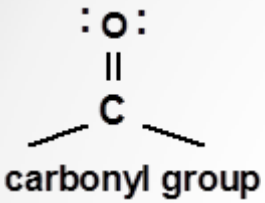
Chem. 108

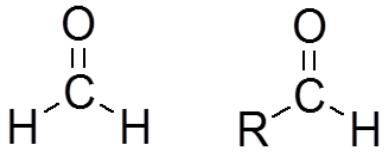
Aldehydes and Ketones

Chapter 9

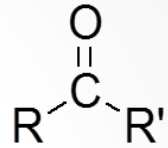
Aldehydes and ketones are simple compounds which contain a carbonyl group (a carbon-oxygen double bond).



aldehyde

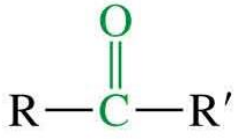
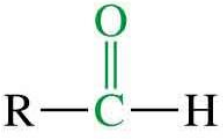
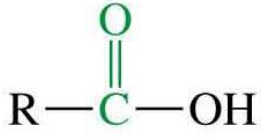
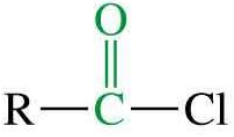
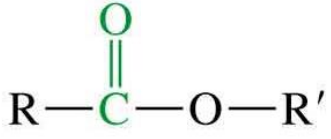
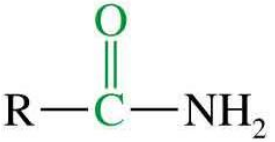


ketone



R can be Ar

Some Common Classes Carbonyl Compounds

Class	General Formula	Class	General Formula
ketones		aldehydes	
carboxylic acids		acid chlorides	
esters		amides	

Aldehydes

RCHO or RCH=O

Nomenclature

Common Names

- Use the common name of the carboxylic acids.
- Drop *-ic acid* and add *-aldehyde*.
  - 1 C: formic acid → formaldehyde
  - 2 C's: acetic acid → acetaldehyde
  - 3 C's: propionic acid → propionaldehyde
  - 4 C's: butyric acid → butyraldehyde.

Structure	IUPAC name	Common name	Structure	IUPAC	Common name
HCO_2H	methanoic acid	**formic acid**	HCHO	methanal	**formaldehyde**
CH_3CO_2H	ethanoic acid	**acetic acid**	CH_3CHO	ethanal	**acetaldehyde**
$CH_3CH_2CO_2H$	propanoic acid	**propionic acid**	CH_3CH_2CHO	propanal	**propionaldehyde**
$CH_3(CH_2)_2CO_2H$	butanoic acid	**butyric acid**	$CH_3(CH_2)_2CHO$	butanal	**butyraldehyde**
$CH_3(CH_2)_3CO_2H$	pentanoic acid	**valeric acid**	$CH_3(CH_2)_3CHO$	pentanal	**valeraldehyde**
$CH_3(CH_2)_4CO_2H$	hexanoic acid	**caproic acid**	$CH_3(CH_2)_4CHO$	hexanal	**caproaldehyde**

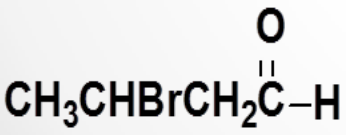
- Substituents locations are given using Greek letters

(α, β, γ, δ) beginning with the carbon next to the carbonyl carbon.

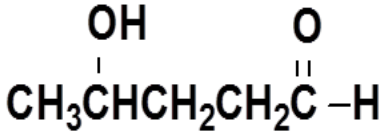
5 4 3 2 1

C—C—C—C—C=O

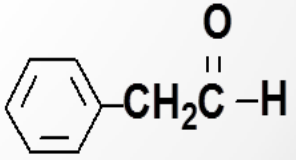
δ γ β α



β-bromobutyraldehyde



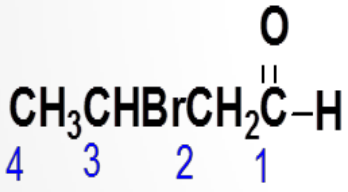
γ-hydroxyvaleraldehyde



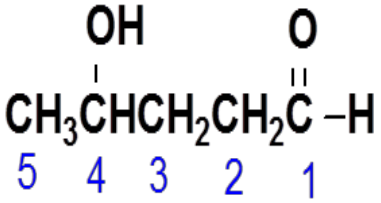
α-phenylacetaldehyde

IUPAC System

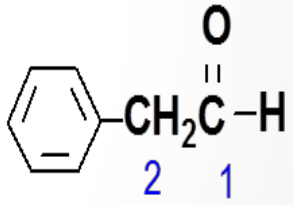
- Select the longest carbon chain containing the carbonyl carbon.
- The **-e** ending of the parent alkane name is replaced by the suffix **-al**.
- The carbonyl carbon is always numbered "1." (It is not necessary to include the number in the name.)



3-bromobutanal



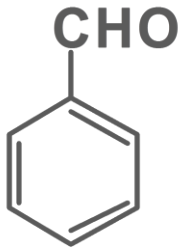
4-hydroxypentanal



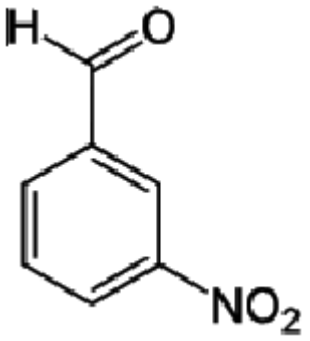
2-phenylethanal

- Aromatic aldehydes are usually designated as derivatives of the simplest aromatic aldehyde,

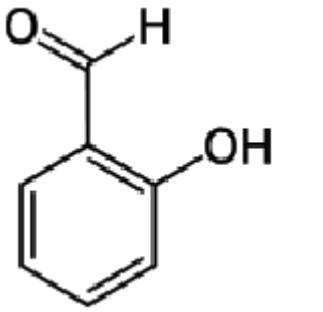
Benzaldehyde



Benzaldehyde



m-Nitrobenzaldehyde
3-Nitrobenzaldehyde



Salicylaldehyde
(*o*-Hydroxybenzaldehyde)
2-Hydroxybenzaldehyde

Ketones

RCOR’ (R and R’=alkyl or aryl)

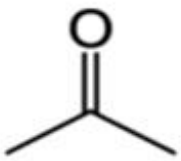
Nomenclature

Common Names

The common name for a ketone is constructed by adding ketone to the names of the two alkyl groups on the C=O double bond, listed in alphabetical order.

IUPAC System

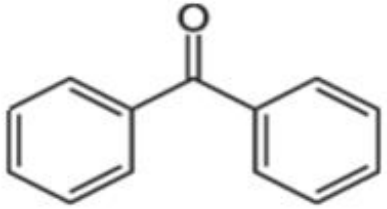
- Select the longest carbon chain containing the carbonyl carbon.
- The -e ending of the parent alkane name is replaced by the suffix -one.
- The chain is numbered in such a way as give the lowest number to the C=O group.



Dimethylketone

acetone

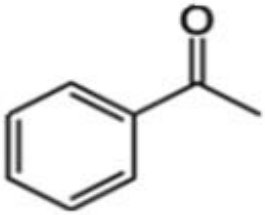
2-Propanone



Diphenylketone

Benzophenone

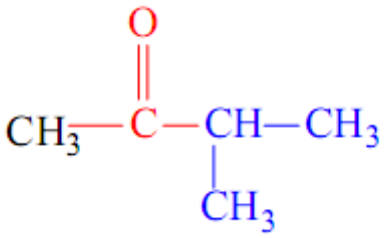
diphenylmethanone



Methylphenylketone

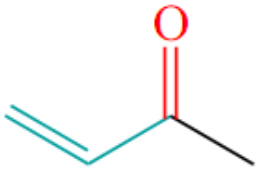
acetophenone

1-Phenyl-2-ethanone



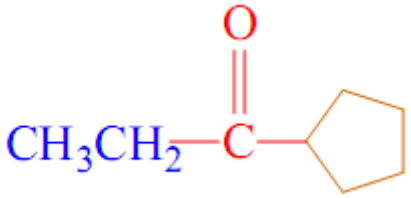
isopropyl methyl ketone

3-Methylbutan-2-one



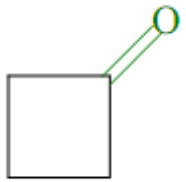
Methyl vinyl ketone

3-buten-2-one



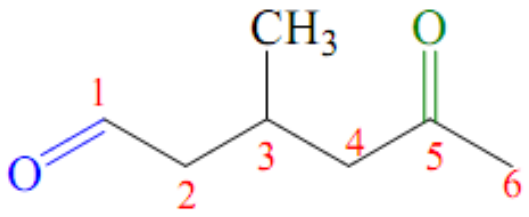
Cyclopentyl ethyl ketone

1-Cyclopentyl-1-propanone

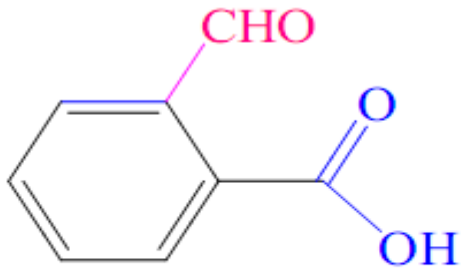


Cyclobutanone

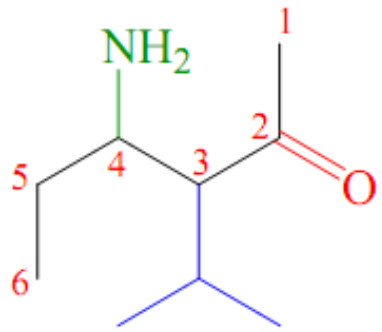
- On a molecule with a higher priority functional group, C=O is *oxo-* and -CHO is *formyl.*
- Aldehyde priority is higher than ketone
- Carboxylic acid priority is higher than aldehyde



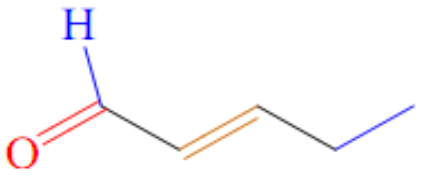
3-Methyl-5-oxohexanal



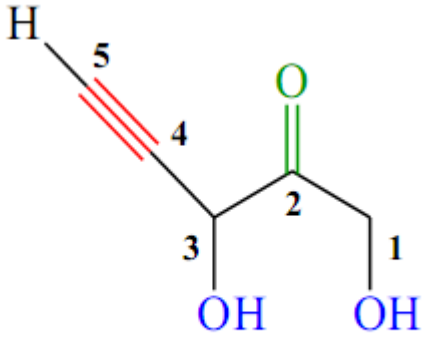
2- formyl benzoic acid



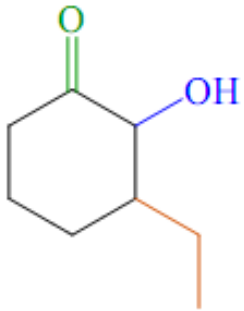
4-amino-3-isopropyl-2-hexanone



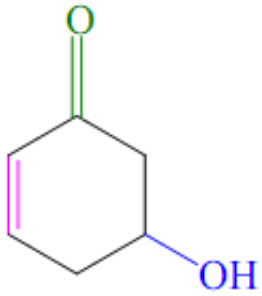
2-pentenal



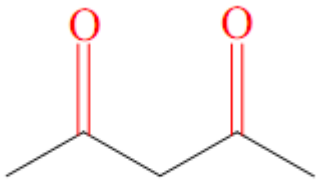
1,3- dihydroxypent-4-yn-2-one



3-Ethyl-2-hydroxycyclohexanone

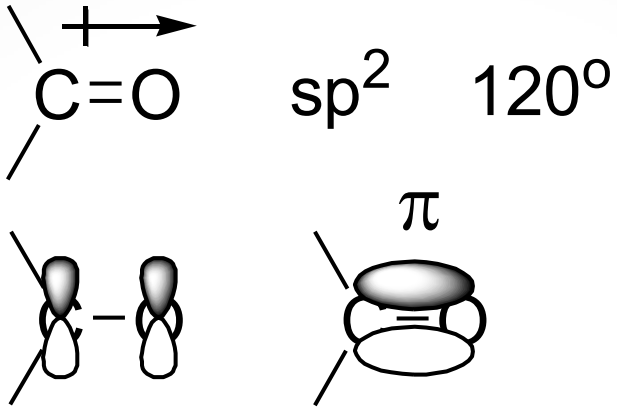


5-hydroxy-2-cyclohexenone

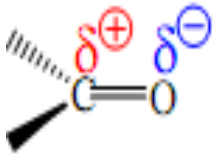


2,4-pentadione

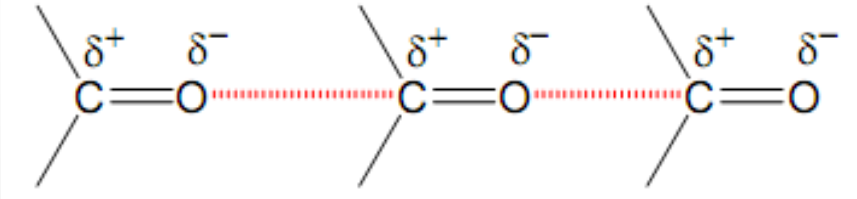
Physical Properties of Aldehydes and Ketones



Carbonyl compounds are polar, containing a dipole along the carbon-oxygen double bond.

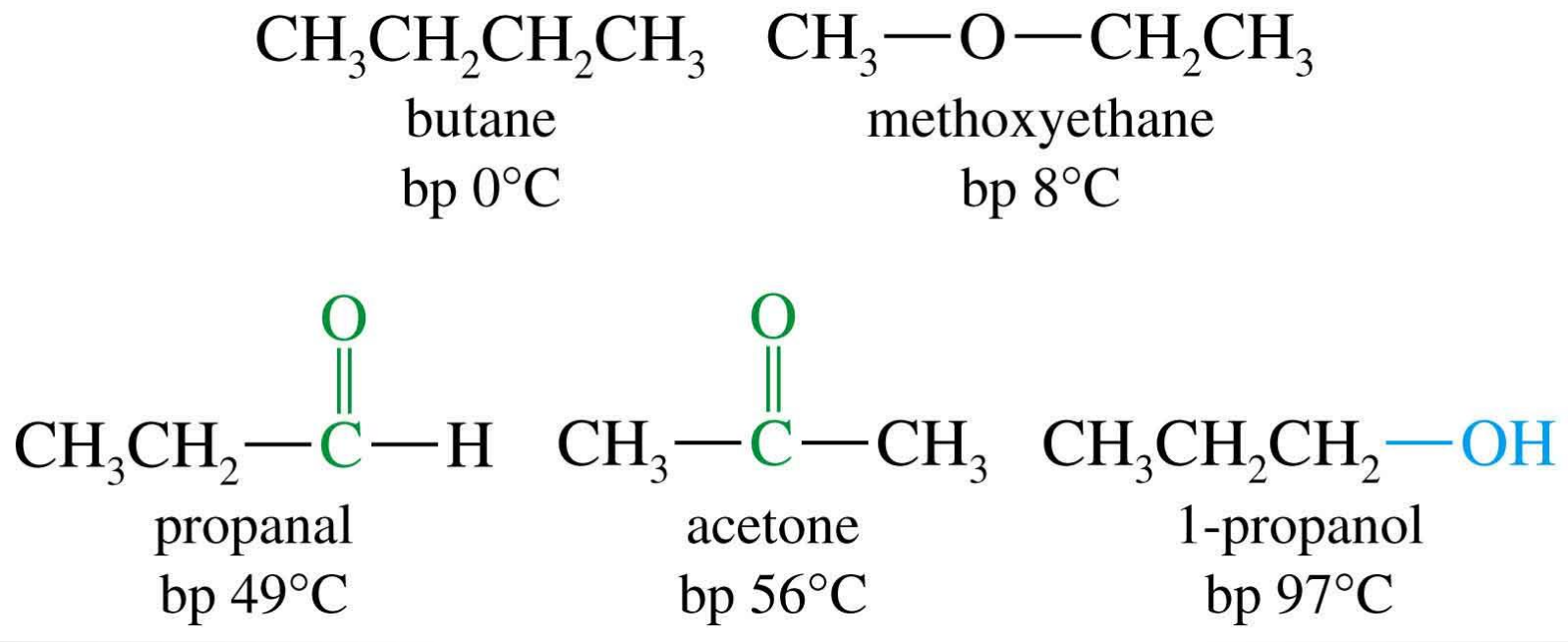


This creates weak attractive forces between carbonyl compounds, but these attractions are not as strong as those that result from hydrogen-bonding.



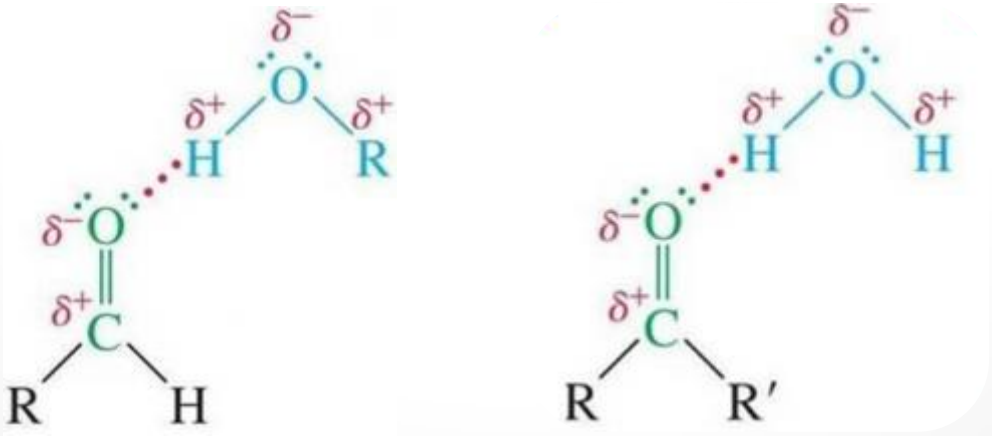
1. Boiling Points

More polar, so higher boiling point than comparable alkane or ether. Cannot H-bond to each other, so lower boiling point than comparable alcohol.



2. Solubility in water

- Carbonyl compounds can not hydrogen-bond to each other, but they can hydrogen-bond to water through the carbonyl oxygen.
- The lower aldehydes and ketones are soluble in water because they form hydrogen bonds with water.
- Aldehydes and ketones with more than six carbons are essentialy insoluble in water.
- The higher aldehydes and ketones are soluble in organic solvents such as; benzene, ether, and carbontetrachlorid.



Preparation of Aldehydes and Ketones

1- Oxidation of Alcohols

- Oxidation of alcohols gives different products depending on the *class of alcohols that is oxidized* and on the *kind of oxidizing agent that is used.*

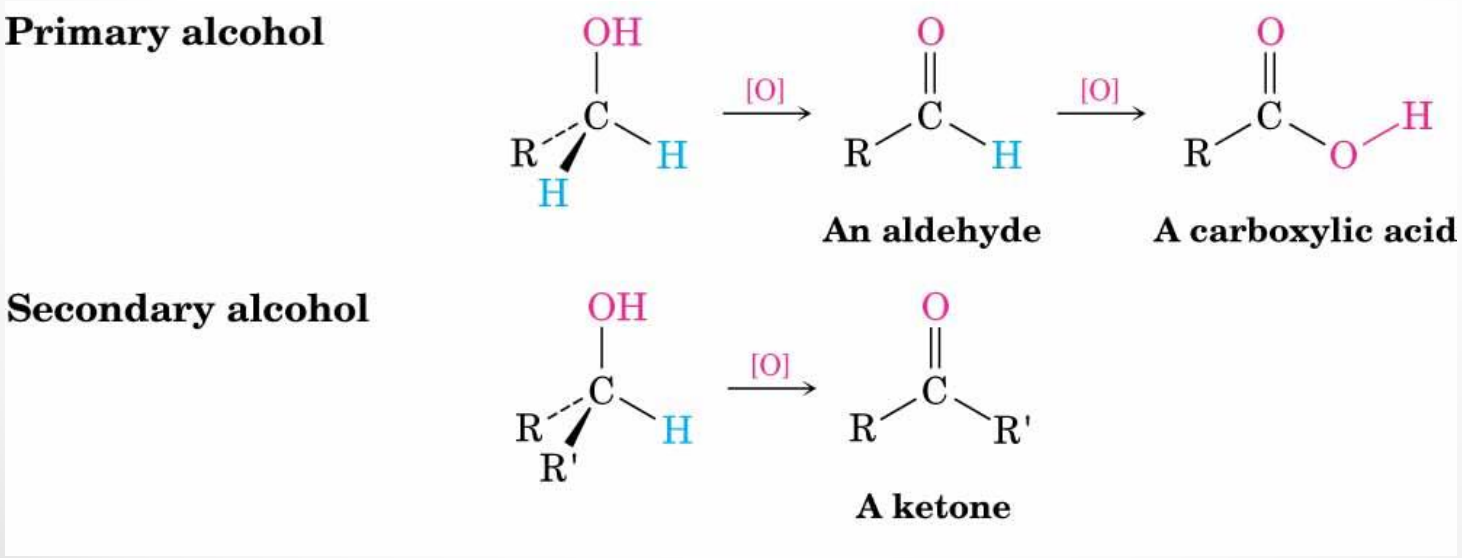
- Oxidizing agent:

  Very strong: $KMnO_4 / H^+ / \Delta$

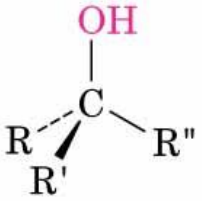
  Strong: $KMnO_4 / OH^-$ or H_2CrO_4 or $K_2Cr_2O_4 / H^+$

  Mild: CrO_3 / pyridine or Cu / 300 °C

.



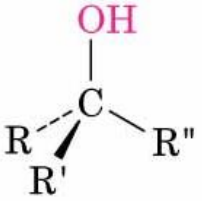
Tertiary alcohol



[O]

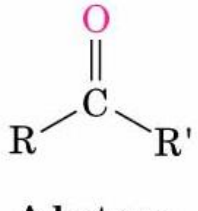
Mild or strong oxidizing

NO reaction



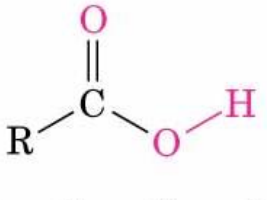
[O]

very strong oxidizing



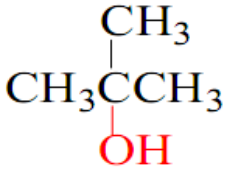
A ketone

+



A carboxylic acid

Examples:

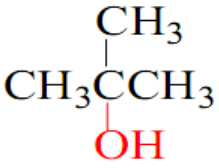


[O]

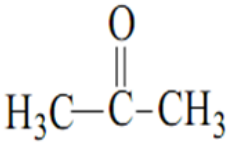
Mild or strong oxidizing

No reaction

t-butyl alcohol



$KMnO_4 / H^+ / \Delta$



Acetone

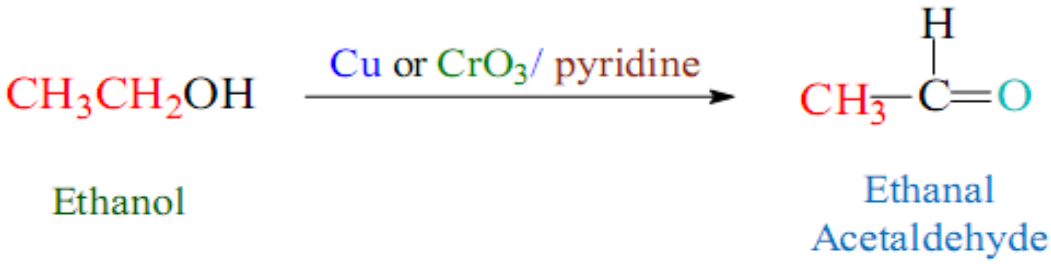
+

HCOOH

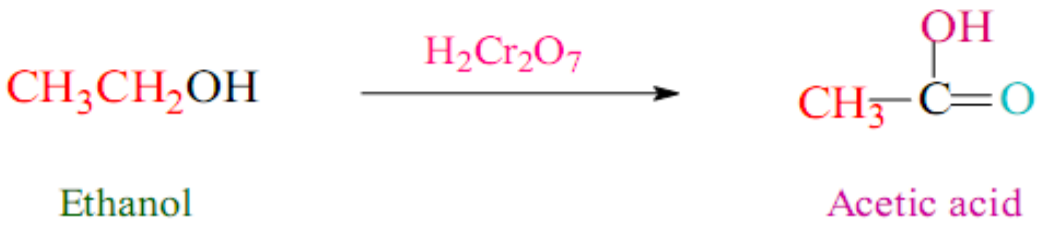
Formic acid

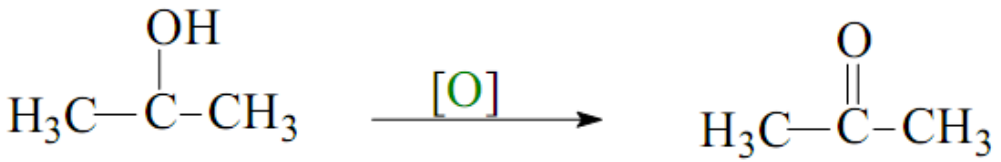
Examples:

with mild oxidizing agent



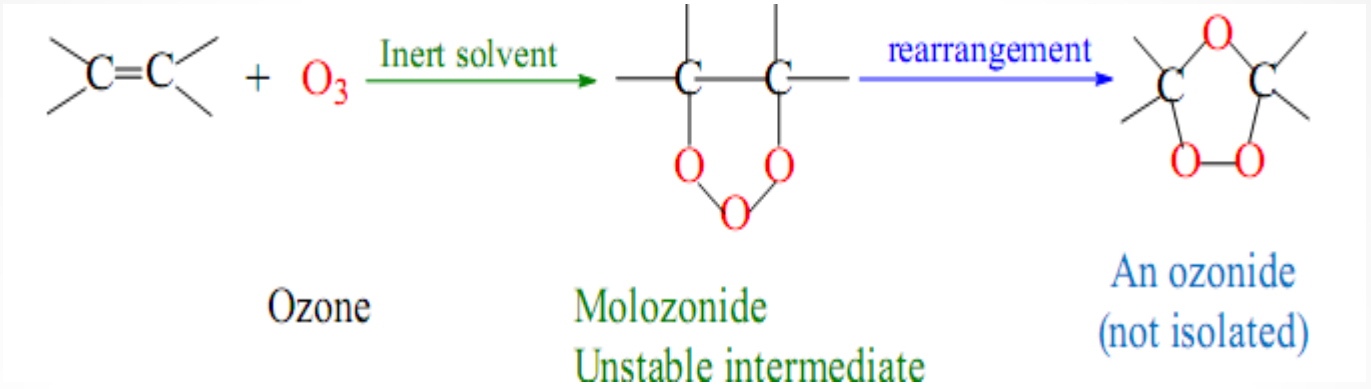
with stronger oxidizing agents

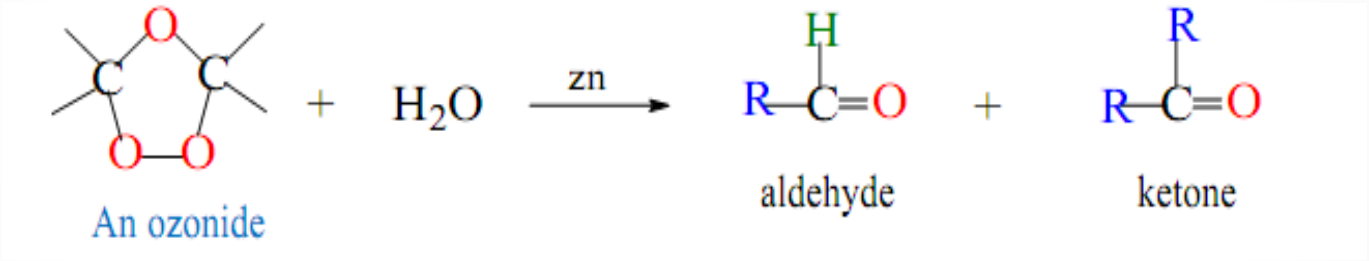




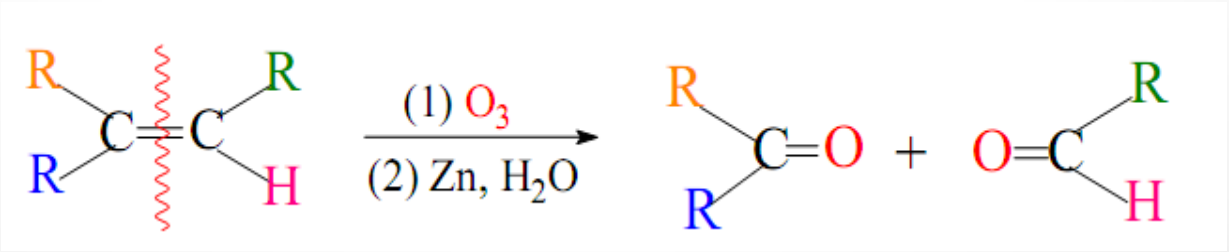
2- Ozonolysis of alkenes

Oxidation of alkenes by ozone O_3

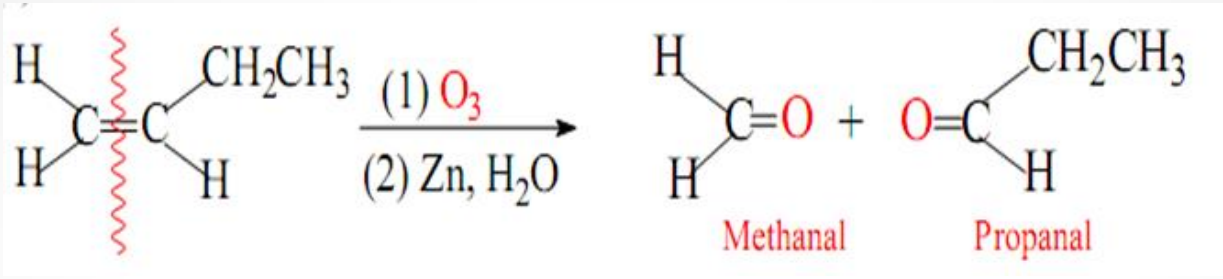


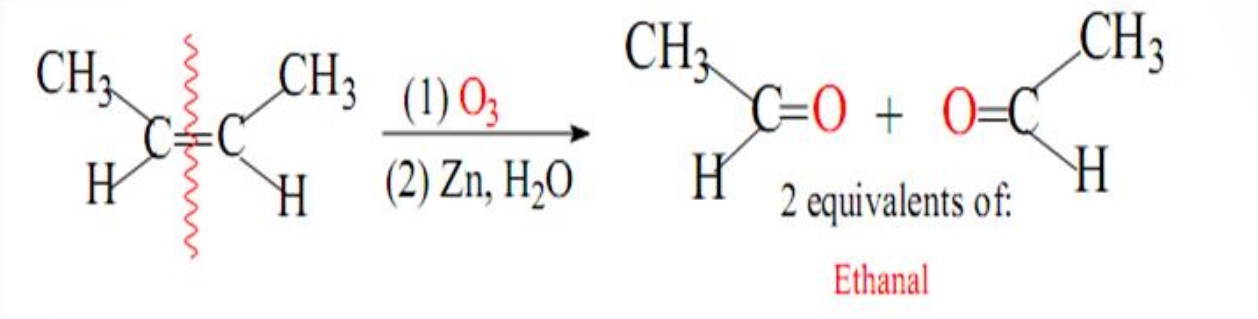


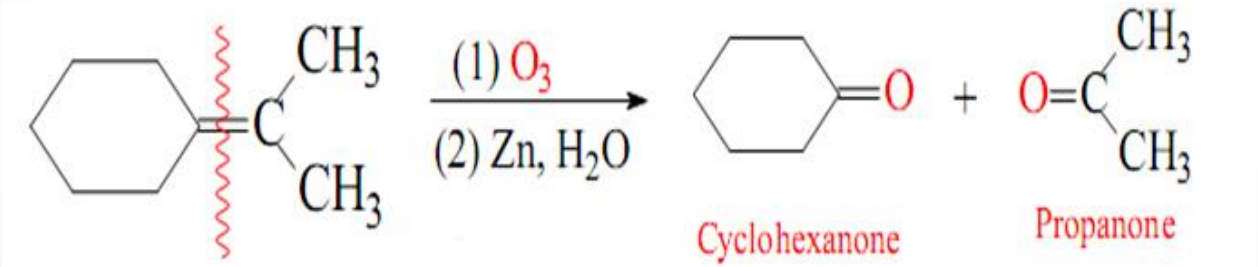
The ozonolysis reaction can be summarized by the following equation:

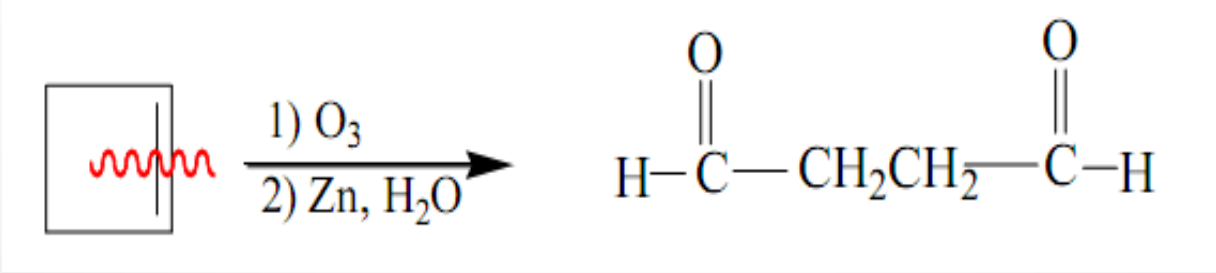


Examples:

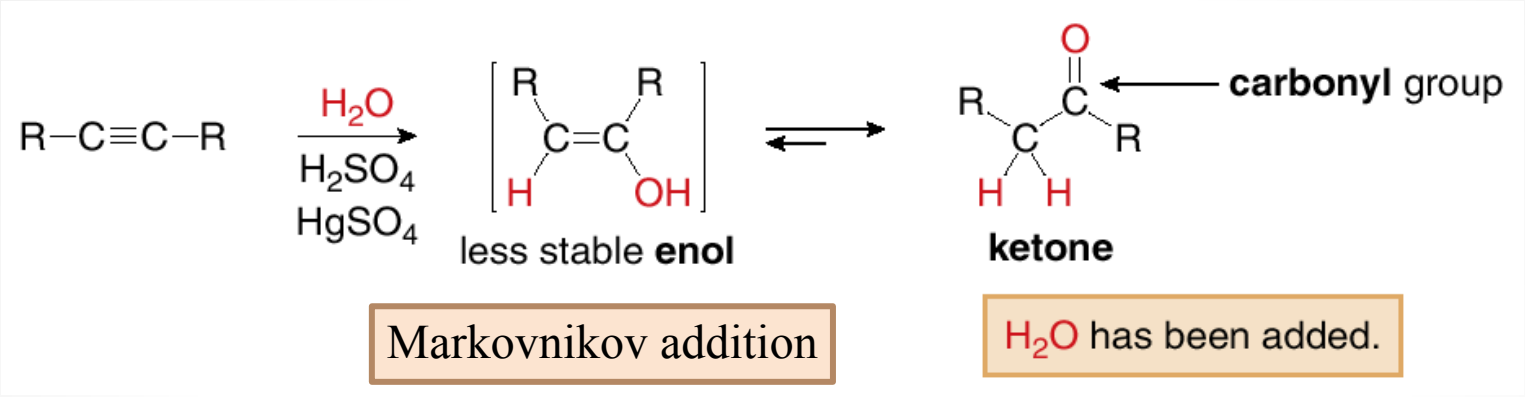

(1) O_3
(2) Zn, H_2O
Methanal
Propanal

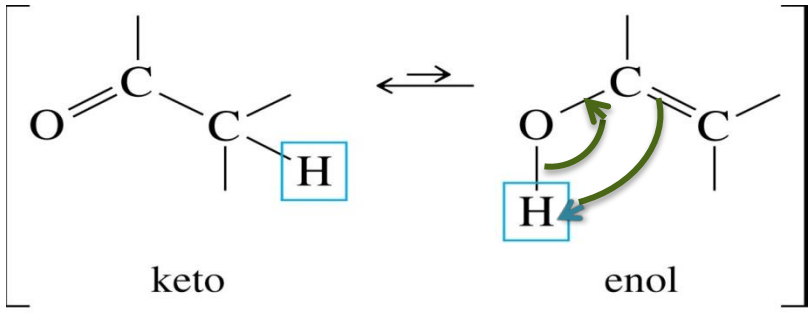

(1) O_3
(2) Zn, H_2O
2 equivalents of:
Ethanal


(1) O_3
(2) Zn, H_2O
Cyclohexanone
Propanone


1) O_3
2) Zn, H_2O

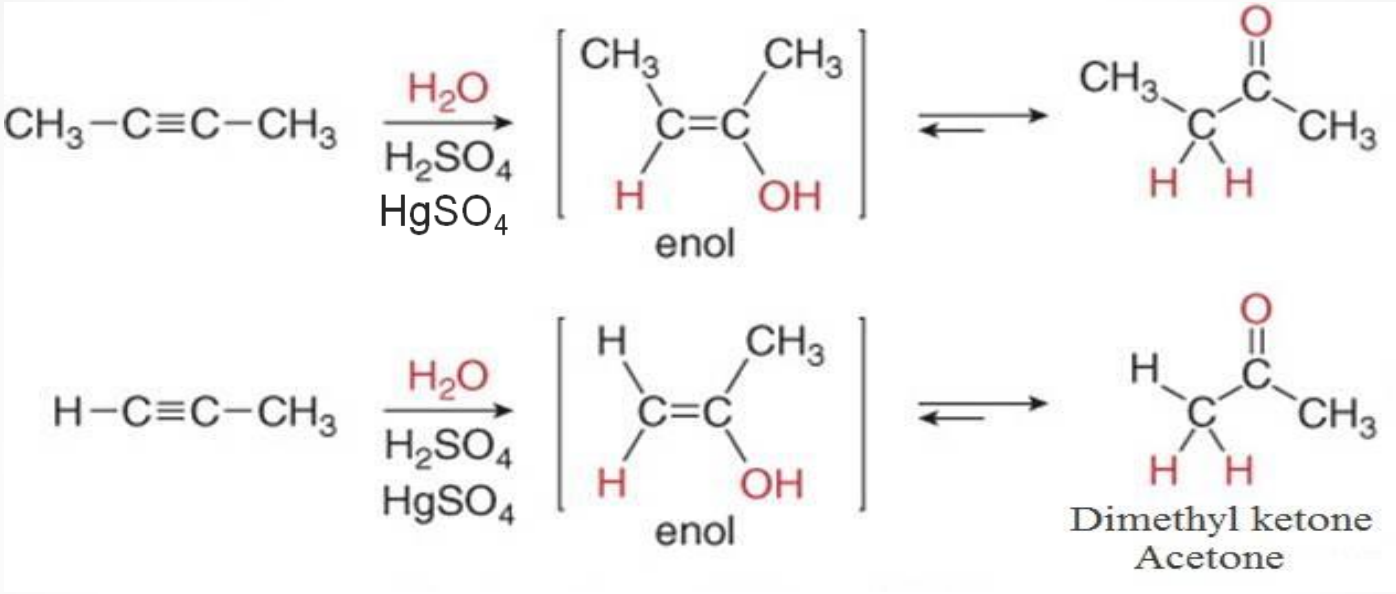
3.Hydration of alkynes: Addition of water

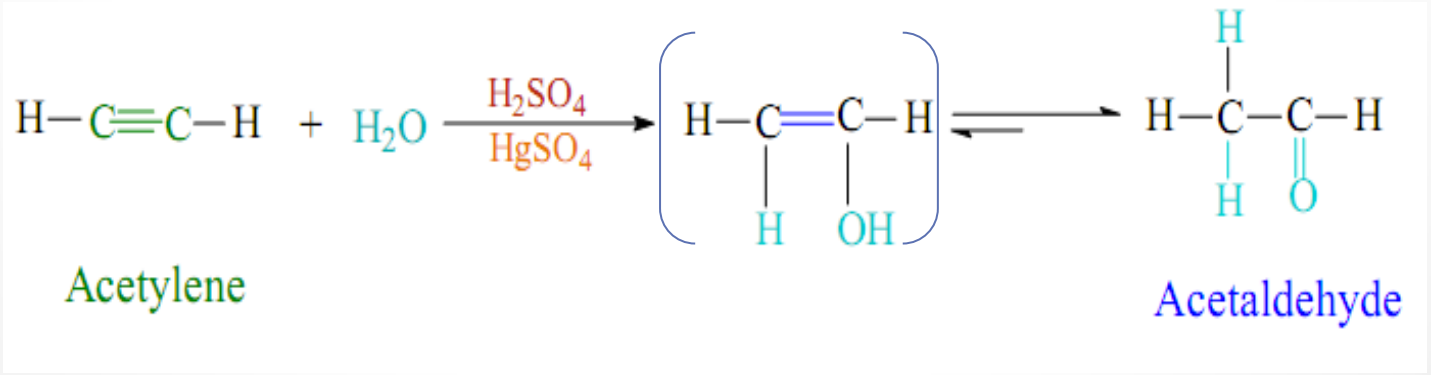




keto–enol tautomerism

Examples:

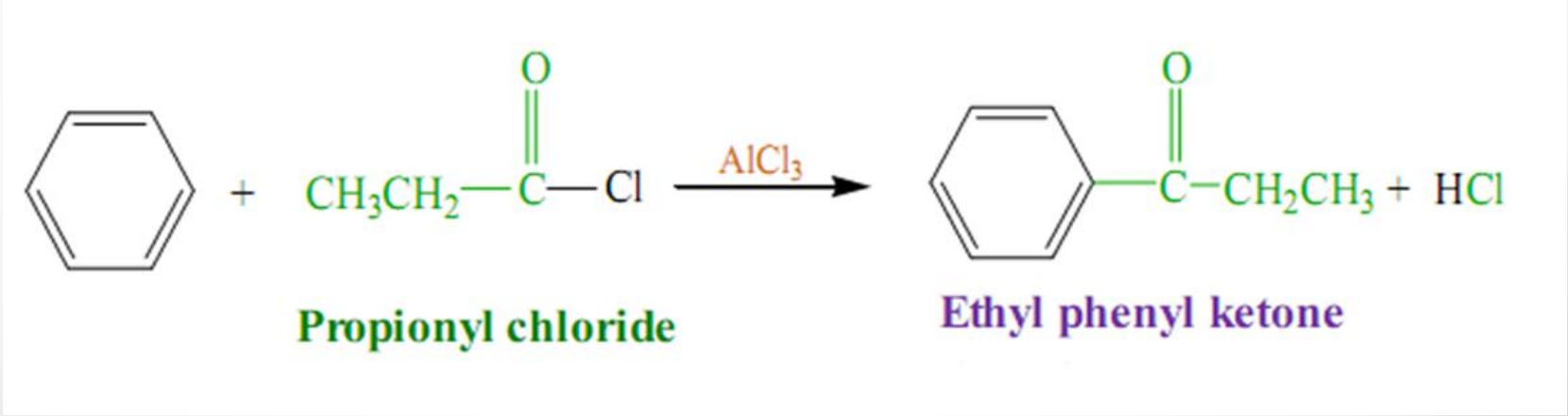

CH3–C≡C–CH3
H2O
H2SO4
HgSO4
CH3
CH3
C=C
H
OH
enol
O
CH3
C
CH3
H
H
H–C≡C–CH3
H2O
H2SO4
HgSO4
H
CH3
C=C
H
OH
enol
O
H
C
CH3
H
H
Dimethyl ketone
Acetone


H–C≡C–H + H2O
H2SO4
HgSO4
H–C=C–H
H
OH
H
H–C–C–H
H
O
Acetylene
Acetaldehyde

4- Friedel-Crafts acylation

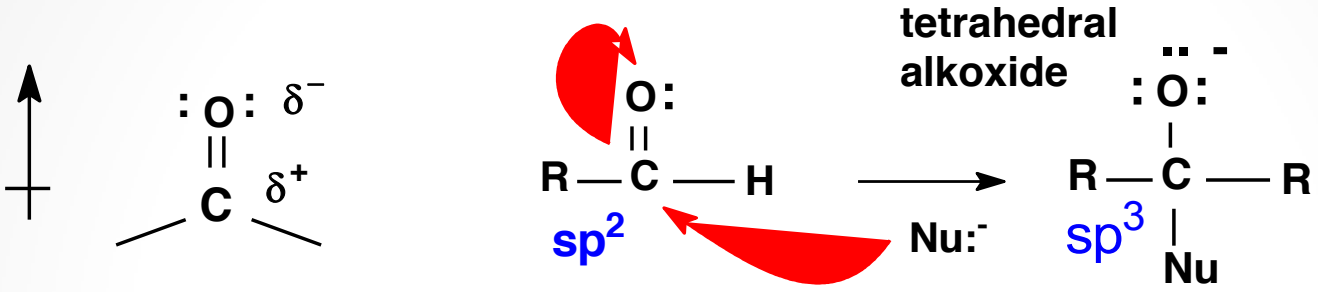
The reaction involves treatment of an aromatic ring with an acylchloride in the presence of $AlCl_3$, which acts as a catalyst.

