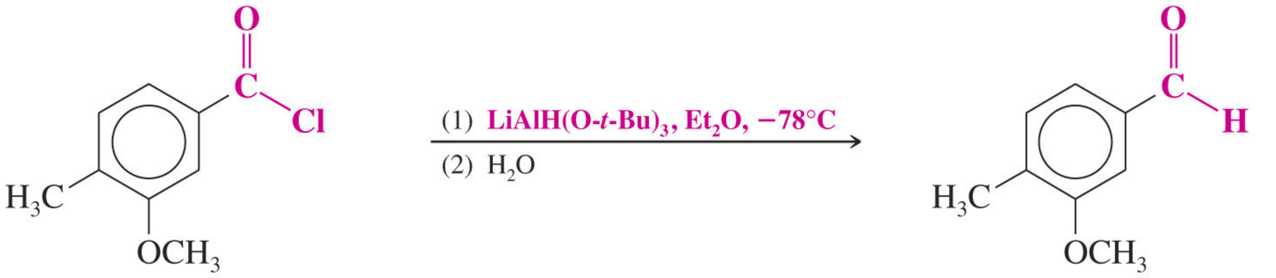


Diisobutylaluminum hydride (abbreviated *i*-Bu_2AlH or DIBAL-H)

- ➔ **Acid chlorides react with lithium tri-*tert*-butoxyaluminum hydride at low temperature to give aldehydes**



$$R\overset{O}{\overset{\|}{C}}OH \xrightarrow{SOCl_2} R\overset{O}{\overset{\|}{C}}Cl \xrightarrow[\text{(2) } H_2O]{\text{(1) } LiAlH(O\text{-}t\text{-}Bu)_3,\ Et_2O,\ -78°C} R\overset{O}{\overset{\|}{C}}H$$

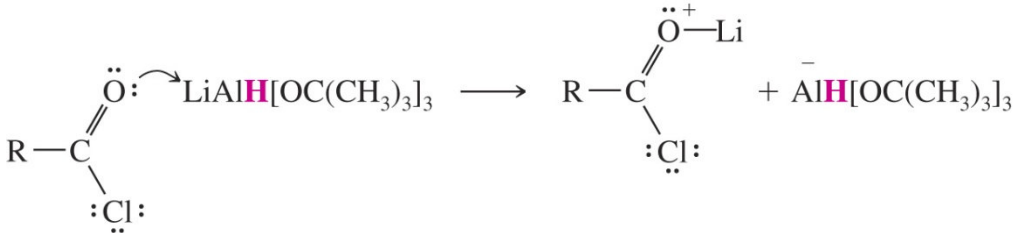


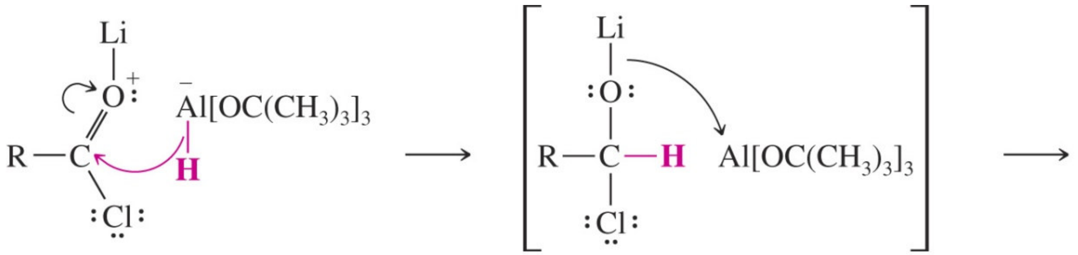
3-Methoxy-4-methylbenzoyl chloride

3-Methoxy-4-methylbenzaldehyde

➔Hydride is transferred to the carbonyl carbon

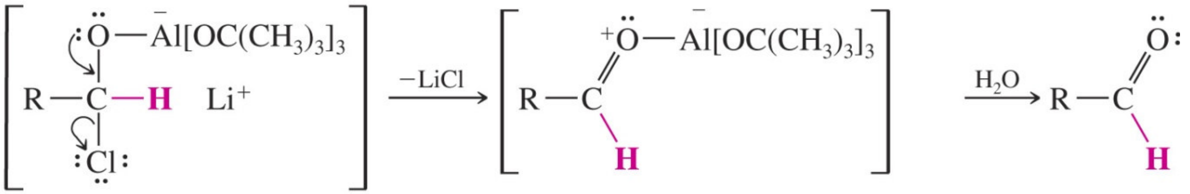
- **As the carbonyl re-forms, the chloride (which is a good leaving group) leaves**





Transfer of a hydride ion to the carbonyl carbon brings about the reduction.

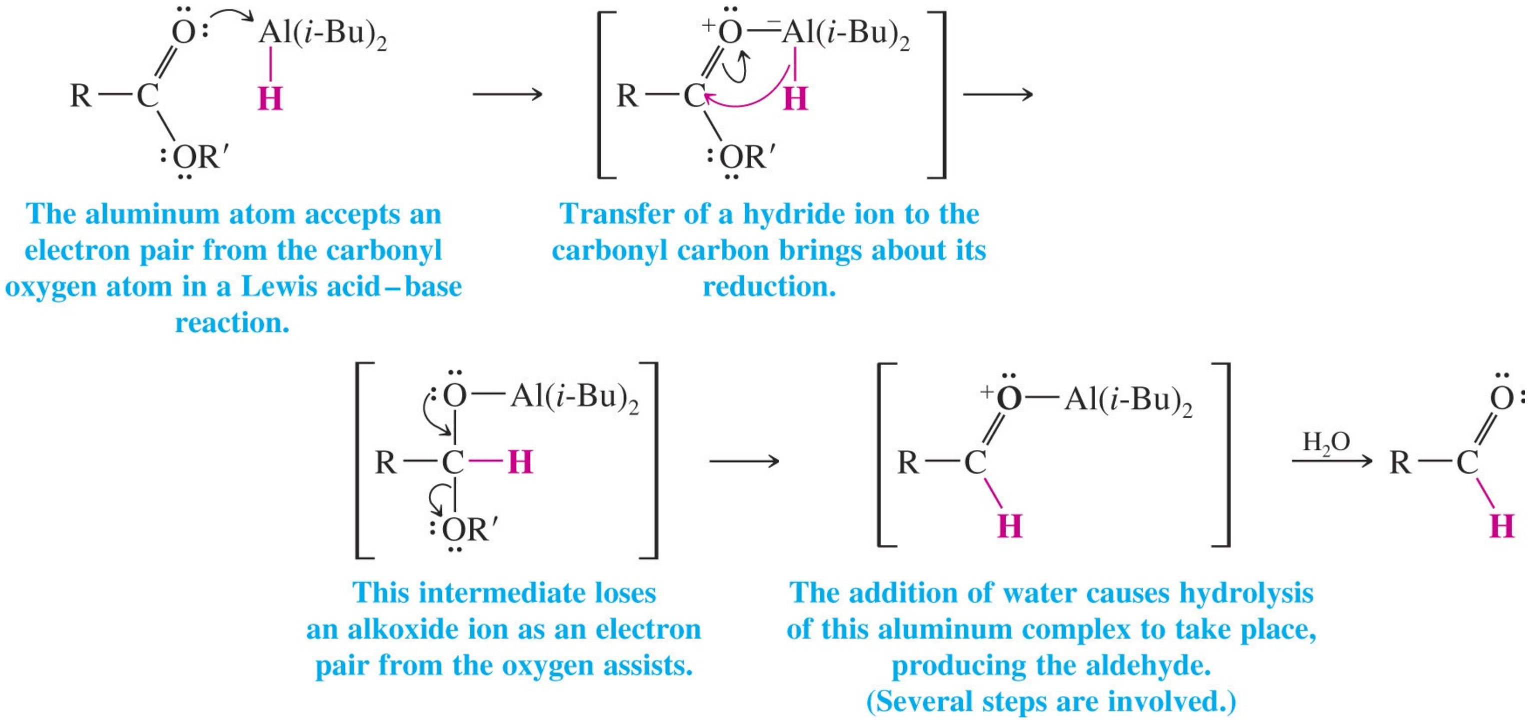
Acting as a Lewis acid, the aluminum atom accepts an electron pair from oxygen.



This intermediate loses a chloride ion as an electron pair from the oxygen assists.

The addition of water causes hydrolysis of this aluminum complex to take place, producing the aldehyde. (Several steps are involved.)

- ➔ **Reduction of an ester to an aldehyde can be accomplished at low temperature using DIBAL-H**
  - **As the carbonyl re-forms, an alkoxide leaving group departs**



The aluminum atom accepts an electron pair from the carbonyl oxygen atom in a Lewis acid–base reaction.

Transfer of a hydride ion to the carbonyl carbon brings about its reduction.

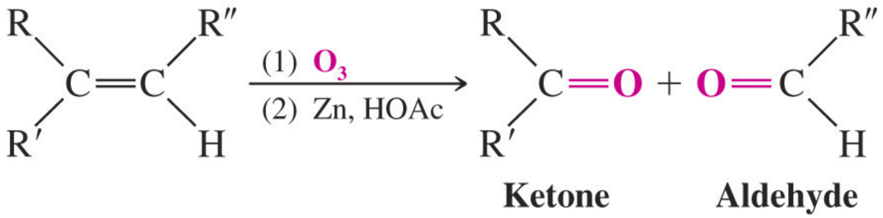
This intermediate loses an alkoxide ion as an electron pair from the oxygen assists.

The addition of water causes hydrolysis of this aluminum complex to take place, producing the aldehyde. (Several steps are involved.)

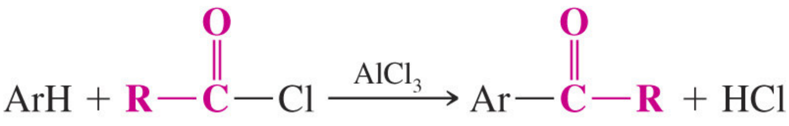
♦ Synthesis of Ketones

● Ketones from Alkenes, Arenes, and 2º Alcohols

➔Ketones can be made from alkenes by ozonolysis



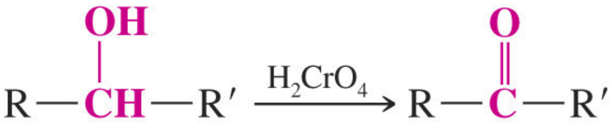
➔Aromatic ketones can be made by Friedel-Crafts Acylation



$$\mathrm{ArH} + \mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl} \xrightarrow{\mathrm{AlCl_3}} \mathrm{Ar{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R} + \mathrm{HCl}$$

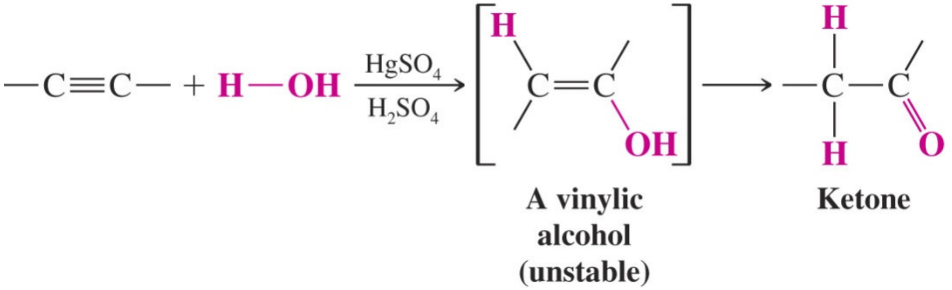
An alkyl aryl ketone

➔Ketones can be made from 2º alcohols by oxidation

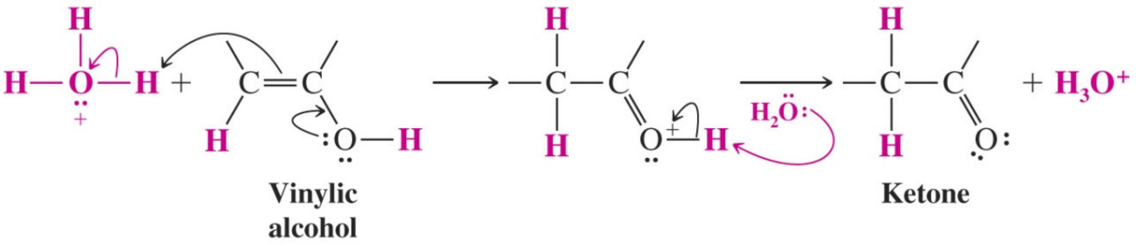


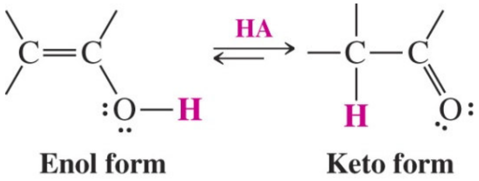
$$\mathrm{R{-}\overset{\overset{\displaystyle OH}{|}}{CH}{-}R'} \xrightarrow{\mathrm{H_2CrO_4}} \mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R'}$$

- **Ketones from Alkynes**
  - ➔ **Markovnikov hydration of an alkyne initially yields a vinyl alcohol (enol) which then rearranges rapidly to a ketone (keto)**



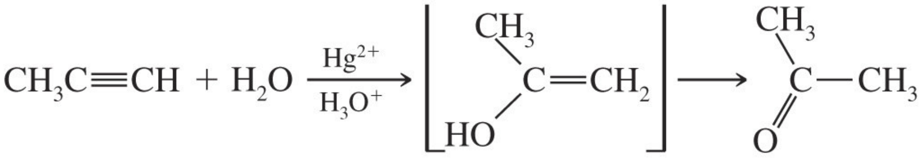
  - ➔ **The rearrangement is called a keto-enol tautomerization (Section 17.2)**
    - **This rearrangement is an equilibrium which usually favors the keto form**



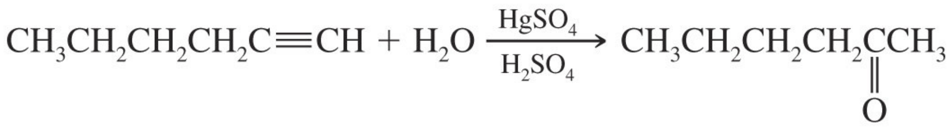


➔ **Terminal alkynes yield ketones because of the Markovnikov regioselectivity of the hydration**

- **Ethyne yields acetaldehyde**
- **Internal alkynes give mixtures of ketones unless they are symmetrical**

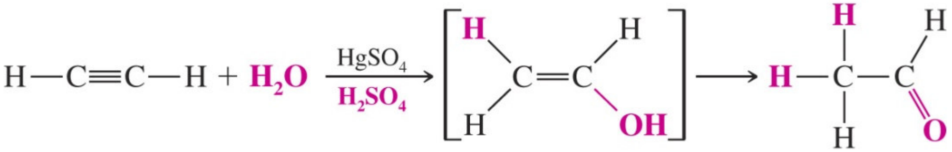


Acetone



$$CH_3CH_2CH_2CH_2C\equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} CH_3CH_2CH_2CH_2\underset{\underset{O}{\|}}{C}CH_3$$

(80%)



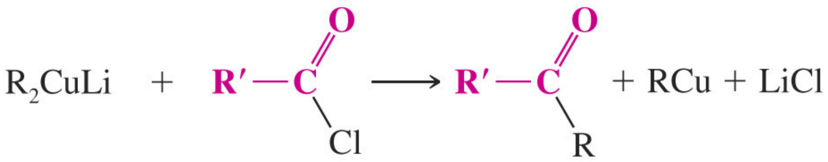
Ethyne

Ethanal (acetaldehyde)

Ketones from Lithium Dialkylcuprates

➔ **An acyl chloride can be coupled with a dialkylcuprate to yield a ketone (a variation of the Corey-Posner, Whitesides-House reaction)**

General Reaction



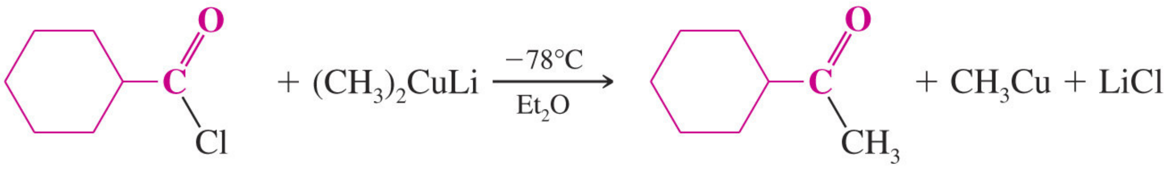
$$R_2CuLi + R'COCl \longrightarrow R'COR + RCu + LiCl$$

Lithium dialkylcuprate

Acyl chloride

Ketone

Specific Example

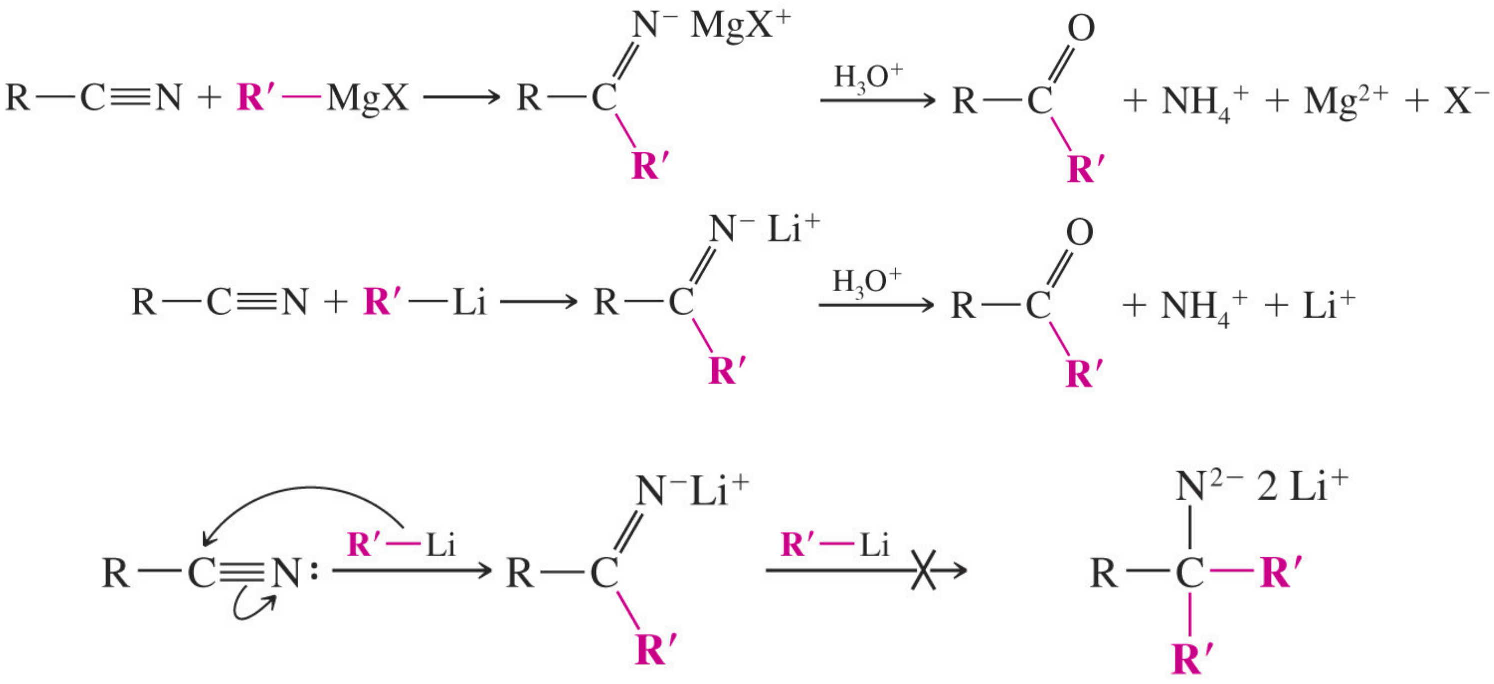


Cyclohexanecarbonyl chloride

(81%)
1-Cyclohexylethanone
(Cyclohexyl methyl ketone)

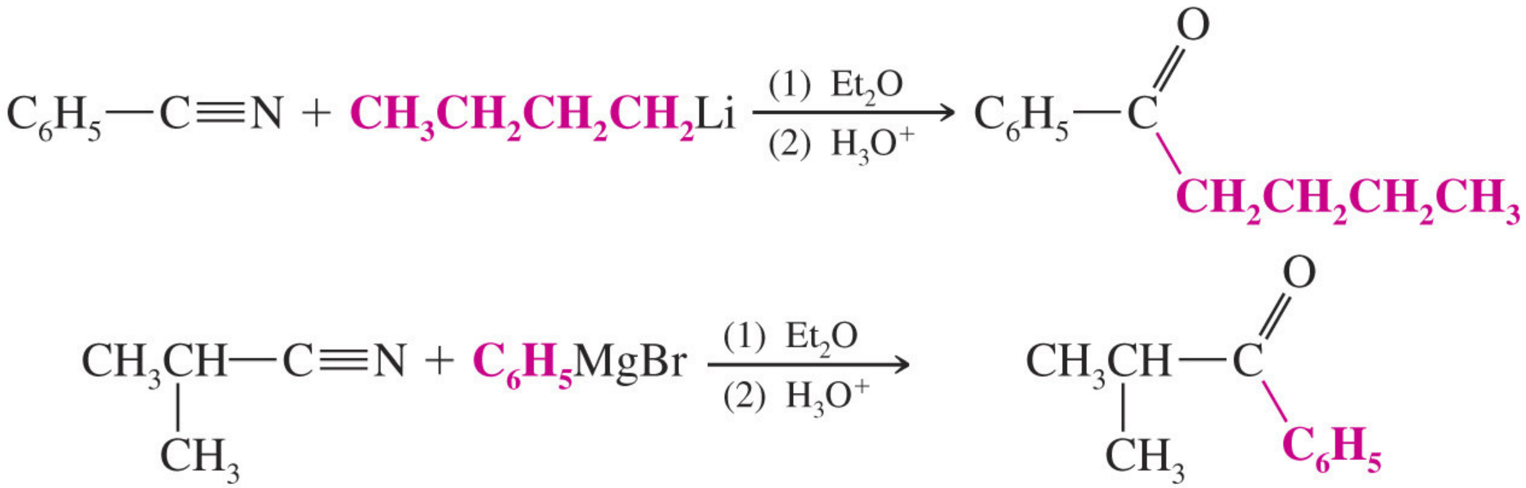
- **Ketones from Nitriles**
  - ➔**Organolithium and Grignard reagents add to nitriles to form ketones**
    - **Addition does not occur twice because two negative charges on the nitrogen would result**

General Reactions



(The dianion does not form.)