Example:

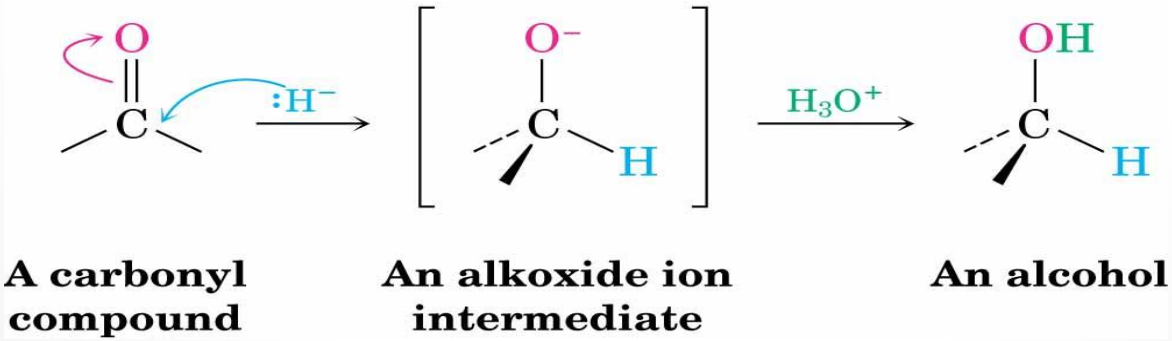


Reactions of Aldehydes and Ketones

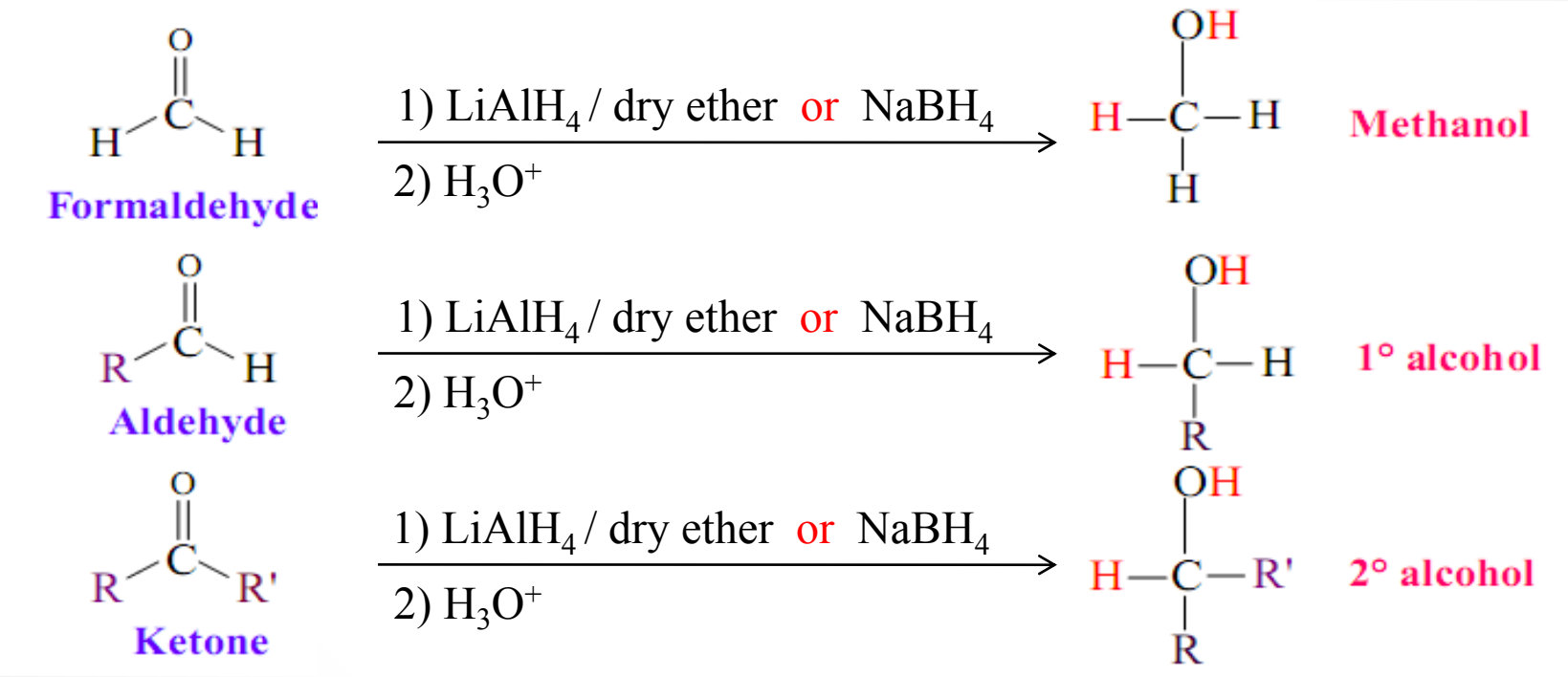
Nucleophilic Addition Reaction to the carbon-oxygen double bond.



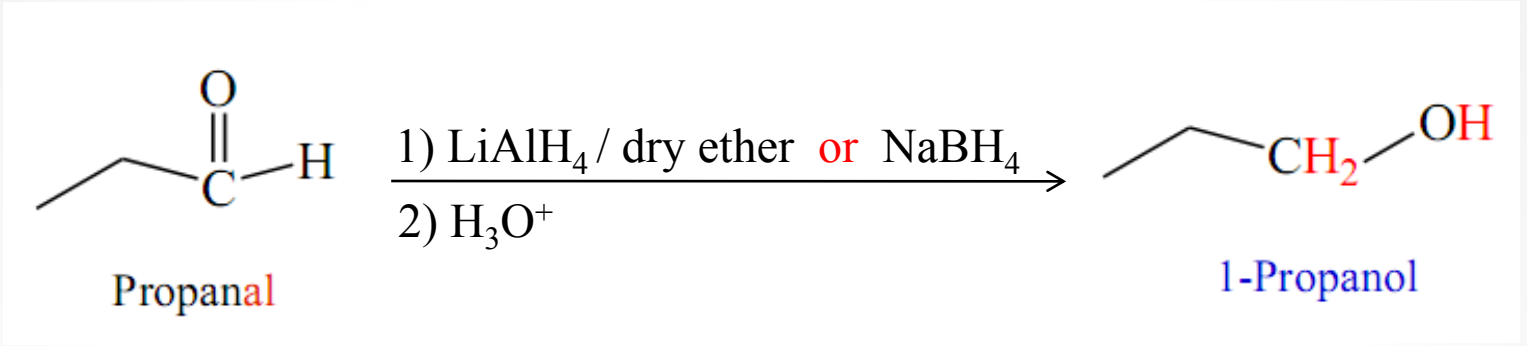
1. Addition of metal hydrides: Formation of alcohols.

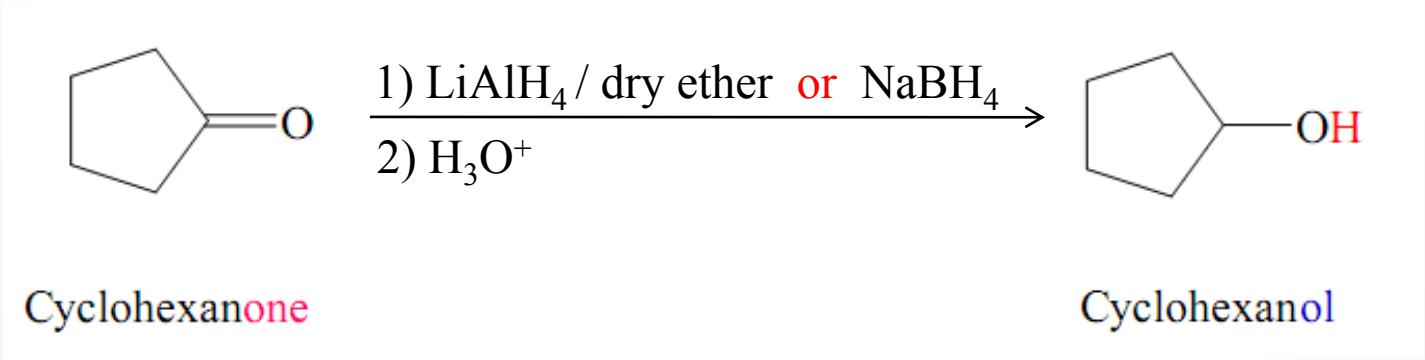


Reduction by hydride reagents, Lithium aluminium hydride $LiAlH_4$ or Sodium boron hydride $NaBH_4$.

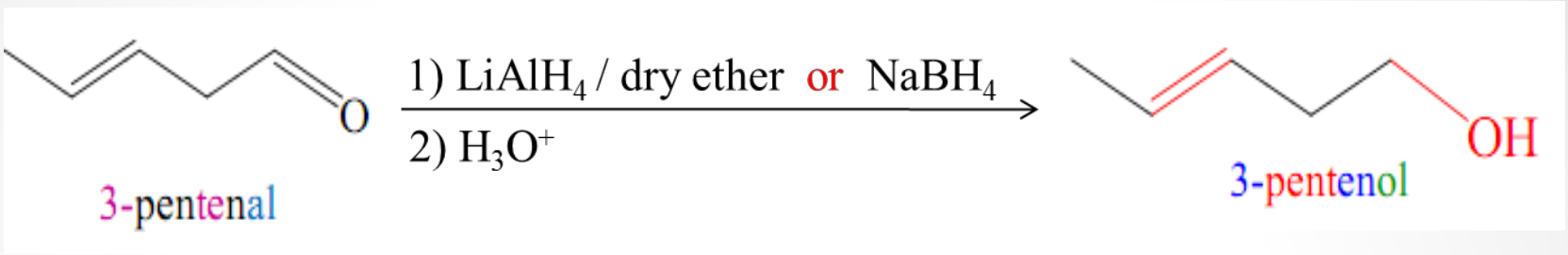


Examples:

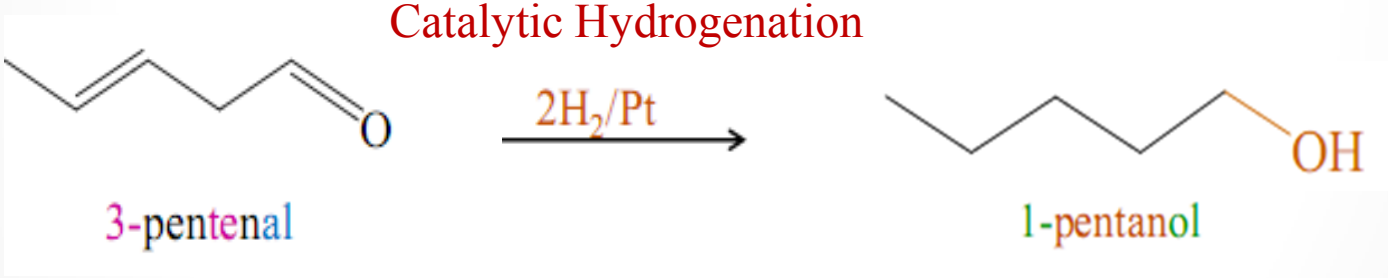

O
C
H
1) LiAlH4 / dry ether or NaBH4
2) H3O+
CH2
OH
Propanal
1-Propanol


O
1) LiAlH4 / dry ether or NaBH4
2) H3O+
OH
Cyclohexanone
Cyclohexanol

Examples:



Catalytic Hydrogenation

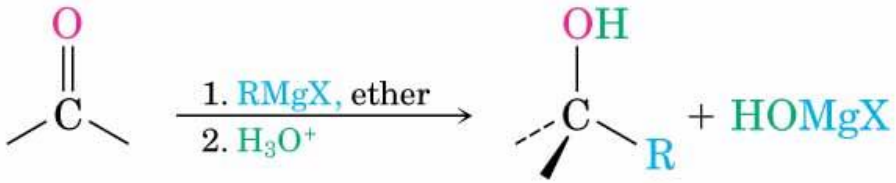


2. Addition of Grignard Reagents : Formation of alcohols.

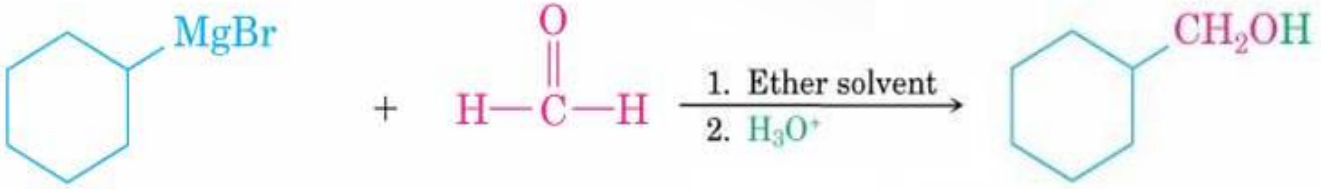
Grignard formation

R = 1°, 2°, or 3° alkyl, aryl, or vinylic
X = Cl, Br, or I

A Grignard reagent

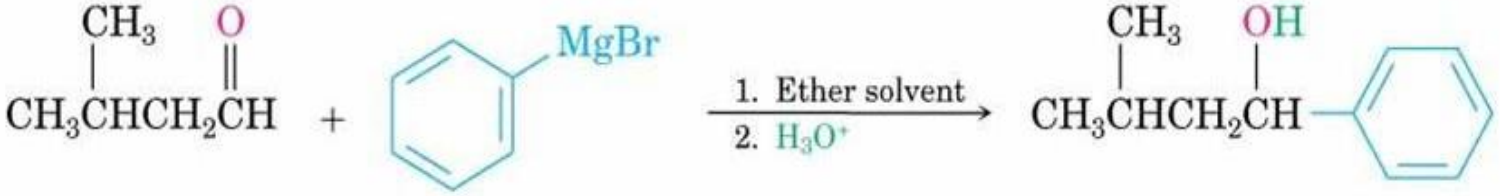


Formaldehyde reaction



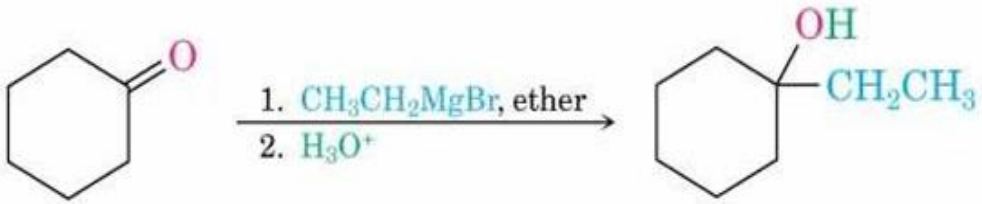
Cyclohexylmagnesium bromide + **Formaldehyde** → **Cyclohexylmethanol (a 1° alcohol)**

Aldehyde reaction



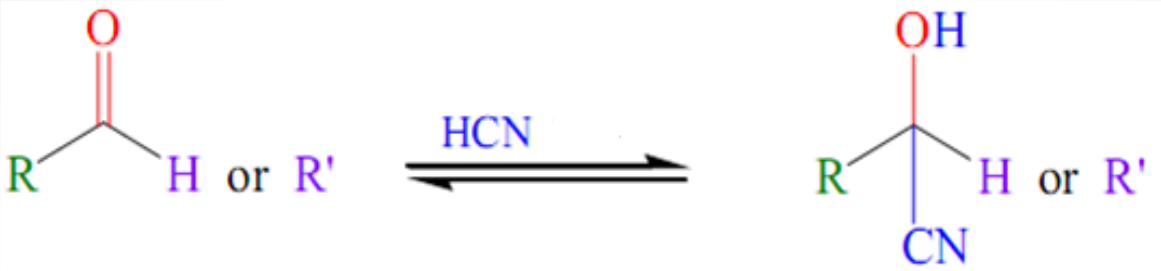
3-Methylbutanal + **Phenylmagnesium bromide** → **3-Methyl-1-phenyl-1-butanol (a 2° alcohol)**

Ketone reaction



Cyclohexanone → **1-Ethylcyclohexanol (a 3° alcohol)**

3. Addition of Hydrogen cyanide: Formation of cyanohydrin.



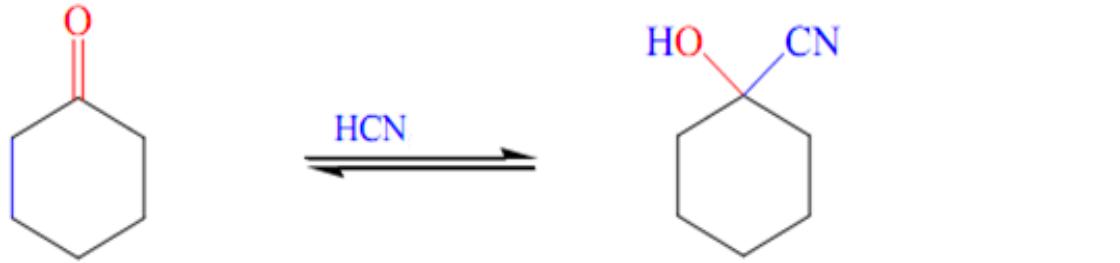
aldehydes or ketones

Cyanohydrin

Examples:

Benzaldehyde

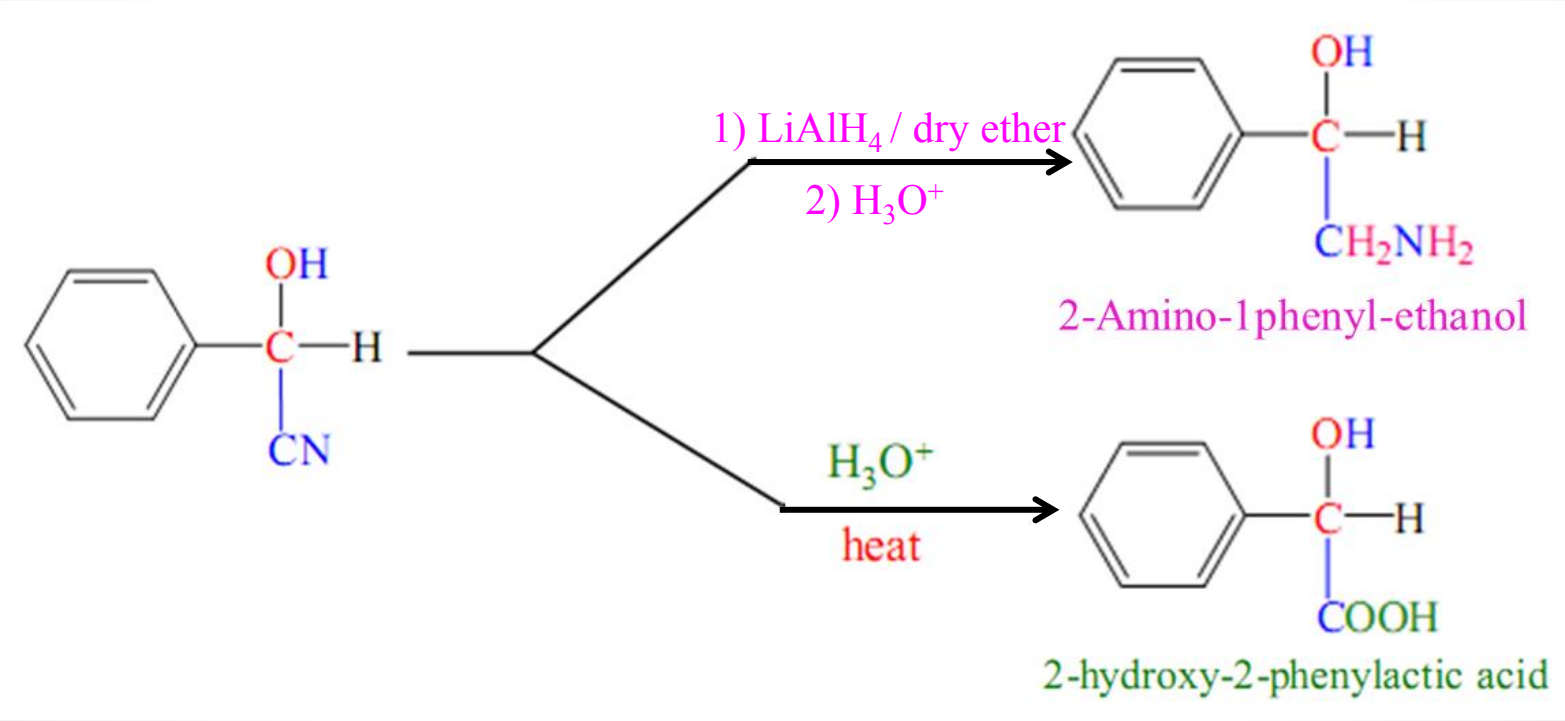
Benzaldehyde cyanohydrin



Cyclohexanone

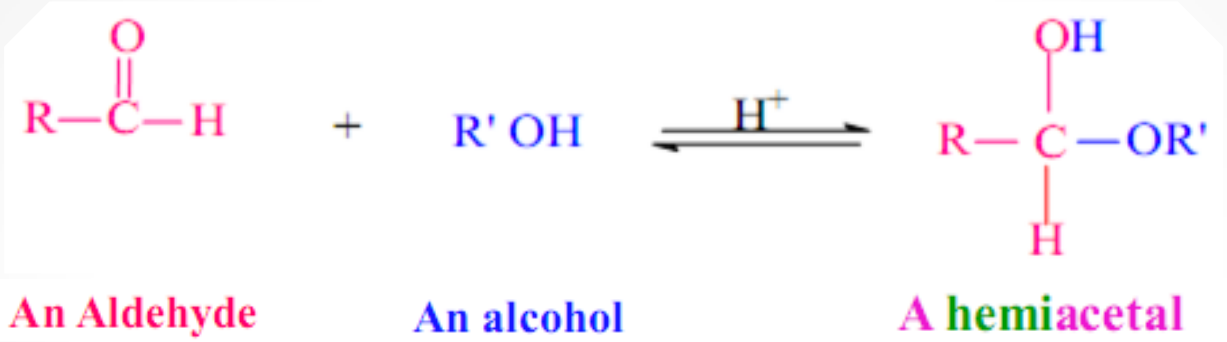
Cyclohexanone cyanohydrin

Cyanohydrins are very useful because the CN group can be converted to other functional groups.

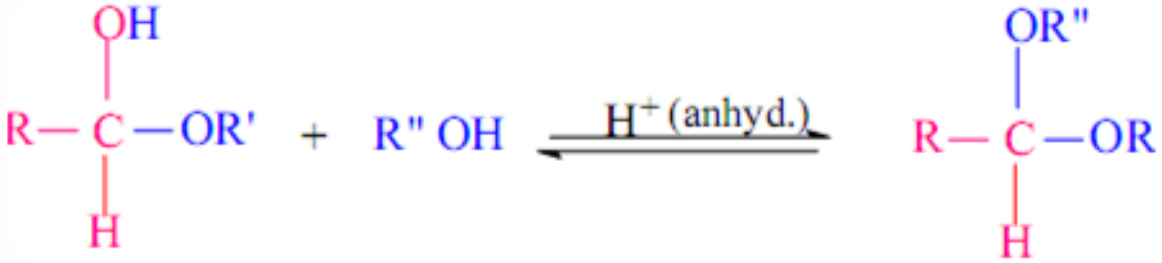


4- Nucleophilic Addition of Alcohols:

A) Formation of Hemiacetals and Acetals

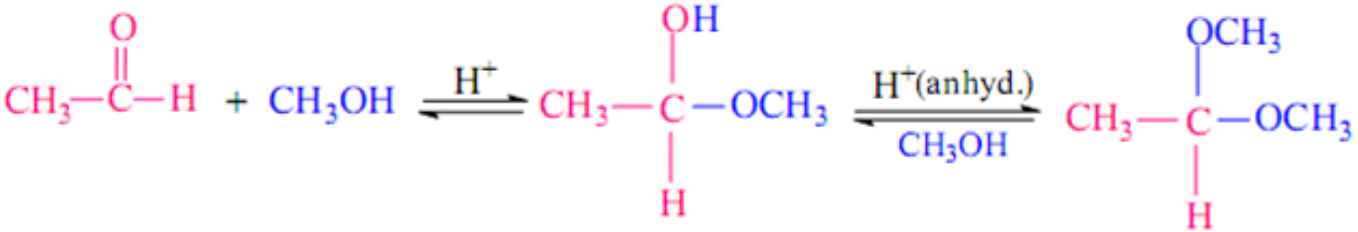


An Aldehyde **An alcohol** **A hemiacetal**



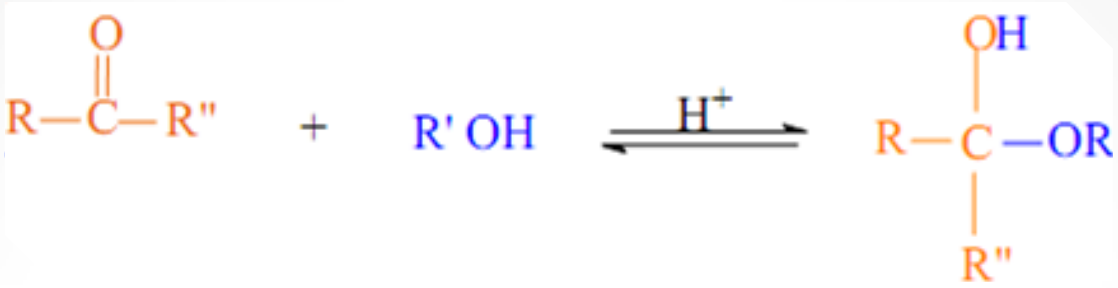
A hemiacetal **An alcohol** **Acetal**

Example:

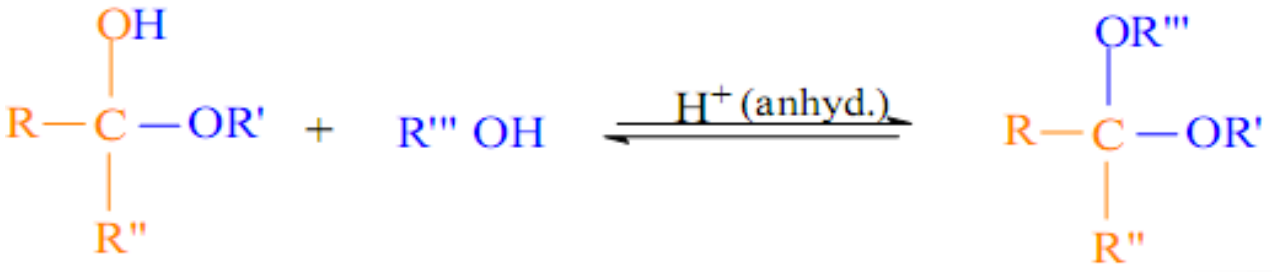


Ethanal **Methanol** **1-Methoxyethanol (A hemiacetal)** **1,1-Dimethoxyethane (An acetal)**

B) Formation of Hemiketals and Ketals

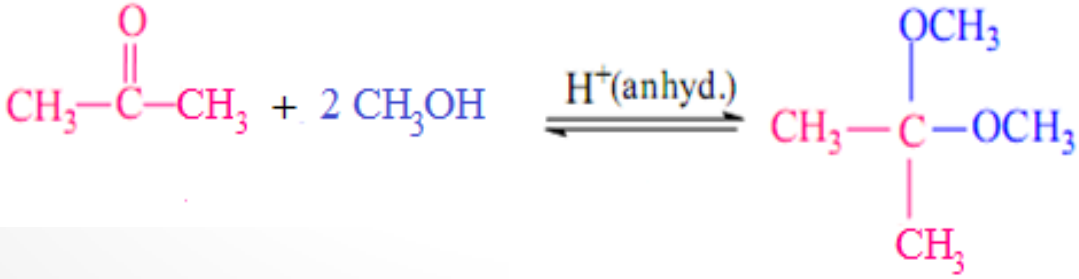


A Ketone **An alcohol** **A hemiketal**



A hemiketal **An alcohol** **ketal**

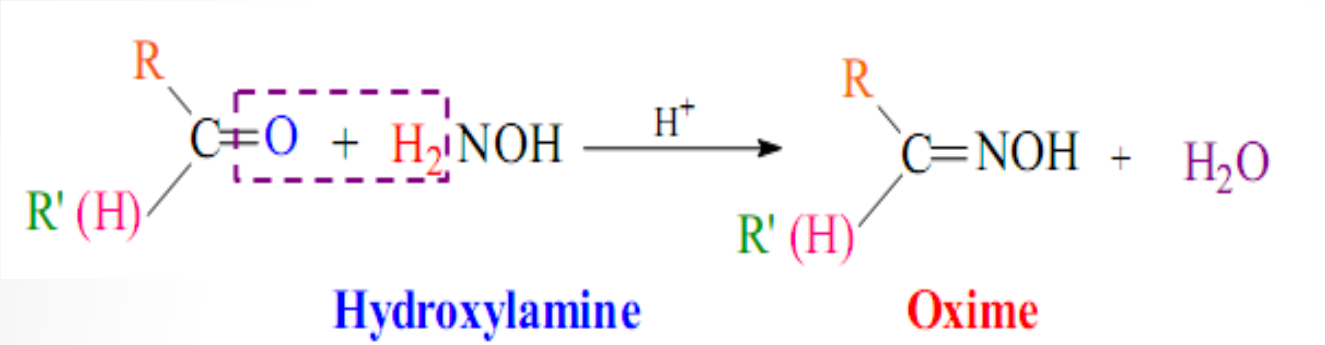
Example:



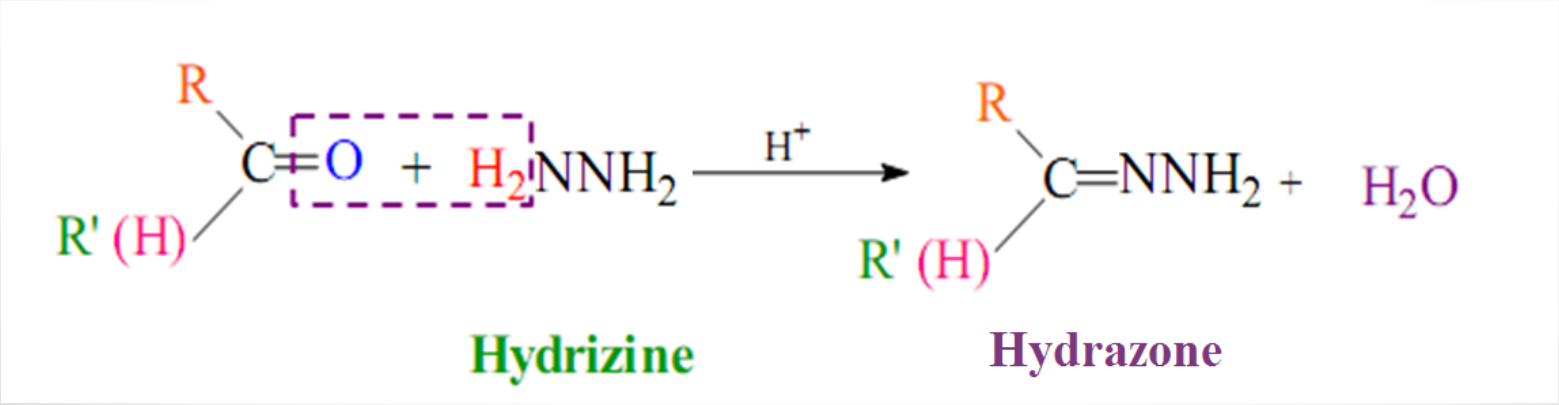
ketal

5- Addition of Ammonia and Ammonia Derivatives

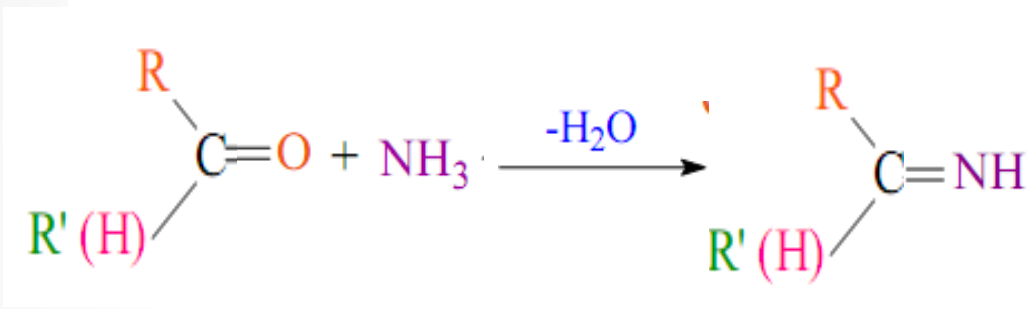
A) The Reaction with Hydroxylamine



B) The Reaction with Hydrazine



C) The Reaction with Ammonia NH_3

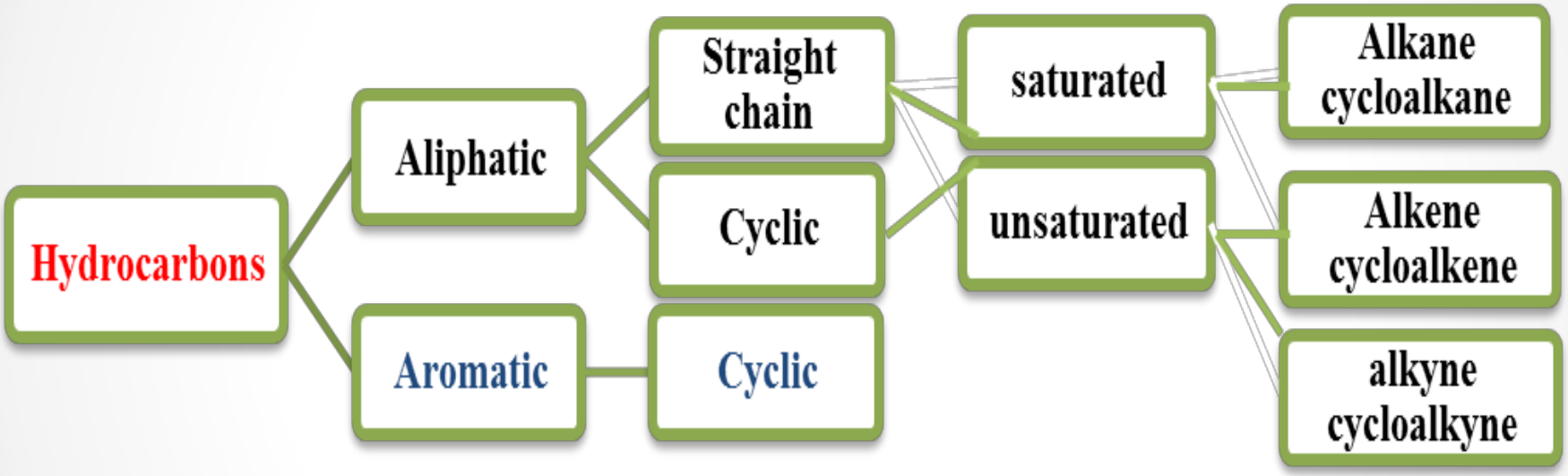


Imine

Chem. 108

Saturated Hydrocarbons: Alkanes

Chapter 2


Hydrocarbons
Aliphatic
Aromatic
Straight chain
Cyclic
Cyclic
saturated
unsaturated
Alkane cycloalkane
Alkene cycloalkene
alkyne cycloalkyne

General Molecular Formula of Hydrocarbons (Homologous Series)

Alkanes	C_nH_{2n+2} Saturated
Cycloalkanes	C_nH_{2n} (containing a single ring)
Alkenes	C_nH_{2n} (containing one double bond)
Alkynes	C_nH_{2n-2} (containing one triple bond)

Alkanes

C_nH_{2n+2} Saturated -ane

Names, Molecular Formula and Structural Formula of the first Ten Alkanes

Carbon	Name	Molecular Formula	Structural Formula
1	Methane	CH_4	CH_4
2	Ethane	C_2H_6	CH_3CH_3
3	Propane	C_3H_8	$CH_3CH_2CH_3$
4	Butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$
5	Pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$
6	Hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$
7	Heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$
8	Octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$
9	Nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$
10	Decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$

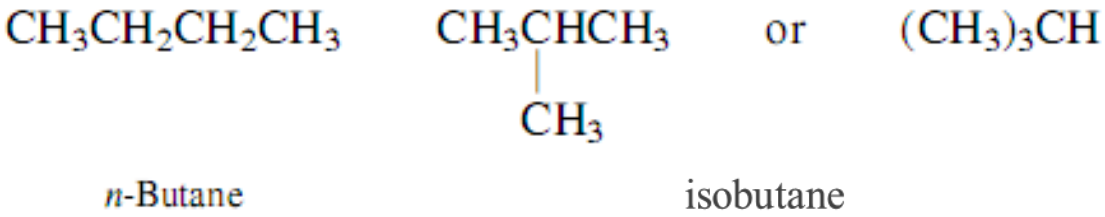
Structural Isomerism

structural isomers:

compounds with identical molecular formula and different structure

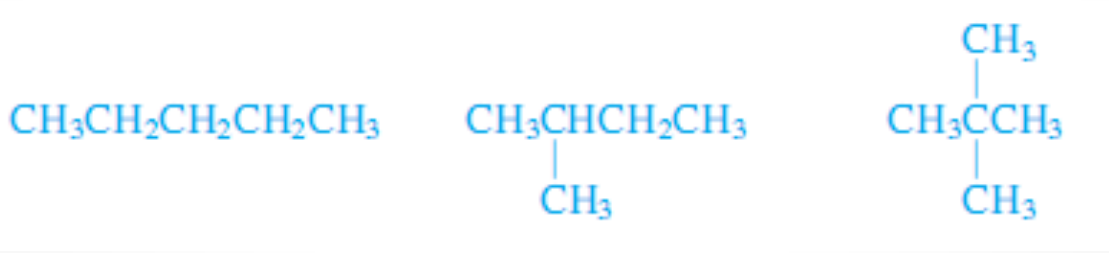
Examples:

C_4H_{10}



n-Butane isobutane

C_5H_{12}

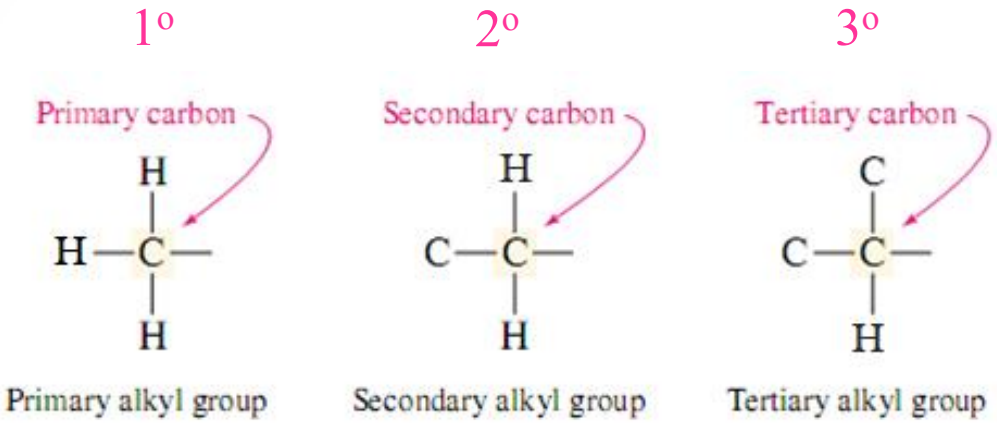


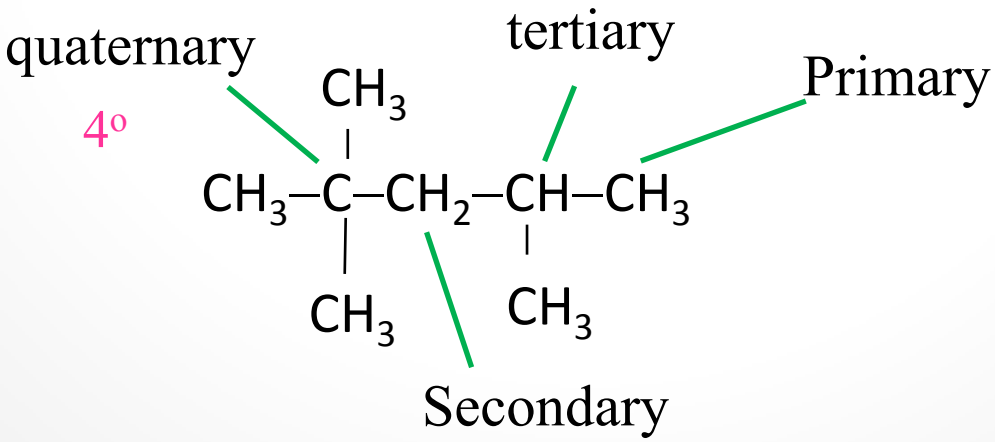
n-Pentane isopentane Neopentane

Alkyl Groups

C_nH_{2n+1}

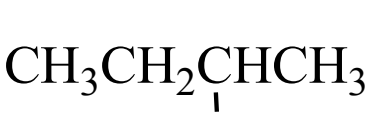
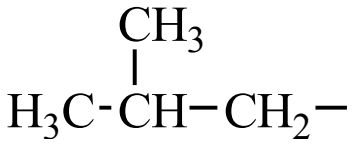
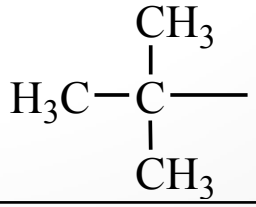
Classes of Carbons and Hydrogens :





Alkyl Groups

-ane ⟶ -yl

Methyl	CH_3-
Ethyl	CH_3CH_2-
n-Propyl	$CH_3CH_2CH_2$-
isopropyl or 1-Methylethyl	
n-Butyl	$CH_3CH_2CH_2CH_2$-
sec-Butyl or 1-Methylpropyl	
isobutyl or 2-Methylpropyl	
tert-Butyl or 1,1-dimethylethyle	

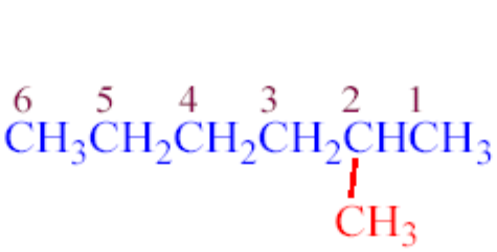
The IUPAC System of Nomenclature

1. Identifying the parent hydrocarbon chain (the longest one)

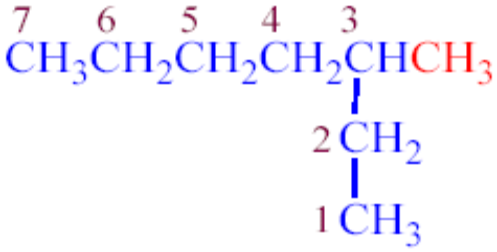
2. Numbering the chain (starting at the end that a side chain is nearer from)

3. Listing the side-chains before the of parent chain

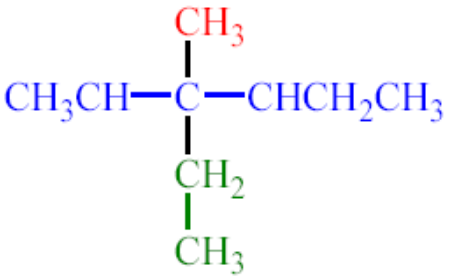
(in alphatbetical order, giving the number of the carbon atom of the parent chain)



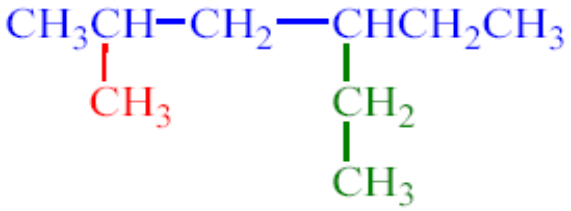
2-Methylhexane



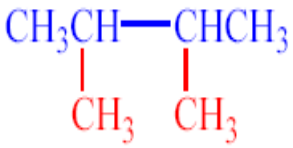
3-Methylheptane



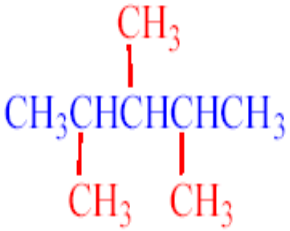
3-Ethyl-3-methylhexane



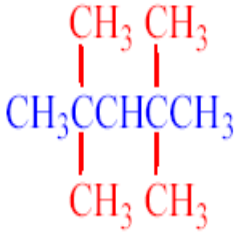
4-Ethyl-2-methylhexane



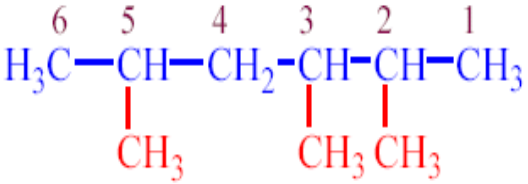
2,3-Dimethylbutane



2,3,4-Trimethylpentane

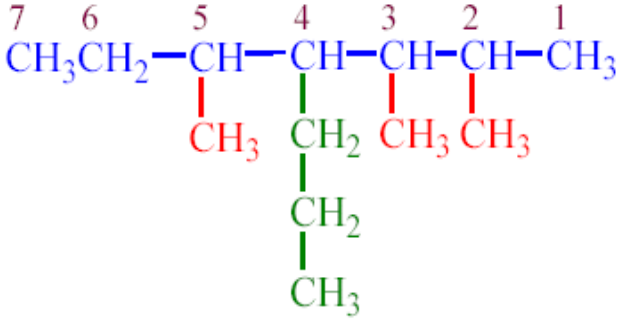


2,2,4,4-Tetramethylpentane



2,3,5-Trimethylhexane

(*not* 2,4,5-Trimethylhexane)



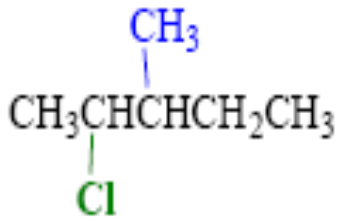
2,3,5-Trimethyl-4-propylheptane

(four substituents)

If any other substituents are found on the parent chain, all these substituents are arranged alphabetically.

- $-NO_2$ nitro
- $-NH_2$ amino
- -CN cyano
- - Cl Chloro
- -Br bromo
- - I iodo

Examples:



2-Chloro-3-methylpentane

CH_3CH_2Cl

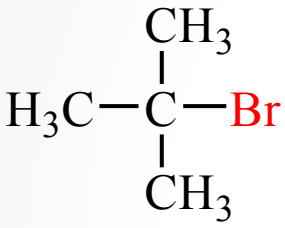
Chloroethane

Ethyl chloride

$CH_3CH_2CH_2Br$

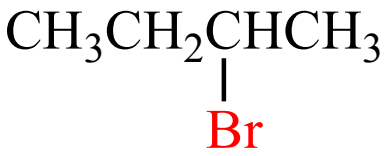
1-Bromopropane

n-Propyl bromide

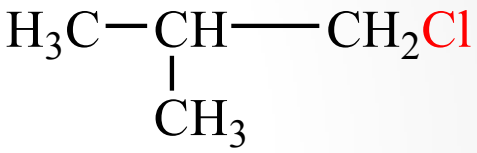


2-Bromo-2-methylpropane

tert-Butyl bromide

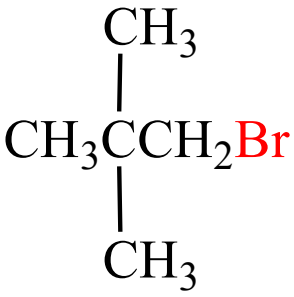


2-Bromobutane



1-Chloro-2-methylpropane

isobutyl chloride



1-Bromo-2,2-dimethylpropane

Neopentyl bromide

Physical properties of alkanes

A Physical States and Solubilities

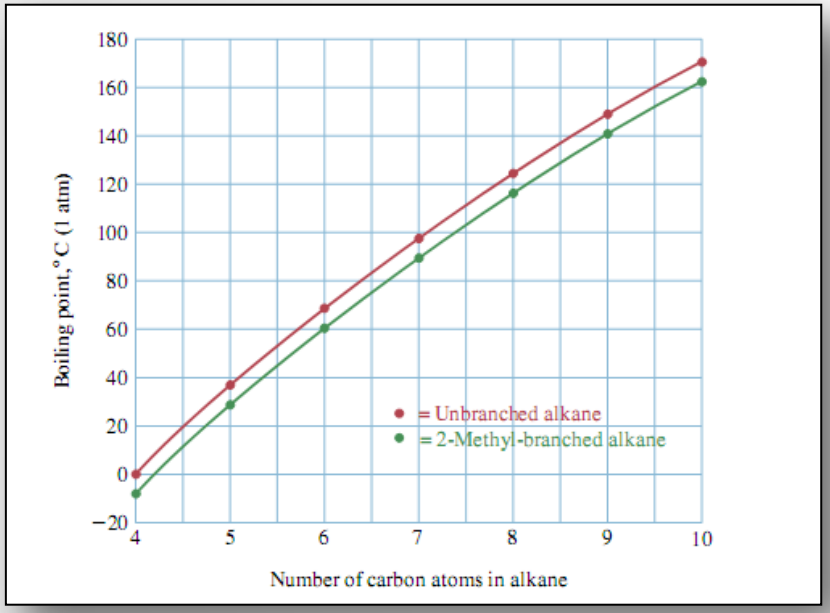
C_1-C_4	colorless gases
C_5-C_{17}	liquids with characteristic odor
C_{20} and more	odorless waxy materials

Alkanes are nonpolar compounds. Thus alkanes are soluble in the nonpolar solvents such as carbon tetrachloride (CCl_4) and benzene (C_6H_6), but they are insoluble in polar solvents such as water.

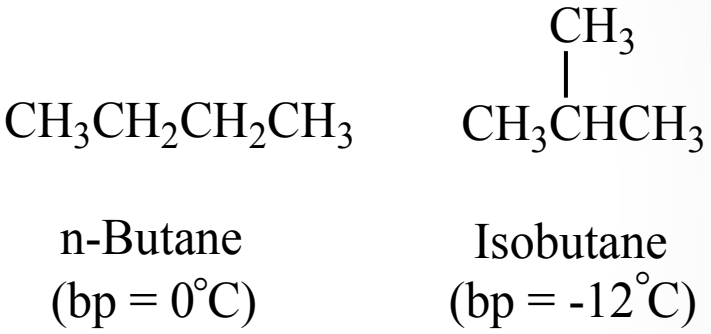
B Boiling Points

The boiling points of the normal alkanes increase with increasing molecular weight.

Branching of the alkane chain lowers the boiling point.



Example:



n-Butane (bp = 0°C)

Isobutane (bp = -12°C)

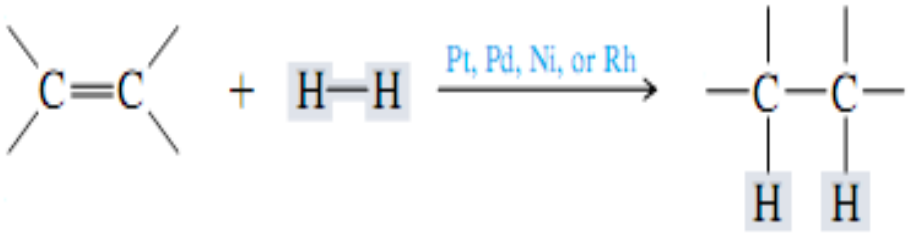
C Melting Points

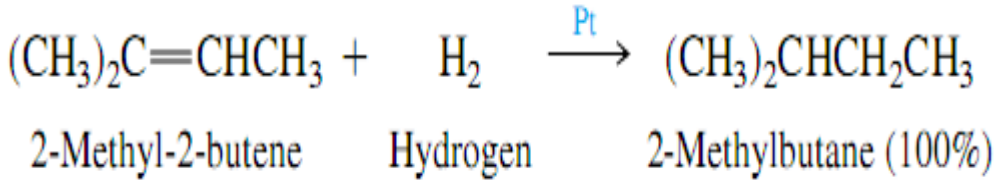
Generally, melting point increases as molecular weight increases, but with no particular pattern.

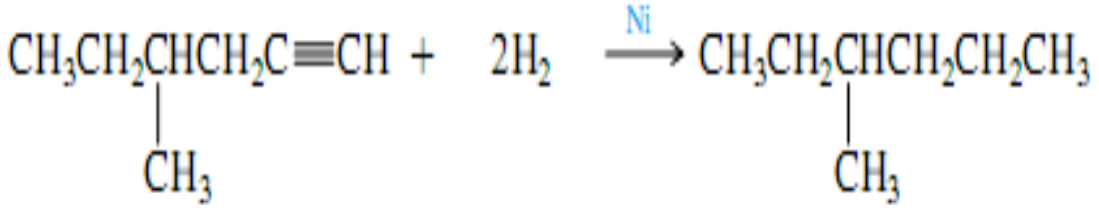
Preparation of alkanes

(1) From Alkenes & Alkynes

Catalytic Hydrogenation

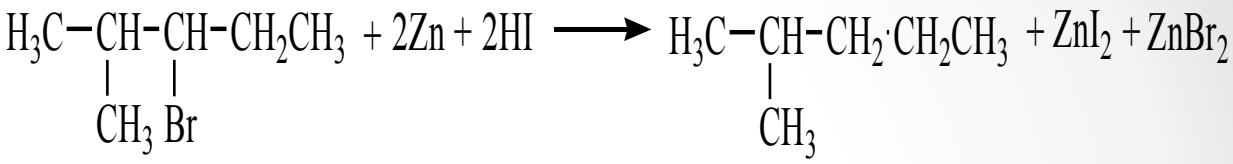






(2) From alkyl Halides

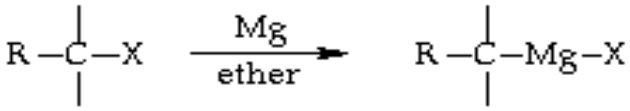
A) Reduction of alkyl halides



3-Bromo-2-methyl-pentane

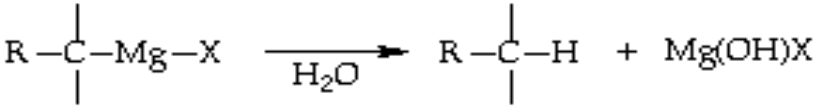
2-Methyl-pentane

B) Hydrolysis of Grignard Reagent

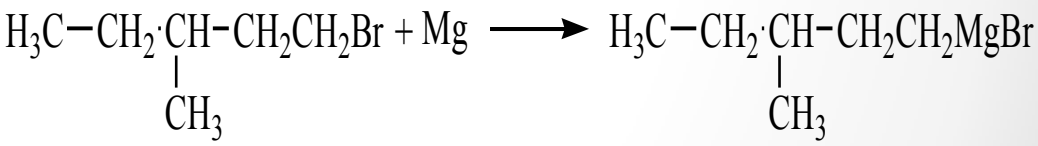


an alkyl halide

a Grignard reagent

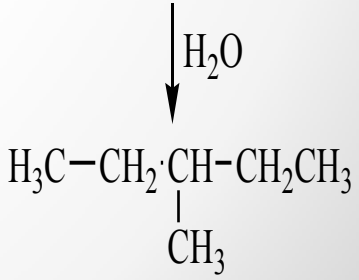


alkane



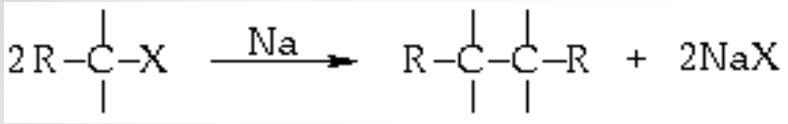
1-Bromo-3-methyl-pentane

Grignard reagent



3-Methyl-pentane

C) Wurtz Reaction

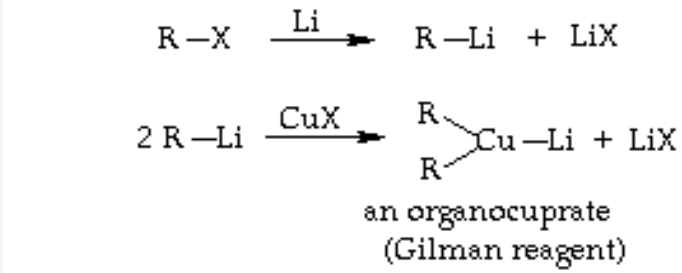


symmetrical alkane

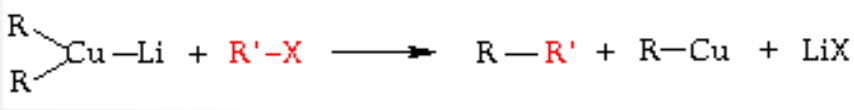
$$2\ CH_3(CH_2)_3CH_2Br + 2\ Na \longrightarrow CH_3(CH_2)_8CH_3 + 2\ NaBr$$

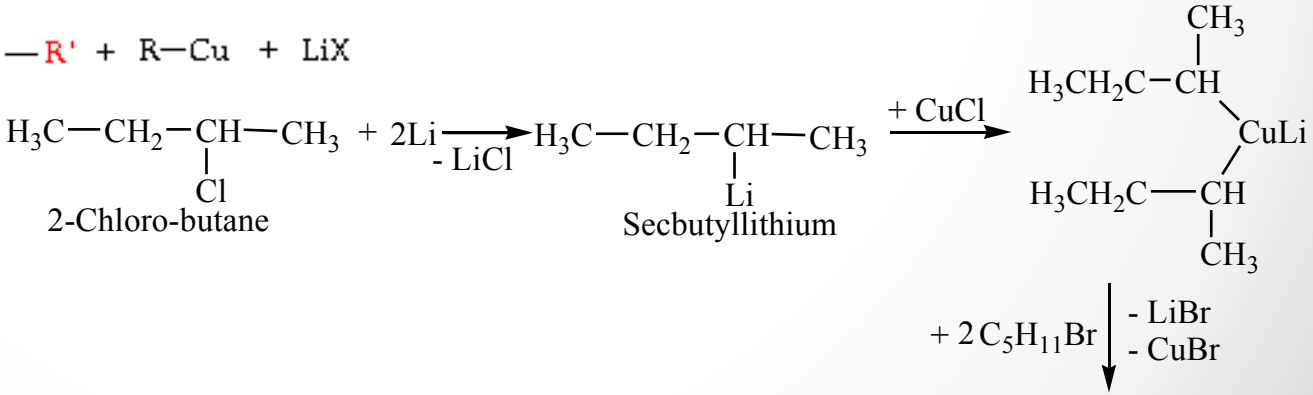
1-Bromo-pentane — Decane

D) Corey-House (Gilman reagent)



an organocuprate (Gilman reagent)

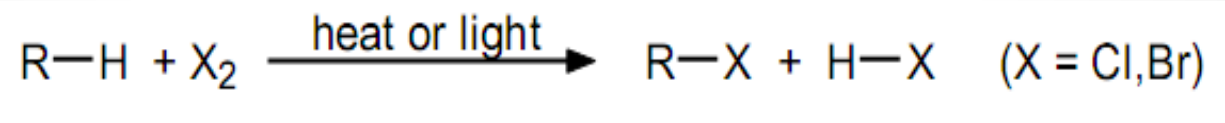




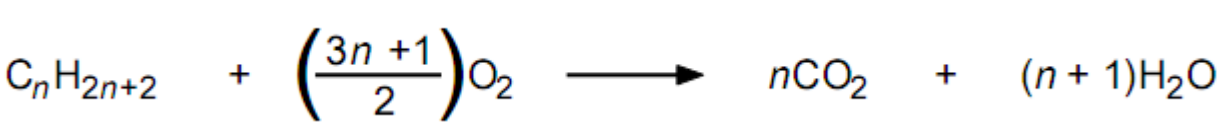
3-Methyl-octane

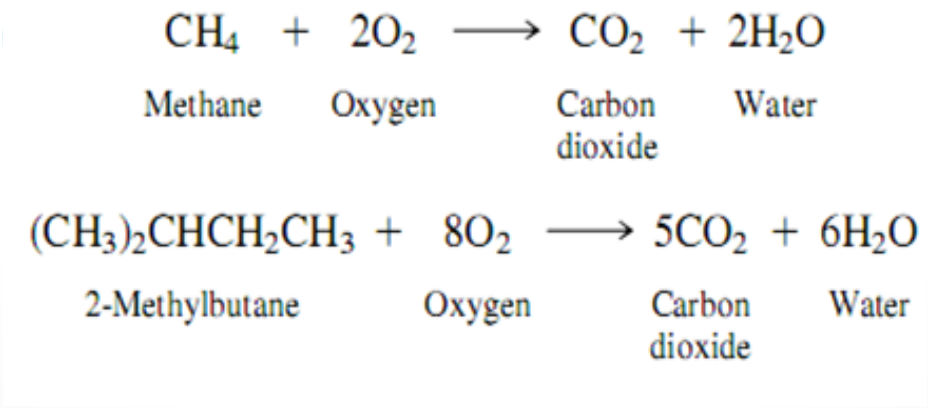
Reactions of alkanes

(1) Halogenation

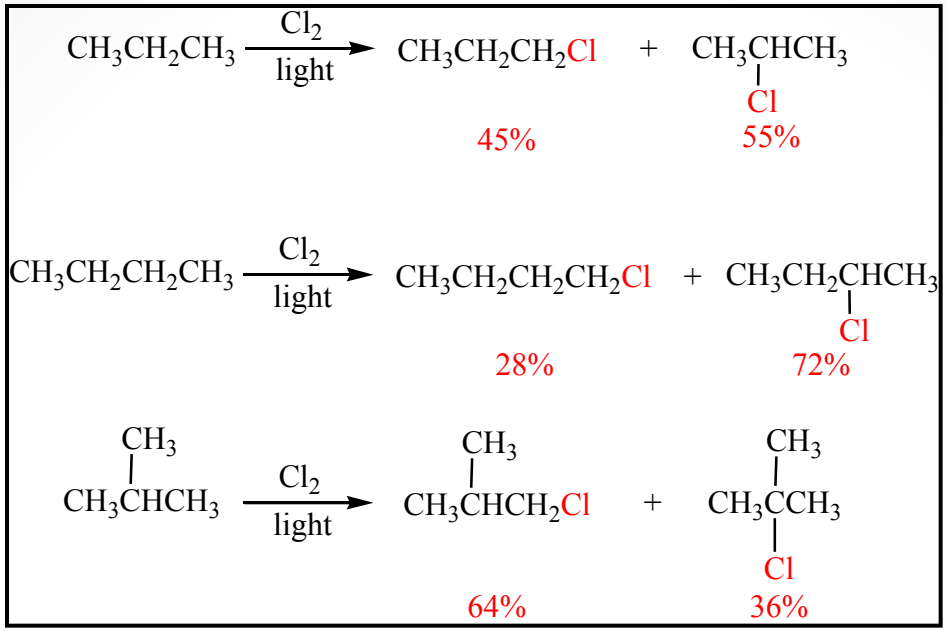


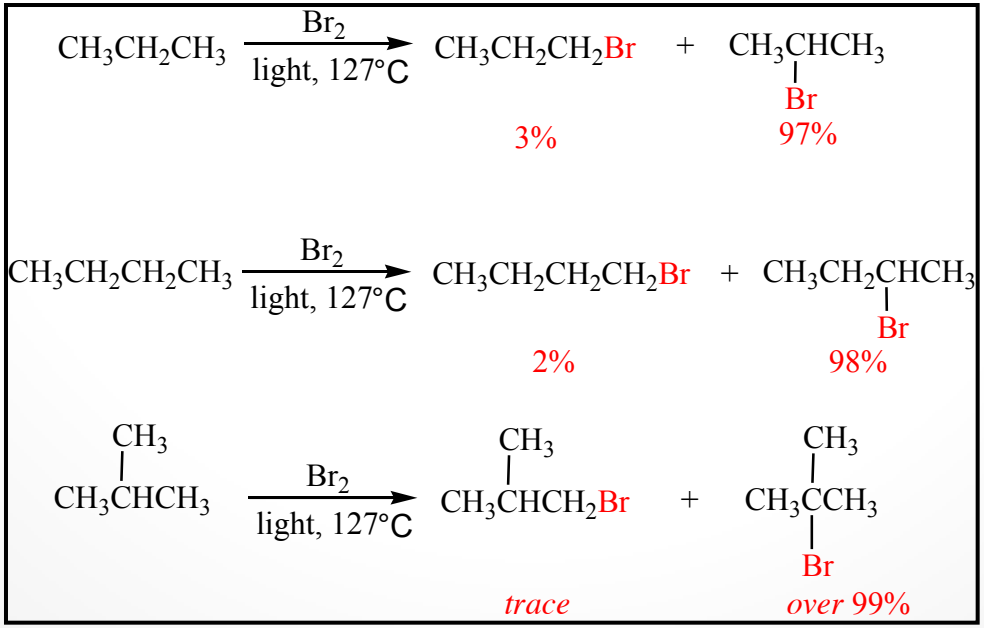
(2) Combustion





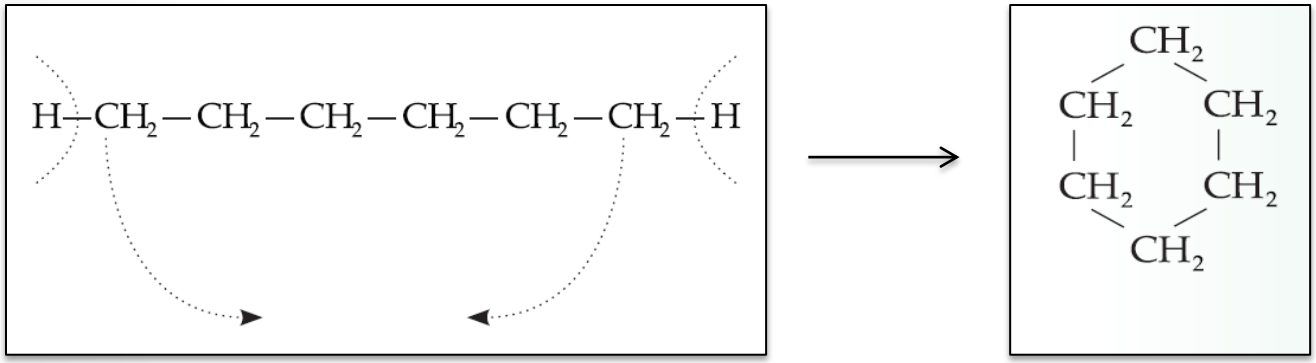
Selectivity in Halogenation Reactions





Cycloalkanes

C_nH_{2n} containing a single ring



$C_nH_{2n+2} \longrightarrow C_nH_{2n}$

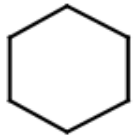
Nomenclature of Cycloalkane

cycol-

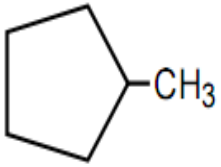
Cyclopropane

Cyclobutane

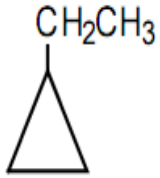
Cyclopentane



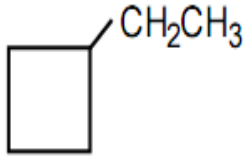
Cyclohexane



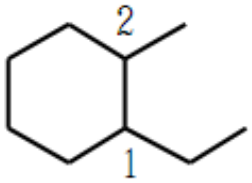
methylcyclopentane



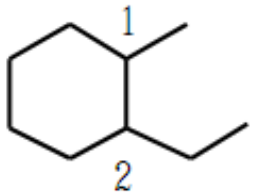
ethylcyclopropane



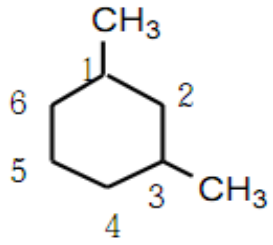
ethylcyclobutane



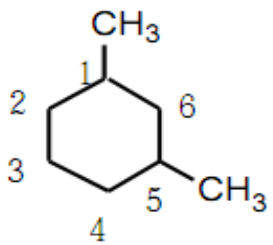
1-Ethyl-2-methylcyclohexane



-not-
2-Ethyl-1-methylcyclohexane

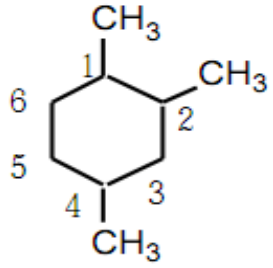


1,3-Dimethylcyclohexane

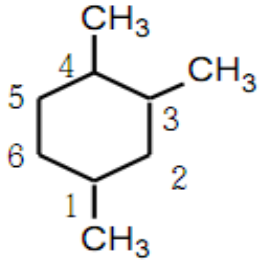


-not-

1,5-Dimethylcyclohexane

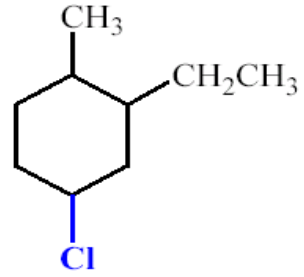


1,2,4-Trimethylcyclohexane
(1 + 2 + 4 = 7)

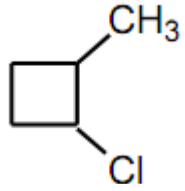


-not-

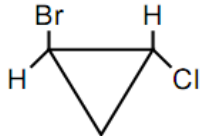
1,3,4-Trimethylcyclohexane
(1 +3 + 4 = 8)



4-Chloro-2-ethyl-1-methylcyclohexane
(not **1-Chloro-3-ethyl-4-methylcyclohexane**)



1-Chloro-2-methylcyclobutane



1-bromo-2-chlorocyclopropane

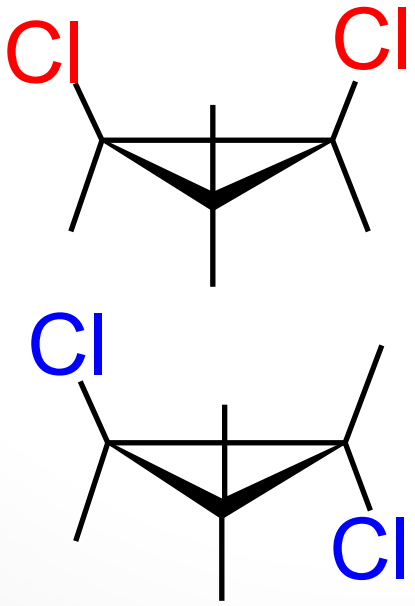
Geometric Isomerism in Cycloalkane

Cis-Trans Isomerism

Ring structures like C=C restrict rotation and therefore can result in cis and trans isomers.

The Trans-isomer is the molecule with branches on OPPOSITE sides of the ring

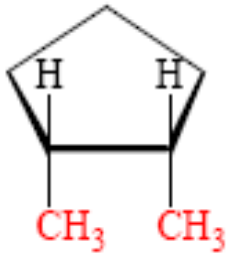
The Cis-isomer is the molecule with branches on the SAME side of the ring.



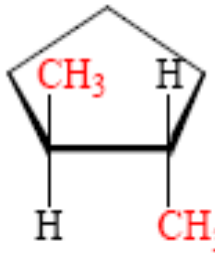
cis-1,2-dichlorocyclopropane

place designation in front of name

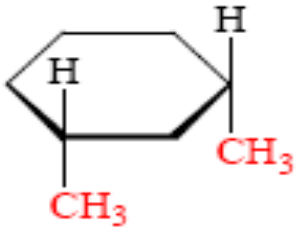
trans-1,2-dichlorocyclopropane



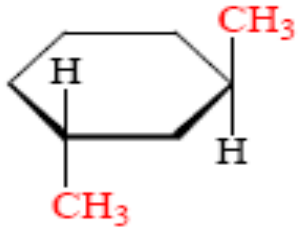
cis-1,2-Dimethylcyclopentane



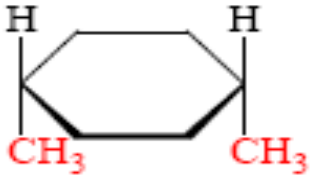
trans-1,2-Dimethylcyclopentane



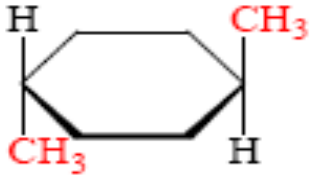
cis-1,3-Dimethylcyclohexane



trans-1,3-Dimethylcyclohexane



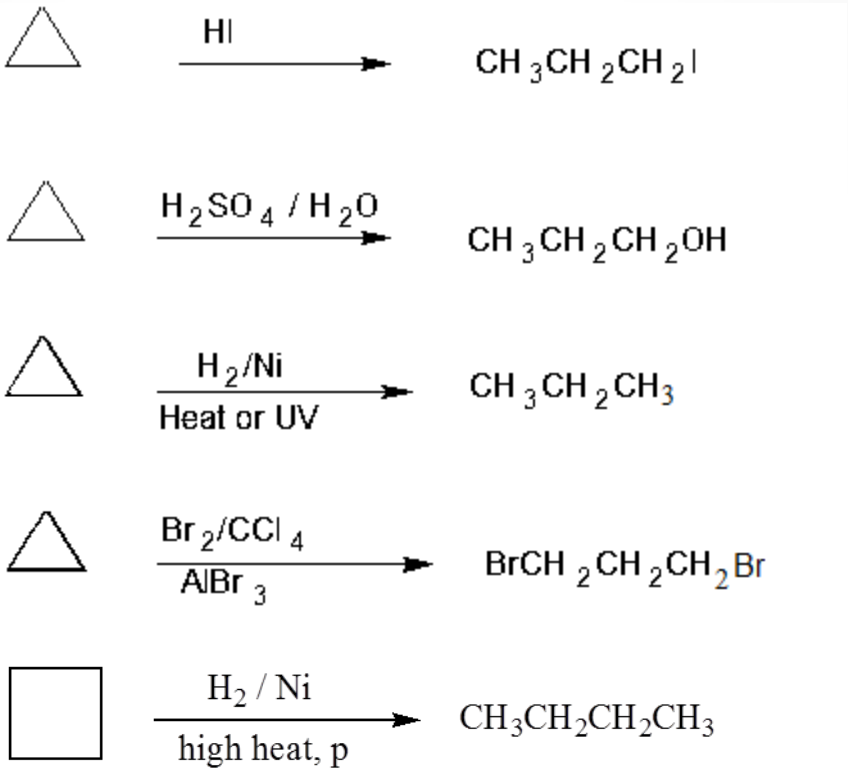
cis-1,4-Dimethylcyclohexane



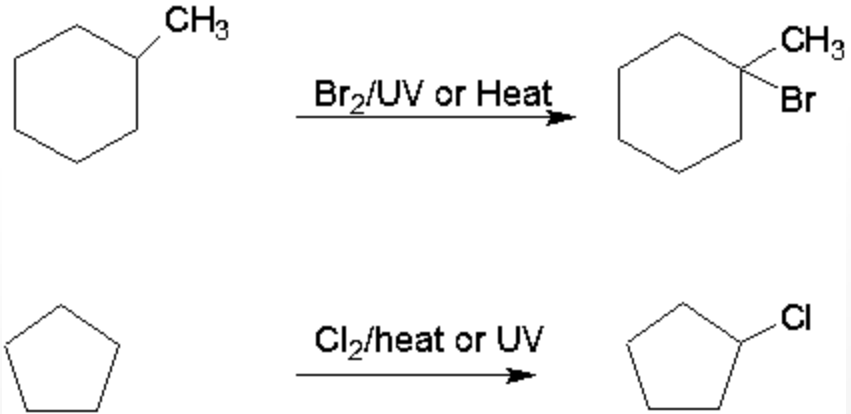
trans-1,4-Dimethylcyclohexane

Reaction of cycloalkanes

- Ring less stable

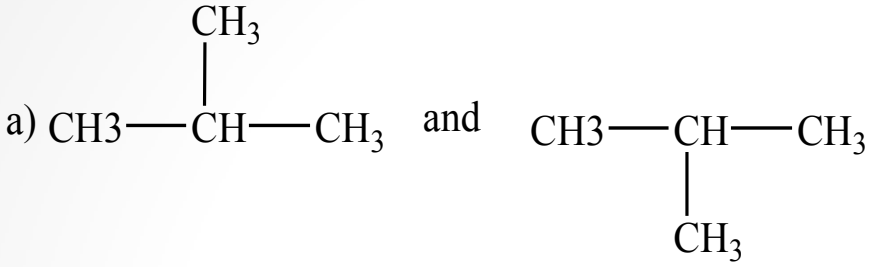


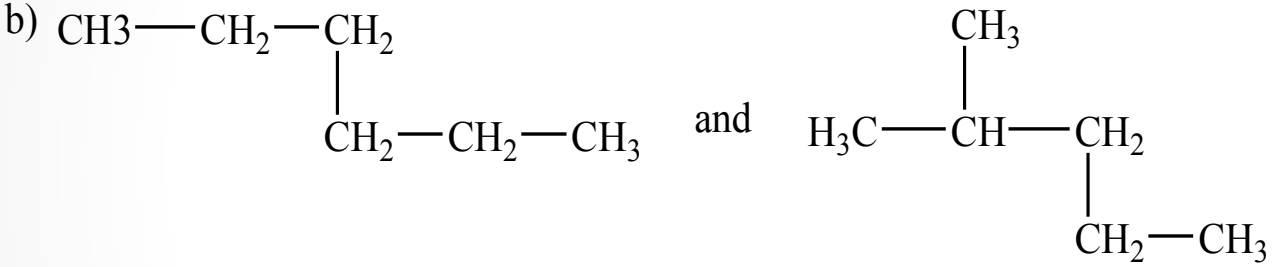
- Ring more stable 5 and 6

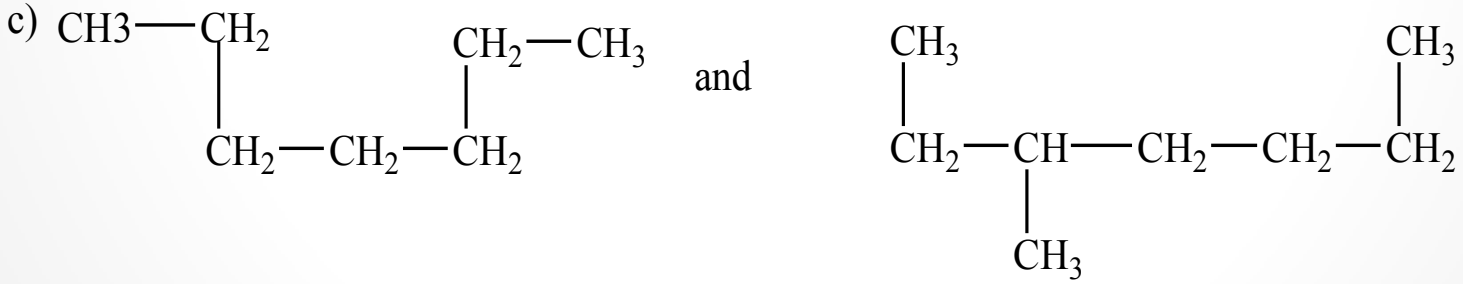


Homework - 2

1- Indicate whether the following pairs of structures are (1) the same, (2) structural isomers, or (3) entirely unrelated.

a) 

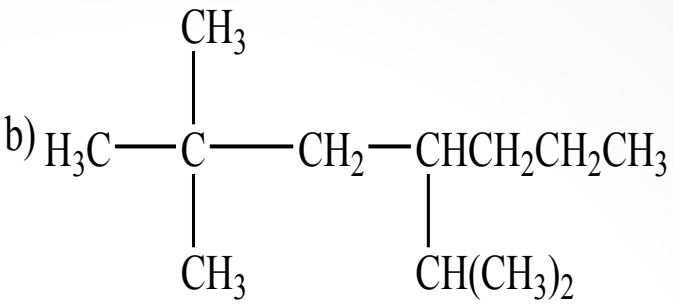
b) 

c) 

2- Arrange the following compounds in order of increasing boiling points : *n*-hexane; 2,2-dimethylbutane; 2-methylpentane.

3- Give IUPC names for the following compounds.

a) $CH_3CHCH_2CH_2CHCH_2CH_2CH_3$ (with CH_3 branches at the 2nd and 5th carbons)

b) 

c) $CHBr_2CHBr_2$

d) CCl_3CH_3

4- Write structural formulas for the following compounds.

A. 2,3-Dimethyl-4-ethylhexane.
B. 2,4-Dimethyl-5-ethyl-4-*t*-butyleheptane.
C. 3,4-Dimethyl-5-ethyl-6-isopropylnonane.

5- Write the condensed structural formula for each of named compounds, and give the correct name for each.

a) 1,4-Dimethylcyclobutane
b) 2,2-Dichloro-5-methylcyclohexane
c) Cis-1,3-Dimethylcyclopropane
d) 1,1-Dibromo-3-methylcyclopentane (note: There are no cis and trans in this case. Why)

108 Chem

Unsaturated Hydrocarbons: Alkenes

Chapter 3

Alkenes or Olefines

C_nH_{2n}

Crabon-carbon double bond

Nomenclature of Alkenes

Common names:

ane ⟶ ylene

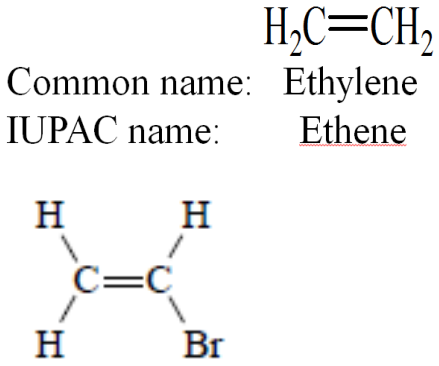
$CH_2=CH-$	vinyl group
$CH_2=CHCH_2-$	allyl group

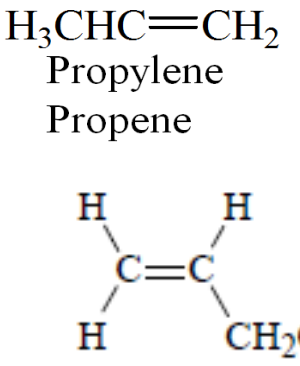
IUPAC rules:

- Determine the parent name by selecting the longest chain that contains the double bond and change the ending of the name of the alkane of identical length from -ane to -ene.
- Number the chain so as to include both carbon atoms of the double bond, and begin numbering at the end of the chain nearer the double bond. Designate the location of the double bond by using the number of the first atom of the double bond as a prefix.

- In cycloalkenes, the double is always found between carbon 1 and carbon 2. It is therefore not necessary to specify the position of the double bond with a number. If substituents are present, the ring must numbered, starting from the double bond, in the direction that gives the substituents the lowest number(s).

Examples



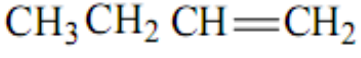


Bromoethene or

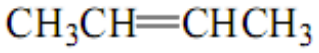
vinyl bromide (common)

3-Chloropropene or

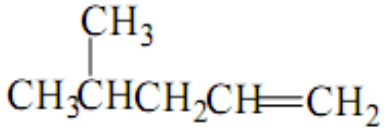
allyl chloride (common)



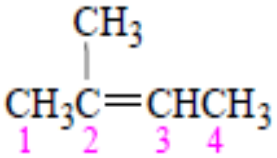
1-Butene
(**not** 3-Butene)



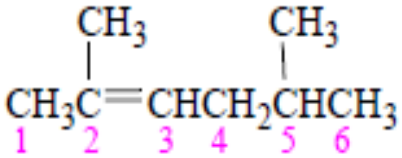
2- Butene



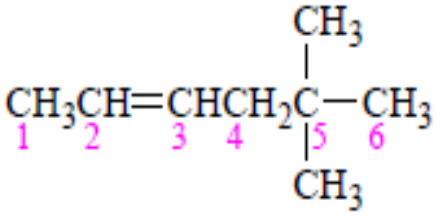
4-Methyl-1-pentene
(**not** 2-Methyl-4-pentene)



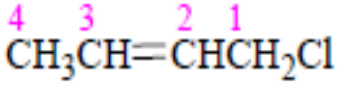
2-Methyl-2-butene
(*not* **3-methyl-2-butene**)



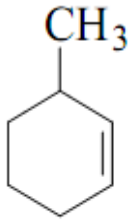
2,5-Dimethyl-2-hexene
(*not* **2,5-dimethyl-4-hexene**)



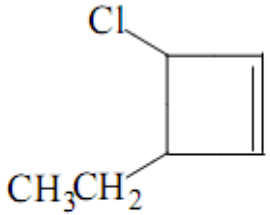
5,5-Dimethyl-2-hexene



1-Chloro-2-butene



3-Methylcyclohexene
(**not** 1-Methyl-2-cyclohexene)



3-Chloro-4-ethylcychlobutene
(**not** 1-Chloro-2-ethylcyclobutene)

Hybridization in Alkanes:

Energy ↑ C $\frac{\uparrow\downarrow}{1s}$ $\frac{\uparrow\downarrow}{2s}$ $\frac{\uparrow}{2p_x}$ $\frac{\uparrow}{2p_y}$ $\frac{}{2p_z}$

Ground state

Promotion →

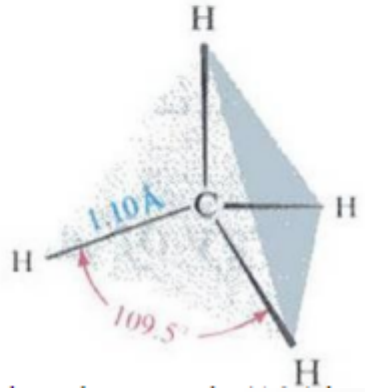
Energy ↑ C^* $\frac{\uparrow\downarrow}{1s}$ $\frac{\uparrow}{2s}$ $\frac{\uparrow}{2p_x}$ $\frac{\uparrow}{2p_y}$ $\frac{\uparrow}{2p_z}$

The excitation of one of the 2s electrons, resulting in the presence of **four unpaired electrons**.

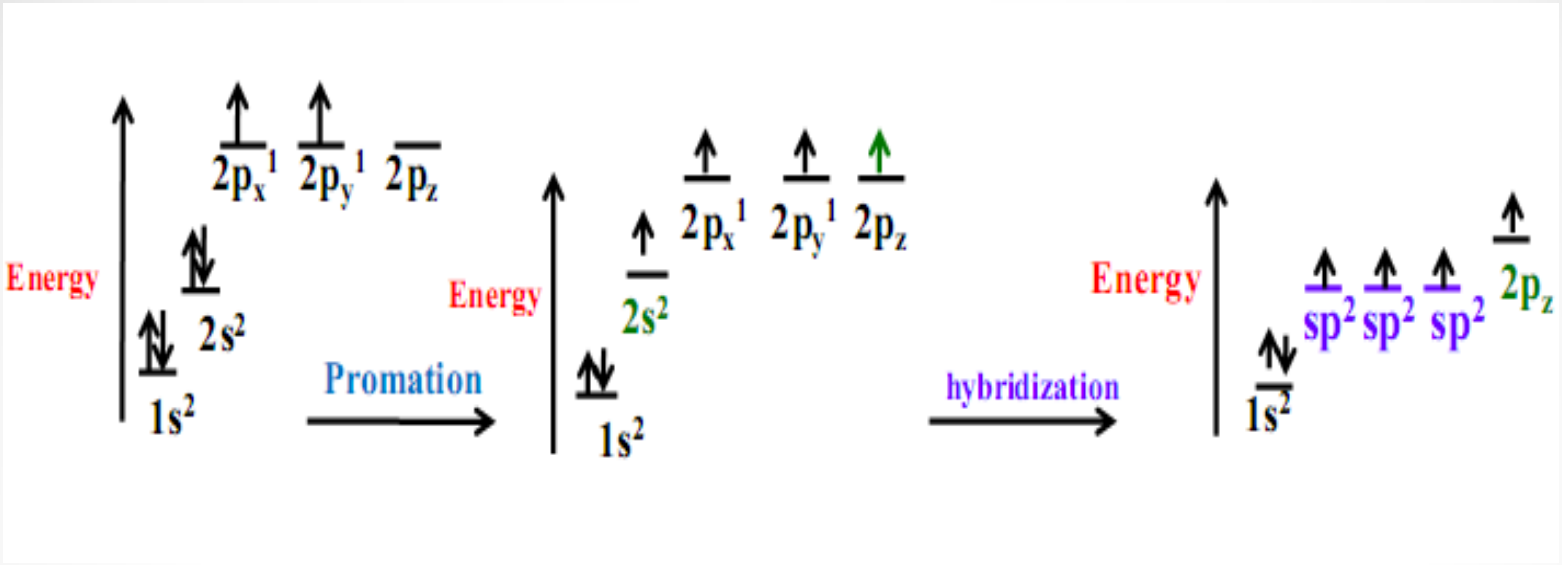
hybridization →

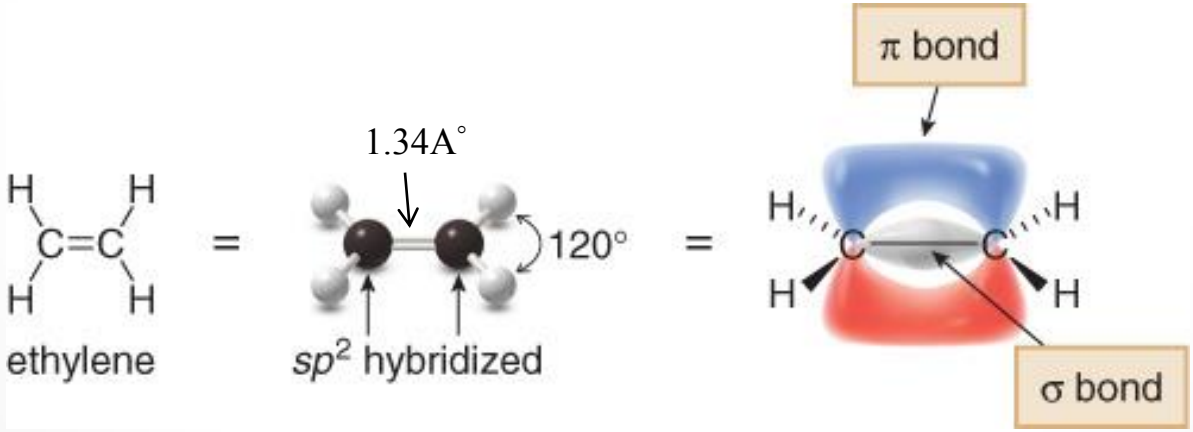
Energy ↑ C^* $\frac{\uparrow\downarrow}{1s}$ $\frac{\uparrow}{sp^3}$ $\frac{\uparrow}{sp^3}$ $\frac{\uparrow}{sp^3}$ $\frac{\uparrow}{sp^3}$

The 2s orbital mixes with the three 2p orbitals to form **four sp^3** hybrids.