Specific Examples



$$C_6H_5-C\equiv N + CH_3CH_2CH_2CH_2Li \xrightarrow[(2)\ H_3O^+]{(1)\ Et_2O} C_6H_5-\overset{\overset{O}{\|}}{C}-CH_2CH_2CH_2CH_3$$

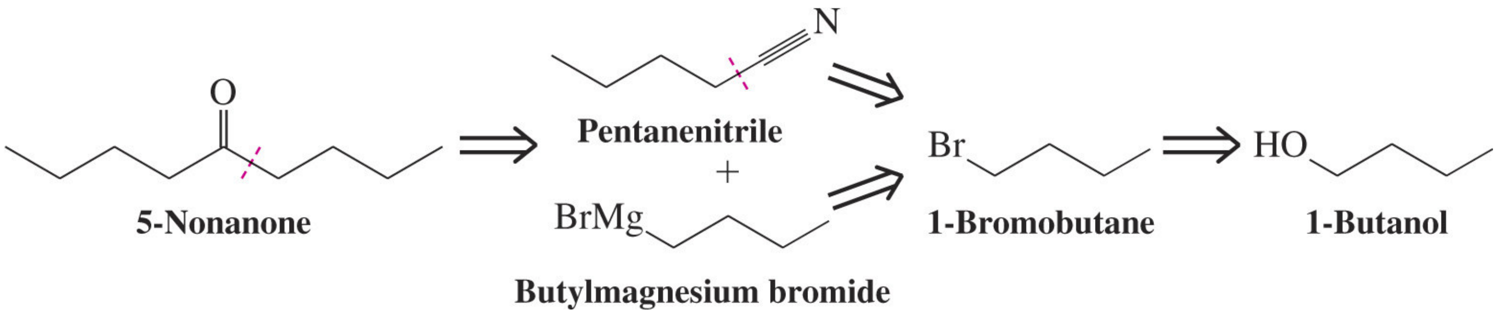
$$CH_3\underset{\underset{CH_3}{|}}{CH}-C\equiv N + C_6H_5MgBr \xrightarrow[(2)\ H_3O^+]{(1)\ Et_2O} CH_3\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-C_6H_5$$

2-Cyanopropane

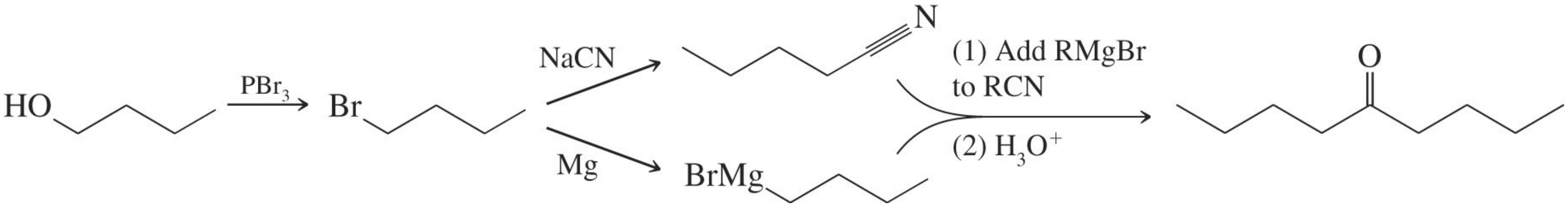
2-Methyl-1-phenylpropanone
(isopropyl phenyl ketone)

- **Solved Problem : Synthesize 5-nonanone using 1-butanol as your only starting material**

Retrosynthetic Analysis



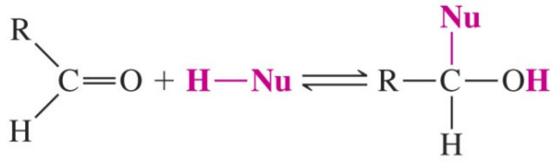
Synthesis



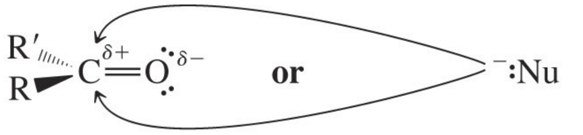
♦ Nucleophilic Addition to the Carbonyl Groups

➔ Addition of a nucleophile to a carbonyl carbon occurs because of the δ+ charge at the carbon

General Reaction



$$RHC{=}O + H{-}Nu \rightleftharpoons R{-}CH(Nu){-}OH$$

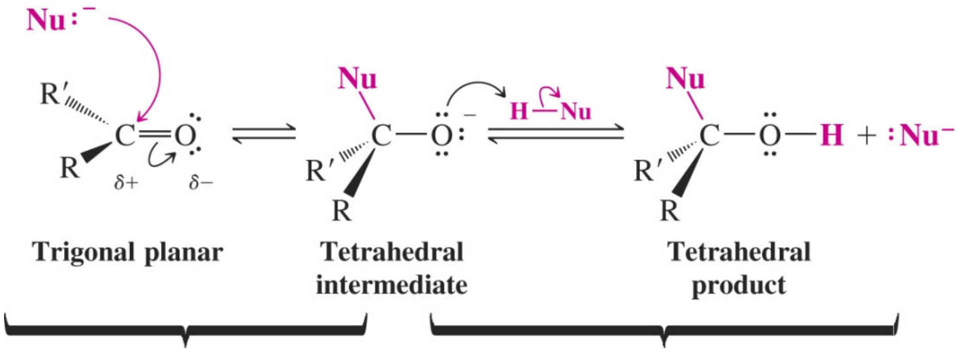


Aldehyde or ketone (R or R′ may be H)

The nucleophile may attack from above or below.

➔ Addition of strong nucleophiles such as hydride or Grignard reagents result in formation of a tetrahedral alkoxide intermediate

- The carbonyl π electrons shift to oxygen to give the alkoxide
- The carbonyl carbon changes from trigonal planar to tetrahedral

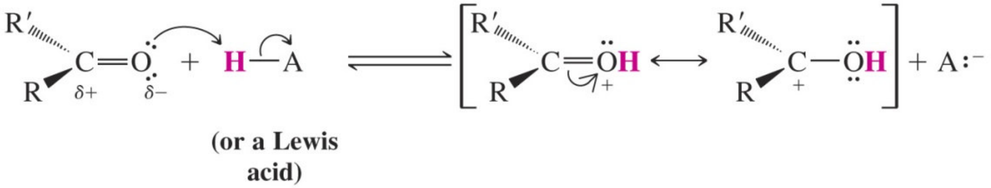


In this step the nucleophile forms a bond to the carbon by donating an electron pair. An electron pair shifts out to the oxygen.

In this step the alkoxide oxygen, because it is strongly basic, removes a proton from H—Nu or some other acid.

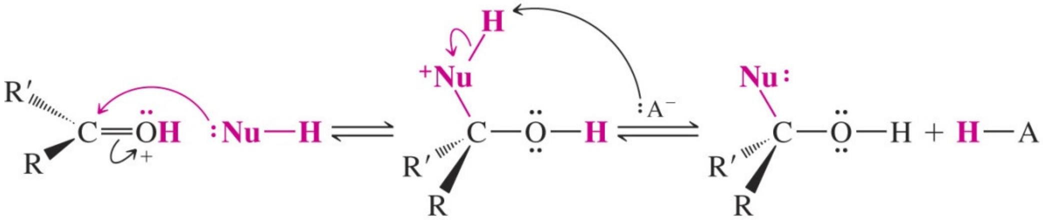
- ➔ **An acid catalyst is used to facilitate reaction of weak nucleophiles with carbonyl groups**
  - **Protonating the carbonyl oxygen enhances the electrophilicity of the carbon**

Step 1



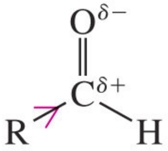
In this step an electron pair of the carbonyl oxygen accepts a proton from the acid (or associates with a Lewis acid), producing an oxonium cation. The carbon of the oxonium cation is more susceptible to nucleophilic attack than the carbonyl of the starting ketone.

Step 2



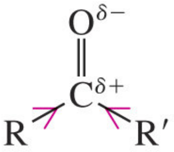
In the first of these two steps, the oxonium cation accepts the electron pair of the nucleophile. In the second step, a base removes a proton from the positively charged atom, regenerating the acid.

- **Relative Reactivity: Aldehydes versus Ketones**
  - ➔ **Aldehydes are generally more reactive than ketones**
    - **The tetrahedral carbon resulting from addition to an aldehyde is less sterically hindered than the tetrahedral carbon resulting from addition to a ketone**
    - **Aldehyde carbonyl groups are more electron deficient because they have only one electron-donating group attached to the carbonyl carbon**



Aldehyde

Carbonyl carbon is more positive.



Ketone

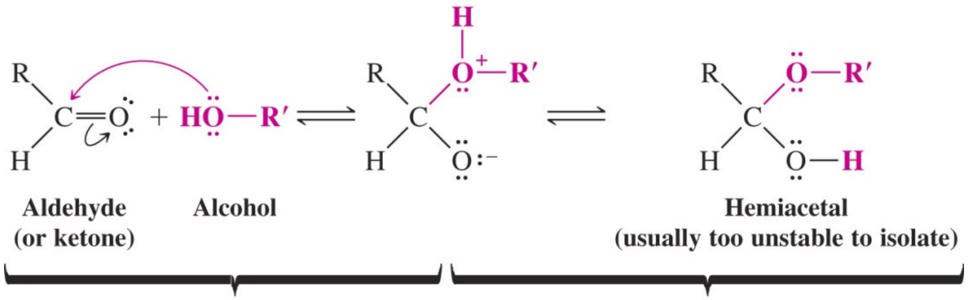
Carbonyl carbon is less positive.

♦ The Addition of Alcohols: Hemiacetals and Acetals

● Hemiacetals

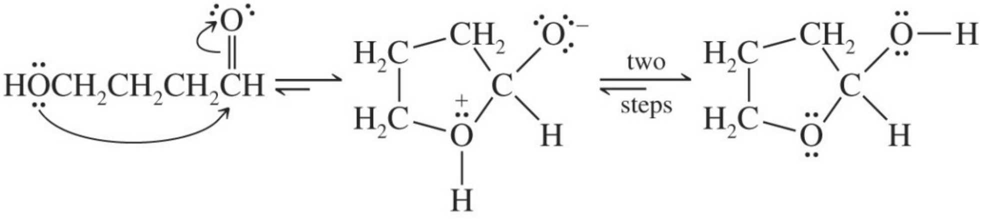
➔ An aldehyde or ketone dissolved in an alcohol will form an equilibrium mixture containing the corresponding hemiacetal

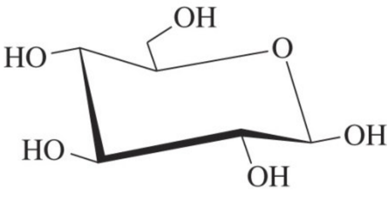
- A hemiacetal has a hydroxyl and alkoxyl group on the same carbon
- Acylic hemiacetals are generally not stable, however, cyclic five- and six-membered ring hemiacetals are



In this step the alcohol attacks the carbonyl carbon.

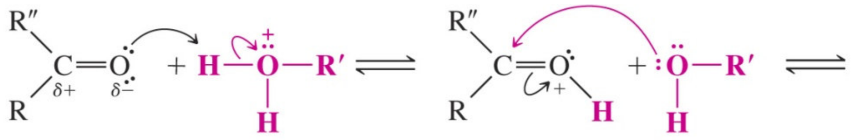
In two intermolecular steps, a proton is removed from the positive oxygen and a proton is gained at the negative oxygen.





(+)-Glucose
(a cyclic hemiacetal)

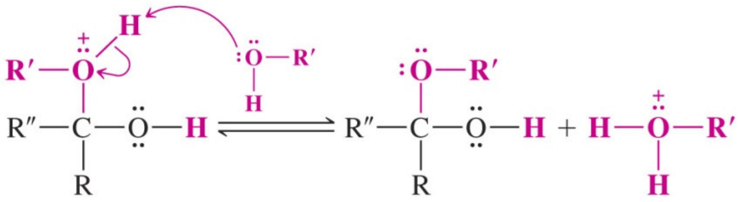
➔Hemiacetal formation is catalyzed by either acid or base



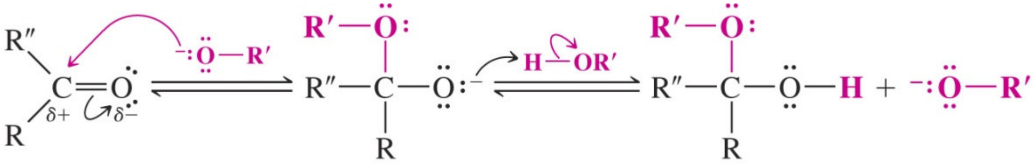
(R″ may be H)

Protonation of the aldehyde or ketone oxygen atom makes the carbonyl carbon more susceptible to nucleophilic attack. [The protonated alcohol results from reaction of the alcohol (present in excess) with the acid catalyst, e.g., HCl.]

An alcohol molecule adds to the carbon of the oxonium cation.



The transfer of a proton from the positive oxygen to another molecule of the alcohol leads to the hemiacetal.



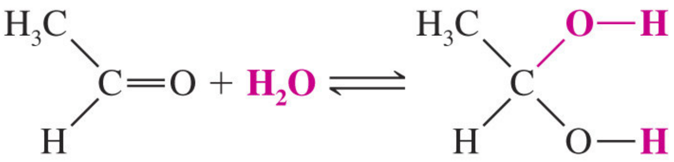
(R″ may be H)

An alkoxide anion acting as a nucleophile attacks the carbonyl carbon atom. An electron pair shifts onto the oxygen atom, producing a new alkoxide anion.

The alkoxide anion abstracts a proton from an alcohol molecule to produce the hemiacetal and regenerates an alkoxide anion.

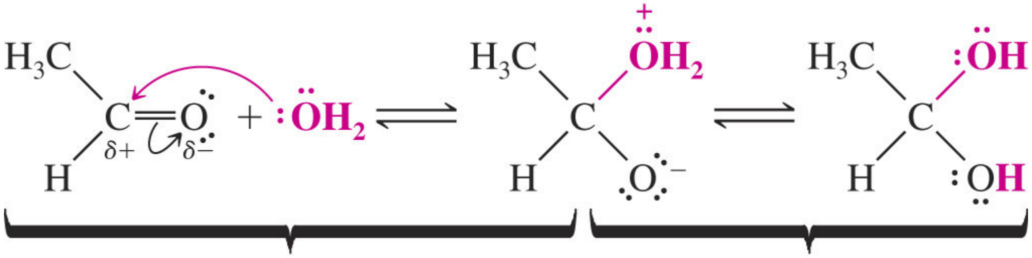
➔ **Dissolving aldehydes (or ketones) in water causes formation of an equilibrium between the carbonyl compound and its hydrate**

- **The hydrate is also called a *gem*-diol (*gem* *i.e.* geminal, indicates the presence of two identical substituents on the same carbon)**
- **The equilibrum favors a ketone over its hydrate because the tetrahedral ketone hydrate is sterically crowded**



Acetaldehyde

Hydrate (a *gem*-diol)

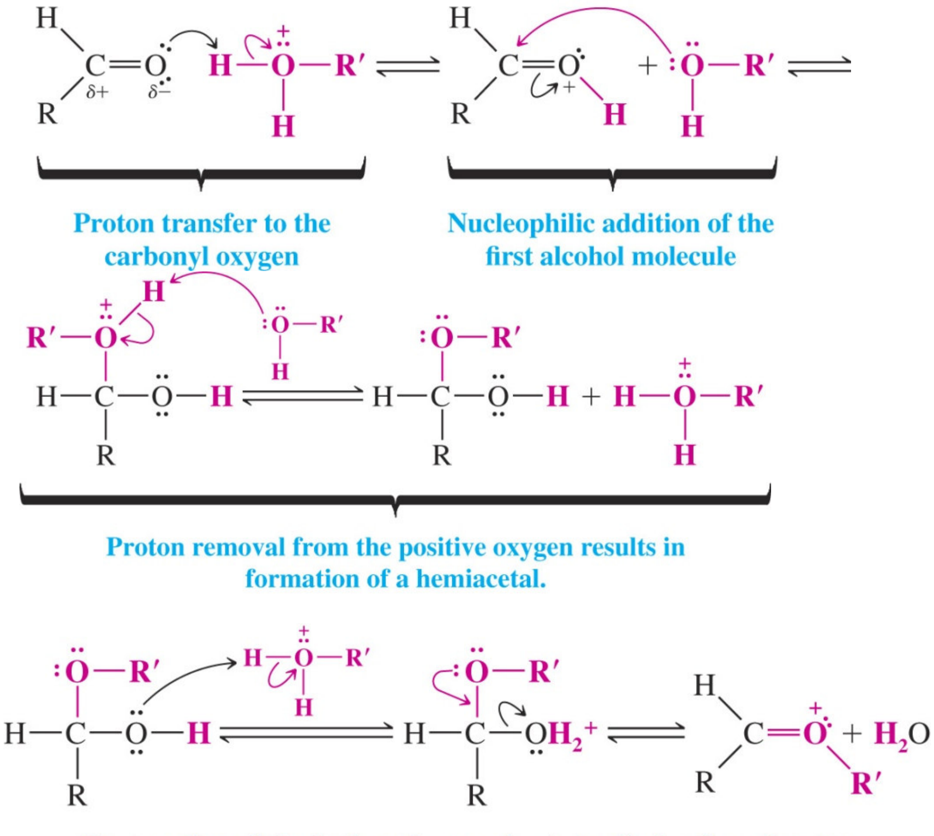


In this step water attacks the carbonyl carbon atom.

In two intermolecular steps a proton is lost from the positive oxygen atom and a proton is gained at the negative oxygen atom.

Acetals

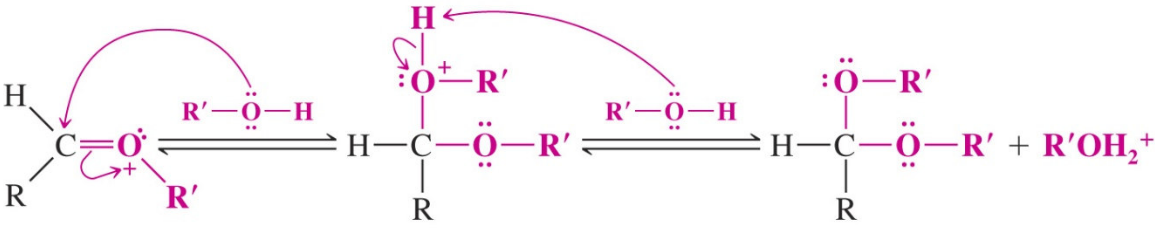
- ➔An aldehyde (or ketone) in the presence of excess alcohol and an acid catalyst will form an acetal
  - Formation of the acetal proceeds via the corresponding hemiacetal
  - An acetal has two alkoxyl groups bonded to the same carbon


Proton transfer to the carbonyl oxygen

Nucleophilic addition of the first alcohol molecule

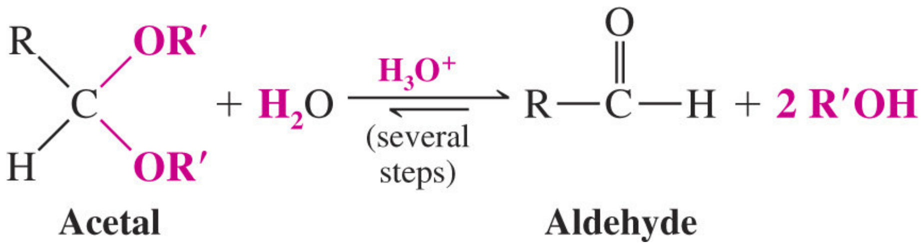
Proton removal from the positive oxygen results in formation of a hemiacetal.

Protonation of the hydroxyl group leads to elimination of water and formation of a highly reactive oxonium cation.



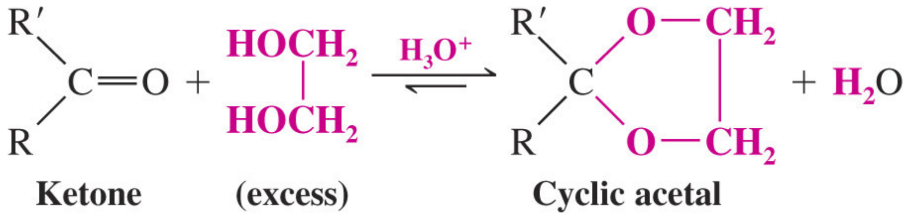
Attack on the carbon of the oxonium ion by a second molecule of the alcohol, followed by removal of a proton, leads to the acetal.

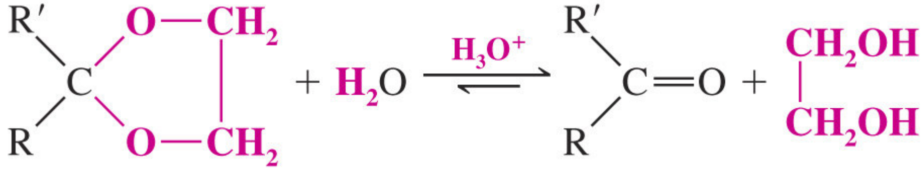
- ➔ **Acetals are stable when isolated and purified**
- ➔ **Acetal formation is reversible**
  - **An excess of water in the presence of an acid catalyst will hydrolyze an acetal to the corresponding aldehyde (or ketone)**



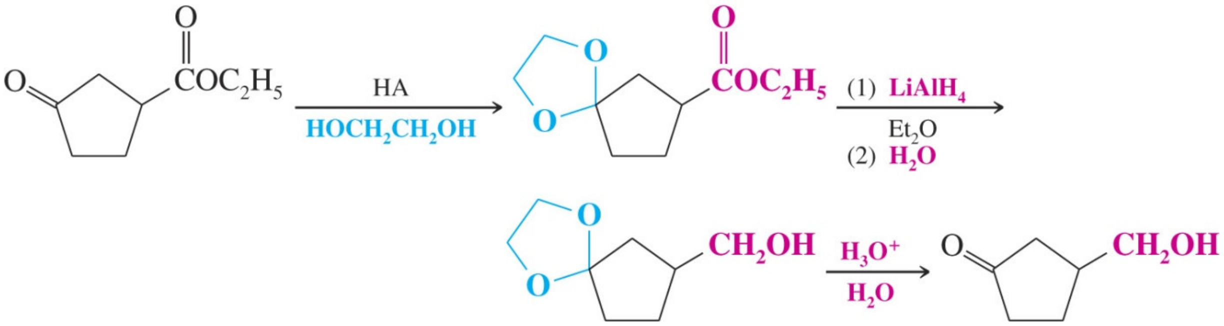
➔ **Acetal formation from ketones and simple alcohols is less favorable than formation from aldehydes**

- **Formation of cyclic 5- and 6- membered ring acetals from ketones is, however, favorable**
- **Such cyclic acetals are often used as protecting groups for aldehydes and ketones**
- **These protecting groups can be removed using dilute aqueous acid**

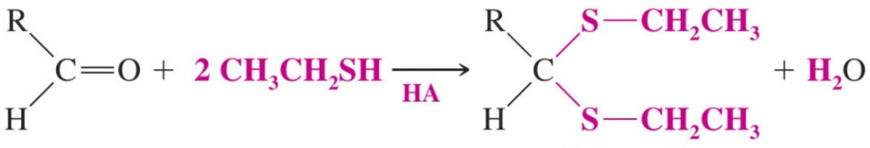




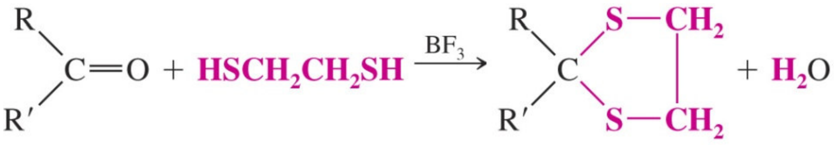
- **Acetals as Protecting Groups**
  - ➔Acetal protecting groups are stable to most reagents except aqueous acid
  - ➔Example: An ester can be reduced in the presence of a ketone protected as an acetal



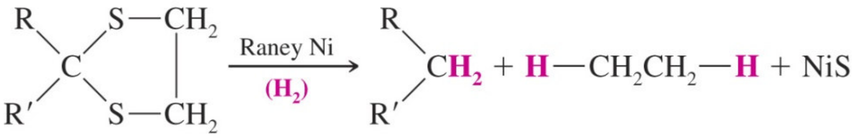
- **Thioacetals**
  - ➔**Thioacetals can be formed by reaction of an aldehyde or ketone with a thiol**
    - **Thioacetals can be converted to CH_2 groups by hydrogenation using a catalyst such as Raney nickel**
    - **This sequence provides a way to remove an aldehyde or ketone carbonyl oxygen**