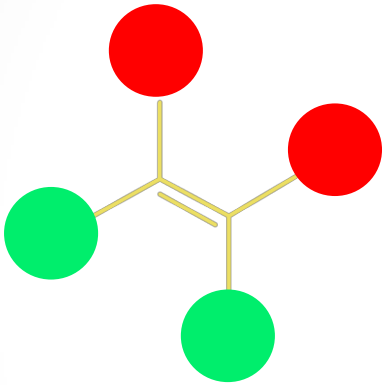
Hybridization in Alkenes:

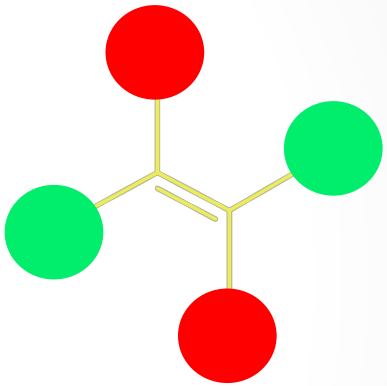




Geometric Isomerism in Alkene

Cis- *Trans* Isomerism





cis (identical or analogous substituents on same side)

trans (identical or analogous substituents on opposite sides)

If either *vinyl* carbon is bonded to two equivalent groups, then no geometric isomerism exists.

$CH_3CH=CHCH_3$

yes

$CH_3CH_2CH=CH_2$

no

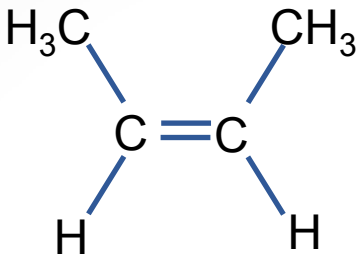
$(CH_3)_2C=CHCH_3$

no

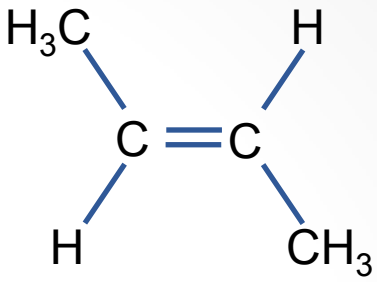
$CH_3CH=C(CH_3)CH_2CH_3$

yes

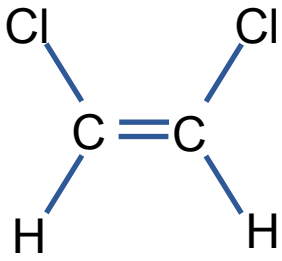
Examples:



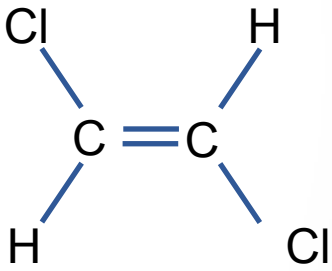
cis-2-Butene



trans-2-Butene



cis-1,2-dichloroethene



trans-1,2-dichloroethene

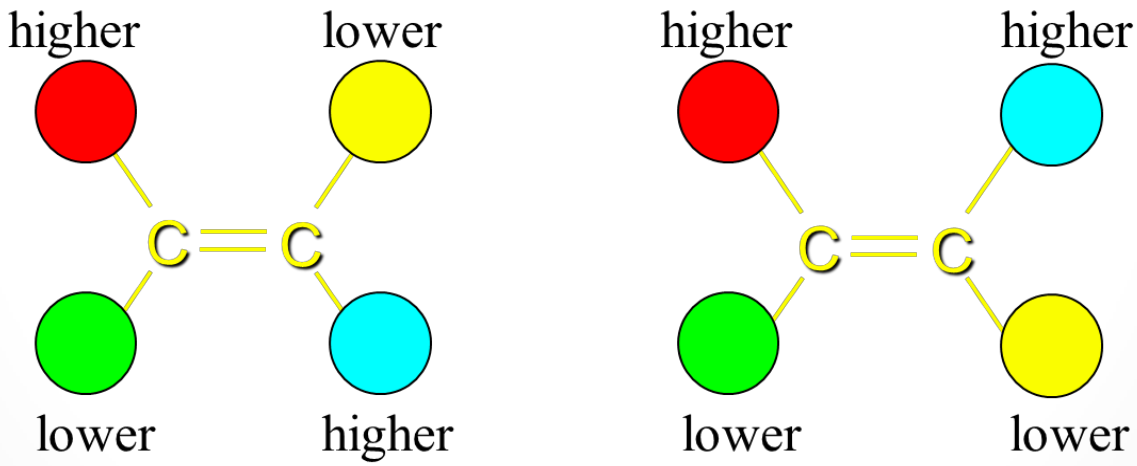
The *E*-*Z* System

E: Entgegen

higher ranked substituents on <u>opposite</u> sides

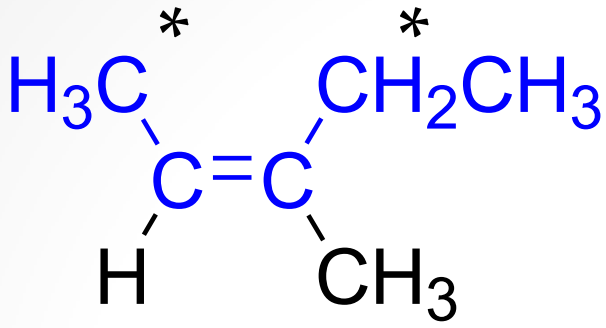
Z: Zusammen

higher ranked substituents on <u>same</u> side

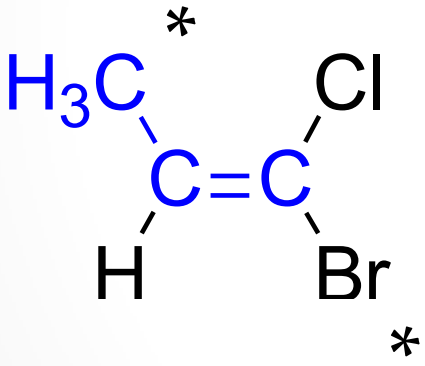


Entgegen *Zusammen*

Examples:



Z-3-methyl-2-pentene



E-1-bromo-1-chloropropene

Physical properties of alkenes

A Physical States and Solubilities

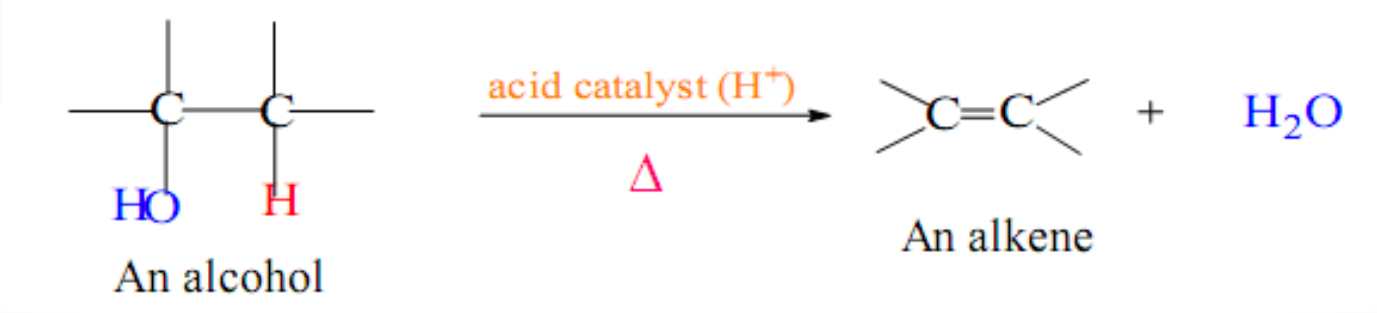
C_1-C_4	gases
C_5-C_{18}	liquids
More than C_{18}	solids

Alkenes are nonpolar compounds. Thus alkenes are soluble in the nonpolar solvents such as carbon tetrachloride (CCl_4) and benzene (C_6H_6), but they are insoluble in polar solvents such as water.

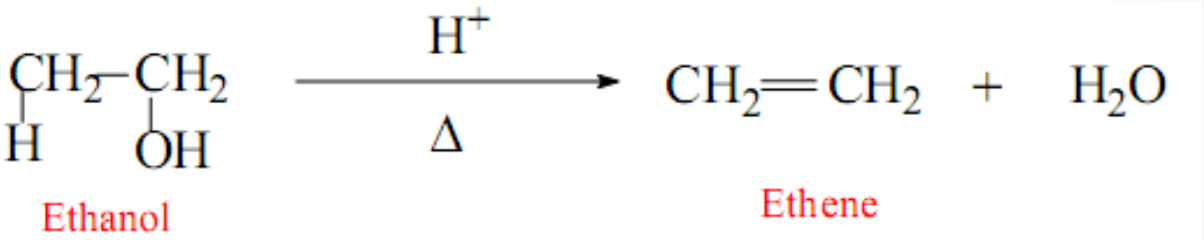
Preparation of alkenes

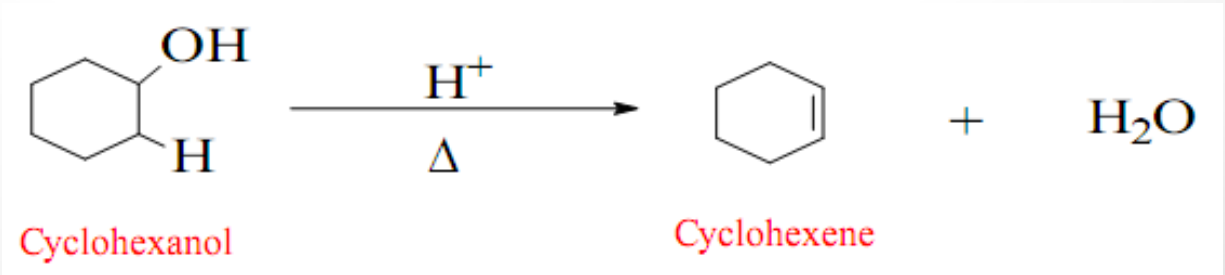
- Alkenes can be prepared from alcohols and alkyl halides by elimination reactions.

1- Dehydration of Alcohols

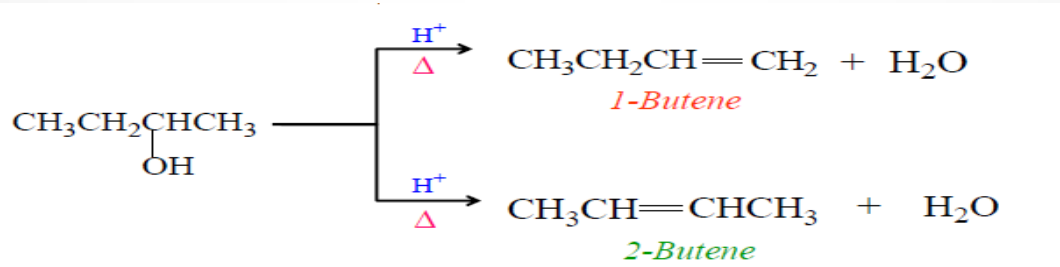


Examples:





Which alkene Predominates?

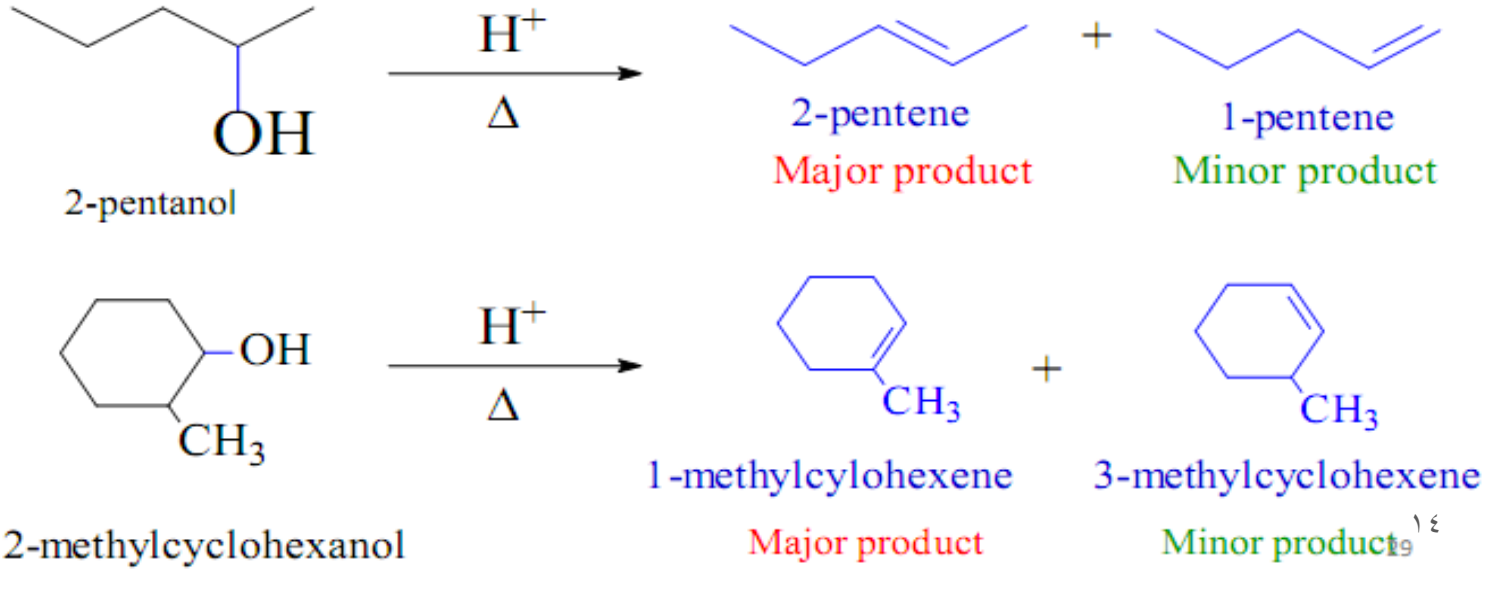


How do you which one is major product?

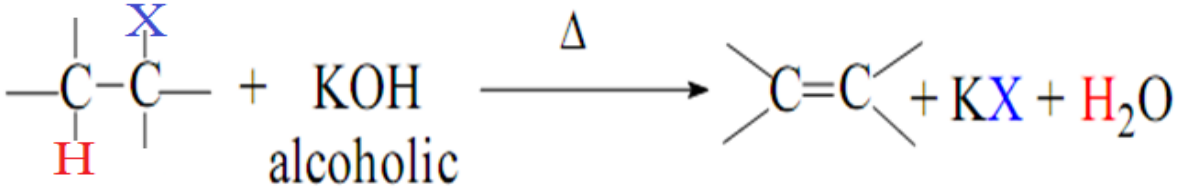
Saytzeff's Rule:

Hydrogen is preferably removed from the carbon with least no. of hydrogen since the alkene formed is more highly branched and is energetically more stable.

Examples:

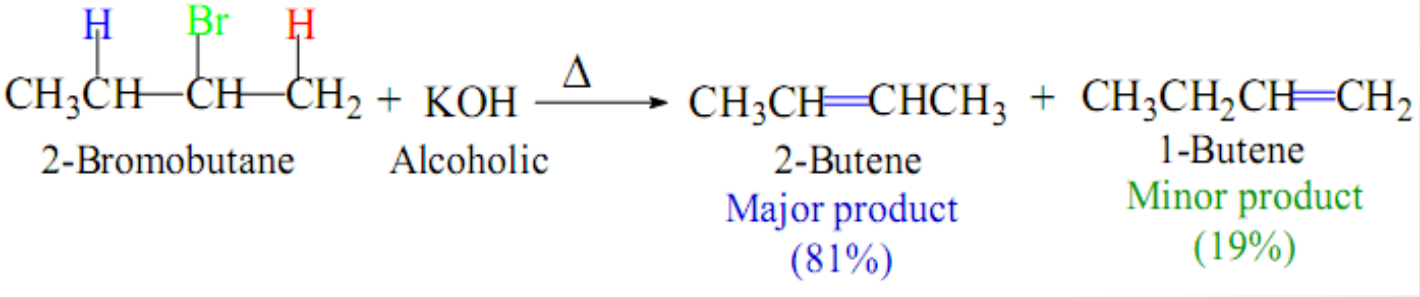


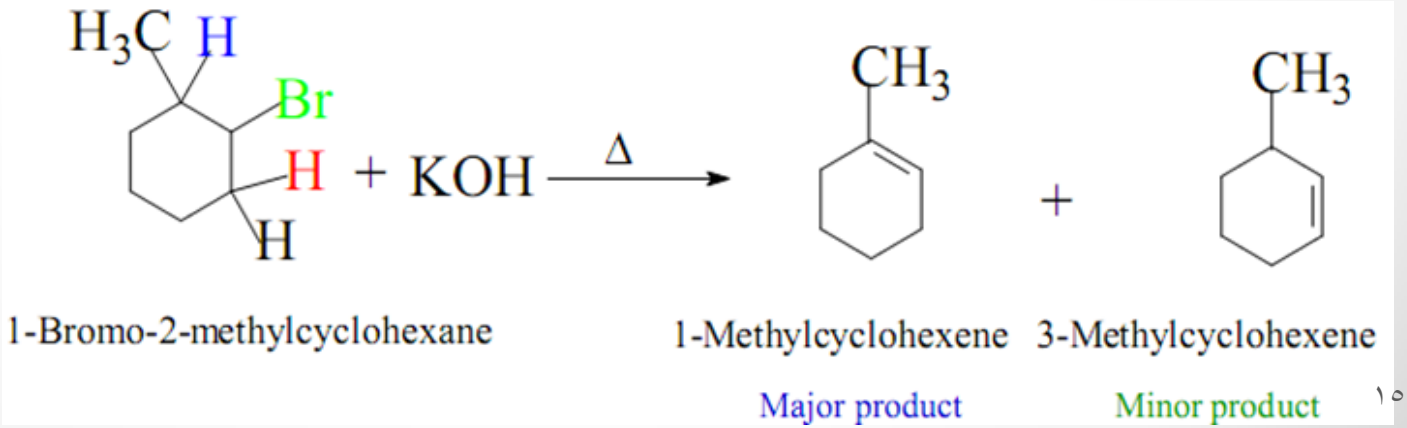
2- Dehydrohaloganation of Alkyl halides



In similar way to that in the dehydration of alcohol, Saytzeff's rule again applies; that is, the alkene with the most alkyl substitution on the double-bonded carbons predominates.

Examples:





Saytzeff orientation:

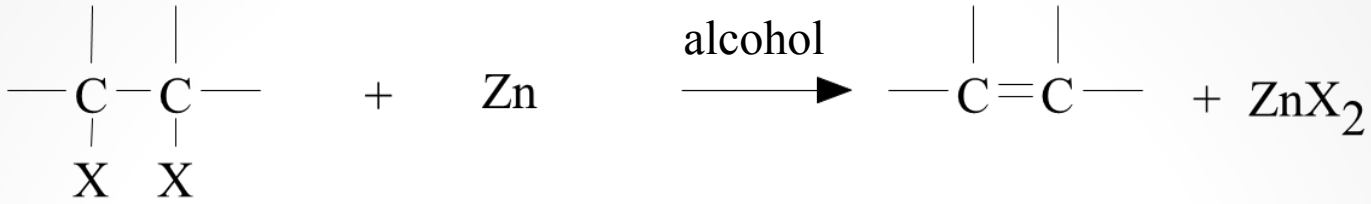
Ease of formation of alkenes:

$R_2C=CR_2 > R_2C=CHR > R_2C=CH_2$, $RCH=CHR > RCH=CH_2 > CH_2=CH_2$

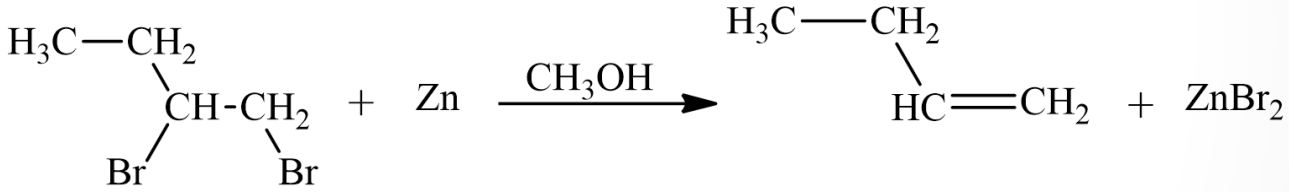
Stability of alkenes:

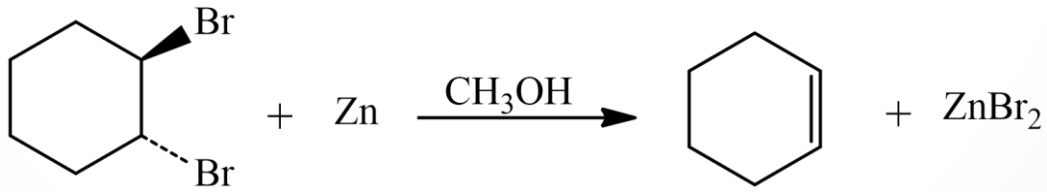
$R_2C=CR_2 > R_2C=CHR > R_2C=CH_2$, $RCH=CHR > RCH=CH_2 > CH_2=CH_2$

3- Dehaloganation of vicinal dihalides



Example:





Reaction of alkenes

1- Addition reactions on the carbon-carbon double bond.

2- Substitution reactions on the saturated alkyl chain.

Addition reactions

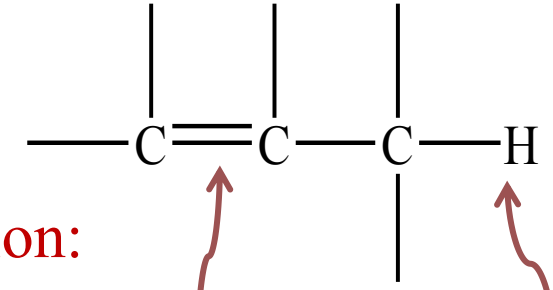
1. Addition of H_2
2. Addtion of X_2
3. Addition of HX.
4. Addition of H-OSO_3H
5. Addition of H_2O
6. Addition of halohydrin XOH
7. Oxidation(visual test for unsaturation)
8. Ozonolysis
9. Polymerization

Substitution reactions

1- Halogenation at High temperature

Substitution reactions

Halogenation at High temperature

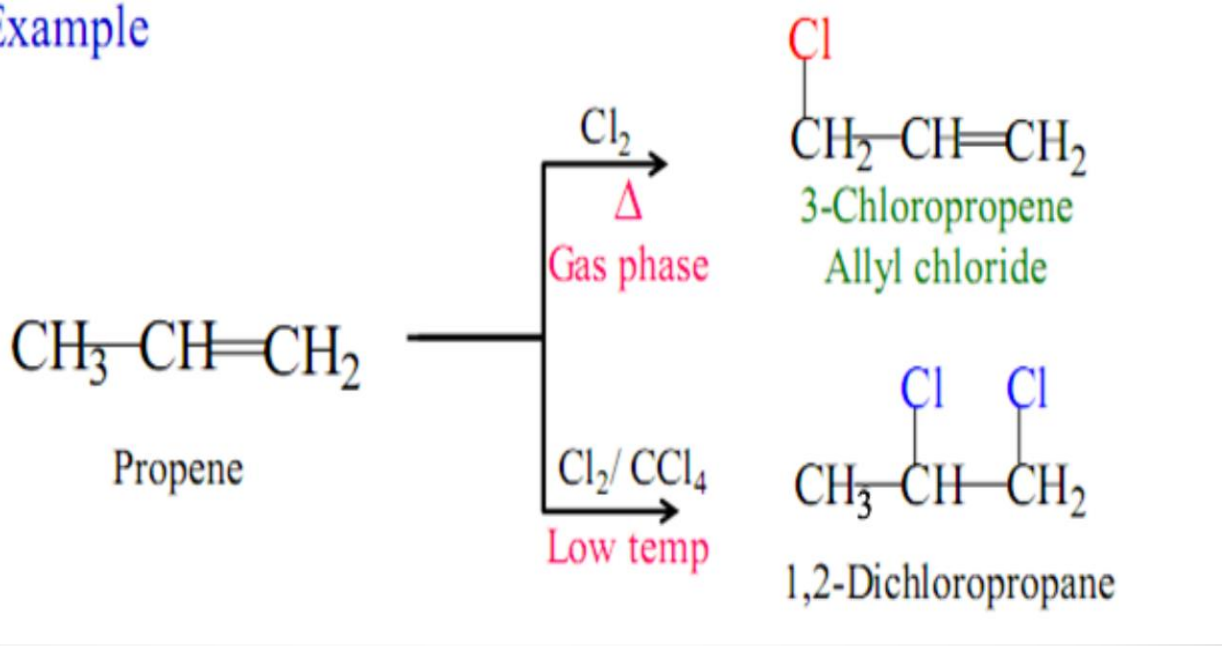


Addition reaction:
low temperature
Absence of light

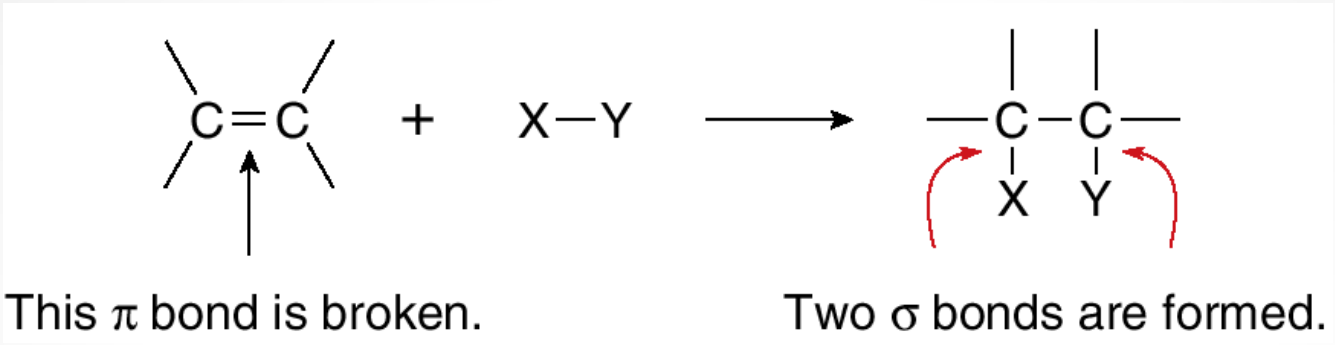
X_2 or X_2

Substitution reaction:
High temperature
or Ultraviolet light

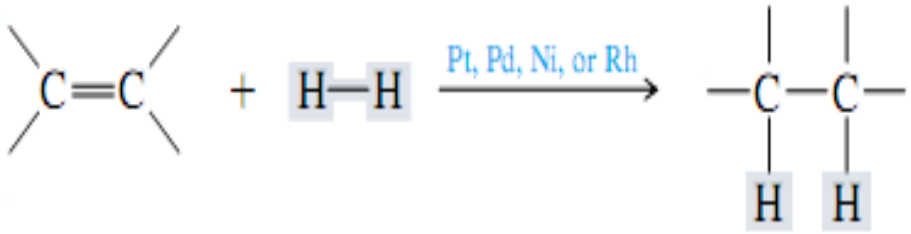
Example



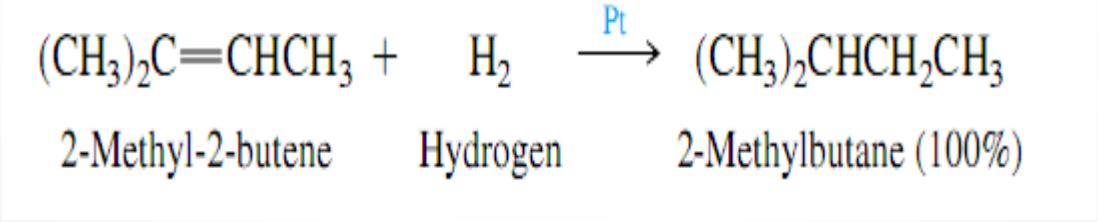
Addition reactions



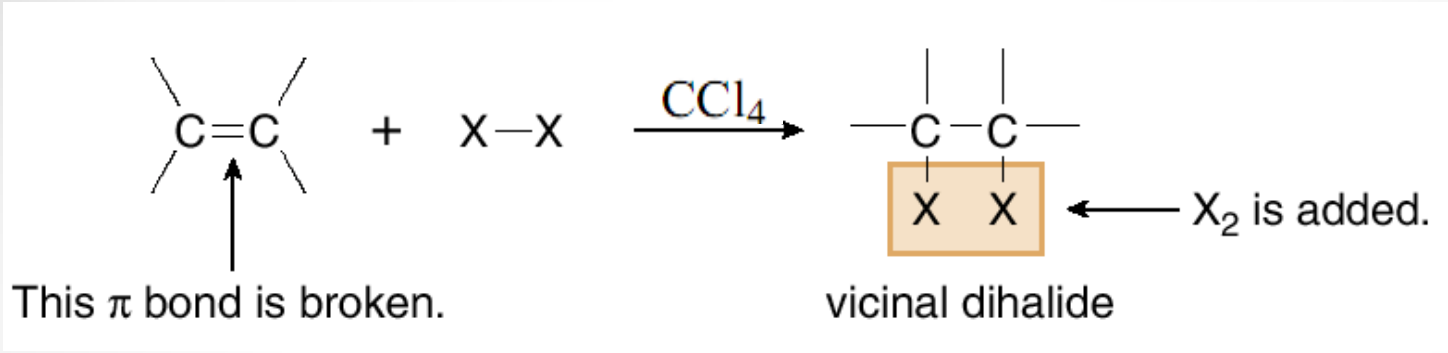
1- Addition of Hydrogen: Catalytic Hydrogenation



Example:

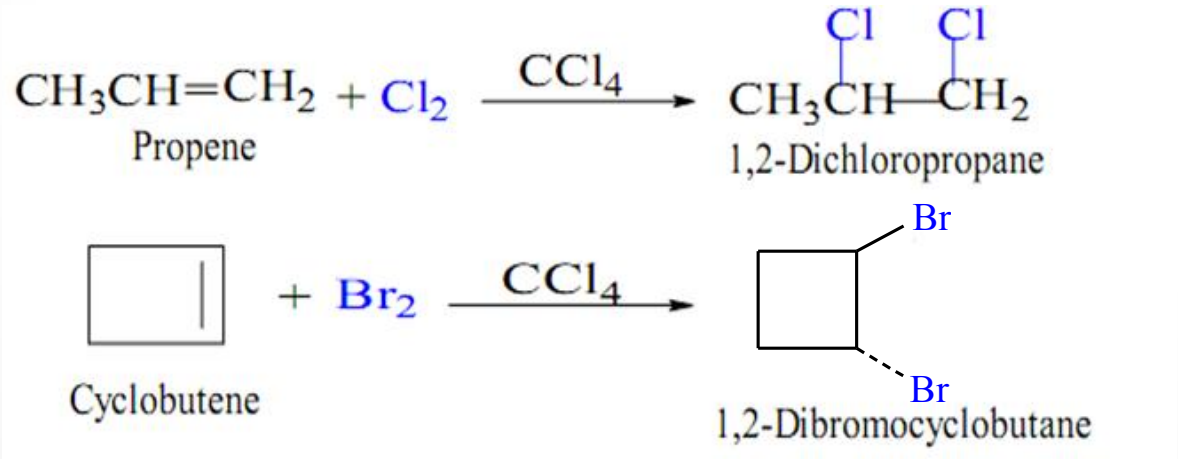


2- Addition of Halogens: Halogenation

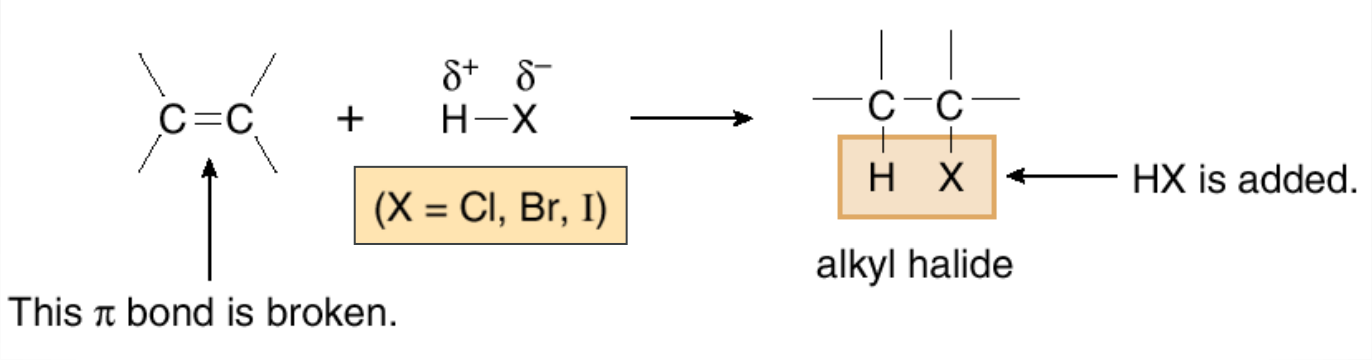


(X= Cl or Br)

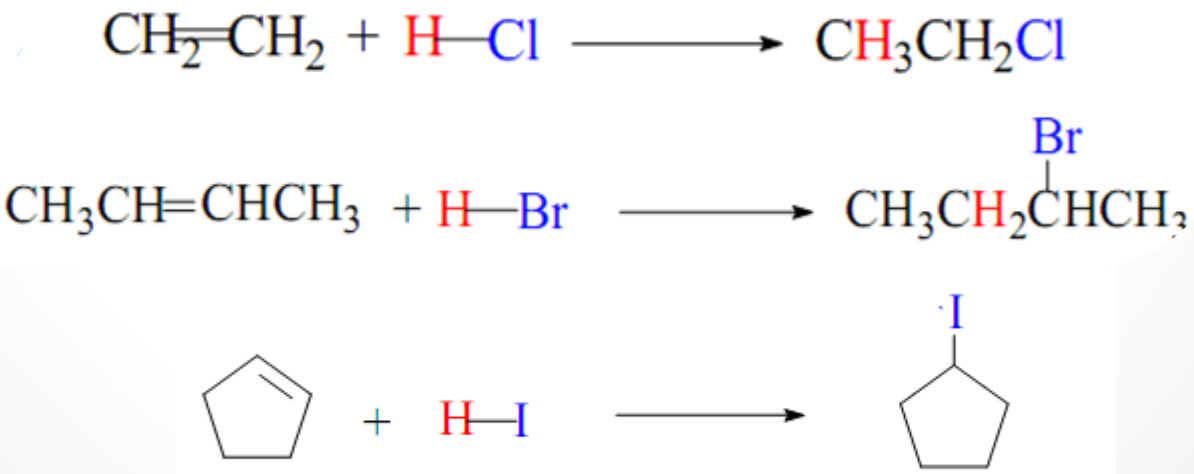
Examples:



3- Addition of Hydrogen Halides: Hydrohalogenation

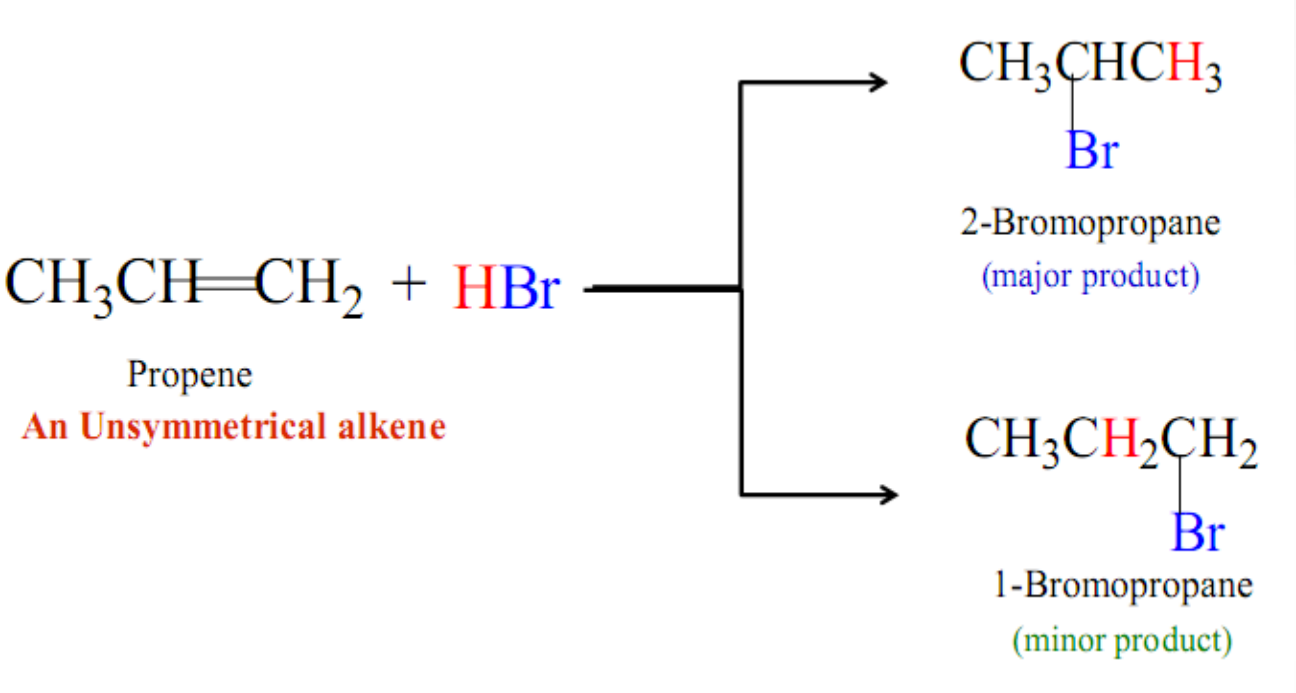


Examples:



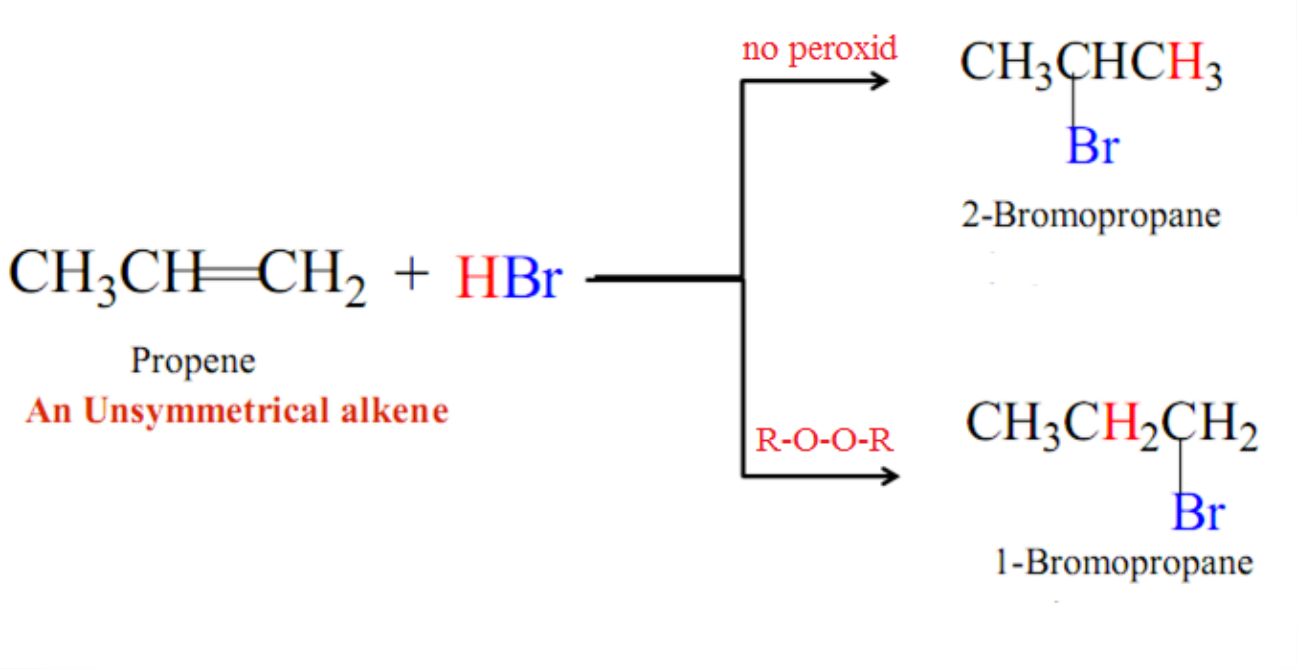
Markovnikov's Rule

With unsymmetrical alkene



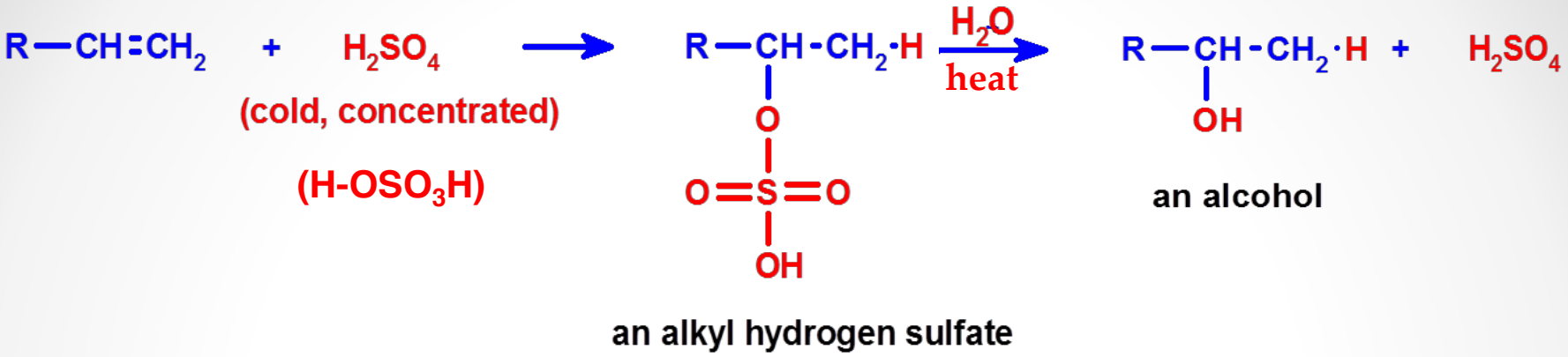
In the addition of an acid to an alkene the hydrogen will go to the vinyl carbon that already has the greater number of hydrogens.

Anti Markovnikov's Rule

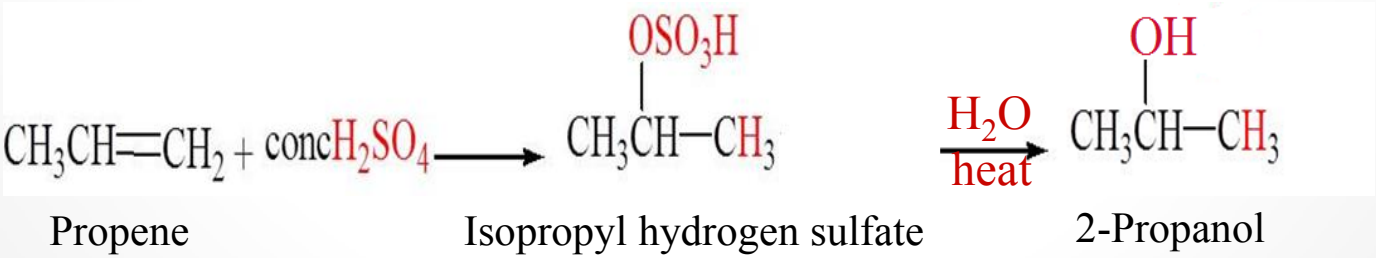


In the addition of an acid to an alkene the hydrogen will go to the vinyl carbon that already has the lowest number of hydrogens.