Thioacetal

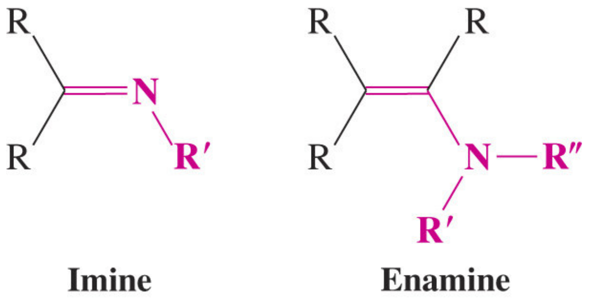


Cyclic thioacetal



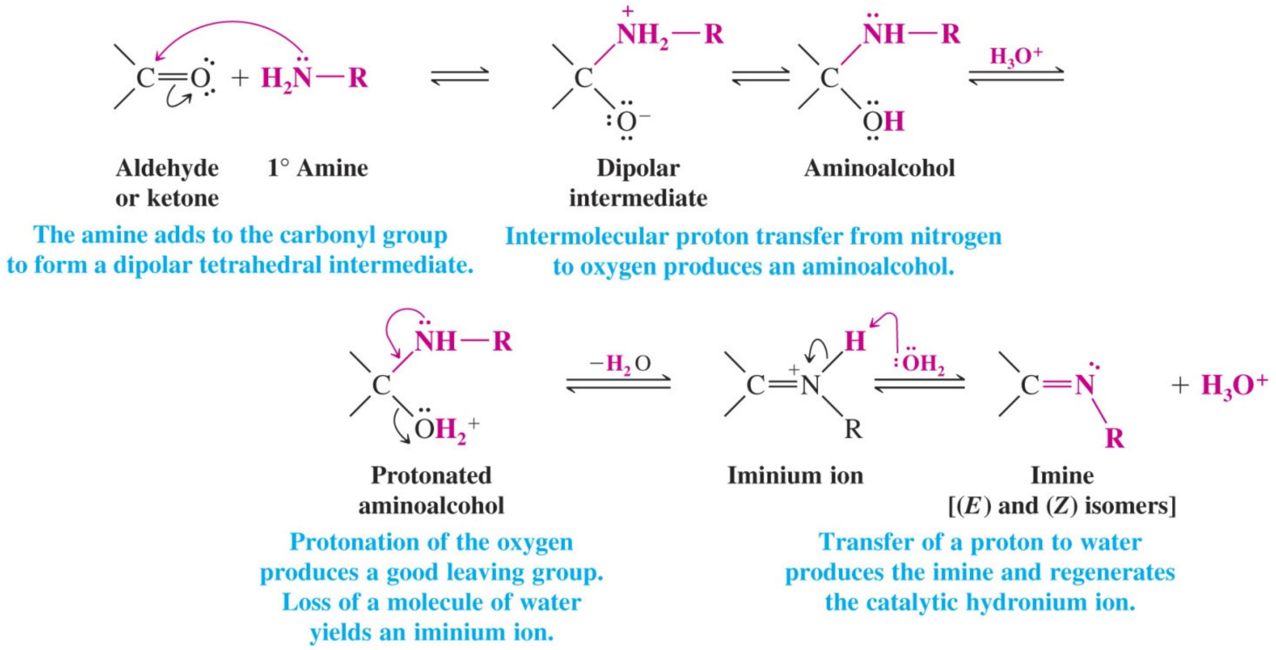
♦ The Addition of Primary and Secondary Amines

- ➔ Aldehydes and ketones react with primary amines (and ammonia) to yield imines
  - ☞ They react with secondary amines to yield enamines



R′, R″ = C;
R = C or H

- **Imines**
  - ➔**These reactions occur fastest at pH 4-5**
    - **Mild acid facilitates departure of the hydroxyl group from the aminoalcohol intermediate without also protonating the nitrogen of the amine starting compound**



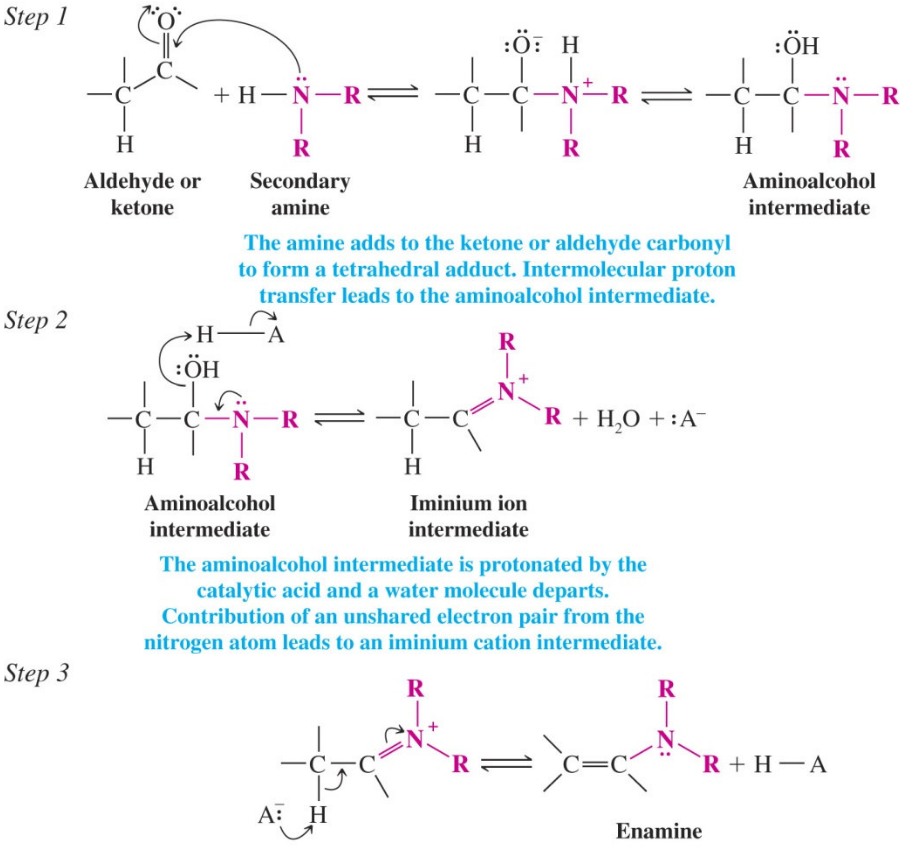
The amine adds to the carbonyl group to form a dipolar tetrahedral intermediate.

Intermolecular proton transfer from nitrogen to oxygen produces an aminoalcohol.

Protonation of the oxygen produces a good leaving group. Loss of a molecule of water yields an iminium ion.

Transfer of a proton to water produces the imine and regenerates the catalytic hydronium ion.

- # Enamines
  - ➔ **Secondary amines cannot form a neutral imine by loss of a second proton on nitrogen**
    - **An enamine is formed instead**



The amine adds to the ketone or aldehyde carbonyl to form a tetrahedral adduct. Intermolecular proton transfer leads to the aminoalcohol intermediate.

The aminoalcohol intermediate is protonated by the catalytic acid and a water molecule departs. Contribution of an unshared electron pair from the nitrogen atom leads to an iminium cation intermediate.

A proton is removed from the carbon adjacent to the iminium group. Proton removal occurs from the carbon because there is no proton to remove from the nitrogen of the iminium cation (as there would have been if a primary amine had been used). This step forms the enamine, neutralizes the formal charge, and regenerates the catalytic acid. (If there had been a proton to remove from the nitrogen of the iminium cation, the final product would have been an imine.)

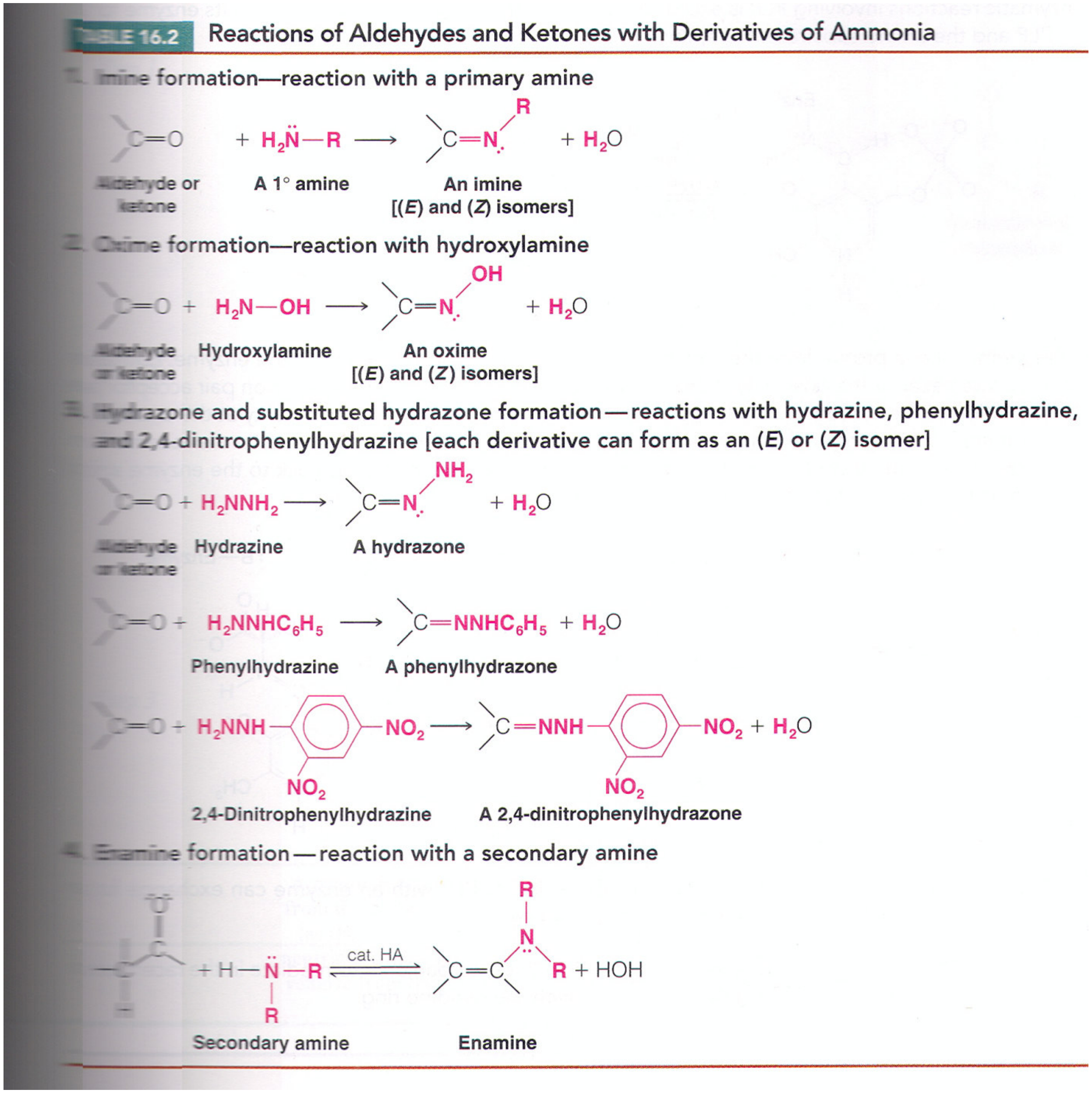


TABLE 16.2 Reactions of Aldehydes and Ketones with Derivatives of Ammonia

1. Imine formation—reaction with a primary amine

$C{=}O + H_2\ddot{N}{-}R \longrightarrow C{=}N{-}R + H_2O$

Aldehyde or ketone | A 1° amine | An imine [(*E*) and (*Z*) isomers]

2. Oxime formation—reaction with hydroxylamine

$C{=}O + H_2N{-}OH \longrightarrow C{=}N{-}OH + H_2O$

Aldehyde or ketone | Hydroxylamine | An oxime [(*E*) and (*Z*) isomers]

3. Hydrazone and substituted hydrazone formation—reactions with hydrazine, phenylhydrazine, and 2,4-dinitrophenylhydrazine [each derivative can form as an (*E*) or (*Z*) isomer]

$C{=}O + H_2NNH_2 \longrightarrow C{=}N{-}NH_2 + H_2O$

Aldehyde or ketone | Hydrazine | A hydrazone

$C{=}O + H_2NNHC_6H_5 \longrightarrow C{=}NNHC_6H_5 + H_2O$

Phenylhydrazine | A phenylhydrazone

$C{=}O + H_2NNH{-}C_6H_3(NO_2)_2 \longrightarrow C{=}NNH{-}C_6H_3(NO_2)_2 + H_2O$

2,4-Dinitrophenylhydrazine | A 2,4-dinitrophenylhydrazone

4. Enamine formation—reaction with a secondary amine

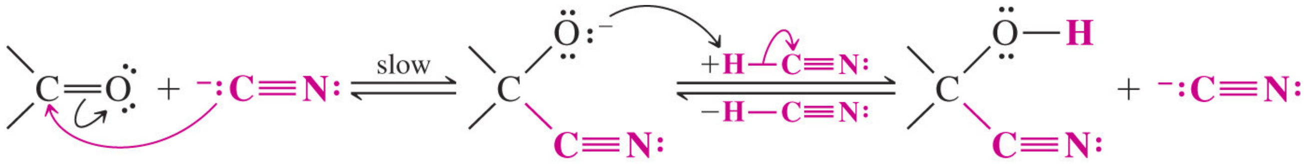
$+ H{-}\ddot{N}{-}R \underset{}{\overset{\text{cat. HA}}{\rightleftharpoons}} C{=}C{-}NR_2 + HOH$

Secondary amine | Enamine

♦ The Addition of Hydrogen Cyanide

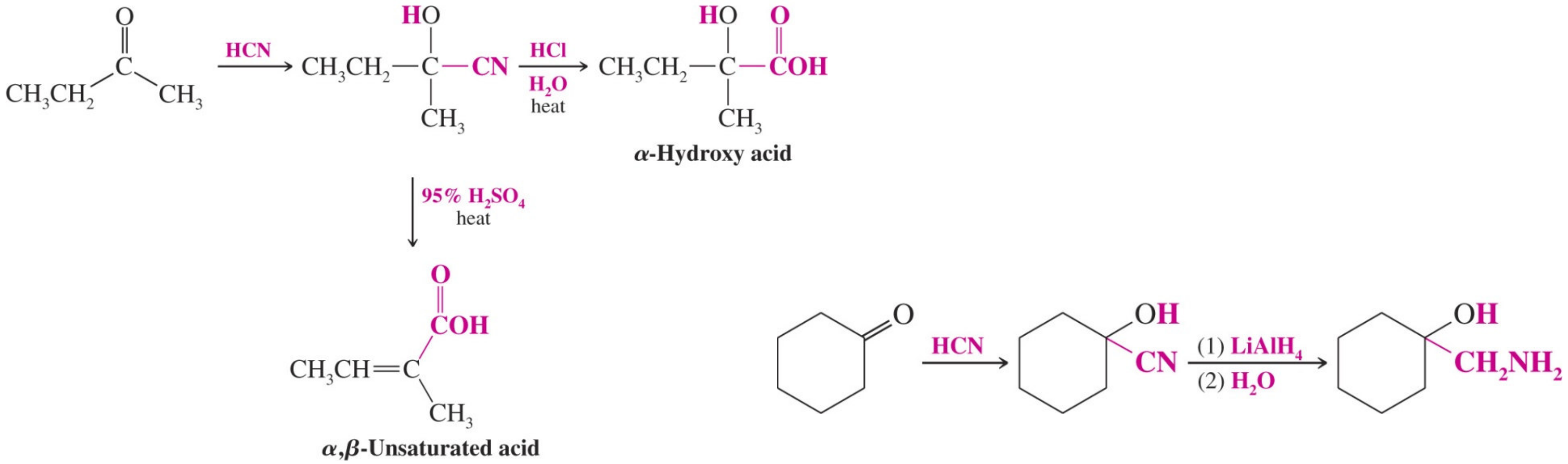
➔ **Aldehydes and ketone react with HCN to form a cyanohydrin**

- **A catalytic amount of cyanide helps to speed the reaction**



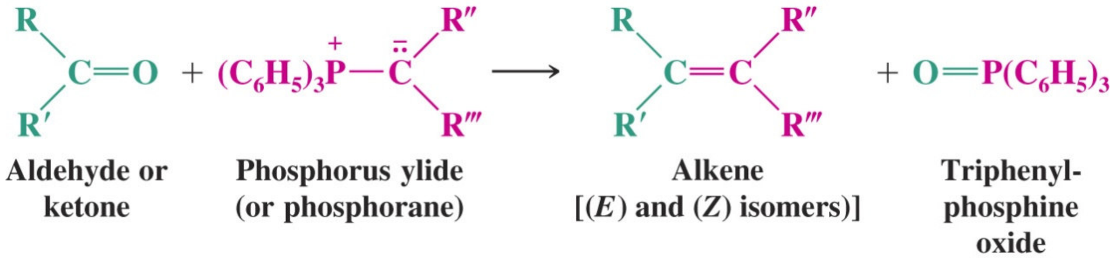
➔ **The cyano group can be hydrolyzed or reduced**

- **Hydrolysis of a cyanohydrin produces an α-hydroxycarboxylic acid (Sec. 18.8H)**
- **Reduction of a cyanohydrin produces a β-aminoalcohol**

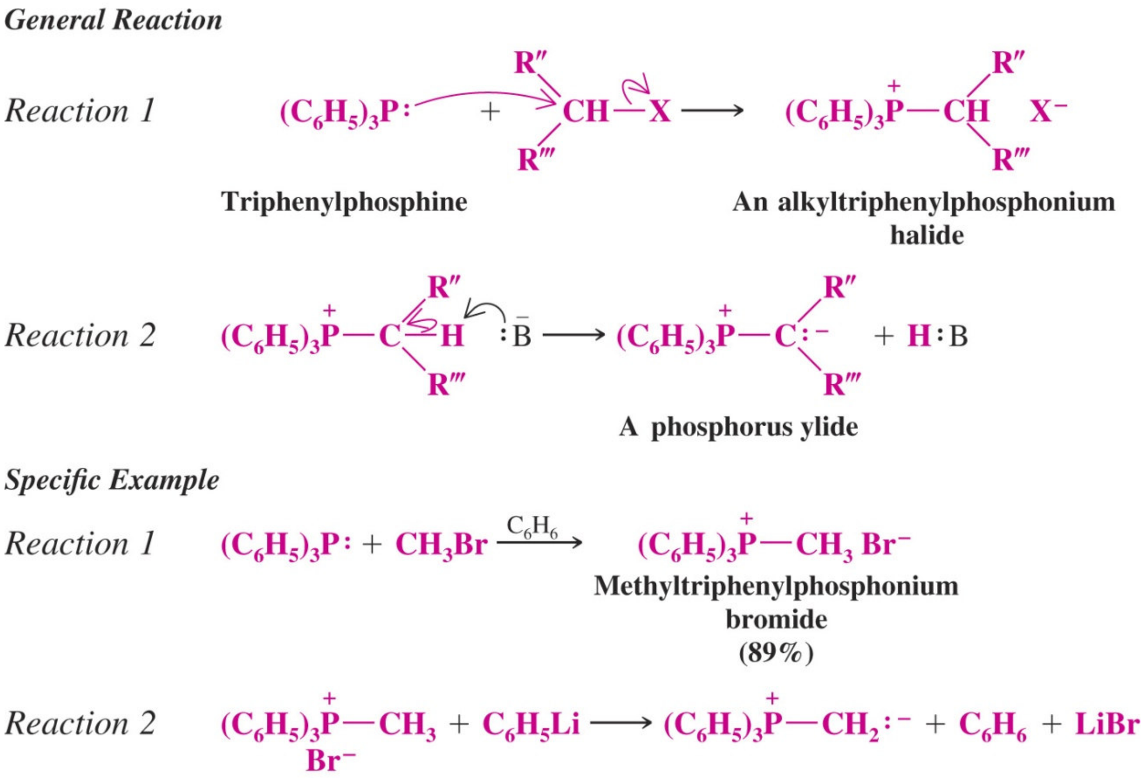


♦ The Addition of Ylides: The Wittig Reaction

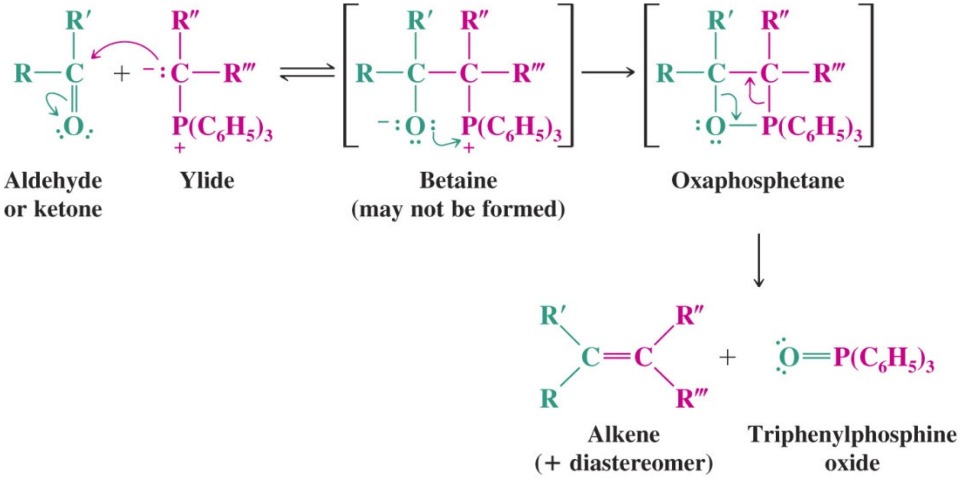
- ➔ **Aldehydes and ketones react with phosphorous ylides to produce alkenes**
  - **An ylide is a neutral molecule with adjacent positive and negative charges**



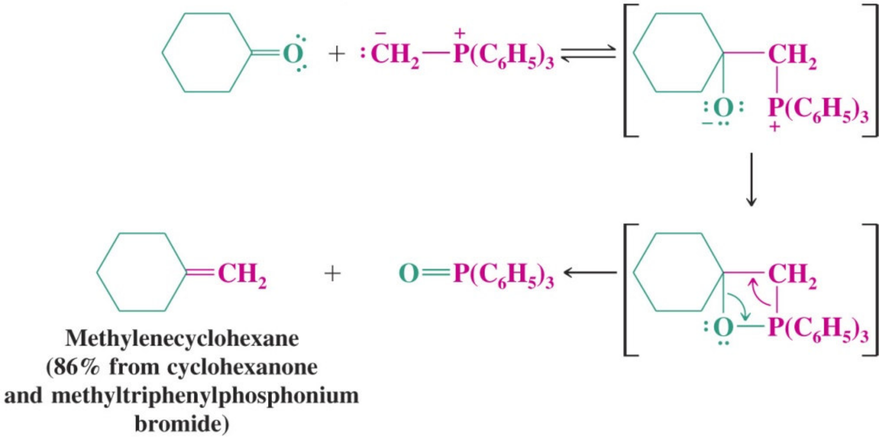
- ➔ **Reaction of triphenylphosphine with a primary or secondary alkyl halide produces a phosphonium salt**
  - **The phosphonium salt is deprotonated by a strong base to form the ylide**



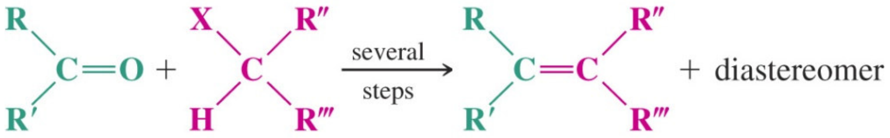
- ➔ **Addition of the ylide to the carbonyl leads to formation of a four-membered ring oxaphosphetane**
  - **The oxaphophetane rearranges to the alkene and triphenylphosphine oxide**
  - **The driving force for the last reaction is formation of the very strong phosphorus-oxygen double bond in triphenylphosphine oxide**



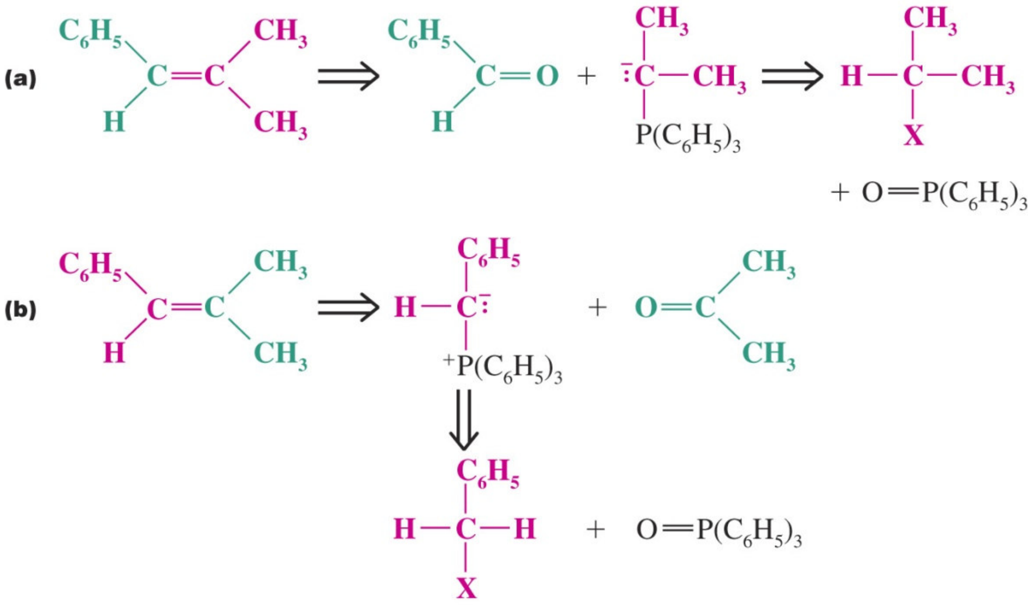
Specific Example



➔**The overall result of a Wittig reaction is formation of a C=C bond from a C=O bond**