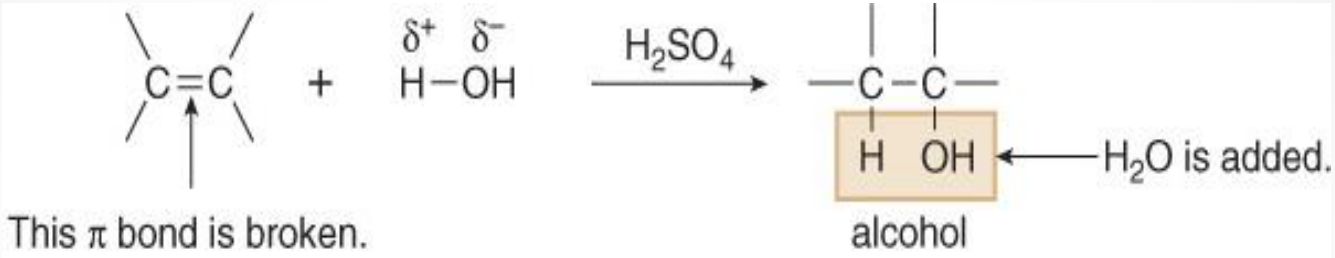
4- Addition of Sulfuric acid



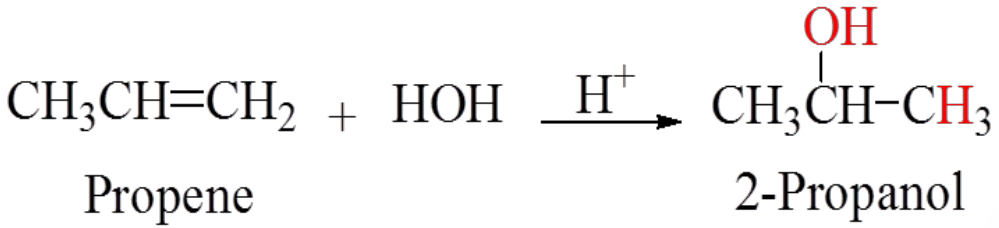
Addition of Sulfuric acid to alkenes also follows Markovnikov's rule, as the example



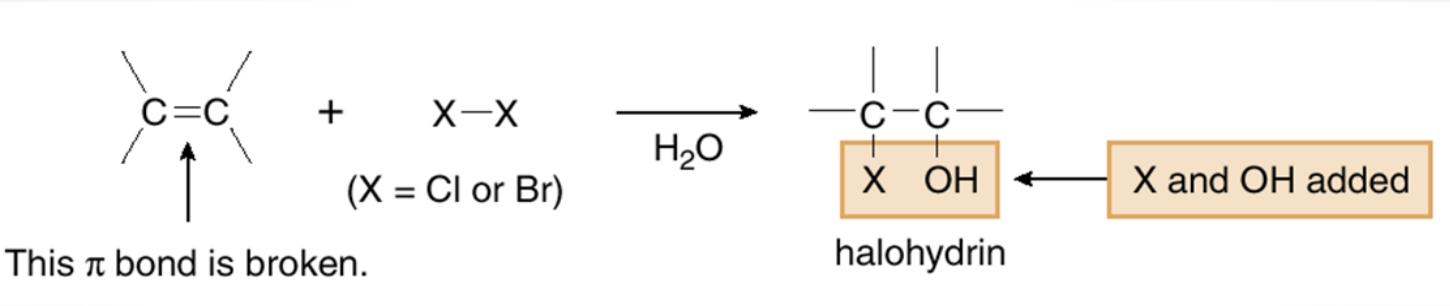
5- Addition of Water : Hydration



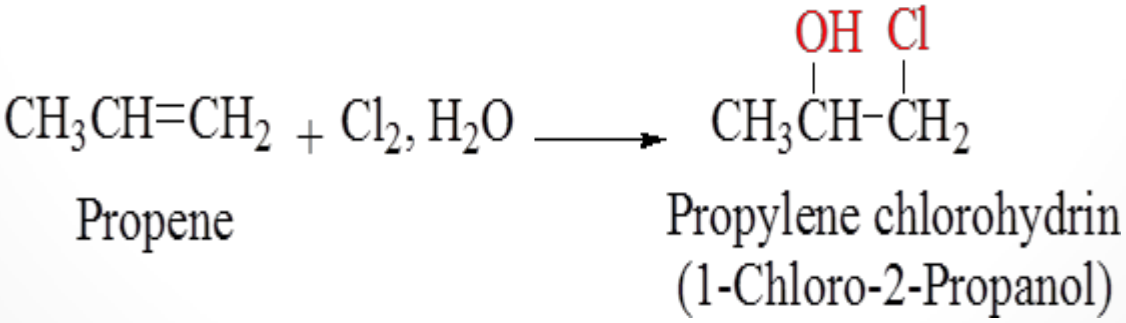
Addition of HOH across the double bond is in accordance with Markovnikov's rule, as the example



6- Addition of HOX : Halohydrin Formation

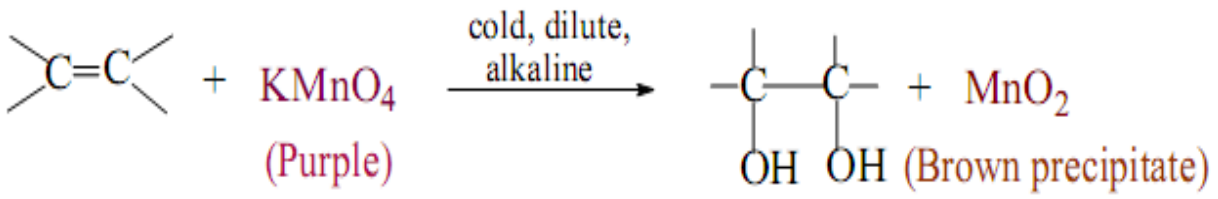


The addition of the chloronium ion, Cl^+ or bromonium ion, Br^+ and the hydroxide ion, OH^-, follows the Markovnikov's rule, as the example.



7- Oxidation of alkenes

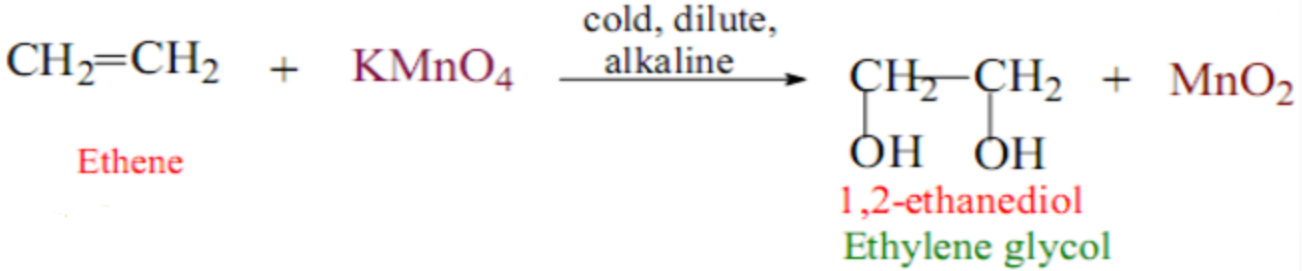
1) Oxidation of alkenes with Permanganate (Baeyer test)



A glycol

syn hydroxylation

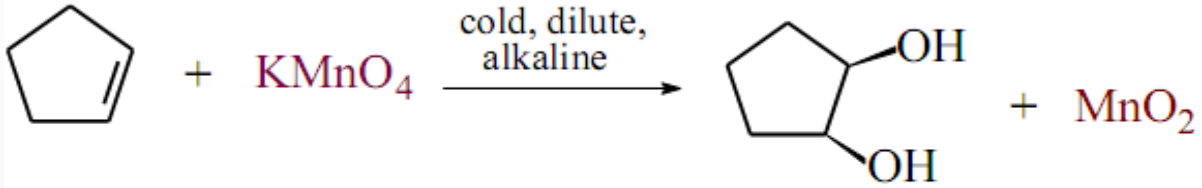
Examples:



Ethene

1,2-ethanediol

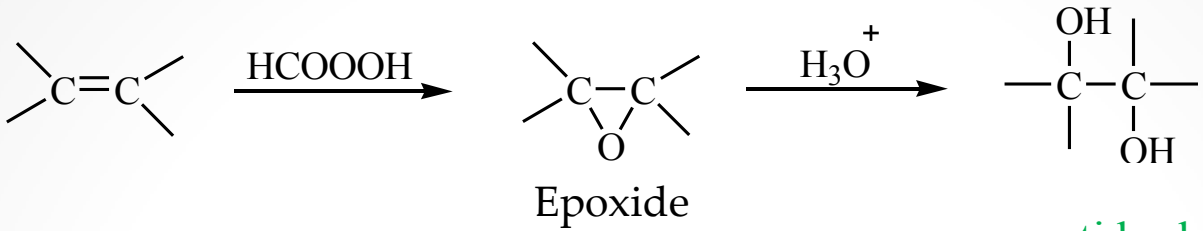
Ethylene glycol



cyclopentene

Cis-1,2-cyclopentadiol

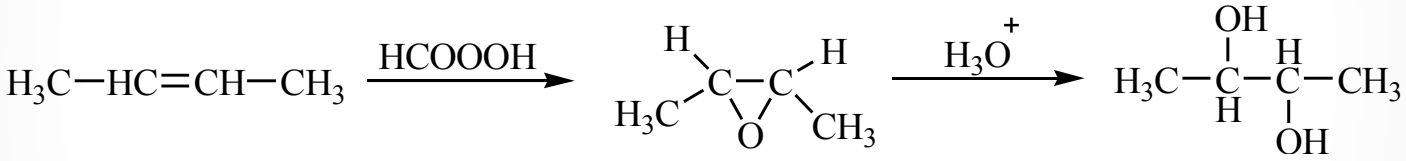
2) Oxidation of alkenes with peroxy acid



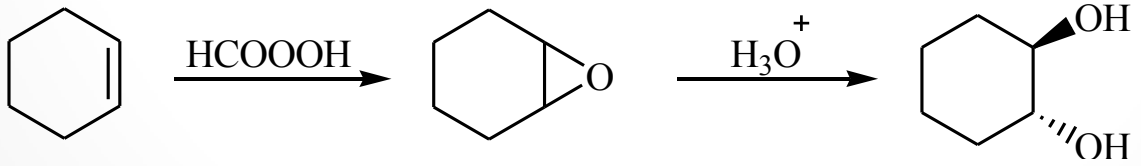
Epoxide

anti hydroxylation

Examples:



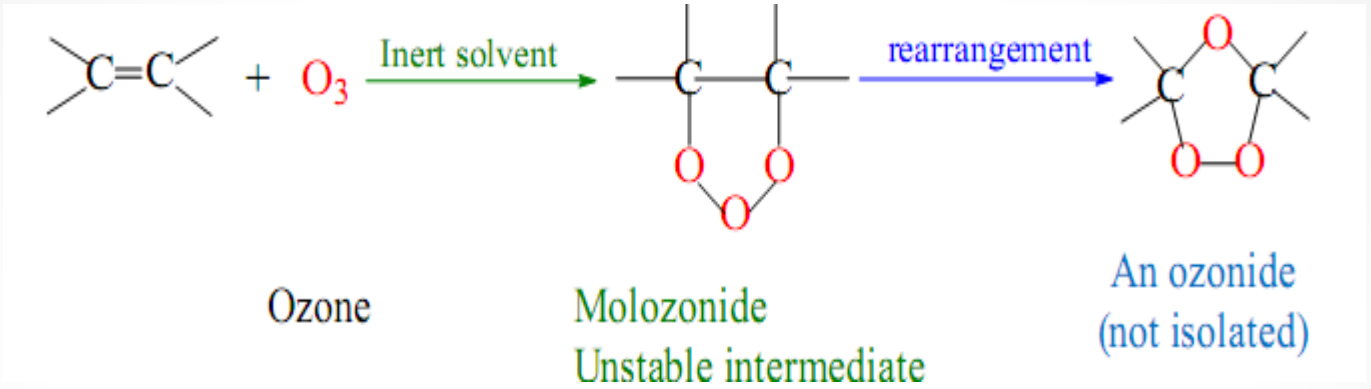
2,3-butanediol

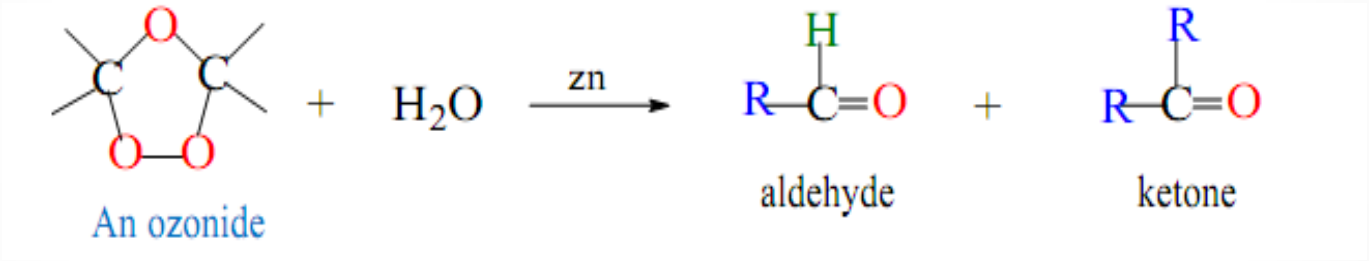


trans-1,2-cyclohexanediol

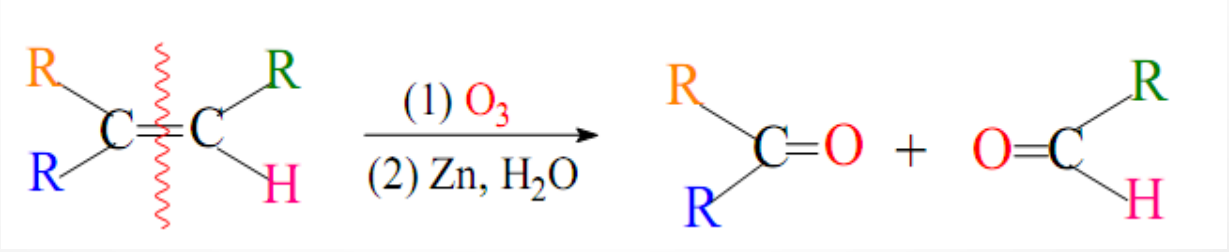
8- Ozonolysis

Oxidation of alkenes by ozone O_3

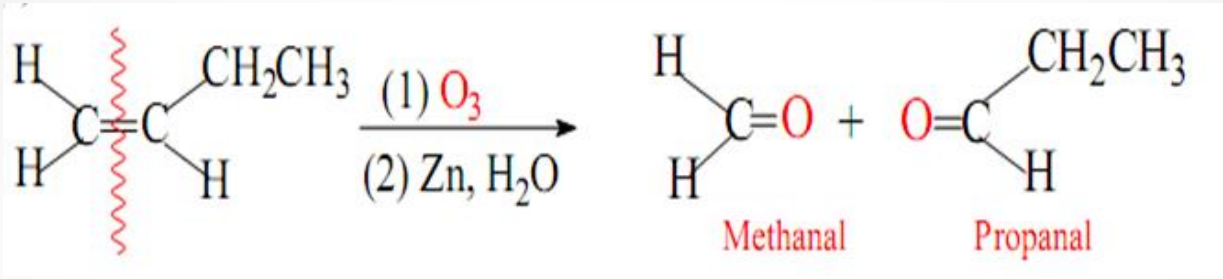


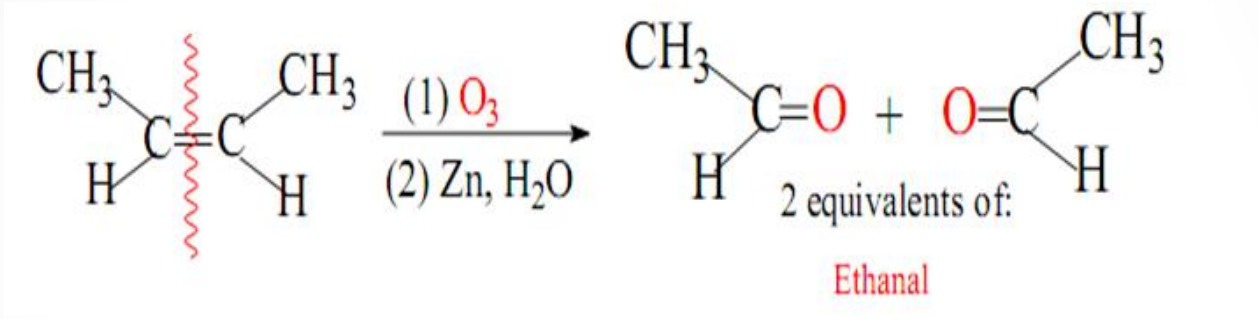


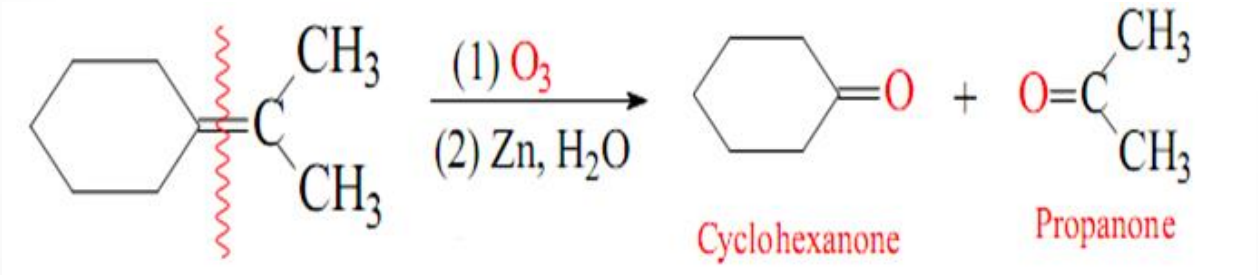
The ozonolysis reaction can be summarized by the following equation:



Examples:

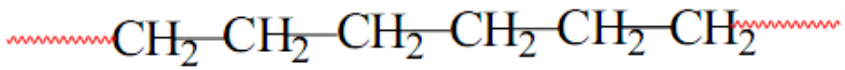

H
H
C
C
CH2CH3
H
(1) O3
(2) Zn, H2O
H
C=O
H
+
O=C
CH2CH3
H
Methanal
Propanal

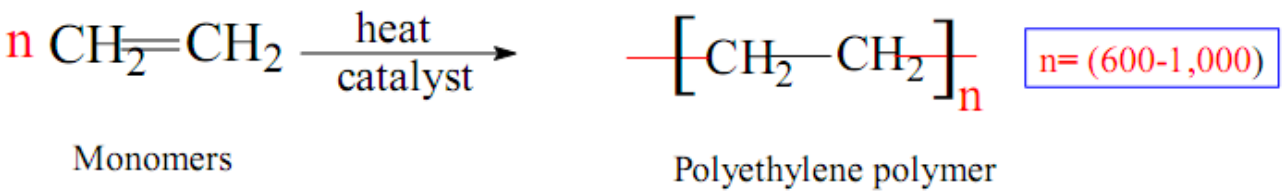

CH3
H
C
C
CH3
H
(1) O3
(2) Zn, H2O
CH3
C=O
H
+
O=C
CH3
H
2 equivalents of:
Ethanal


CH3
C
CH3
(1) O3
(2) Zn, H2O
=O
+
O=C
CH3
CH3
Cyclohexanone
Propanone

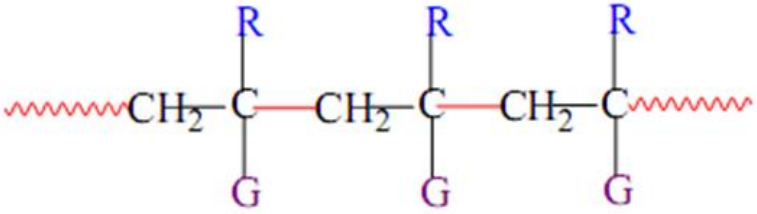
9- Polymerization

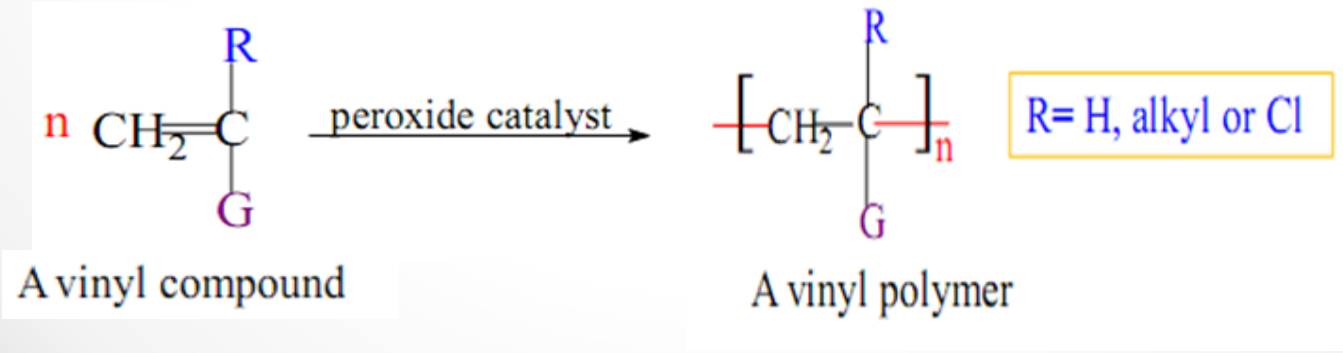
A)





B)





Homework

1- Which of the following compounds can exist as *cis-trans* isomers? Draw the structures of the geometric isomers.

a) $CH_2=CHCH_2CH_2CH_3$

b) $CH_3CH_2CH=CHCH_2CH_3$

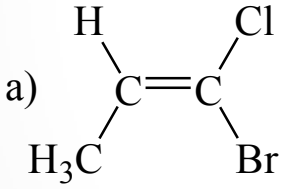
2- Draw the structures of the following compounds.

a) *trans*-4-Octene

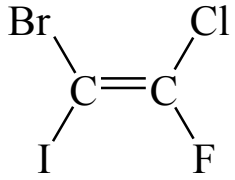
b) *cis*-1,2-Dichloropropene

3- Name the following compounds using the *E,Z* .

a)



b)



4- Write the structure of the major product expected on reaction of

a) 1-butene with H_2SO_4

b) 2-methylpropene with aqueous bromine

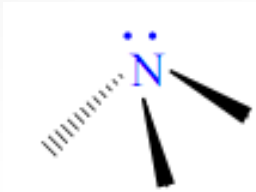
c) 1-methylcyclopentene with water

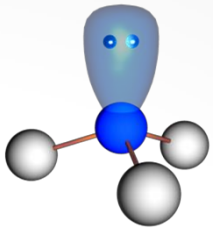
d) The ozonolysis of 2-methyl-2-pentene

Chem. 108

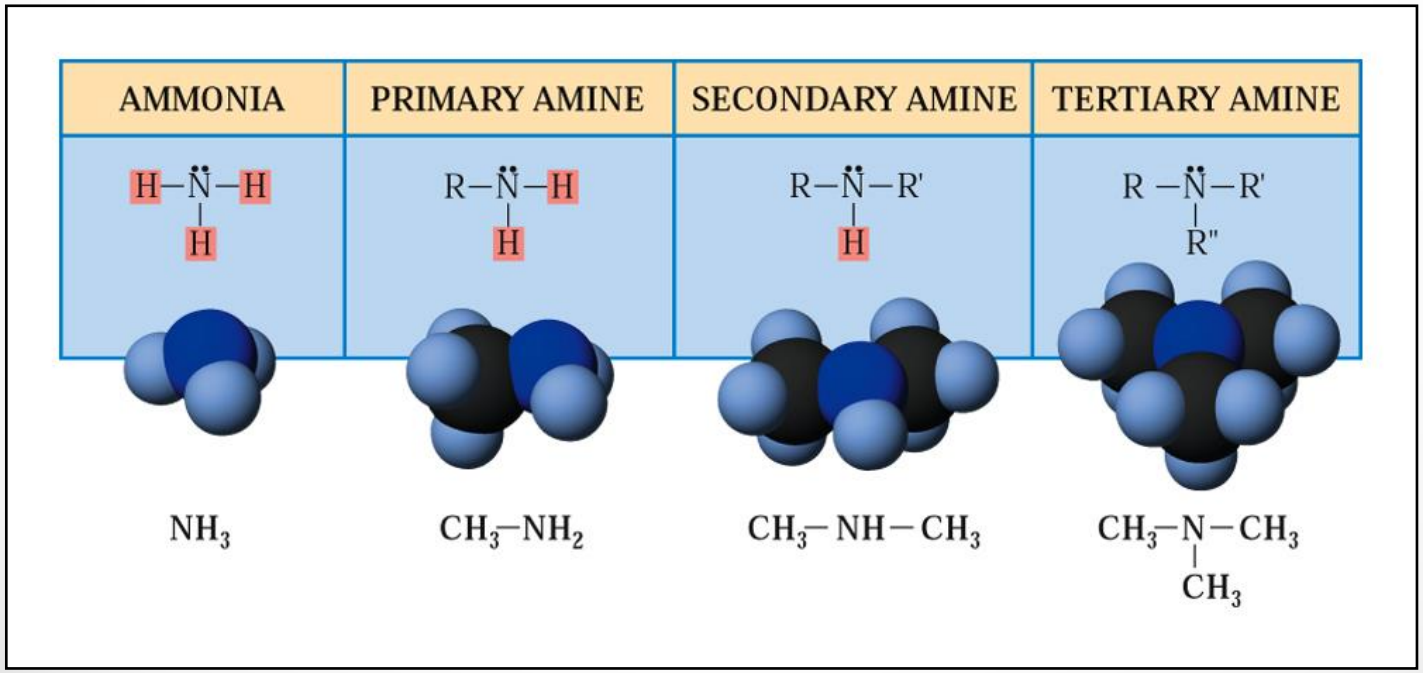
Amines

Chapter 11

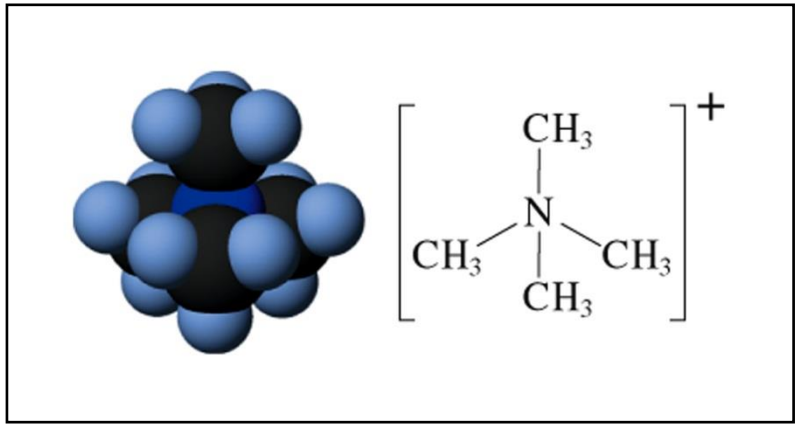




- Amines are organic nitrogen compounds, formed by replacing one or more hydrogen atoms of ammonia (NH_3) with alkyl or aryl groups.
- Amines are classified as 1°, 2°, or 3° based on the number of alkyl groups bonded to the nitrogen atom.



- When a fourth group bonds to the nitrogen through this lone pair, the product is a quaternary ammonium ion, which has a positive charge and forms ionic compounds with anions.



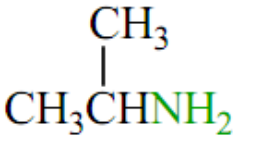
- Amines are stronger bases and better nucleophiles than other neutral organic compounds.

Nomenclature of Amines

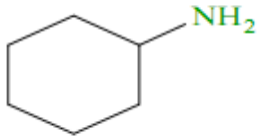
Common Name

- Name the alkyl group bonded to the nitrogen atom and add the word amine, forming a single word (alkylamine).
- Secondary and Tertiary amines having identical alkyl groups are named using the prefix di- or tri- with the name of the primary amine (Dialkylamine or Trialkyamine)

Methylamine

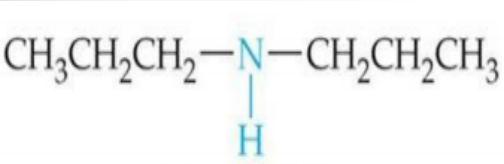


Isopropylamine

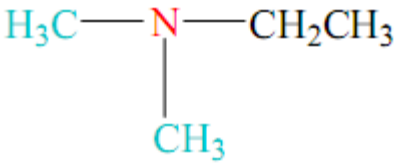


cyclohexylamine

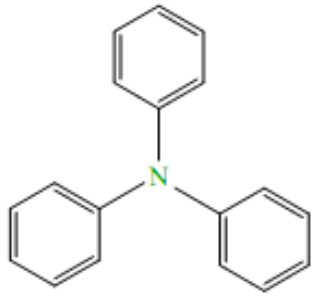
Ethylpropylamine



Dipropylamine



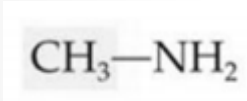
Ethyldimethylamine



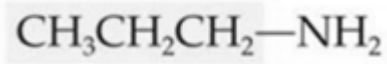
Triphenylamine

IUPAC System

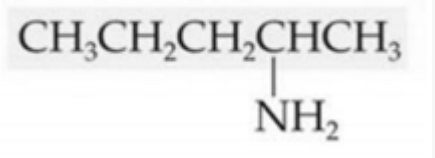
- If the compound does not contain a functional group except amino group, In this system find the longest chain and give it a suitable name and the amino group is considered as substituent, and its position on the chain is indicated by the lowest possible number.
- Substituents attached to the nitrogen are indicated by using "N-" as the location number.



Aminomethane



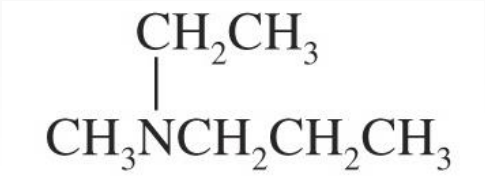
1-Aminopropane



2-Aminopentane

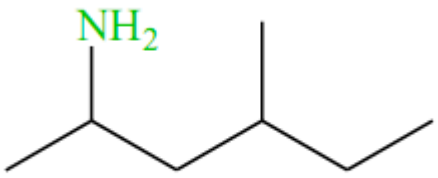
N-Ethyl-1-aminopropane

N,N-Dimethyl-1-aminopropane

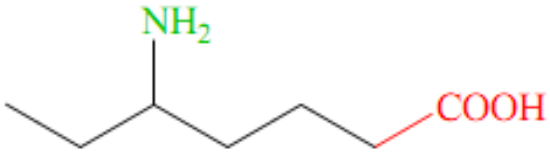


N-Ethyl,N-methyl-1-aminopropane

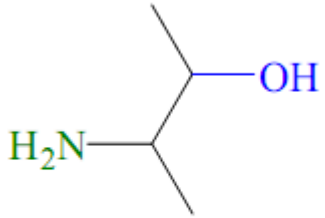
Nomenclature of multifunctional compounds



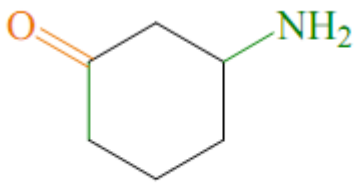
2-Amino-4-methylhexane



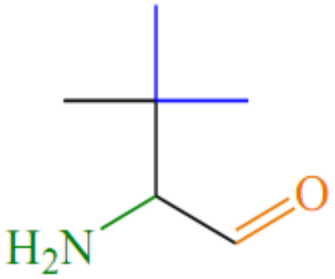
5-Aminoheptanoic acid



3-Amino-2-butanol

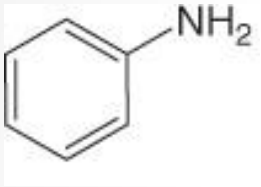


3-Aminocyclohexanone

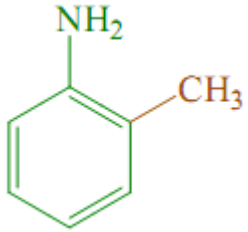


2-Amino-3,3-dimethyl-butanal

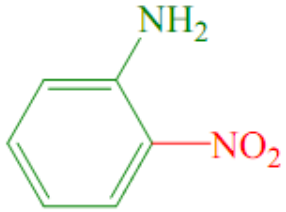
- Aromatic amines are named as derivatives of aniline. Substituents attached to the nitrogen are indicated by using "N-" as the location number.



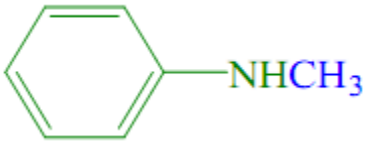
Aniline



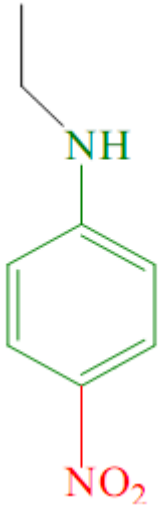
2-Methylaniline



2-Nitroaniline



N-Methylaniline



N-Ethyl-4-nitroaniline

4-Chloro-N-ethyl,N-methylaniline

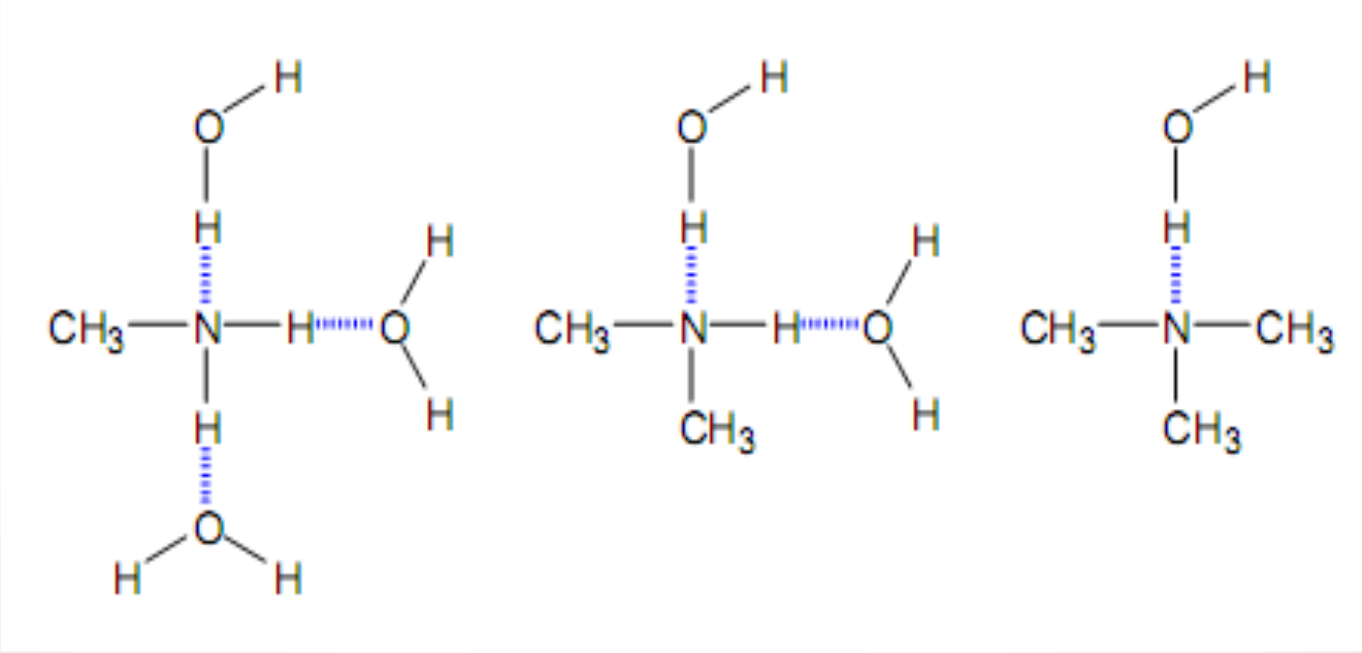
Precedence Order of Functional Groups

Class	Functional group	Prefix	suffix
Carboxylic acids Cyclic alknes or alkenes with COOH group	COOH		oic acid carboxylic acid
Aldehydes Cyclic alknes or alkenes with CHO group	-CHO	Formyl	al carbaldehyde
ketone	-C=O	oxo	one
Alcohols	-OH	hydroxy	ol
Amines	$-NH_2$	amino	amine
Ethers	-OR	alkoxy	-
Alkenes and aAlkynes	= & ≡ bonds	-	ene & yne

Physical properties of Amines

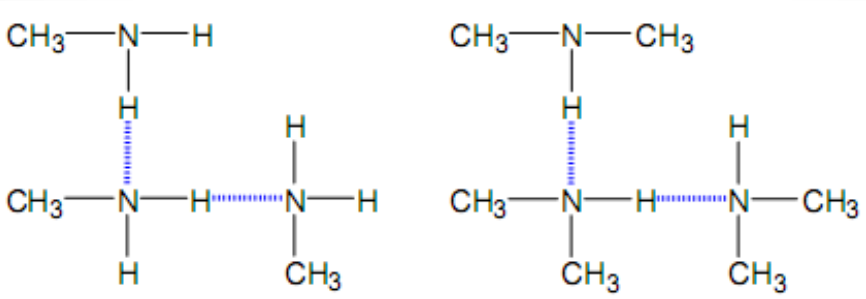
1. Solubility in water

- 1°, 2°, and 3° amines with small alkyl groups are very soluble in water due to hydrogen bonding with the solvent.
- Solubility decreases as the molecules get heavier.
- Aromatic amines are insoluble in water.

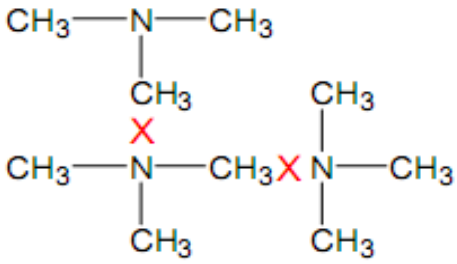


2. Boiling point

- 1° and 2° amines can hydrogen bond to each other:



- 3° amines cannot hydrogen bond to each other:



$CH_3CH_2CH_2CH_3$

Butane, bp 0 °C
MW = 58

$CH_3CH_2CH_2NH_2$

Propylamine, bp 48 °C
MW = 59

$CH_3CH_2CH_2OH$

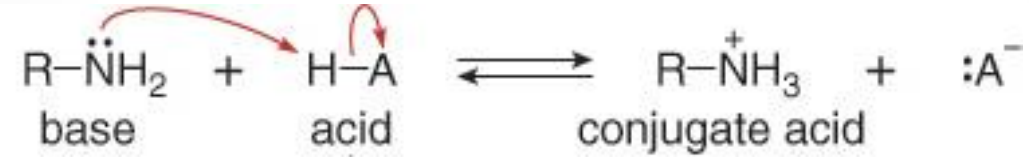
Propanol, bp 97 °C
MW = 60

Boiling Point:

↑ Carboxylic acid
Alcohols
1°/2° Amines
3° Amines/Alkanes

Basicity of Amines

- Amines are basic because they possess a pair of unshared electrons, which they can share with other atoms.

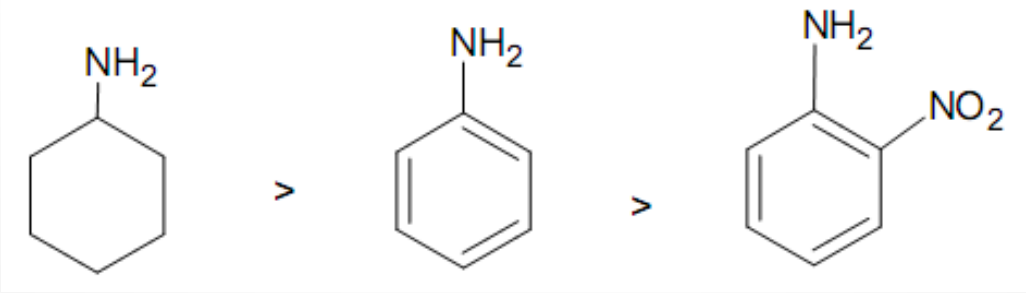


- Groups that donate or supply electrons will increase the basicity of amines while groups that decrease the electron density around the nitrogen decrease the basicity of the molecule.

$$(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$$

Most basic — Least basic

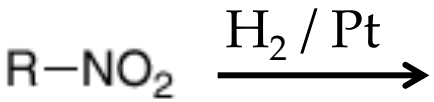
- Aromatic amines are less basic strength than aliphatic amines.



Preparation of Amines

1- Reduction of N-containing compounds (nitro compounds, nitriles, amides, and oximes)

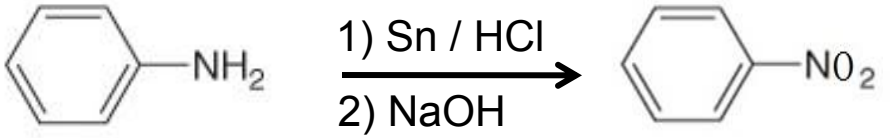
Nitro compounds



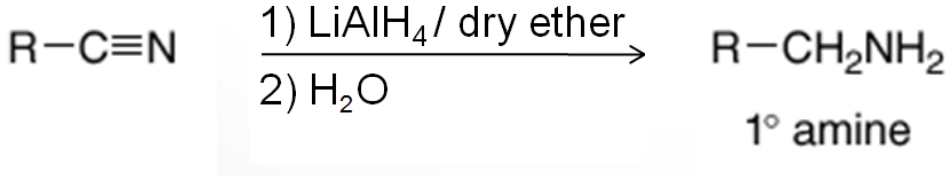
1) Sn / HCl / 2) NaOH

or

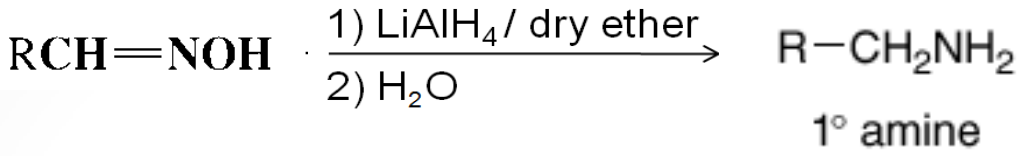
$LiALH_4$ / dry ether / 2) H_2O



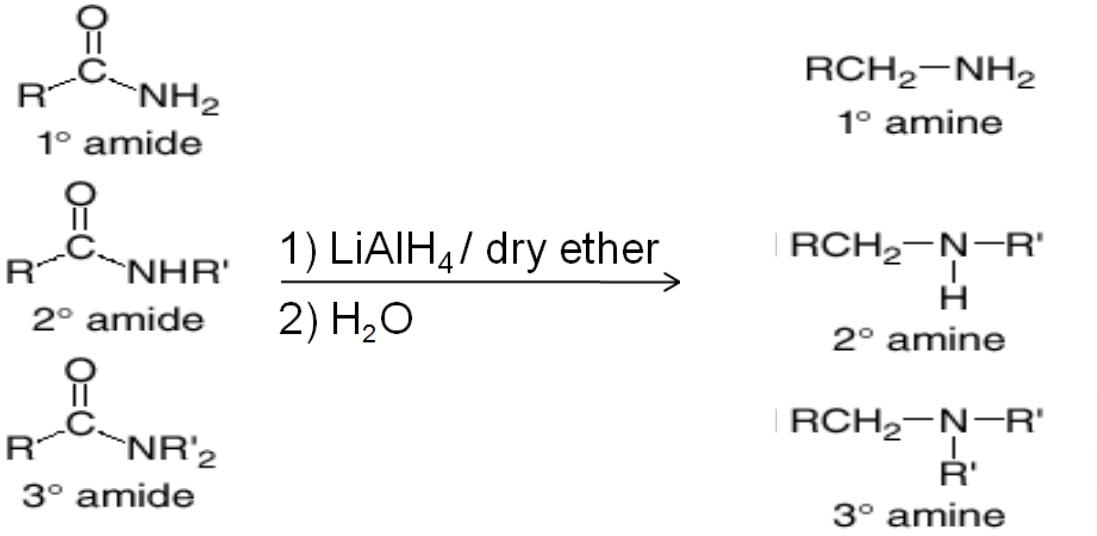
Nitrile



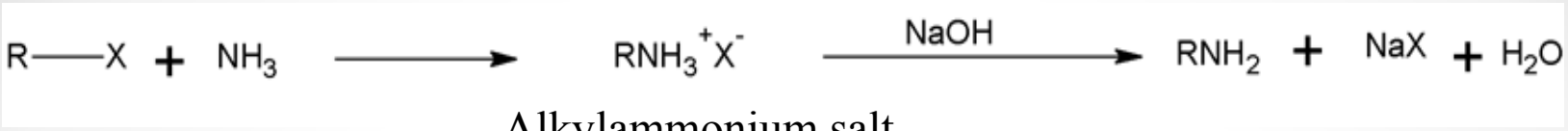
Oxime



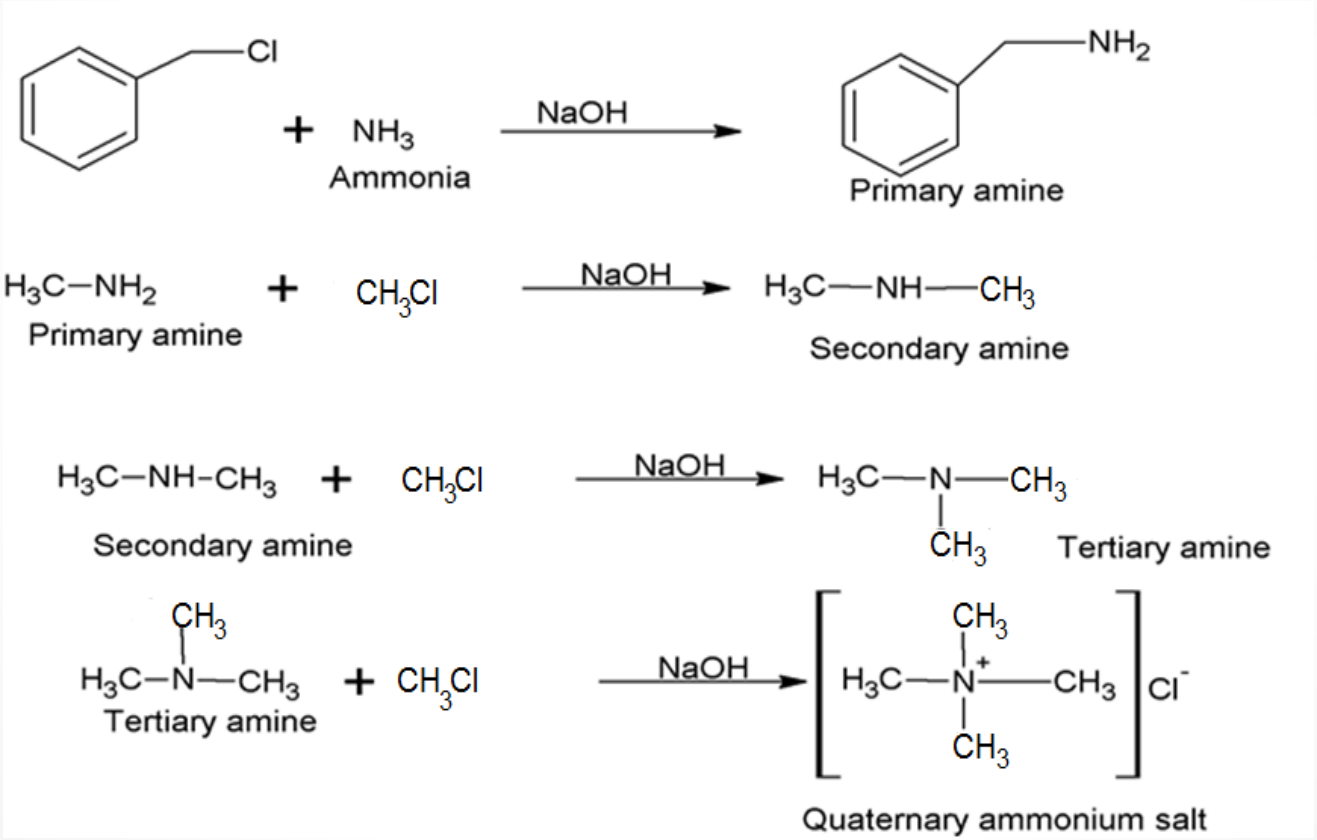
Amides



2- Alkylation Of Ammonia



Alkylammonium salt

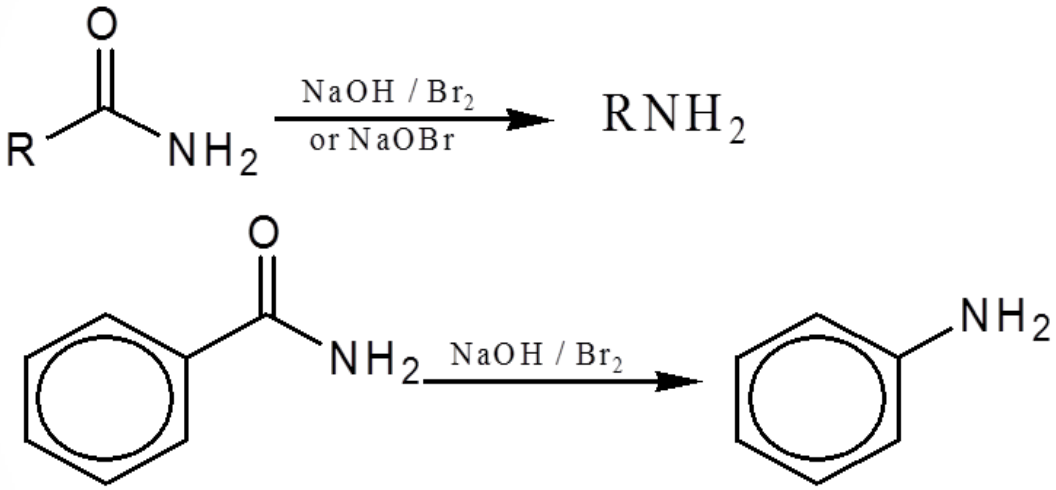


Tetramethylammonium chloride

3- Hoffman Degradation Of Amides

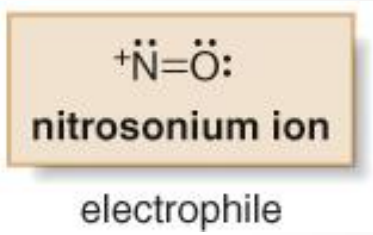
By the action of Sodium hypobromite NaOBr

It will reduce 1 carbon atom in this reaction



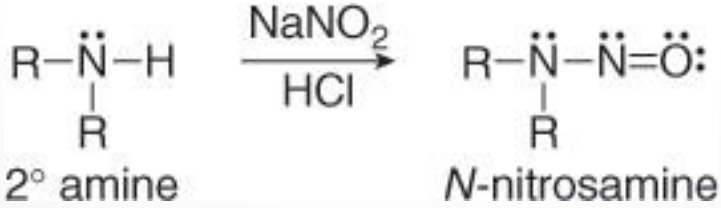
Reactions Of Amines

Reaction of Amines with Nitrous Acid

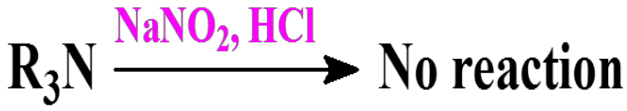


- Nitrous acid reacts with 1° alkylamines and arylamines to form diazonium salts. This reaction is called diazotization.