➔Solved Problem: Make 2-Methyl-1-phenylprop-1-ene by a Wittig reaction



(a) $(CH_3)_2CHBr + (C_6H_5)_3P \longrightarrow (CH_3)_2CH{-}\overset{+}{P}(C_6H_5)_3\ Br^- \xrightarrow{RLi}$

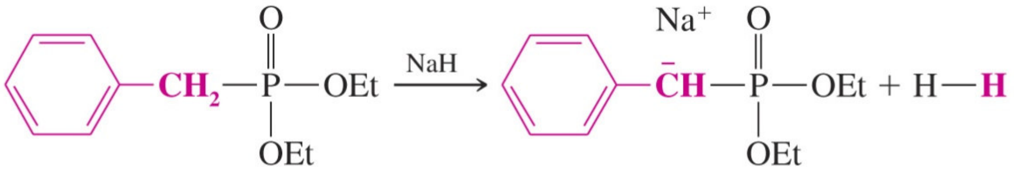
$(CH_3)_2\ddot{C}{-}P(C_6H_5)_3 \xrightarrow{C_6H_5CHO} (CH_3)_2C{=}CHC_6H_5 + (C_6H_5)_3P{=}O$

(b) $C_6H_5CH_2Br + (C_6H_5)_3P \longrightarrow C_6H_5CH_2{-}\overset{+}{P}(C_6H_5)_3\ Br^- \xrightarrow{RLi}$

$C_6H_5\ddot{C}H{-}P(C_6H_5)_3 \xrightarrow{(CH_3)_2C{=}O} C_6H_5CH{=}C(CH_3)_2 + (C_6H_5)_3P{=}O$

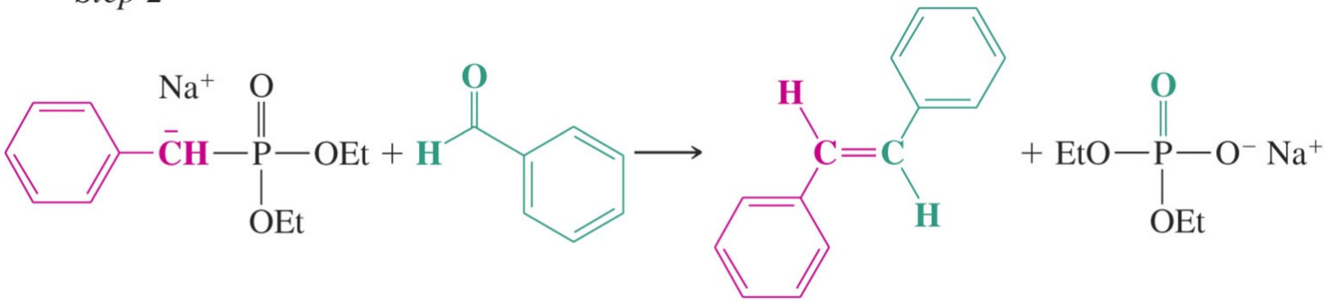
➔ **The Horner-Wadsworth-Emmons reaction employs a phosphonate ester and generally leads to formation of an (*E*)-alkene**

Step 1

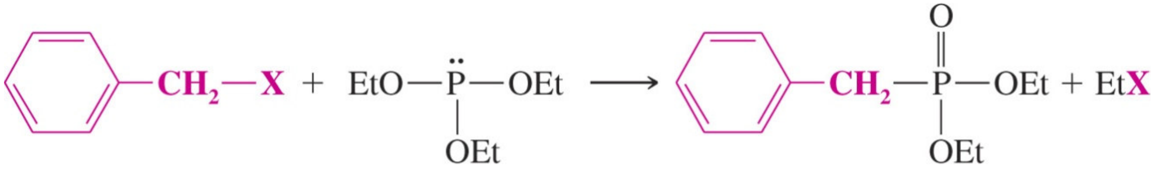


A phosphonate ester

Step 2



(84%)



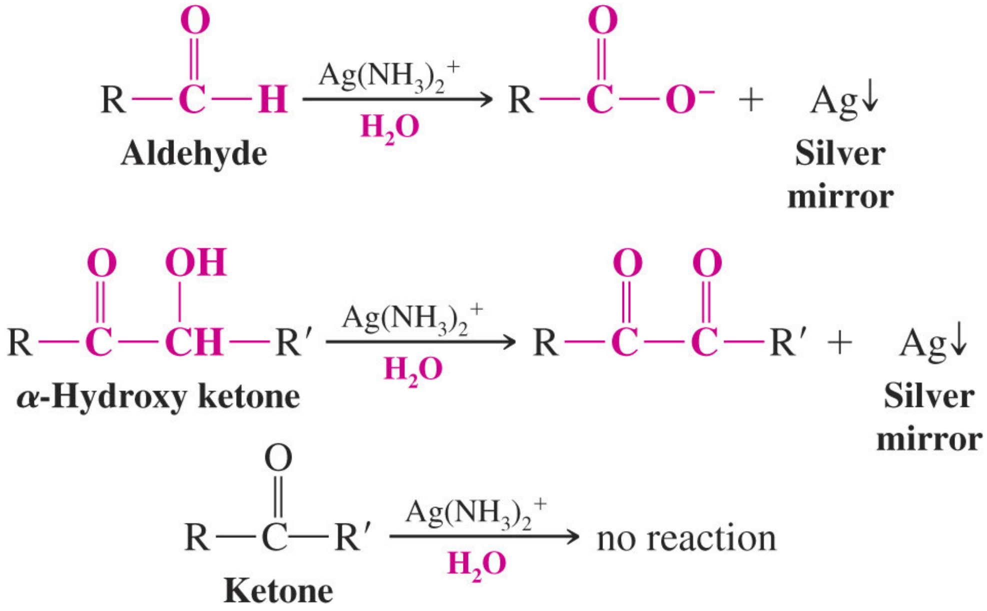
Triethyl phosphite

♦ Chemical Analysis of Aldehydes and Ketones

● Tollens' Test (Silver Mirror Test)

➔ **Aldehydes and ketones can be distinguished from each other on the basis of the Tollens test**

- **The presence of an aldehyde results in formation of a silver mirror (by oxidation of the aldehyde and reduction of the silver cation)**
- **α-Hydroxyketones also give a positive Tollens' test**



$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow[H_2O]{Ag(NH_3)_2^+} R-\overset{O}{\overset{\|}{C}}-O^- + Ag\downarrow$$

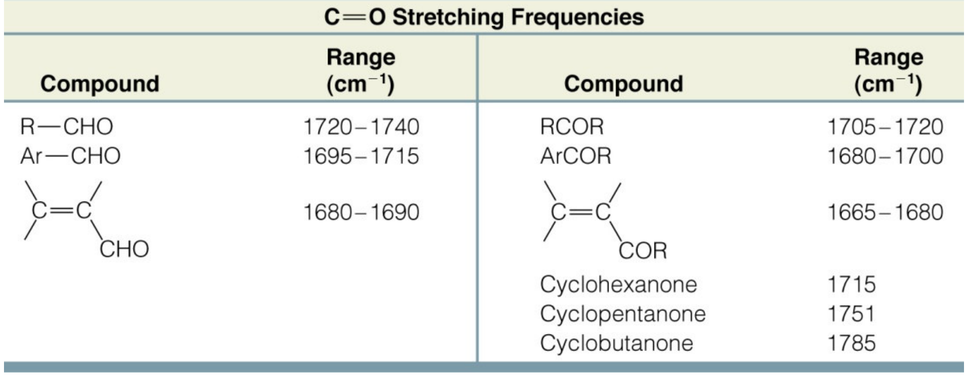
$$R-\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{CH}}-R' \xrightarrow[H_2O]{Ag(NH_3)_2^+} R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R' + Ag\downarrow$$

$$R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow[H_2O]{Ag(NH_3)_2^+} \text{no reaction}$$

♦ Spectroscopic Properties of Aldehydes and Ketones

● IR Spectra of Aldehydes and Ketones

➔ Aldehydes and ketones have strong carbonyl stretching frequencies in the 1665-1780 cm^{-1} region

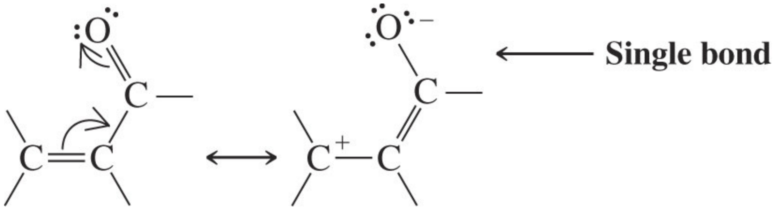


C=O Stretching Frequencies

Compound	Range (cm^{-1})	Compound	Range (cm^{-1})
R—CHO	1720–1740	RCOR	1705–1720
Ar—CHO	1695–1715	ArCOR	1680–1700
$\mathrm{C{=}C{-}CHO}$	1680–1690	$\mathrm{C{=}C{-}COR}$	1665–1680
		Cyclohexanone	1715
		Cyclopentanone	1751
		Cyclobutanone	1785

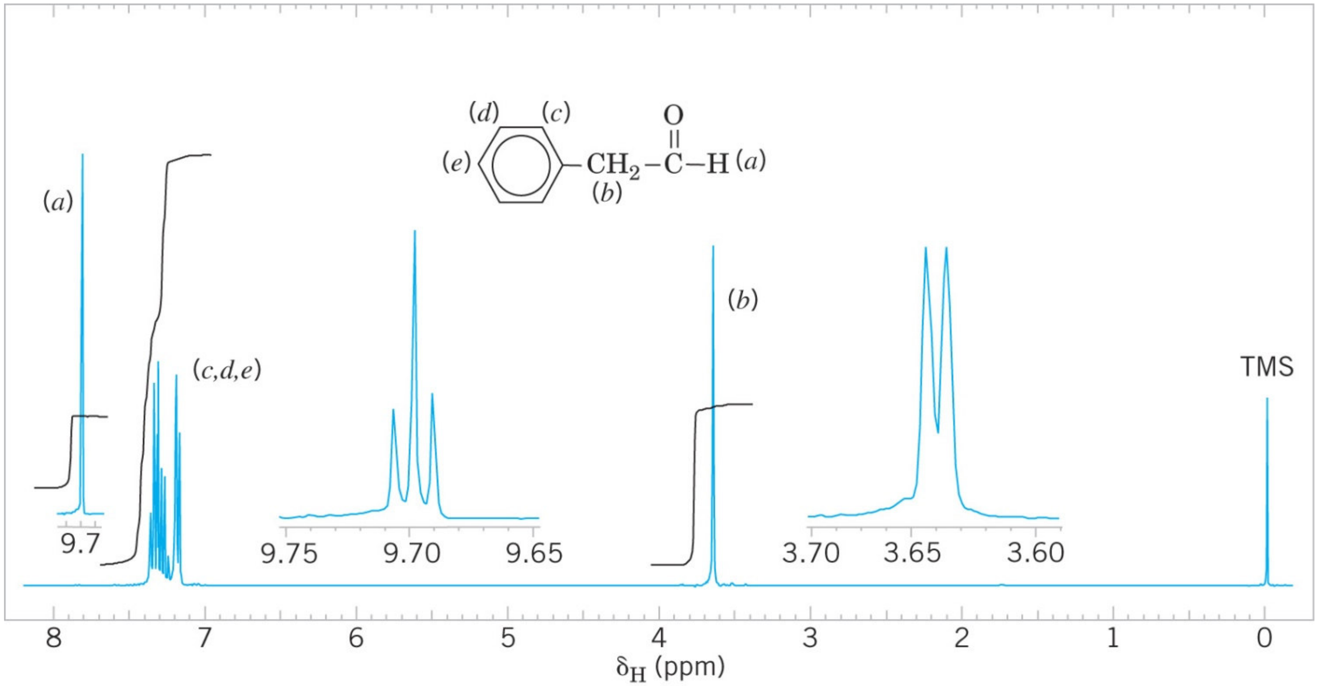
➔ Conjugation shifts the IR frequency about 40 cm^{-1} lower because the carbonyl has less double bond character