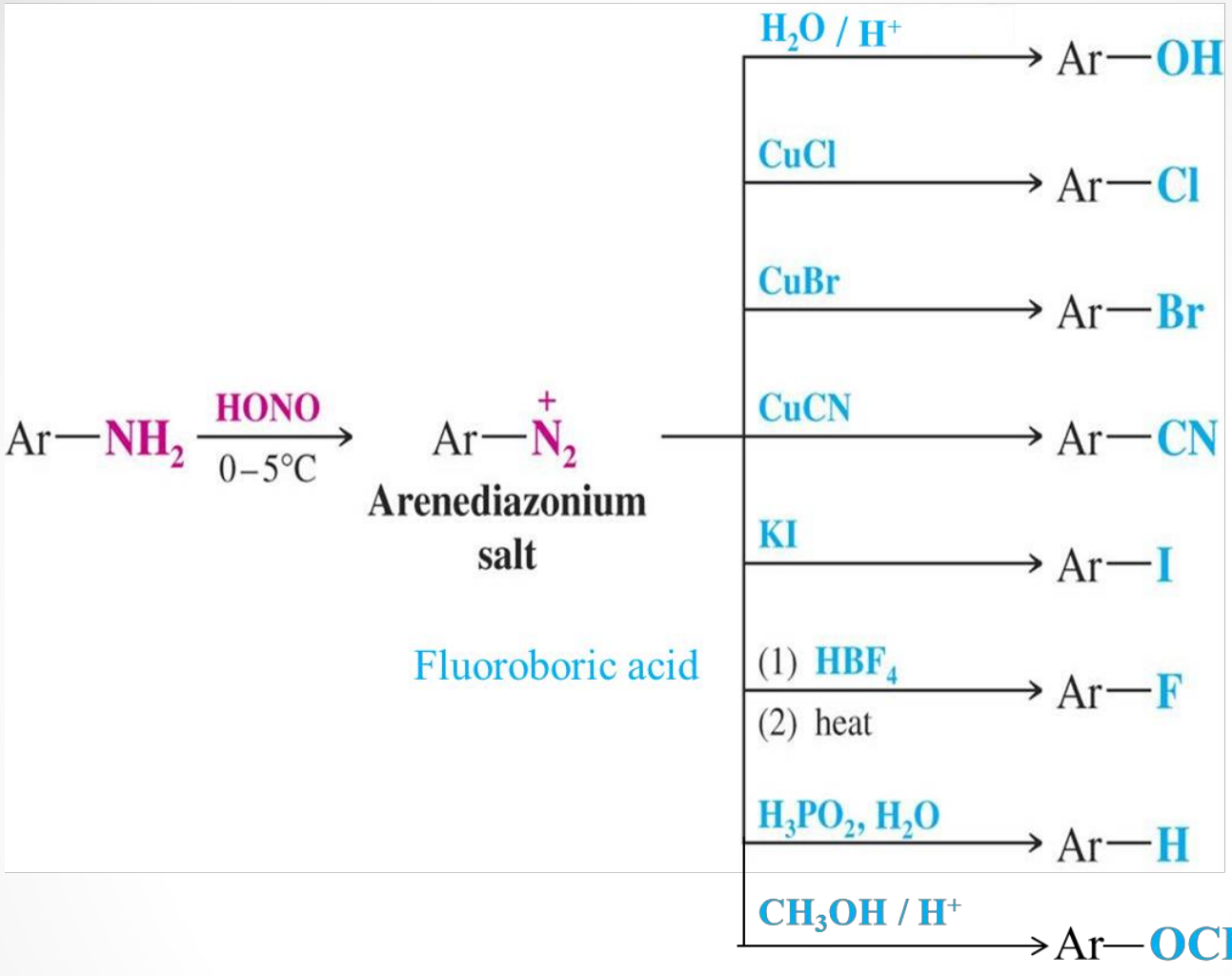
- 2° Alkylamines and aryl amines react with nitrous acid to form *N*-nitrosamines.



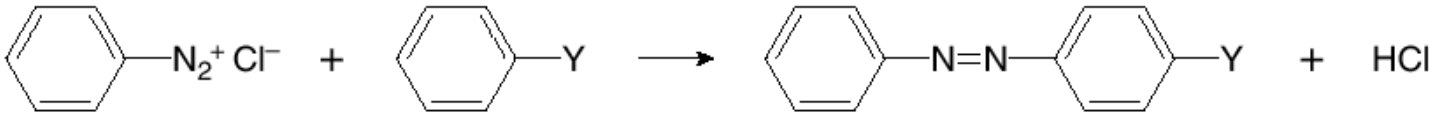
- 3° Alkylamines react with nitrous acid to form
  Water -soluuble ammoium salts.



- 3° aryl amines react with nitrous acid to form
  p-nitroso aromatic compounds



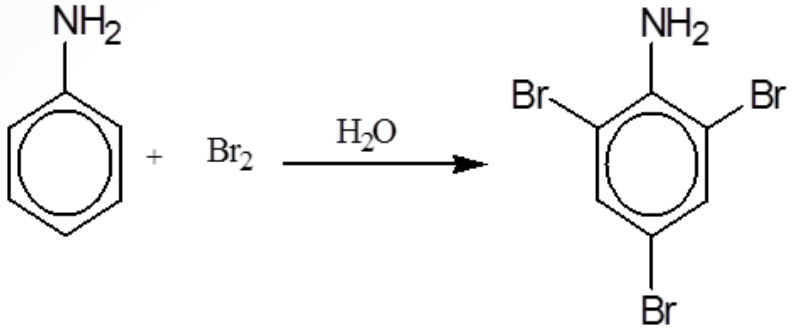
Azo coupling

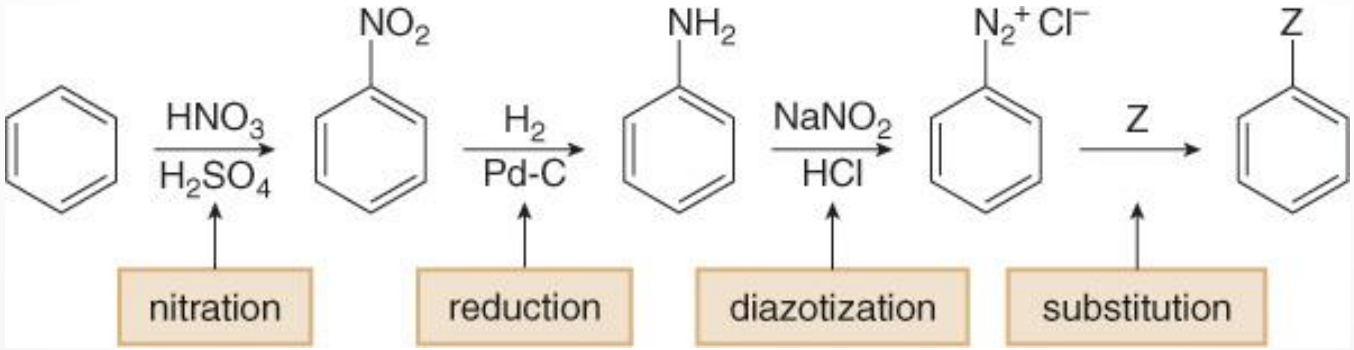


Y = NH_2, NHR, NR_2, OH (a strong electron-donor group)

azo compound

Halogenation





Chem. 108

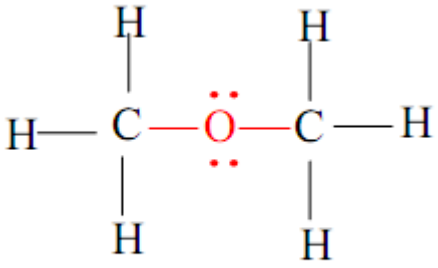
Ethers and Epoxides

Chapter 8

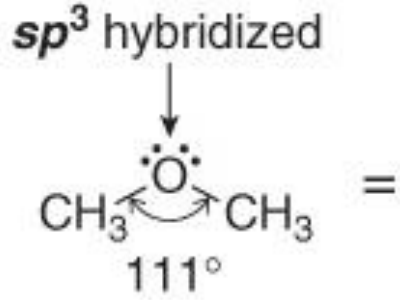
Ethers

Ether is a class of organic compounds that contain an ether group R–O–R.

For the simplest ether, Dimethyl ether



Lewis structure



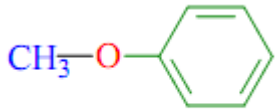
=

Classification of Ethers

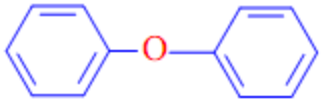
(I) Aliphatic Ethers

Butylmethylether

(II) Aromatic Ethers



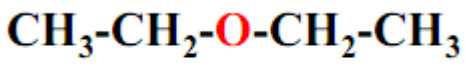
Methyl phenylether



Diphenylether

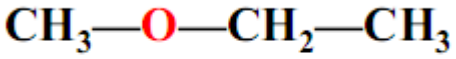
Types of Ethers

1- Simple Ethers or Symmetrical Ethers



Diethyl ether

2- Mixed Ethers or Unsymmetrical Ethers



Ethylmethyl ether

Nomenclature

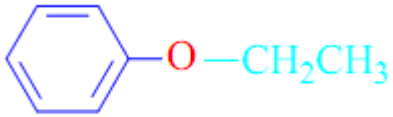
Common Names

The two-alkyl groups bonded to the functional group (- O -) are written alphabetically followed by the word ether.

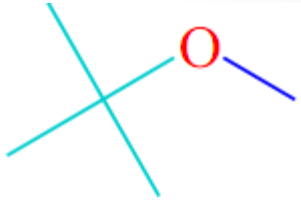
Examples:

$CH_3 - O - C_2H_5$

Ethyl methyl ether



Ethyl phenyl ether

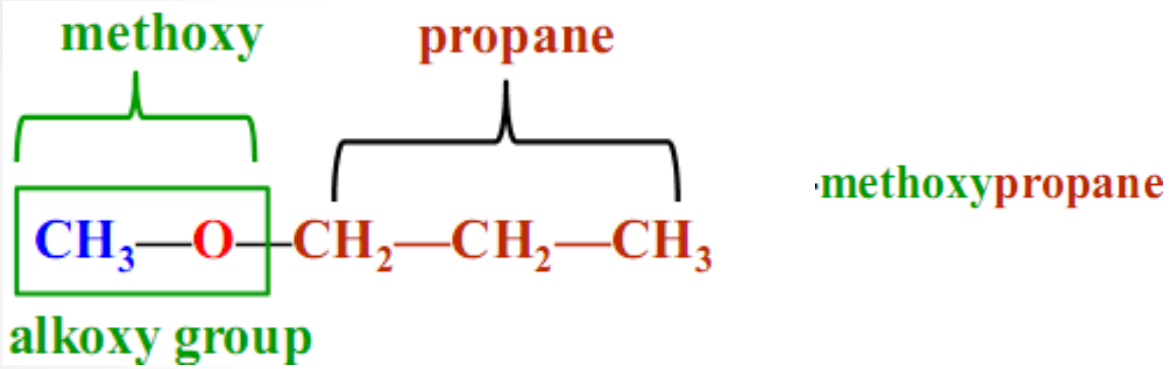


Methyl t-butylether

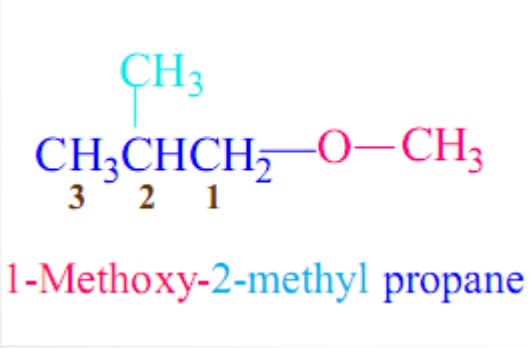
IUPAC System

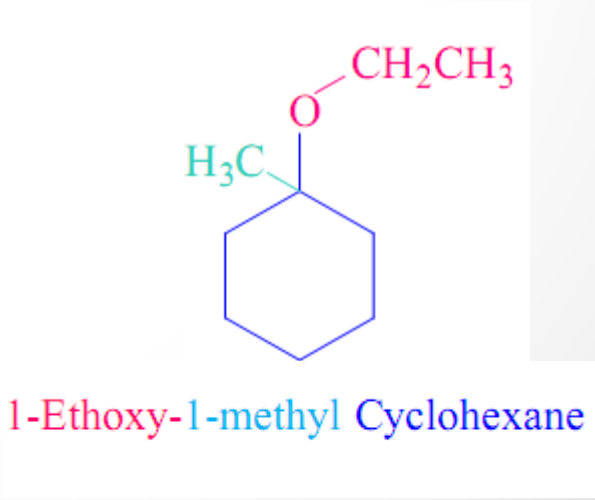
The shorter alkyl group and the oxygen are named as an alkoxy group attached to the longer alkane.

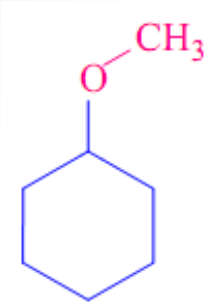
They are named as alkoxyalkanes.



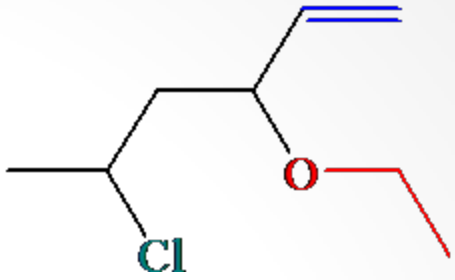
Examples:



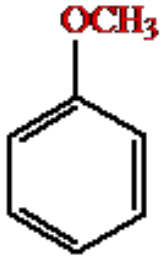




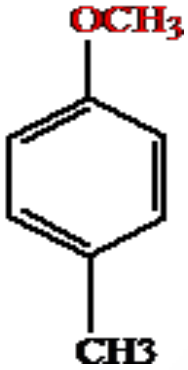
Methoxy cylohexane



5-Chloro-3-ethoxy-hex-1-ene



Methoxybenzene



P-Methoxytoluene

Physical Properties

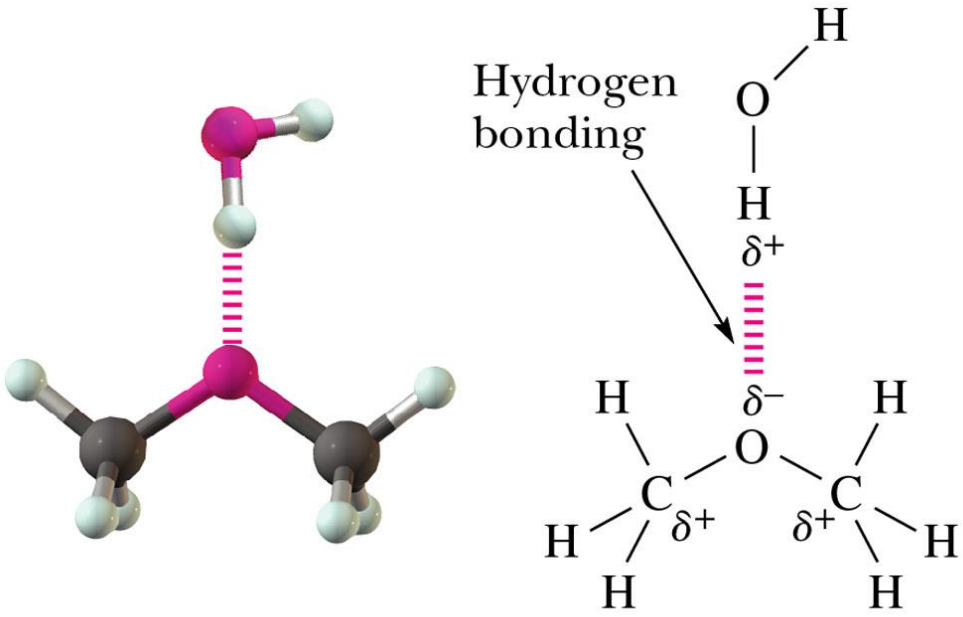
Boiling Points of Ethers:

hydrogen bonds cannot form between ether molecules

$CH_3CH_2CH_2CH_3$	$CH_3-O-CH_2CH_3$	$CH_3CH_2CH_2OH$
Butane	Methoxyethane	1-Propanol
(butane)	(ethyl methyl ether)	(Propyl alcohol)
M.W. = 58	M.W. = 60	M.W. = 60
b.p. = - 0.5°C	b.p. = 7.9 °C	b.p. = 97.2°C

Solubility of Ethers:

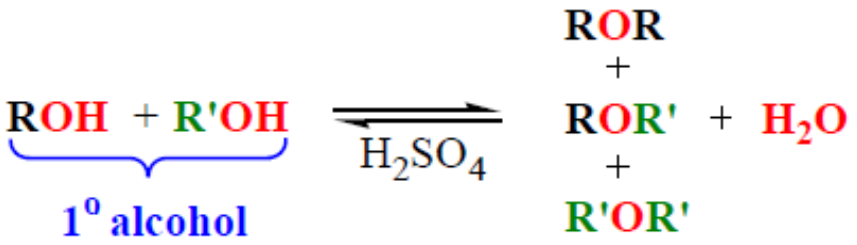
Ethers are soluble in water, due to their hydrogen bond formation with water molecules.

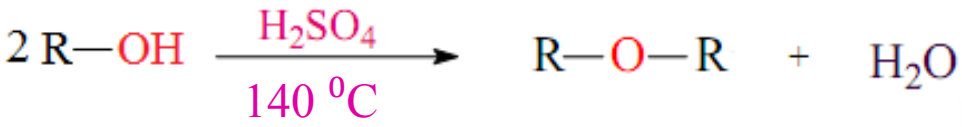


The solubility decreases with increase in the number of carbon atoms.

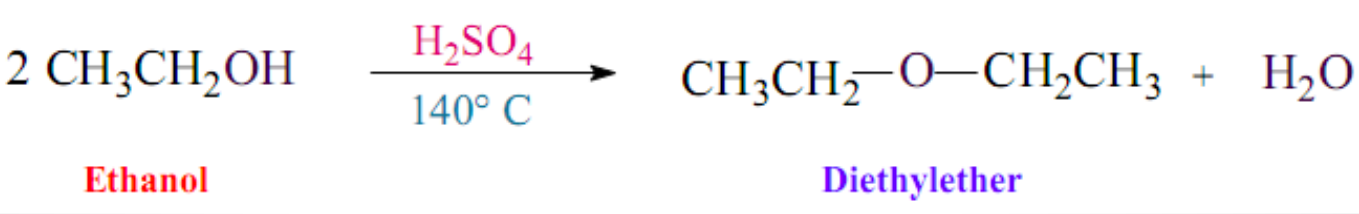
Preparation of Ethers

1- Dehydration of Alcohols

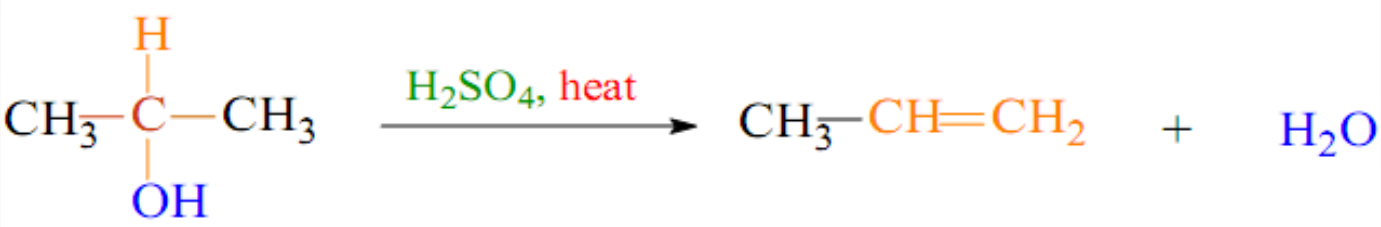


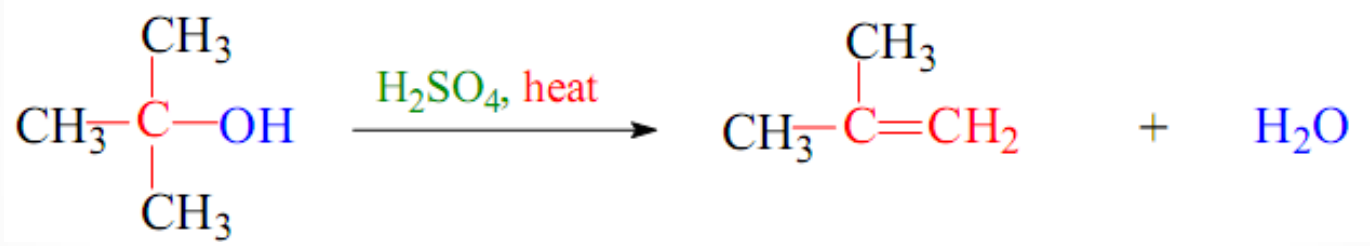


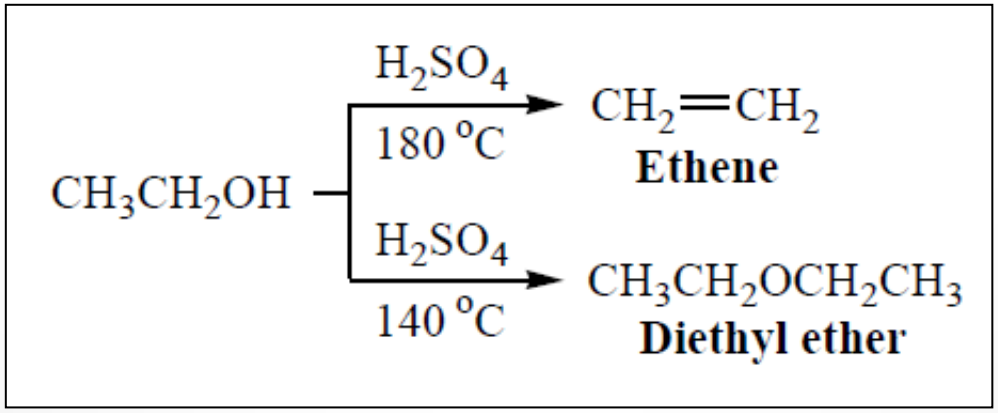
Example:



- The dehydration of 2° and 3° alcohol is unsuccessful to get ethers as alkenes are formed easily.

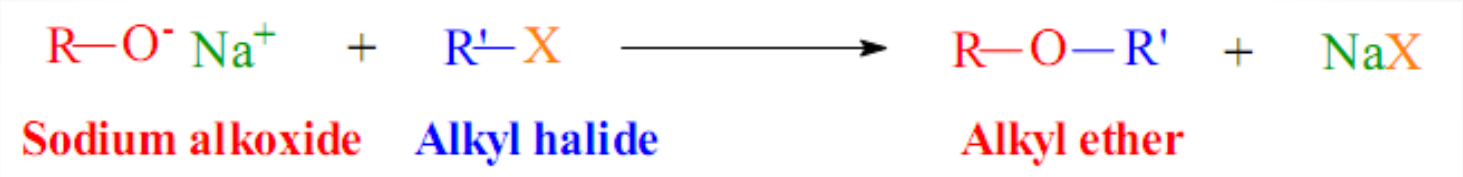


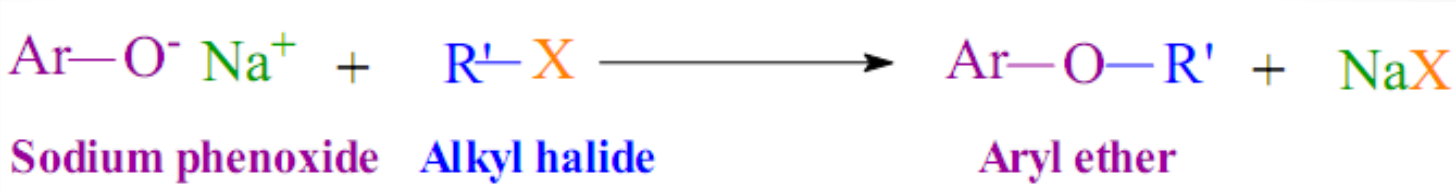




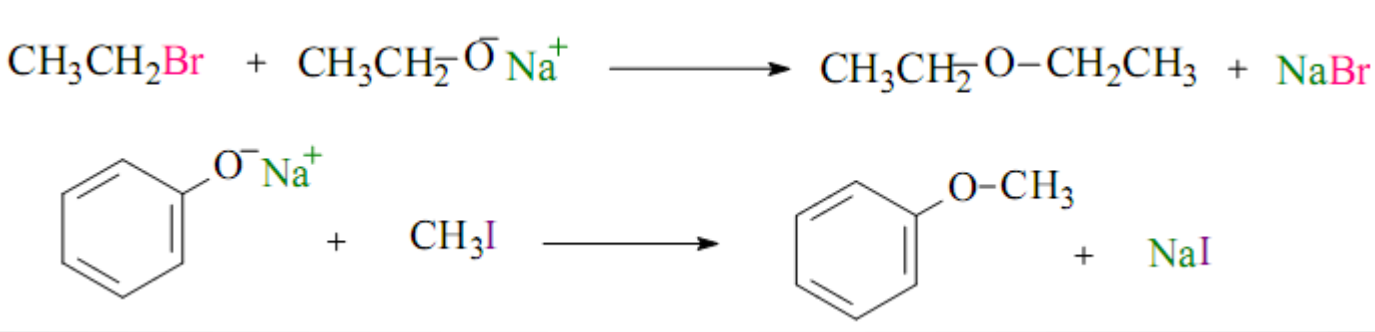
2- Williamson Synthesis

- The reaction of a sodium alkoxide RONa or a sodium phenoxidex ArONa with an alkyl halide to form an ether.
- The reaction involves nucleophilic substitution of an alkoxide ion for a halide ion.

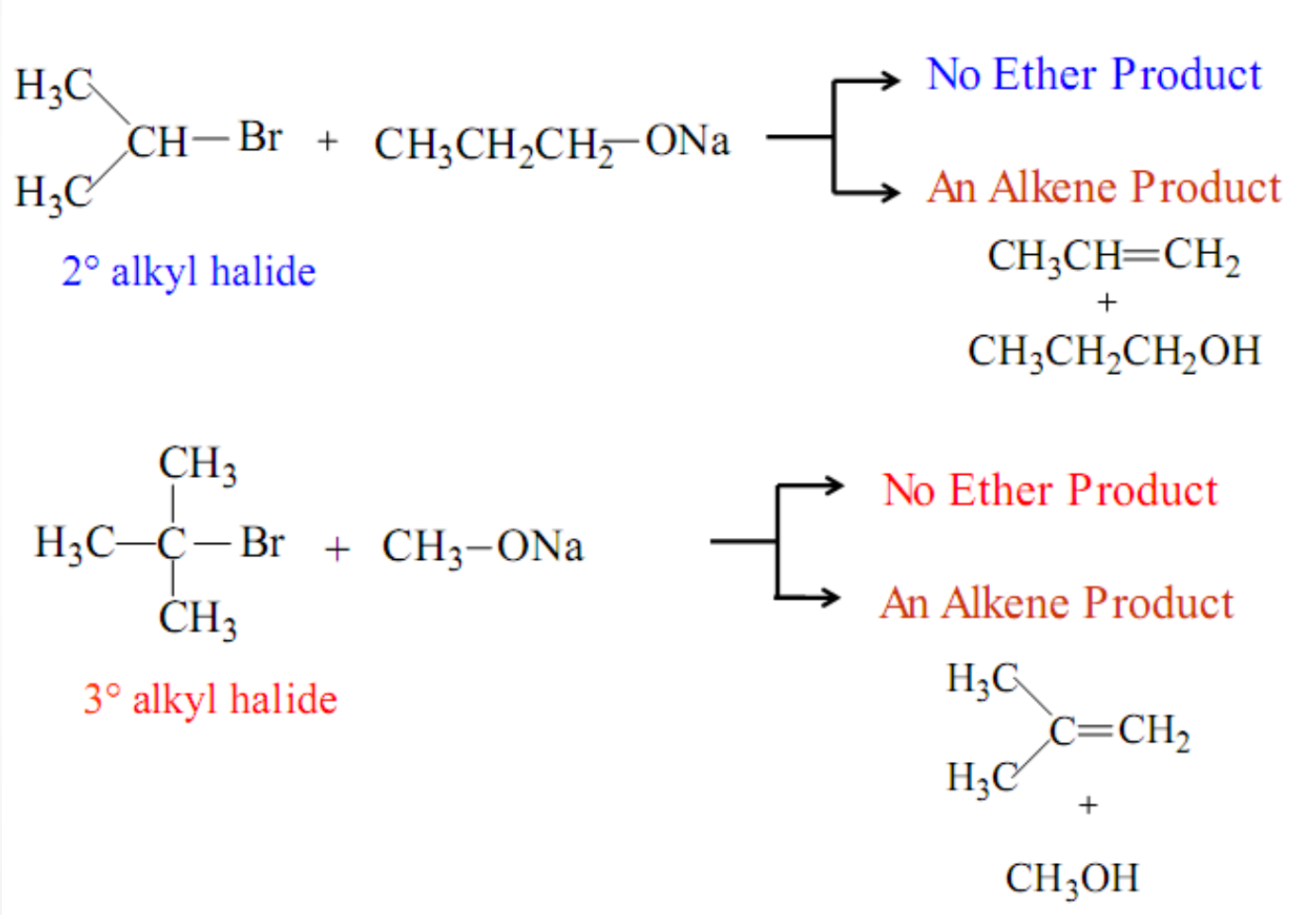




Examples:



- If a secondary (2°) or tertiary alkyl halide (3°) is used, an alkene is the only reaction product and no ether is formed.

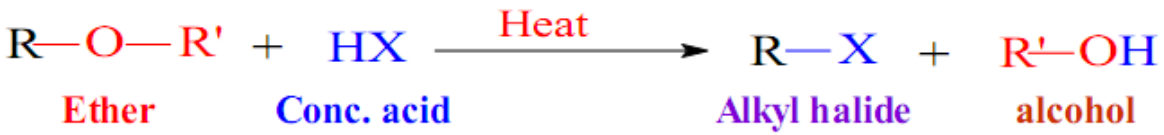


Reactions of Ethers

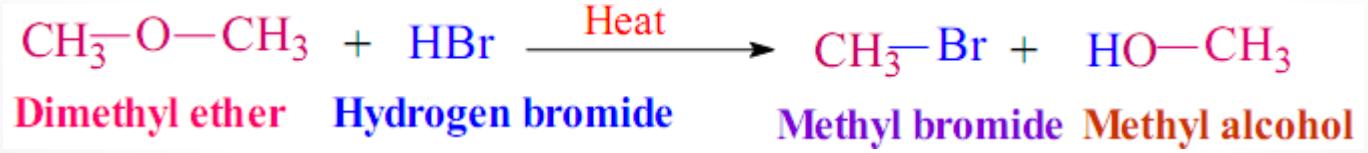
Cleavage of Ethers by Acids

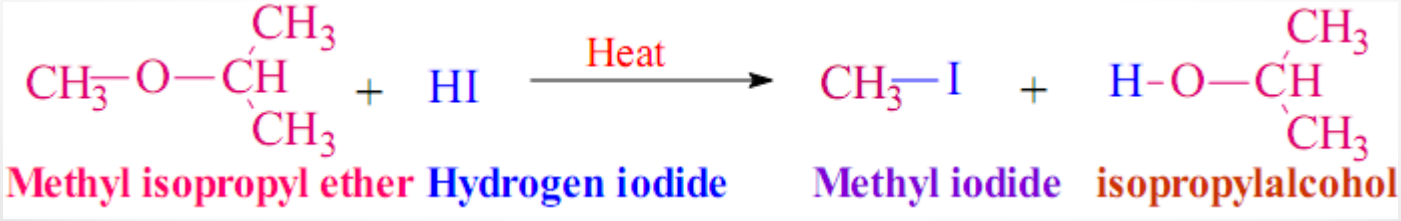
Substitution Reactions with strong acids HX,
X could be; I or Br.

Ethers are cleaved by HX to an alcohol and a haloalkane



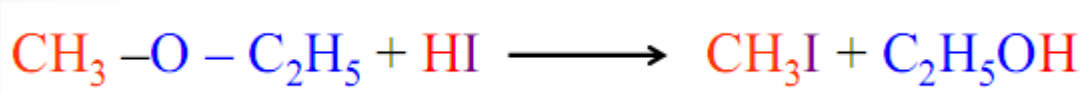
Examples:





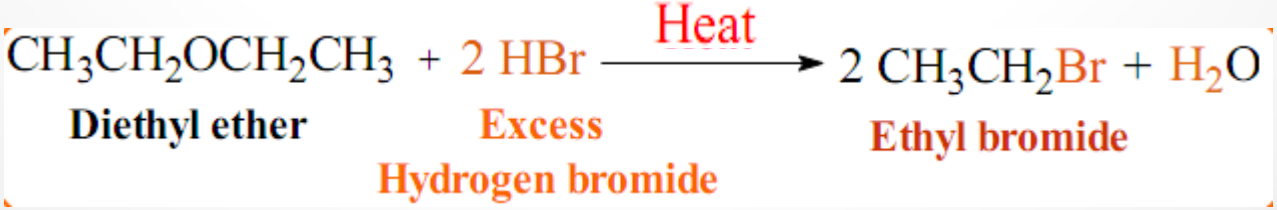
Point of cleavage:

- If both the alkyl groups are primary or secondary, the smaller alkyl group gets converted to the alkyl halide predominantly.



- If one of the alkyl group is tertiary, the point of cleavage is such that the tertiary alkyl halide is formed as the major product

- If two or more equivalents of acid are used further dehydration can occur on formed alcohols which may react further to form a second mole of alkyl halide.



Epoxides (Cyclic Ethers)

Epoxide: a cyclic ether in which oxygen is one atom of a three-membered ring.

epoxide or oxirane

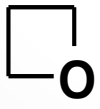
Nomenclature

Although cyclic ethers have IUPAC names, their common names are more widely used.

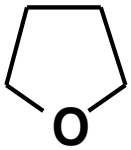
IUPAC: prefix ox- shows oxygen in the ring

the suffixes -irane, -etane, -olane, and -ane show three, four, five, and six atoms in a saturated ring.

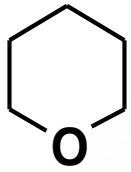
Oxirane (Ethylene oxide)



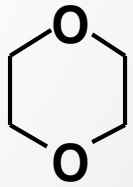
Oxetane



Oxolane (Tetrahydrofuran)



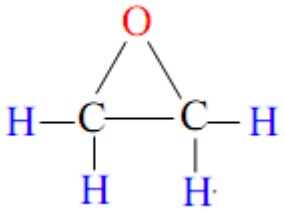
Oxane (Tetrahydropyran)



1,4-Dioxane

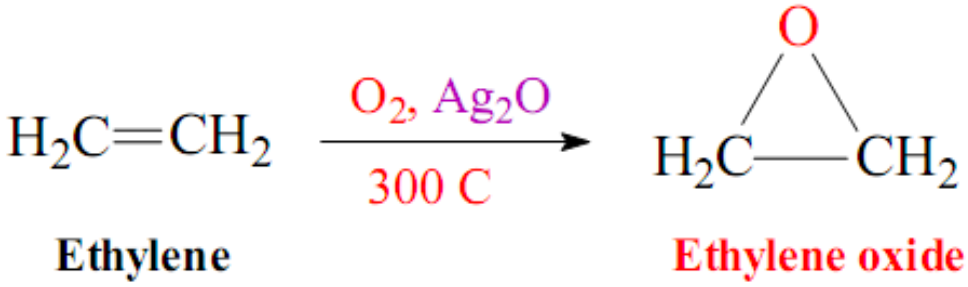
Preparation of Epoxides

The simplest and the most important epoxide is ethylene oxide.



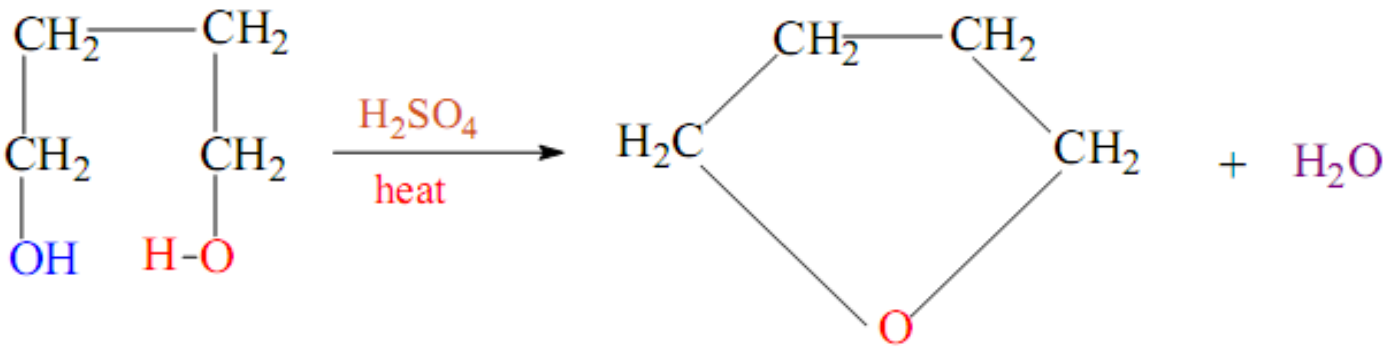
1. Air Oxidation of Ethylene

By air oxidation of ethylene and silver oxide catalyst.

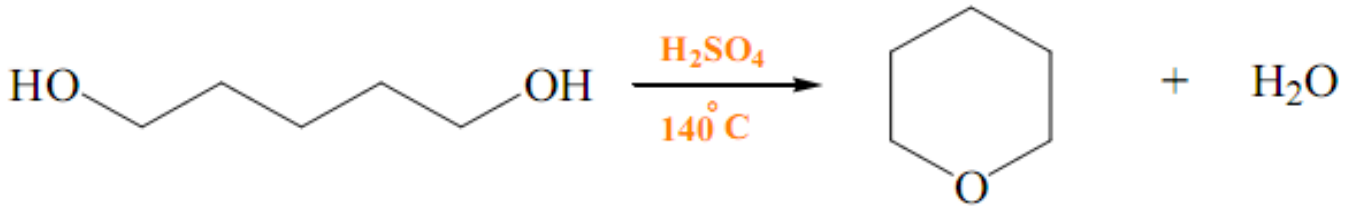


2. Dehydration of dialcohols

Examples:



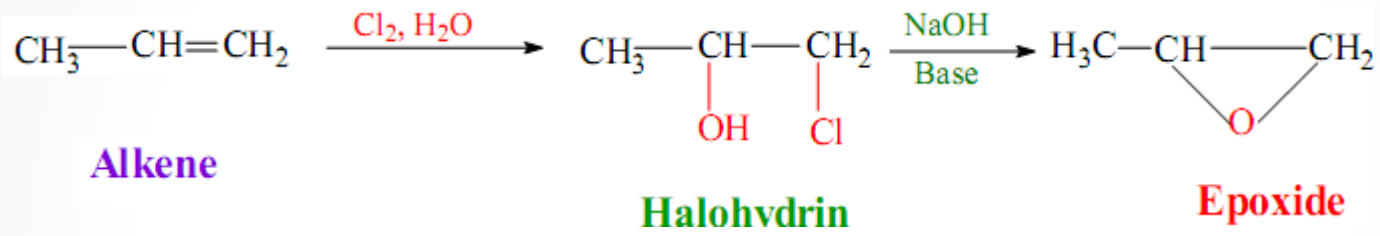
1,4- Butanediol **Tetrahydrofuran (THF)**

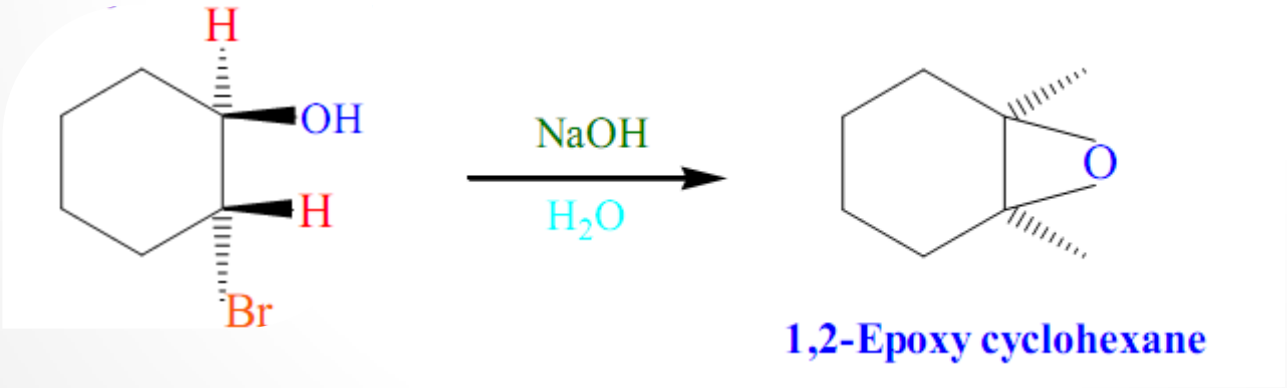


1,5- pentanediol **Tetrahydropyran**

3-Conversion of Vicinal Halohydrins to Epoxides

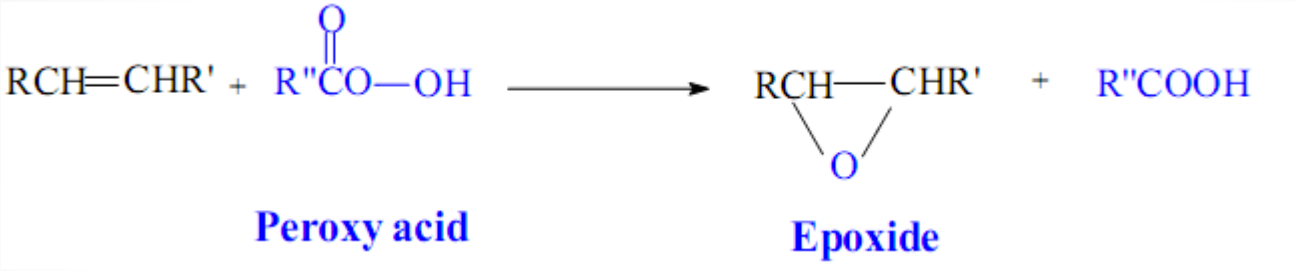
Examples:



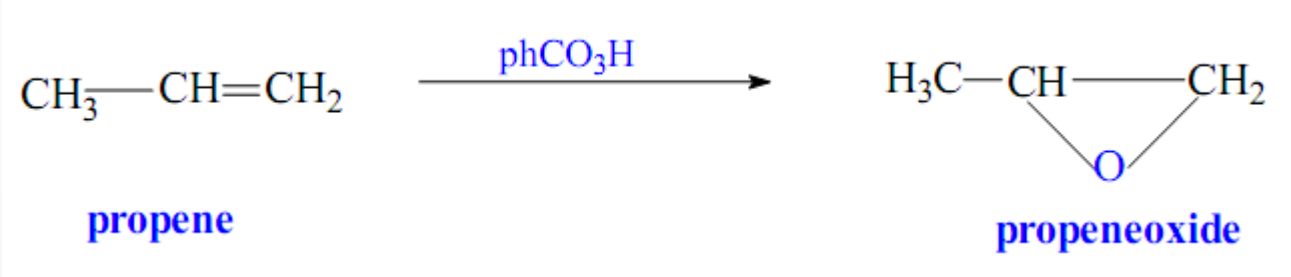


4. Epoxidation method

Epoxides are often prepared from reacting with organic peroxy acids (peracids) ex; $CH_3C(O)OOH$ in a process called epoxidation.

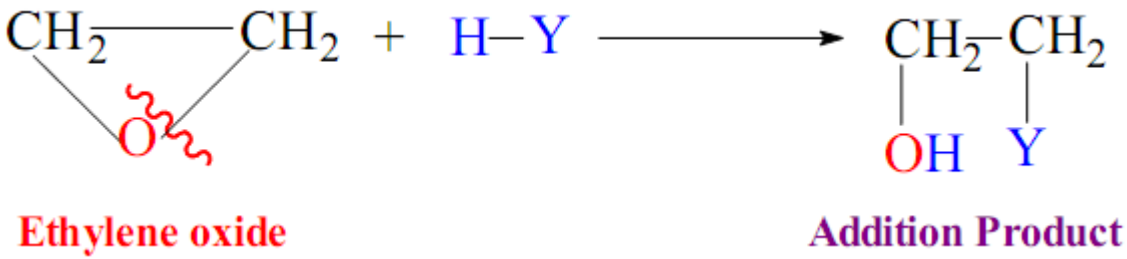


Example:

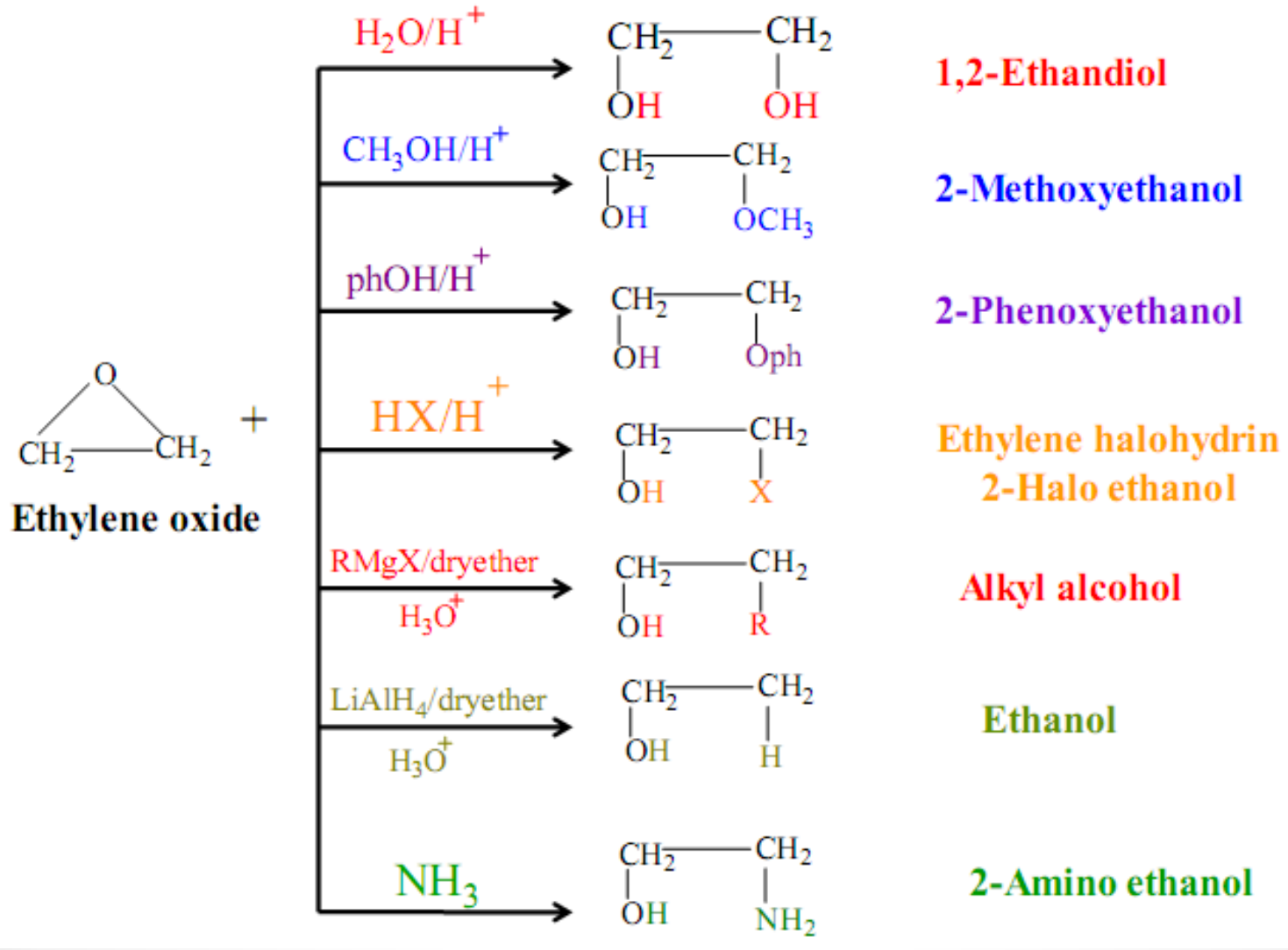


Reactions of Epoxids

Epoxides are highly strained and easily undergo ring-opening reactions under both acidic and basic conditions.



Reactions of Epoxids



Chem. 108

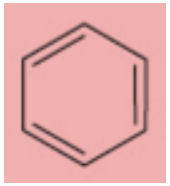
Benzene and Aromatic Compounds

Chapter 5

- The term *aromatic* was used to designate compounds with spicy or sweet-smelling odors.

- Today the expressing *aromatic compounds* came to mean *benzene and derivatives of benzene.*

Structure of Benzene: Resonance Description



C_6H_6

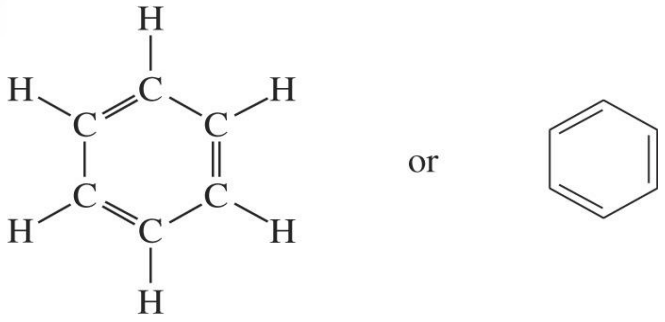
1.It contains a six-membered ring and three additional degrees of unsaturation.

2.It is planar.

3.All C—C bond lengths are equal.

The Kekule Structure for Benzene

- Kekule was the first to formulate a reasonable representation of benzene:

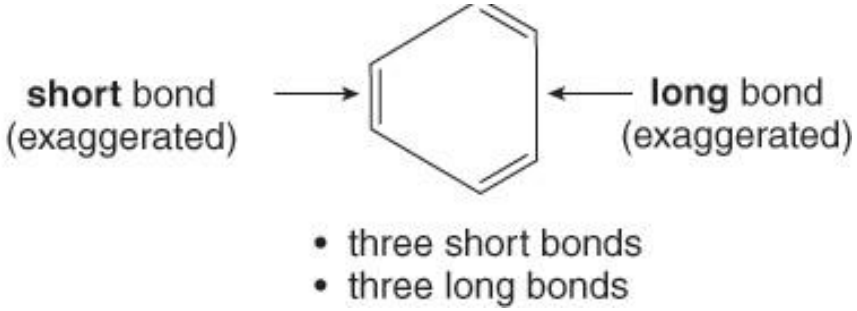


The Kekulé formula for benzene

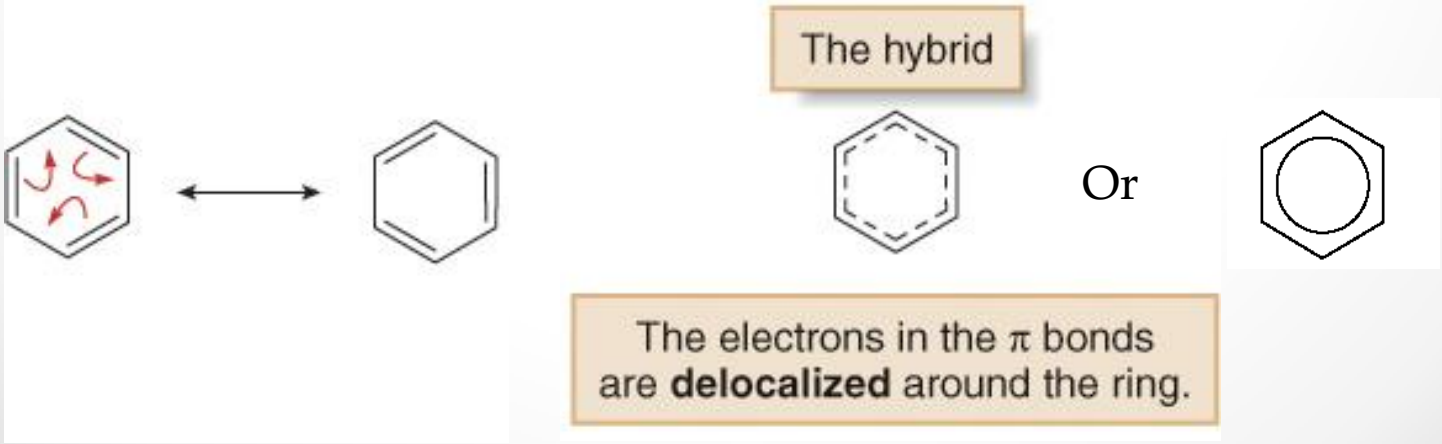
- The Kekule structure suggests alternating double and single carbon-carbon bonds.

- Based on the Kekule structure one would expect there to be two different 1,2-dibromobenzenes but there is only one.

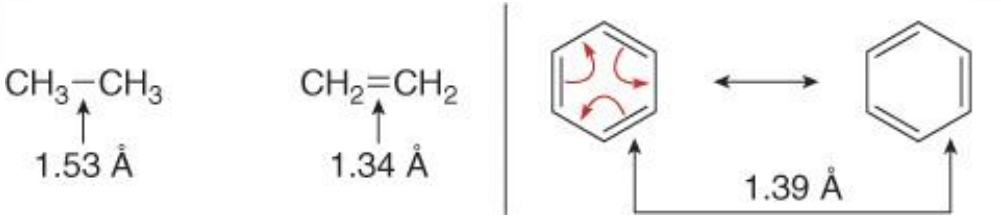
- The Kekule structures satisfy the first two criteria but not the third, because having three alternating π bonds means that benzene should have three short double bonds alternating with three longer single bonds.



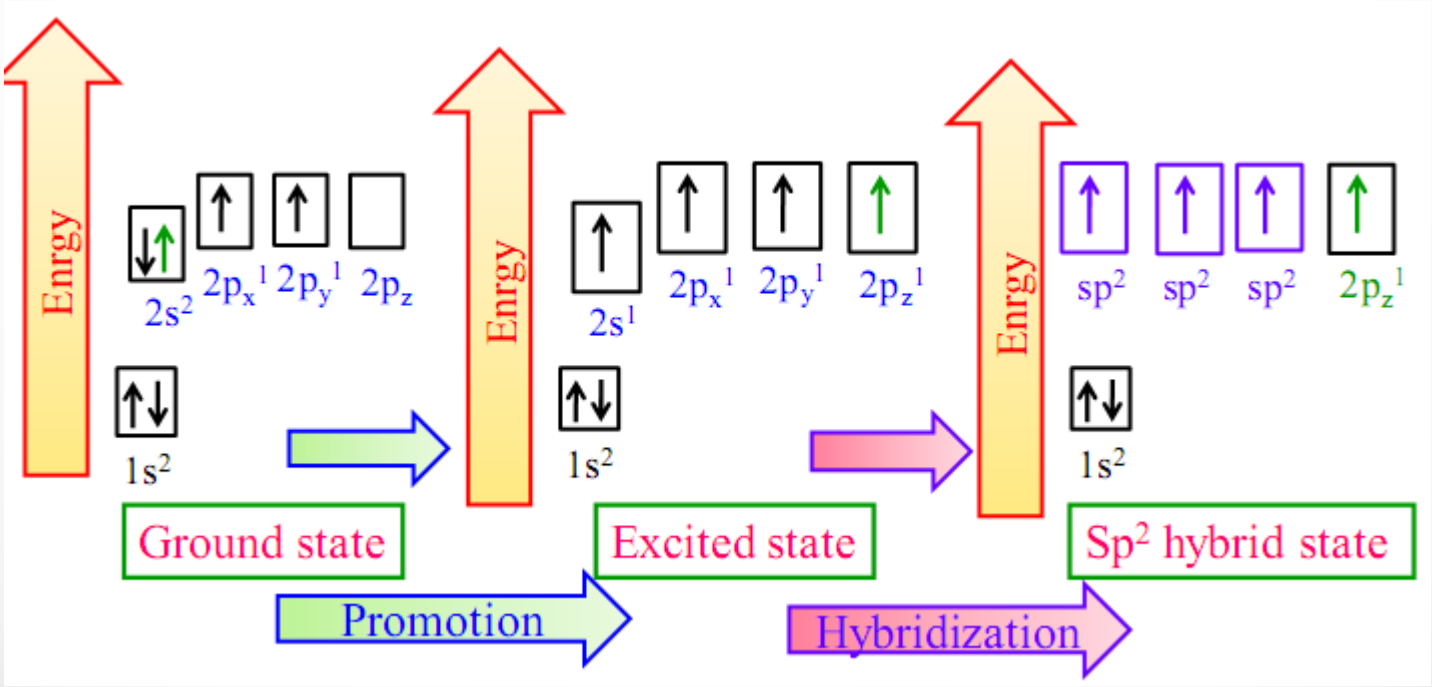
The true structure of benzene is a resonance hybrid of the two Lewis structures, with the dashed lines of the hybrid indicating the position of the π bonds.

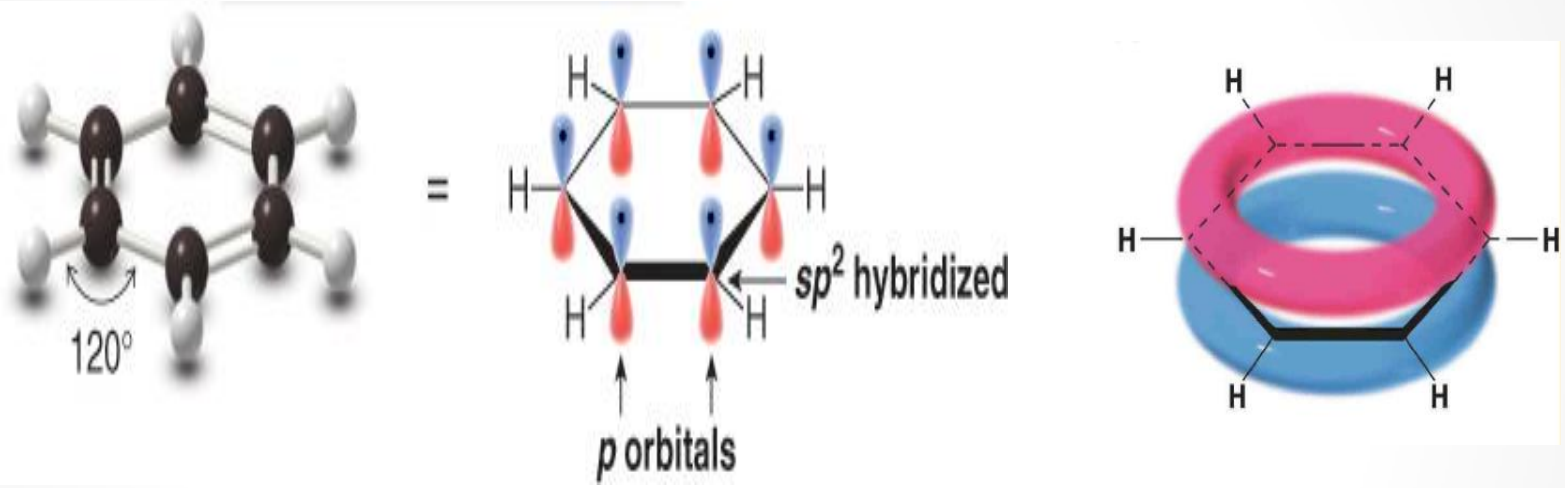


In benzene, the actual bond length (1.39 Å) is intermediate between the carbon—carbon single bond (1.53 Å) and the carbon—carbon double bond (1.34 Å).

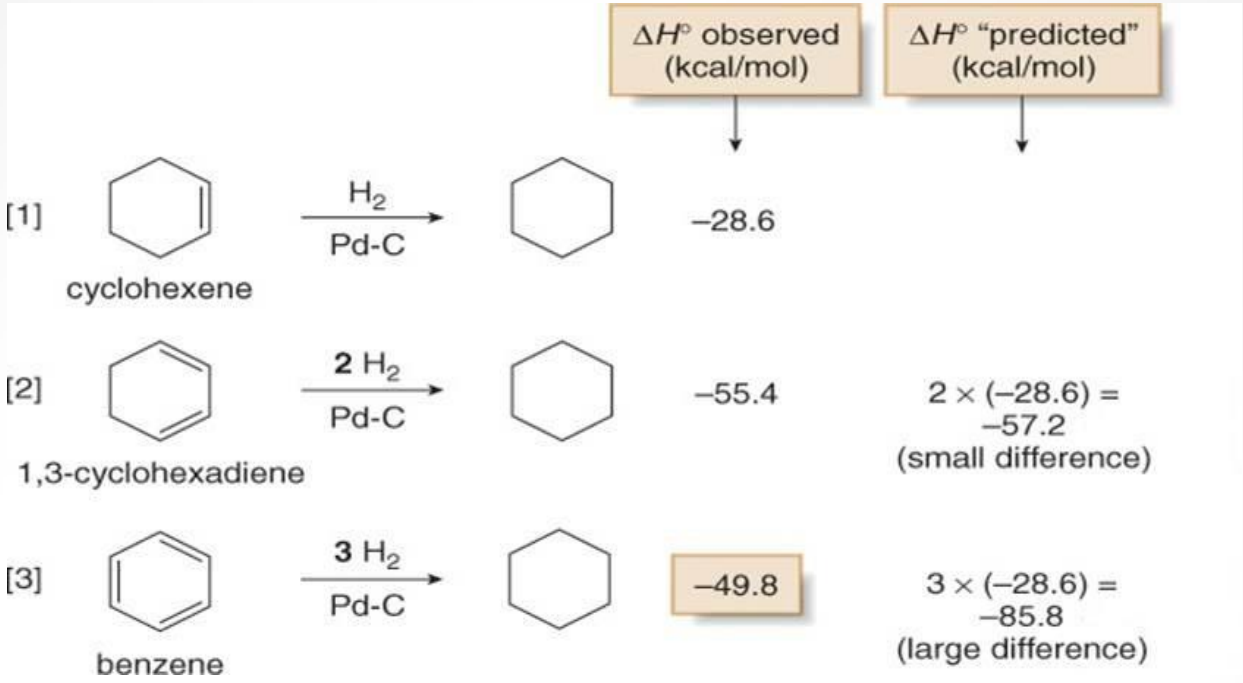


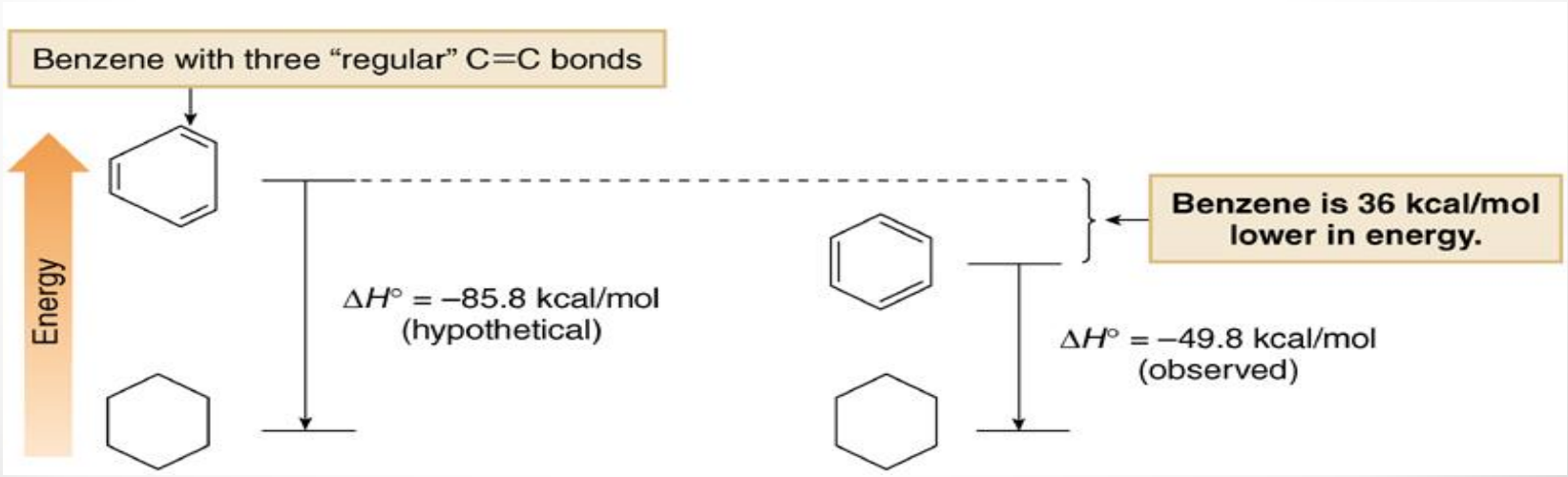
Benzene-Molecular Orbital Description:



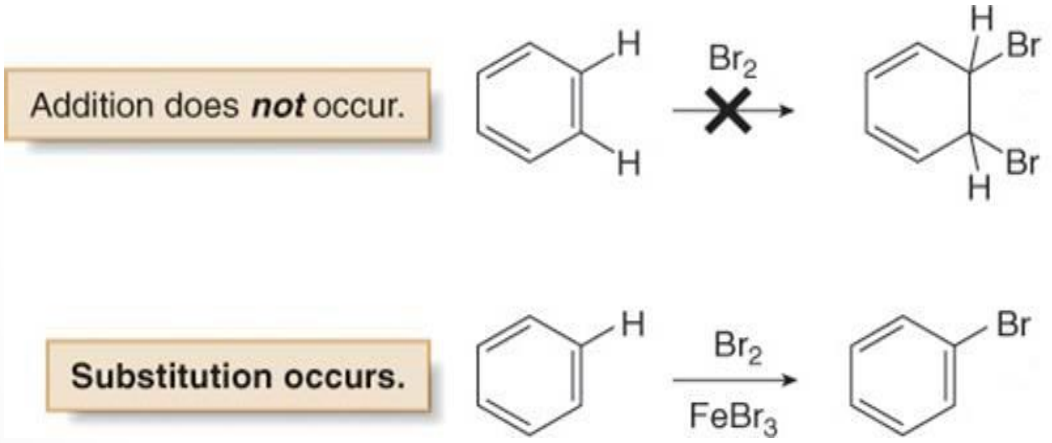

120°
=
H
H
H
H
H
H
sp2 hybridized
p orbitals
H
H
H
H
H
H

Stability of Benzene:





- The low heat of hydrogenation of benzene means that benzene is especially stable even more so than conjugated polyenes. This unusual stability is characteristic of aromatic compounds.
- Benzene's unusual behavior is not limited to hydrogenation. Benzene does not undergo addition reactions typical of other highly unsaturated compounds, including conjugated dienes.



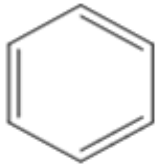
Aromatic Character: The (4n + 2) π Rule

Hückel's Rule

- A molecule must be cyclic.
- A molecule must be planar.
- A molecule must be completely conjugated.
- A molecule must satisfy Hückel's rule, and contain a particular number of π electrons.

  4n+2 π electrons (n= 0, 1, 2, 3, ….= 2, 6, 10, 14, ….)

Examples:

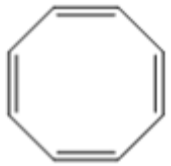


Benzene

3π-bonds = 6 pi electrons

4n+2= 6 ; n= 1

Aromatic



Cyclooctatetraene

4π-bonds = 8 pi electrons

4n+2= 8 ; n= 3/2

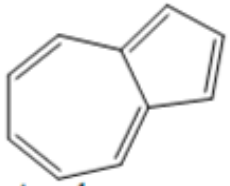
Not aromatic

Cyclopentadiene

The hybridization of the top C is **sp^3**

Not planar, not fully conjugated

Not aromatic

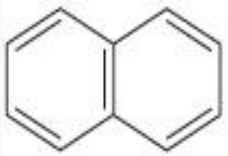


Azulene

5π-bonds = 10 pi electrons

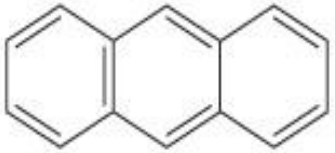
4n+2= 10 ; n= 2

Aromatic



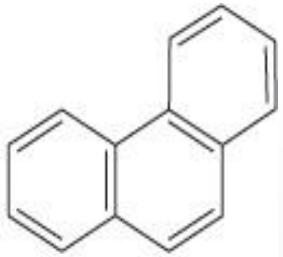
naphthalene

10 π electrons



anthracene

14 π electrons



phenanthrene

14 π electrons

The hybridization of the top C is sp^3

Not planar, not fully conjugated

$4n+2 = 4$; $n = 1/2$

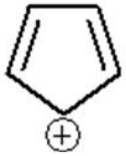
Not aromatic

$4n+2 = 2$; $n = 0$

Aromatic

The hybridization of the top C is sp^3

Not planar, not fully conjugated

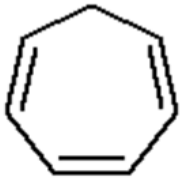


$4n+2 = 4$; $n = 1/2$

Not aromatic

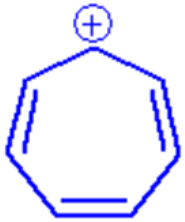
$4n+2 = 6$; $n = 1$

Aromatic



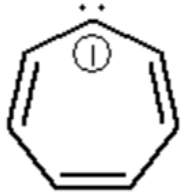
The hybridization of the top C is sp^3

Not planar, not fully conjugated



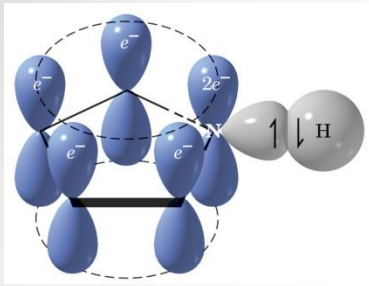
$4n+2 = 6$; $n = 1$

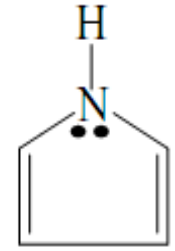
Aromatic



$4n+2 = 8$; $n = 3/2$

Not aromatic



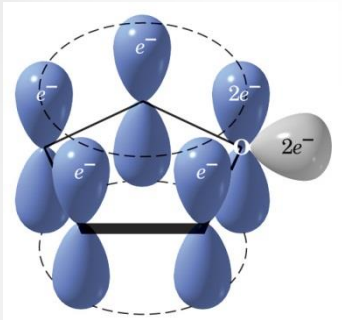


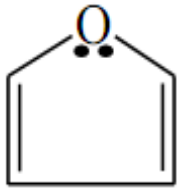
Pyrrol

2π-bonds + 1 lone pair = 6 pi electrons

4n+2= 6 ; n= 1

Aromatic



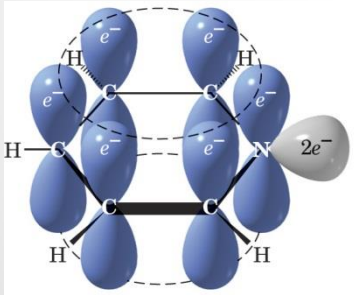


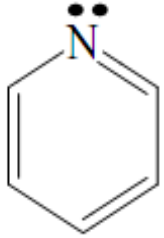
Furan

2π-bonds + 1 lone pair = 6 pi electrons

4n+2= 6 ; n= 1

Aromatic





Pyridine

the lone pair is perpendicular to the π-system

3π-bonds + 0 lone pair = 6 pi electrons

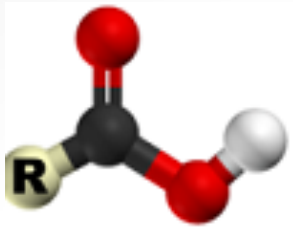
4n+2= 6 ; n= 1

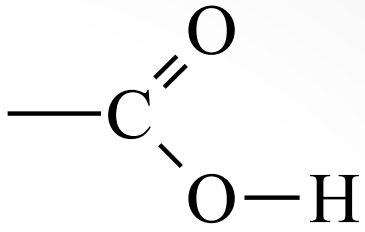
Aromatic

Chem. 108

Carboxylic Acids And Their Derivatives

Chapter 10





- Carboxylic acids are strong organic acids which contain the carboxyl group (-COOH, -CO_2H)

- Carboxylic acids are classified as aliphatic or aromatic depending on whether R or an Ar is attached to the carboxylic group R-COOH or Ar-COOH

Nomenclature

Formula	IUPAC alkan -oic acid	Common prefix – ic acid
HCOOH	methanoic acid	formic acid
CH_3COOH	ethanoic acid	acetic acid
CH_3CH_2COOH	propanoic acid	propionic acid
$CH_3CH_2CH_2COOH$	butanoic acid	butyric acid

Naming Rules

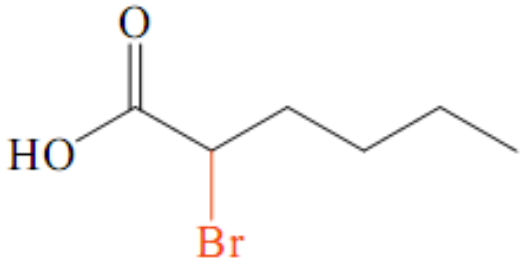
- Identify longest chain
- (IUPAC) Number carboxyl carbon as 1
- (Common) Assign α, β, γ, δ to carbon atoms adjacent to carboxyl carbon

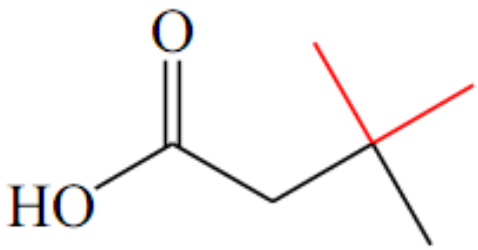
5 4 3 2 1

C—C—C—C—C=O

δ γ β α ← used in common names

Examples:



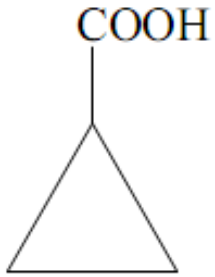


IUPAC: 2- bromohexanoic acid 3,3-dimethylbutanoic acid

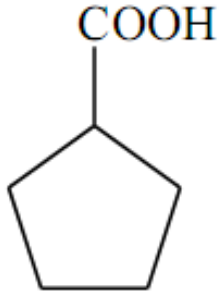
Common: α- bromohexanoic acid β,β-dimethylbutyric acid

Naming Cyclic Carboxylic Acids

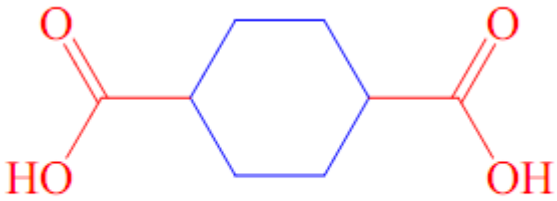
- Cyclic compounds containing one or more COOH groups attached to the ring are **named by identifying the name of the ring followed by the word** carboxylic acid or dicarboxylic acids etc.



Cyclopropane carboxylic acid

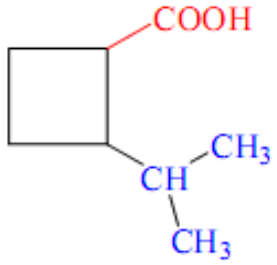


Cyclopentanecarboxylic acid

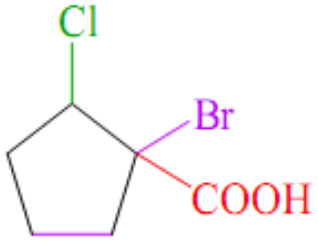


1,4-Cyclohexane**di**carboxylic acid

- The carbon atom bearing the carboxylic group is numbered 1 and the substituents are numbered relative to it.



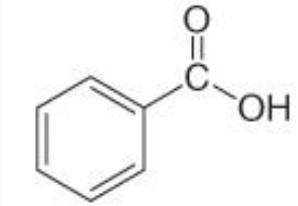
2-Isopropylcyclobutane carboxylic acids



1-Bromo-2-chlorocyclopentane carboxylic acids

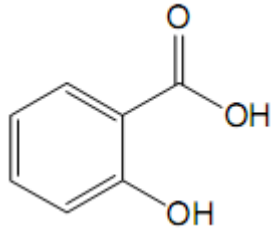
Naming Aromatic Carboxylic Acids

- The simplest aromatic carboxylic acid is benzoic acid.
- Substituted benzoic acids are named with benzoic acid as the parent name.
- Derivatives are named using numbers to show the location of substituents relative to the carboxyl group.
- The ring carbon attached to the carboxyl group is the #1 position.



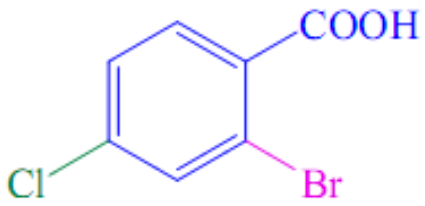
Benzoic acid

Benzene carboxylic acid

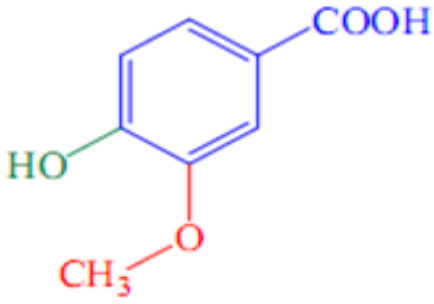


Salicylic acid

2-Hydroxybenzoic acid

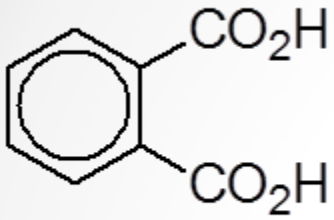


2-Bromo-4-chloro benzoic acid

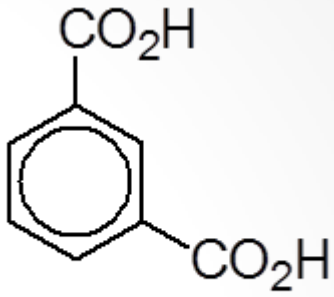


4-hydroxy-3-methoxybenzoic acid

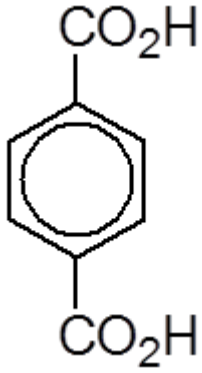
1,2-dicarboxylic acid



Phthalic acid
Benzene-1,2-dicarboxylic acid



isophthalic acid
Benzene-1,3-dicarboxylic acid

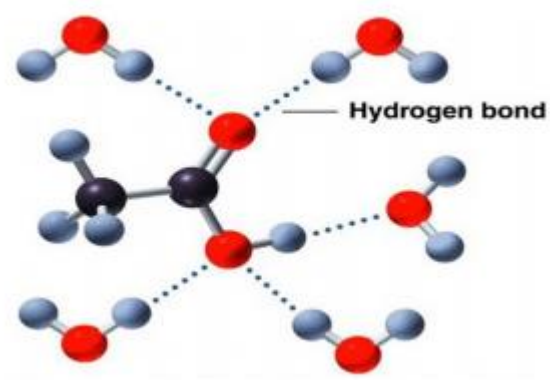


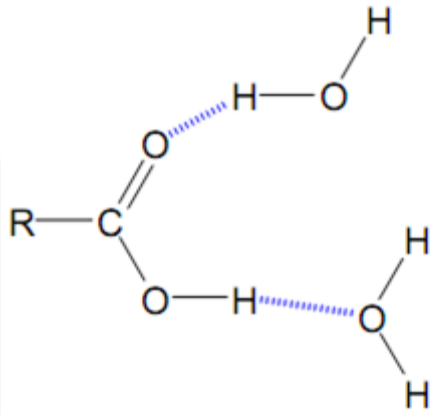
Terephthalic acid
Benzene-1,4-dicarboxylic acid

Physical Properties of Carboxylic Acids

1. Solubility

- The carboxylic acid are highly polar organic compounds.
- This polarity results from the presence of a strongly polarized carbonyl (C=O) group and hydroxyl (O-H) group.





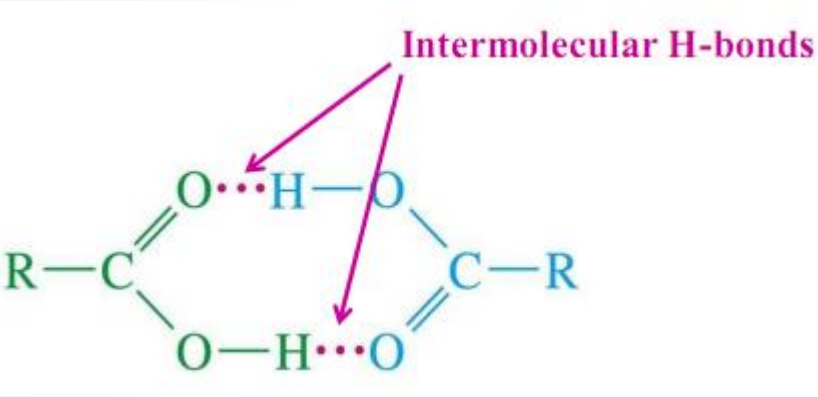
Water Solubility:

Carboxylic acid
Alcohols
Aldehydes/Ketones
Ethers
Alkanes

- As the number of carbons in a carboxylic acid series becomes greater, the solubility in water decreases.
- Aromatic carboxylic acids are insoluble in water.

2. Boiling Point

Carboxylic acids are polar compounds and form very strong intermolecular hydrogen bonds to form a dimer.



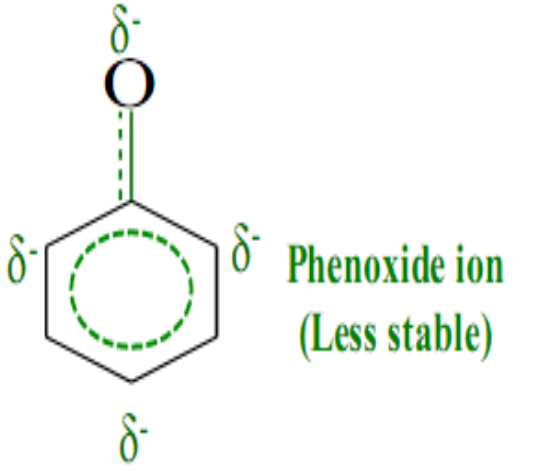
Boiling Point:

Carboxylic acid
Alcohols
Aldehydes/Ketones
Ethers
Alkanes

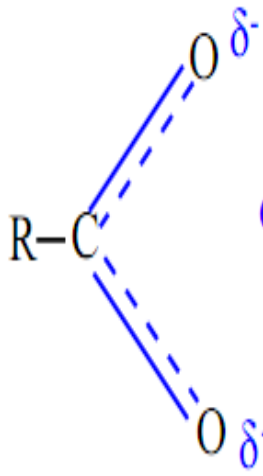
- As the number of carbons in a carboxylic acid series becomes greater, the boiling point increases.

Acidity and Acid Strength

- The most important chemical property of carboxylic acids chemistry is their acidic nature.
- The mineral acids (HCl, HBr, HI, H_2SO_4, H_3PO_4) are defined as "strong acids" because they undergo complete dissociation.
- Carboxylic acids are strong organic acids , they are much more acidic than alcohols.
- Carboxylic acids are stronger acids than phenols.