- Single bonds stretch more easily than double bonds



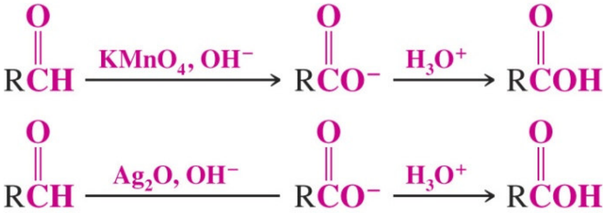
➔ Vibrations of the C-H bond in an aldehyde gives two weak but characteristic bands at 2700-2775 and 2820-2900 cm^{-1}

- **NMR Spectra of Aldehydes and Ketones**
  - ➔ **^{13}C NMR Spectra**
    - **Aldehyde and ketone carbonyl carbons give characteristic signals at δ 180-220**
  - ➔ **^{1}H NMR Spectra**
    - **Aldehyde protons give sharp signals at δ 9-12**
    - **The aldehyde proton often shows coupling to the protons on the α-carbon**
    - **Protons on the α carbon generally appear at δ 2.0-2.3**



♦ Oxidation of Aldehydes and Ketones

➔ Aldehydes are generally much more easily oxidized than ketones



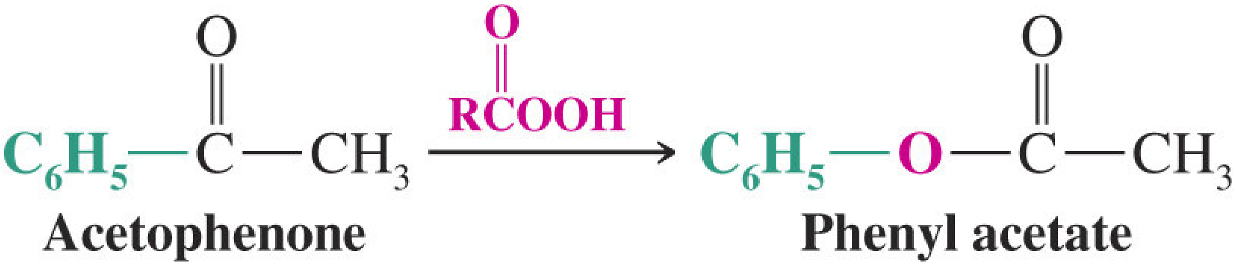
$$R\overset{O}{\overset{\|}{C}}H \xrightarrow{KMnO_4,\ OH^-} R\overset{O}{\overset{\|}{C}}O^- \xrightarrow{H_3O^+} R\overset{O}{\overset{\|}{C}}OH$$

$$R\overset{O}{\overset{\|}{C}}H \xrightarrow{Ag_2O,\ OH^-} R\overset{O}{\overset{\|}{C}}O^- \xrightarrow{H_3O^+} R\overset{O}{\overset{\|}{C}}OH$$

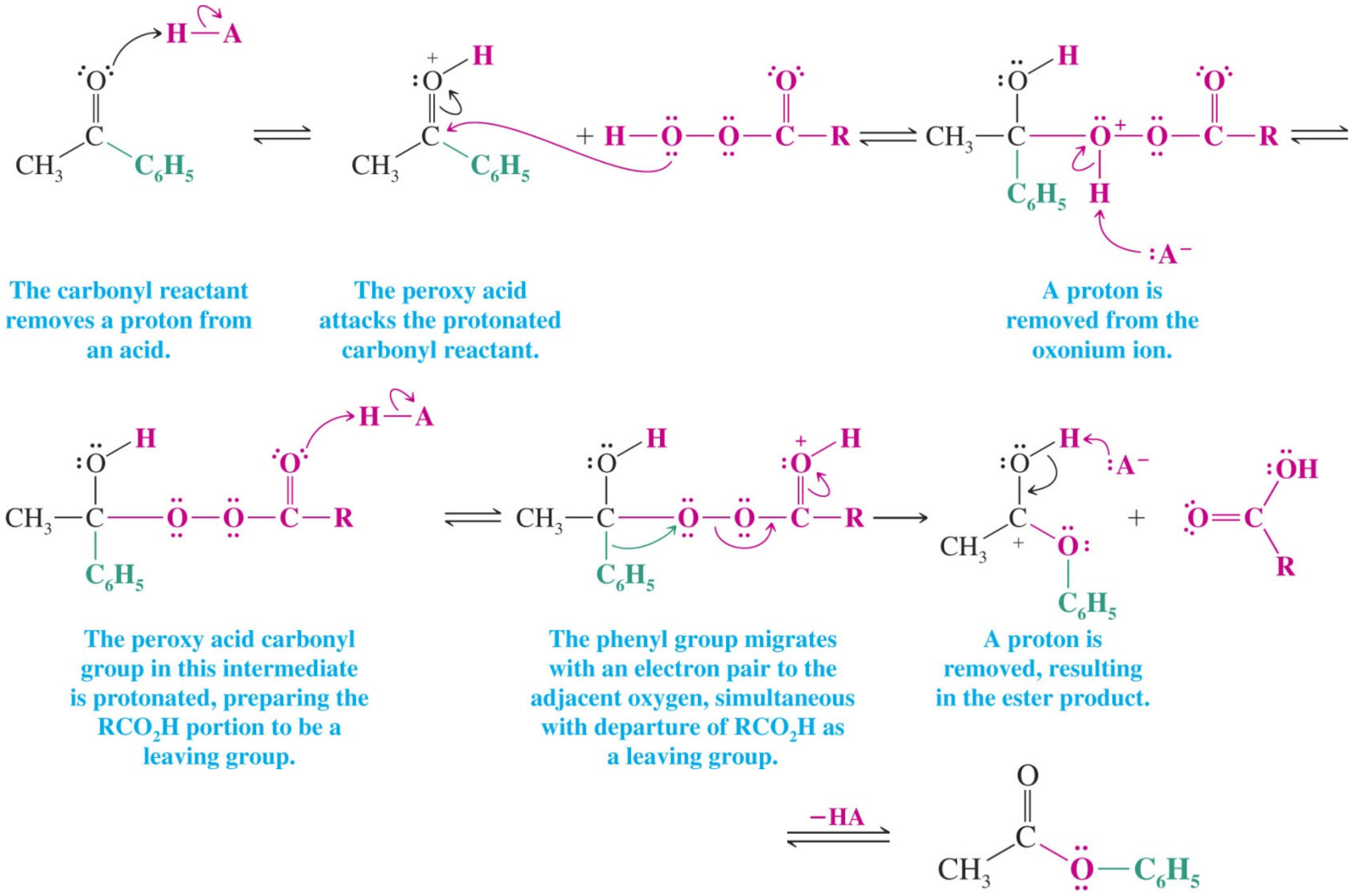
● The Baeyer-Villiger Oxidation of Aldehydes and Ketones

➔ The Baeyer-Villeger reaction results in insertion of an oxygen atom adjacent to a ketone or aldehyde carbonyl

- Oxidation of a ketone yields an ester
- A peroxyacid such as *m*-chloroperbenzoic (MCPBA) acid is used



$$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{R\overset{O}{\overset{\|}{C}}OOH} C_6H_5-O-\overset{O}{\overset{\|}{C}}-CH_3$$



The carbonyl reactant removes a proton from an acid.

The peroxy acid attacks the protonated carbonyl reactant.

A proton is removed from the oxonium ion.

The peroxy acid carbonyl group in this intermediate is protonated, preparing the RCO_2H portion to be a leaving group.

The phenyl group migrates with an electron pair to the adjacent oxygen, simultaneous with departure of RCO_2H as a leaving group.

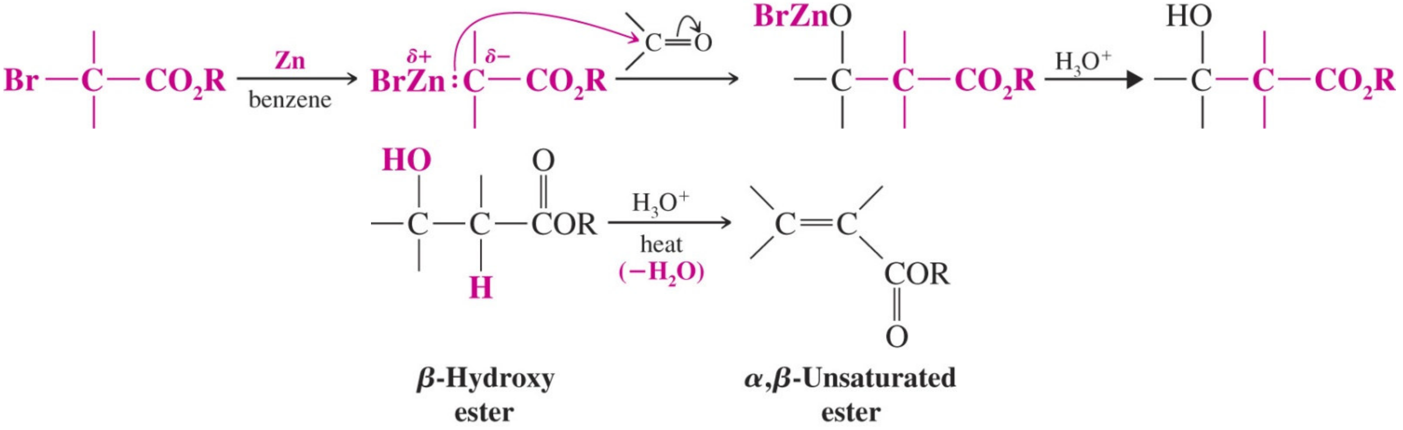
A proton is removed, resulting in the ester product.

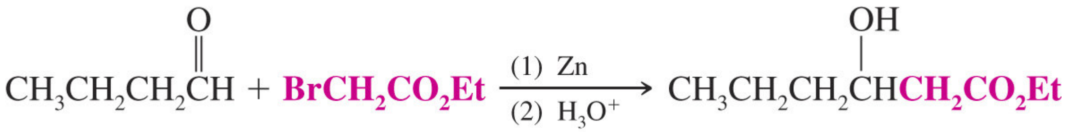
➔The migratory aptitude of a group attached to a carbonyl is
H > phenyl > 3° alkyl > 2° alkyl > 1° alkyl > methyl

♦ The Addition of Organometallic Reagents: The Reformatsky Reaction

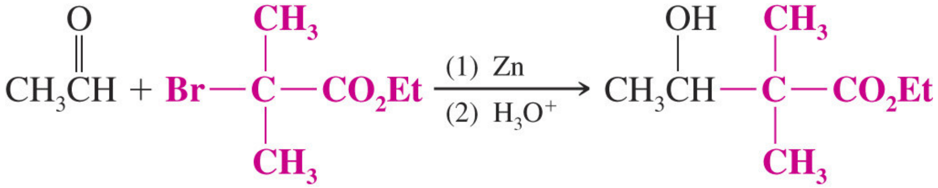
➔ **The Reformatsky reaction involves addition of an organozinc reagent to an aldehyde or ketone**

- **The organozinc reagent is made from an α-bromo ester; the reaction gives a β-hydroxy ester**
- **The β-hydroxyester is easily dehydrated to an α,β-unsaturated ester**





$$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}H + BrCH_2CO_2Et \xrightarrow[(2)\ H_3O^+]{(1)\ Zn} CH_3CH_2CH_2\overset{OH}{\overset{|}{C}}HCH_2CO_2Et$$



$$CH_3\overset{O}{\overset{\|}{C}}H + Br-\underset{CH_3}{\overset{CH_3}{C}}-CO_2Et \xrightarrow[(2)\ H_3O^+]{(1)\ Zn} CH_3\overset{OH}{C}H-\underset{CH_3}{\overset{CH_3}{C}}-CO_2Et$$