Phenoxide ion
(Less stable)



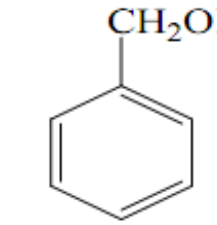
Carboxylate ion
(More stable)

Preparation of Carboxylic acids

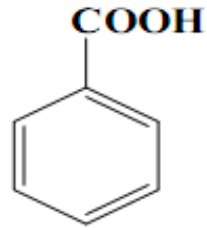
1. Oxidation:

A. Oxidation of primary alcohols and aldehydes

CH_3CH_2OH (Ethyl alcohol) $\xrightarrow[\text{or } K_2Cr_2O_4 / H^+]{KMnO_4 / H^+ / \Delta}$ CH_3COOH (Acetic acid)

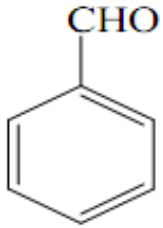


Benzyl alcohol $\xrightarrow[\text{or } K_2Cr_2O_4 / H^+]{KMnO_4 / H^+ / \Delta}$

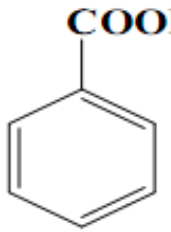


Benzoic acid

CH_3CHO (Acetaldehyde) $\xrightarrow{[O]}$ CH_3COOH (Acetic acid)

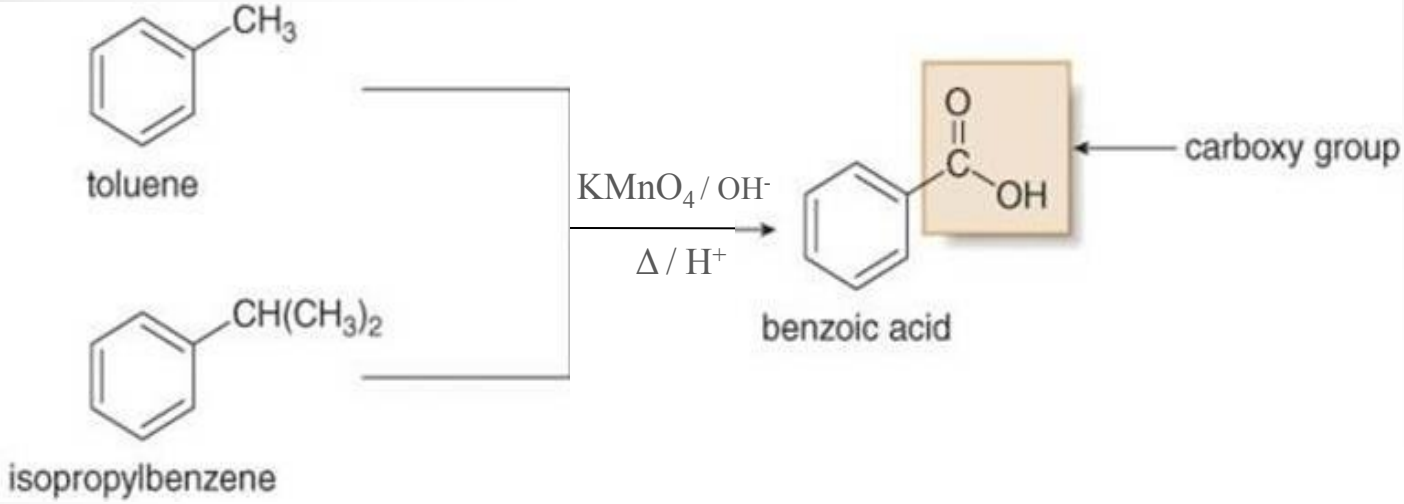


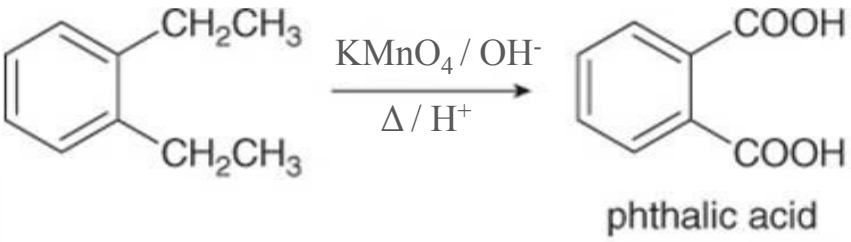
$\xrightarrow{[O]}$



Benzaldehyde → Benzoic acid

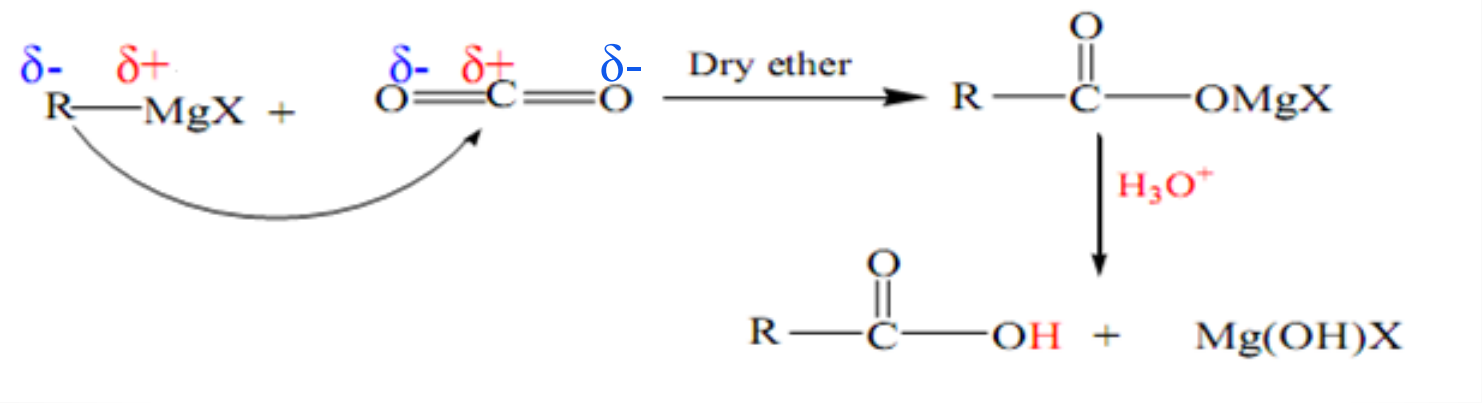
B. Oxidation of Alkylbenzene



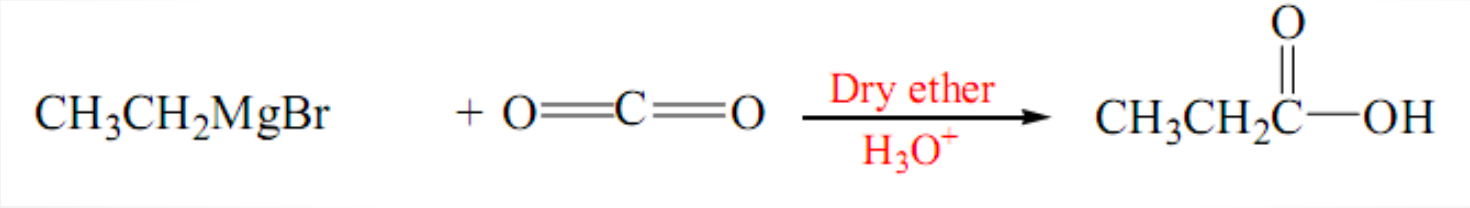


2. Carbonation of Grignard Reagents:

The addition of Grignard reagents to CO_2 in form of dry ice gives an acid with one more carbon more than the original Grignard reagent.



Example:

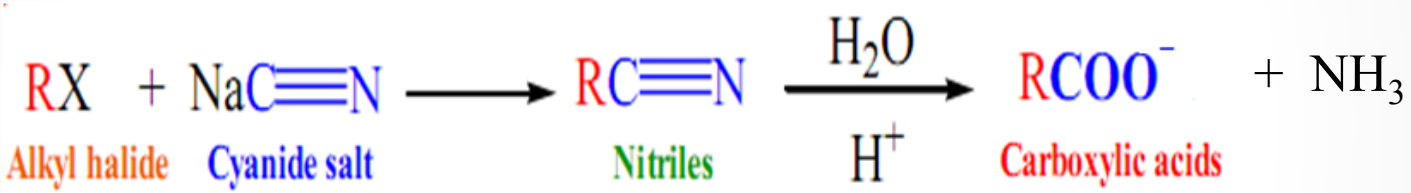


3. Hydrolysis of Nitriles:

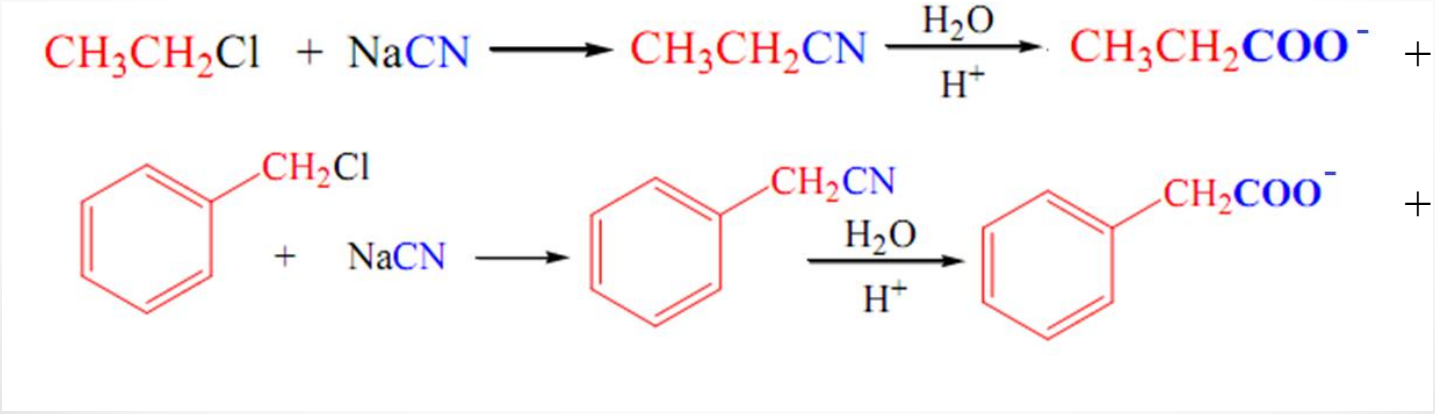
Nitriles:

$RC{\equiv}N$ or $ArC{\equiv}N$

- They are prepared by reacting a 1° or 2° alkyl halide with cyanide salt.
- Acid hydrolysis of a nitriles yields a carboxylic acids.



Examples:

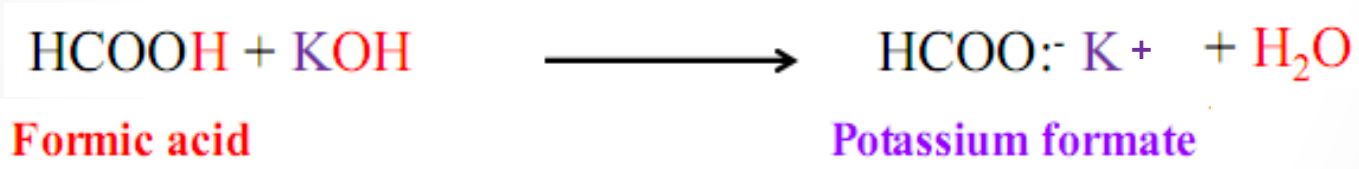


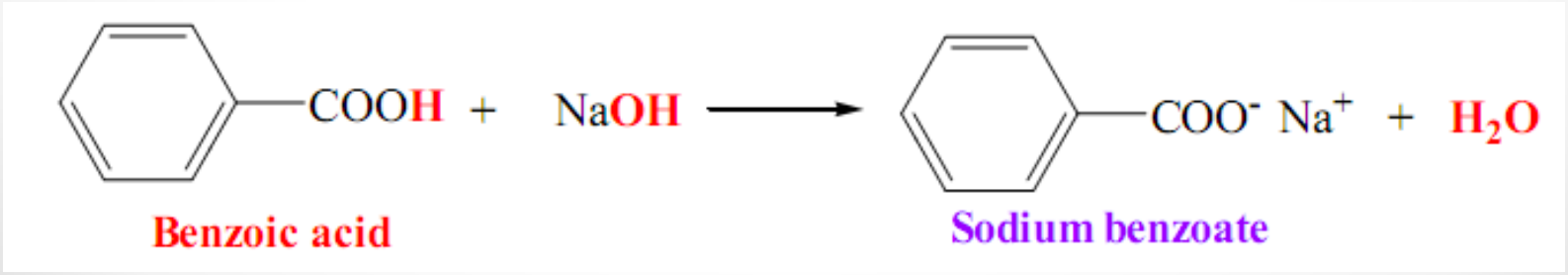
Reactions of Carboxylic acids

1. Reaction with Bases : Salt formation

The carboxyl hydrogen is replaced by metal ion, M^+

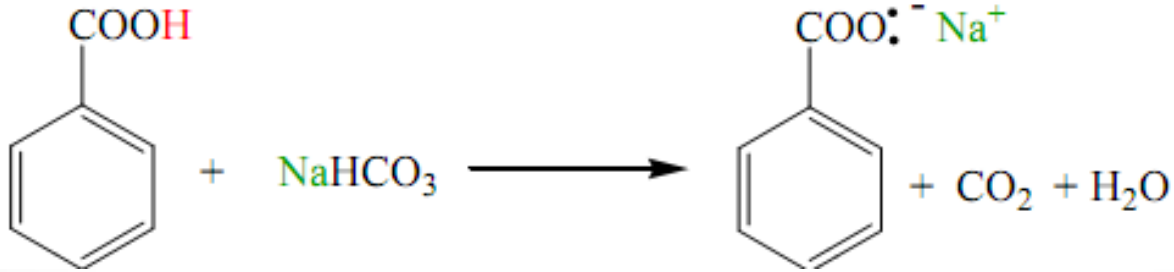
A) With strong base:

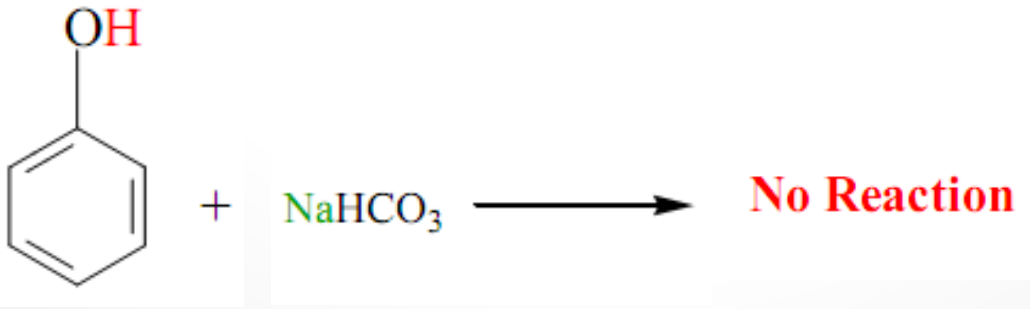




B) With weak base

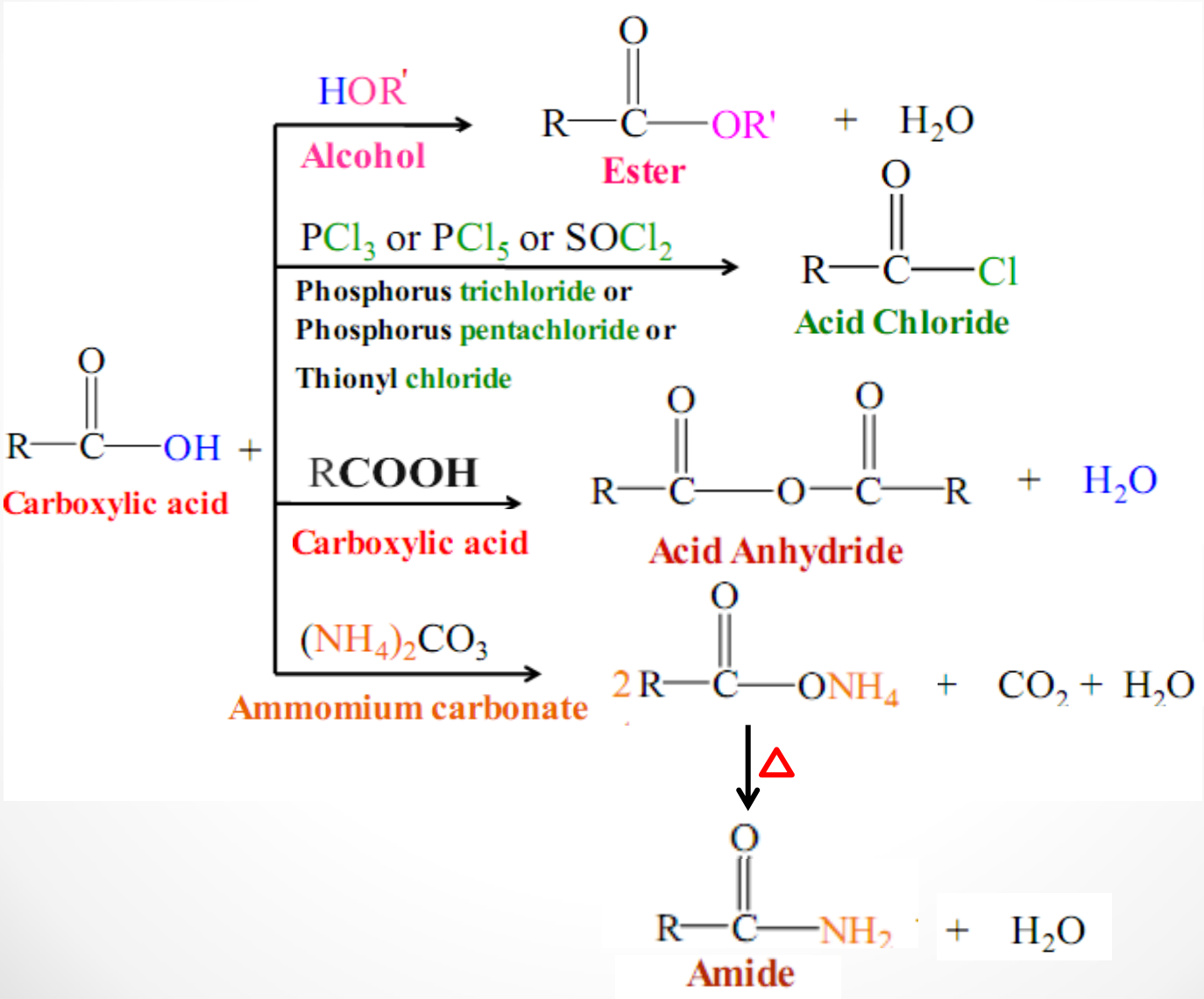
- Weaker acids like phenols react only with strong bases like (NaOH or KOH) and will not react with $NaHCO_3$



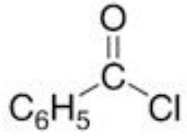
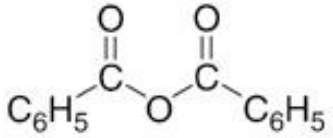
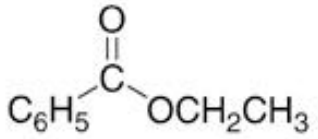
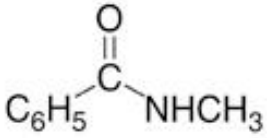


2. Reaction with Nucleophiles to form acid derivatives:

- When the OH of a carboxylic acid is replaced by a nucleophile, :Nu , a carboxylic acid derivative is produced.



Derivatives of Carboxylic acids

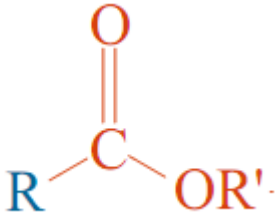
Compound	Name ending	Example	Name
acid chloride	**-yl chloride** or **-carbonyl chloride**		benzoyl chloride
anhydride	**anhydride**		benzoic anhydride
ester	**-ate**		ethyl benzoate
amide	**-amide**		*N*-methylbenzamide

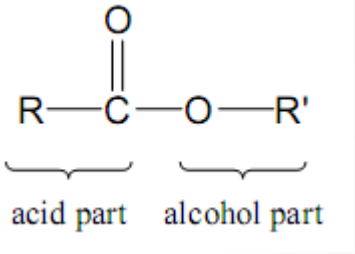
Nomenclature

Nomenclature: the functional derivatives' names are derived from the common or IUPAC names of the corresponding carboxylic acids.

1. Esters:

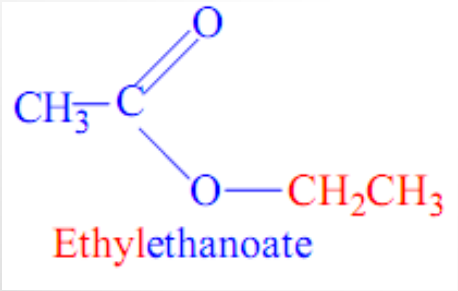
alkyl alkanoate



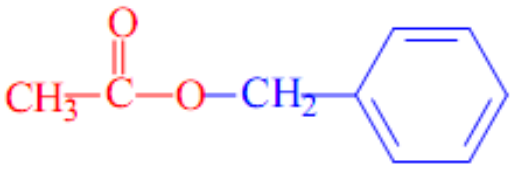


Change –ic acid to –ate preceded by the alkyl is derived from the alcohol, R'OH.

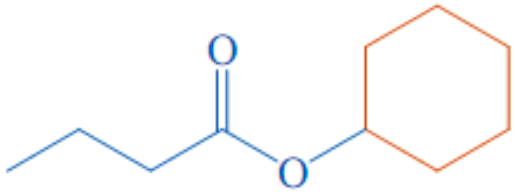
Examples:



Ethylethanoate

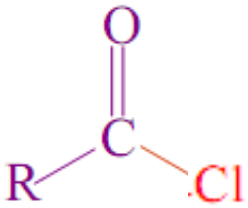


Benzyl ethanoate



Cyclohexyl butanoate

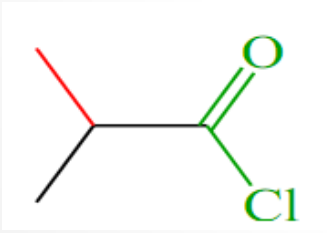
2. Acid Chlorides:



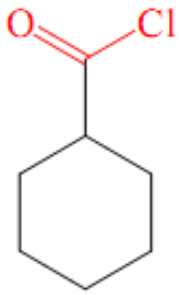
Change –ic acid to –yl chloride

Alkanoyl chloride

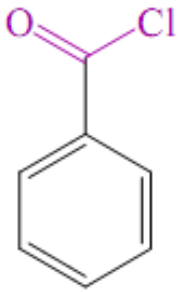
Examples:



2-methylpropanoyl chloride

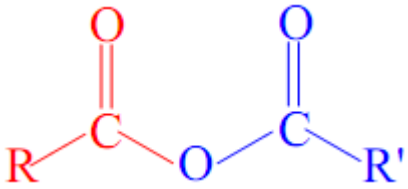


cyclohexanoyl chloride



Benzoyl chloride

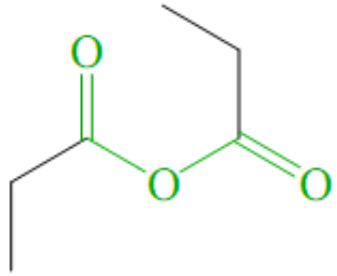
3. Acid Anhydride:



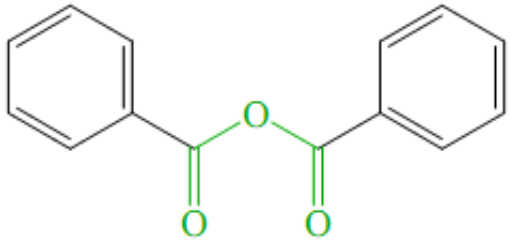
Change acid to anhydride

alkanoic anhydrides

Examples:

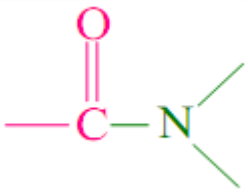


Propanoic anhydride



Benzoic anhydride

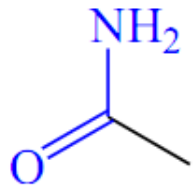
4. Amides:



Change -oic acid to –amide

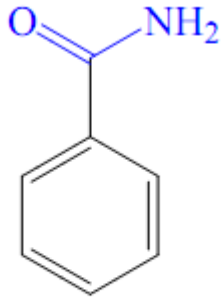
alkanamide

Examples:

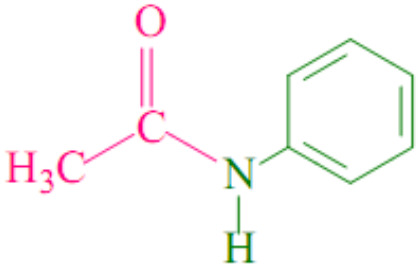


Acetamide

Ethanamide



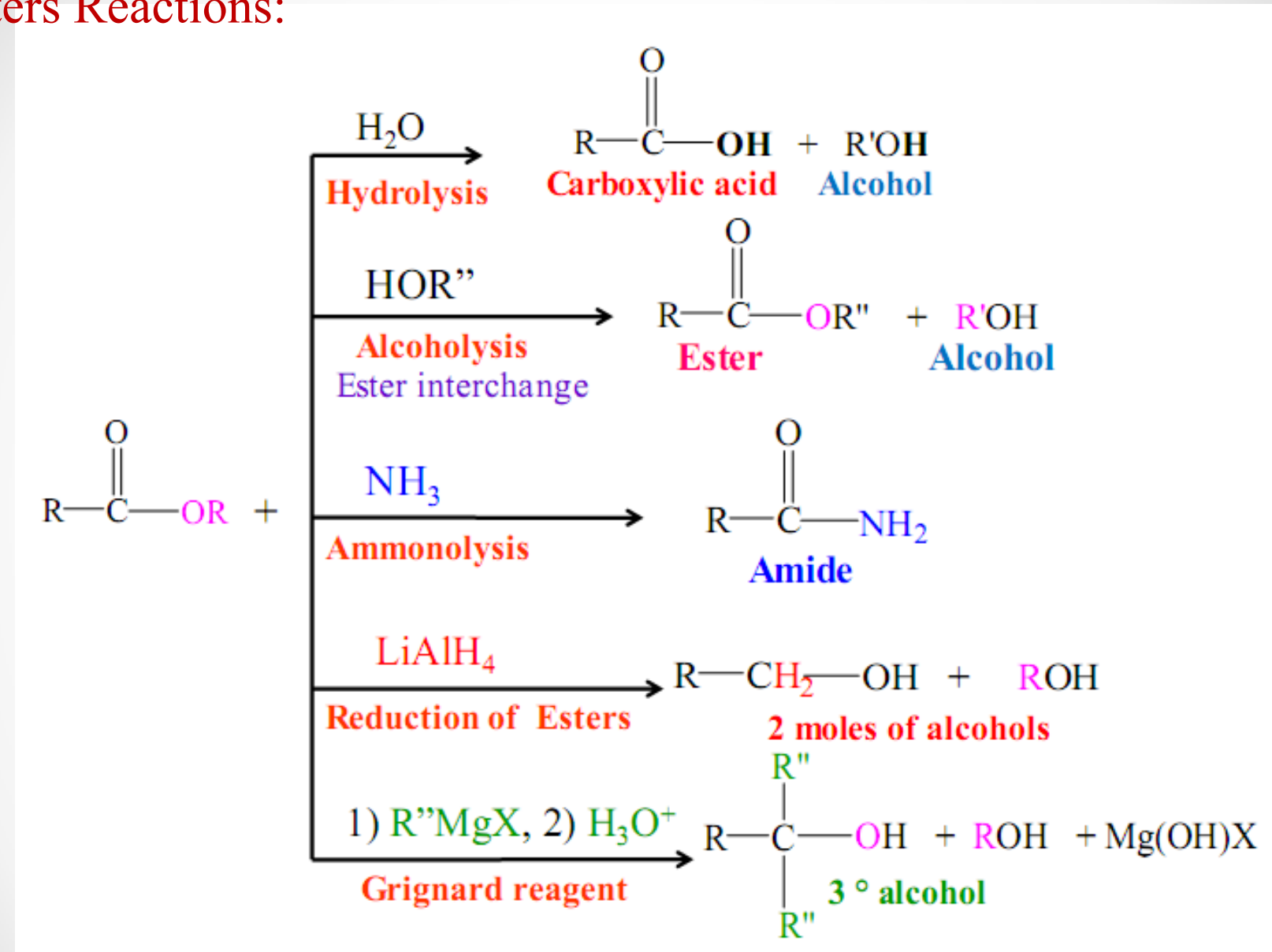
Benzamide



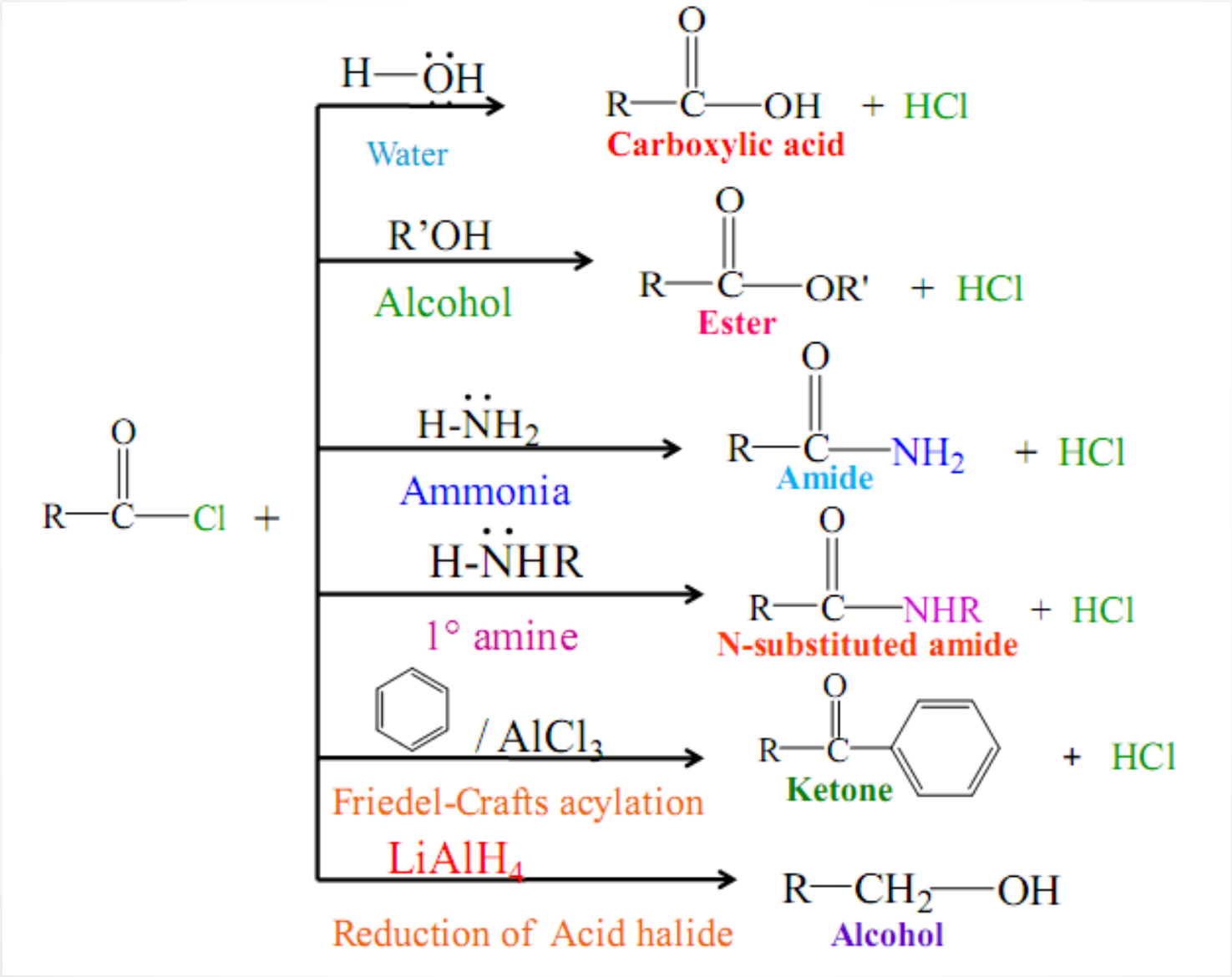
Acetanilide

N-phenylethanamide

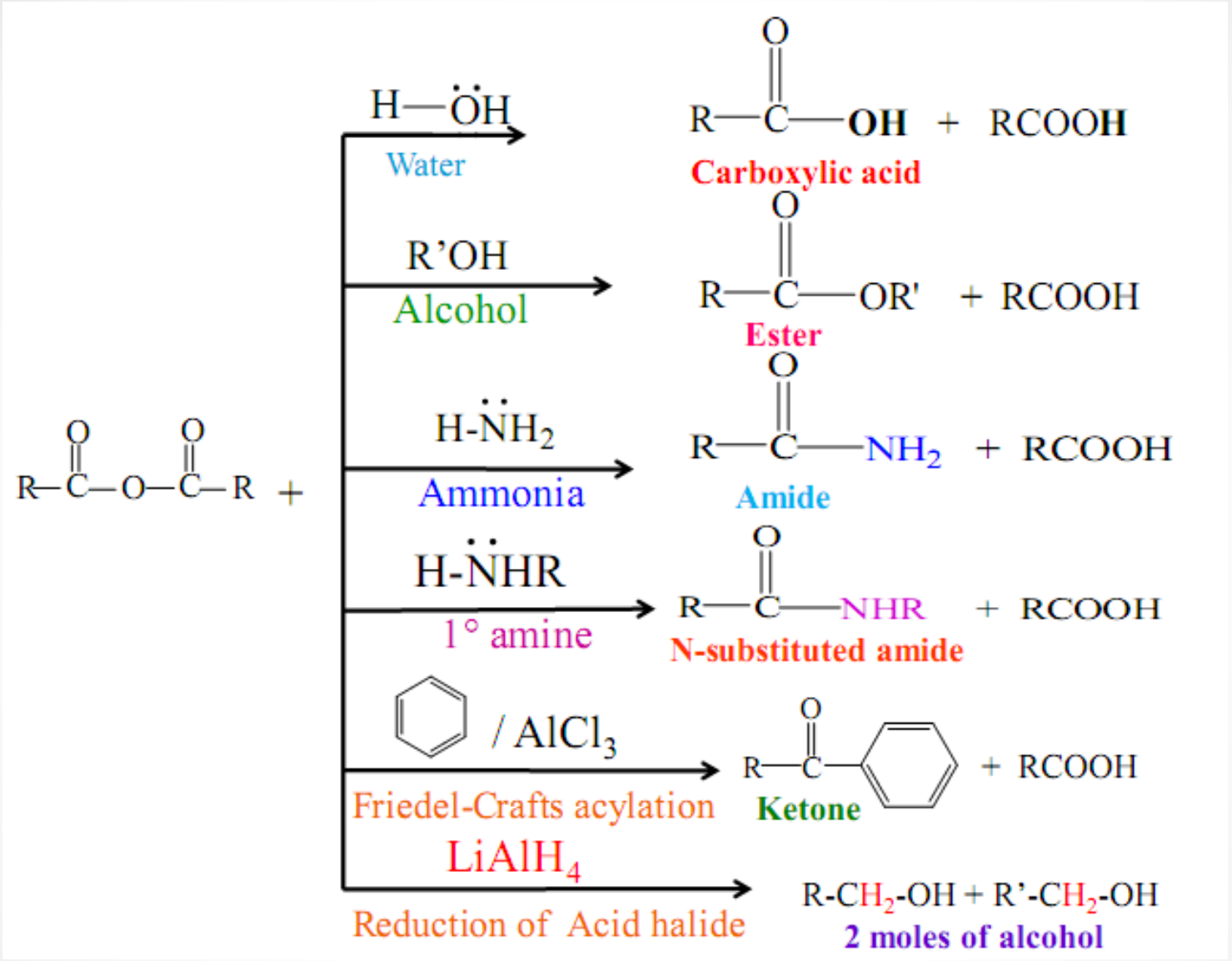
Esters Reactions:



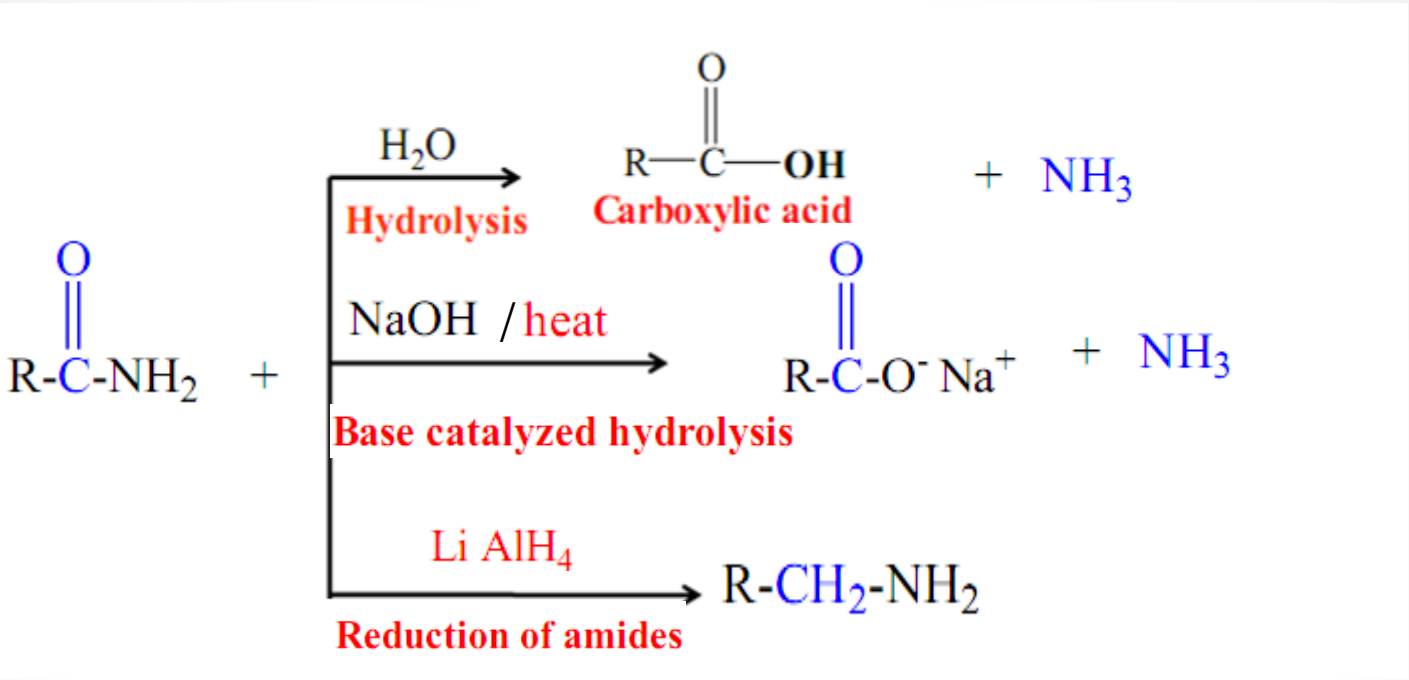
Acid Chlorides Reactions:



Acid Anhydride Reactions:

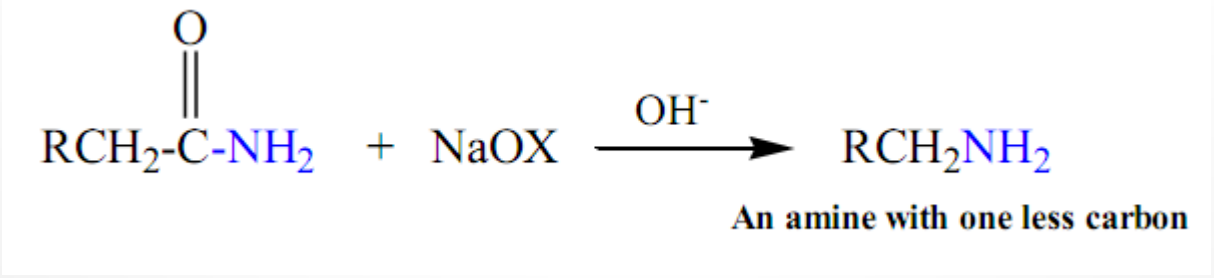


Amides Reactions:



4- Reaction of amides with alkaline hypohalite solution:

Reduced to amines containing one less carbon atom



Chem. 108

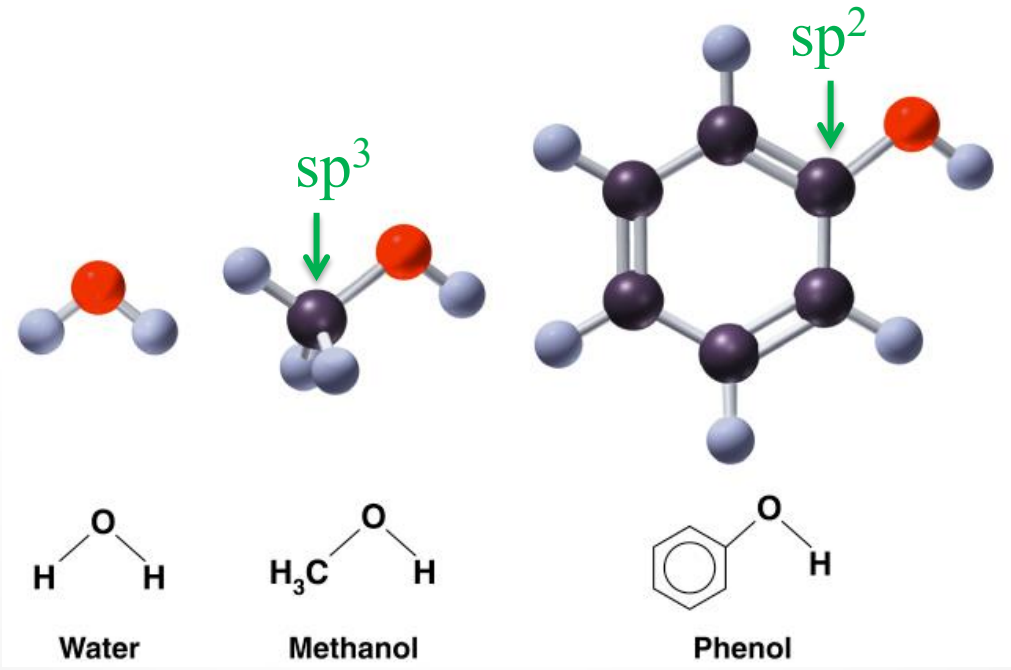
Alcohols and Phenols

Chapter 7

Alcohols and Phenols

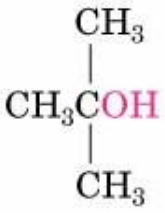
The Hydroxyl group (-OH)

- The **hydroxyl group** (—**OH**) is found in the **alcohol** and **phenol** functional groups.
  - in **alcohols**, a hydroxyl group is connected to a carbon atom.
  - in **phenols**, —OH is connected to a benzene ring.



Types of Alcohols

1- Monohydroxyls: containing one hydroxyl group



***tert*-Butyl alcohol**
(2-Methyl-2-propanol)

2- Dihydroxyls (glycols) : containing two hydroxyl groups

$HOCH_2CH_2OH$

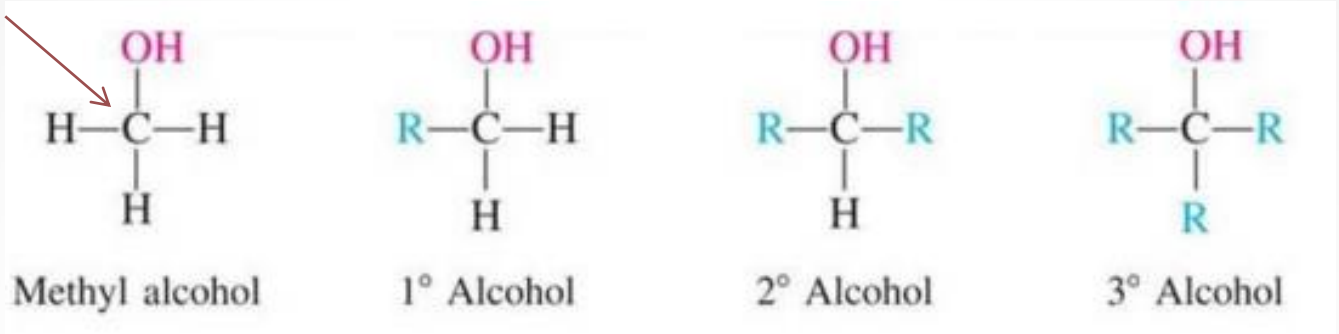
Ethylene glycol
(1,2-Ethanediol)

3- Polyhydroxyls : containing more than two hydroxyl groups

Glycerol
(1,2,3-Propanetriol)

Classification of Alcohols

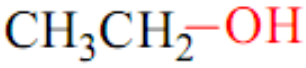
Carbinol Carbon



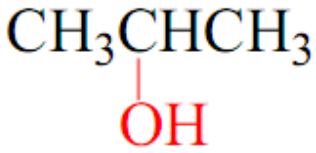
Nomenclature of Alcohols

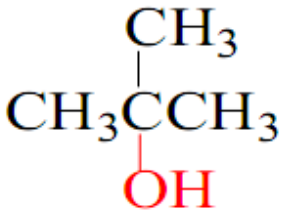
Common Nomenclature:

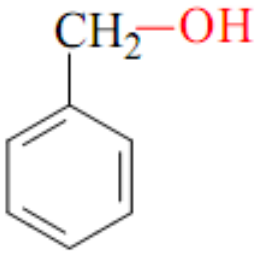
Alkyl + alcohol

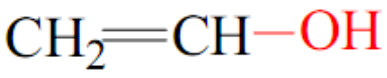


Ethyl alcohol









Vinyl alcohol

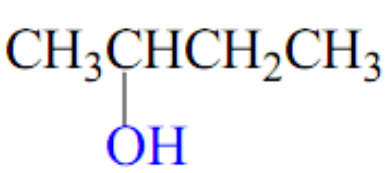
Isopropyl alcohol

t-butyl alcohol

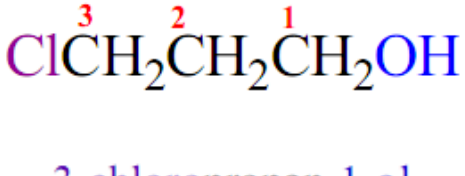
Benzyl alcohol

IUPAC Nomenclature:

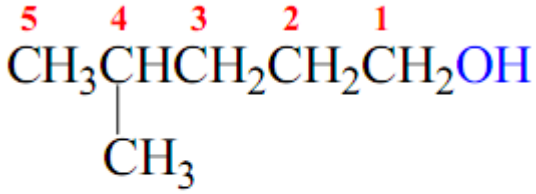
- Select the longest carbon chain containing the hydroxyl group.
- derive the parent name by replacing the *-e* ending of the corresponding alkane with *-ol*.
- Number the chain from the end nearer the hydroxyl group.



2-Butanol

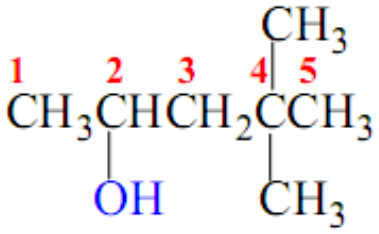


3-chloropropan-1-ol

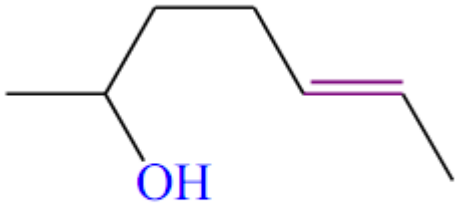


4-Methylpentan-1-ol

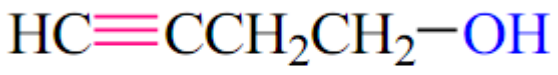
Not 2-Methylpentan-5-ol



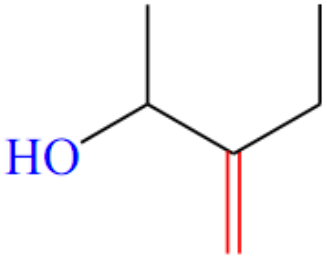
4,4-Dimethylpentan-2-ol



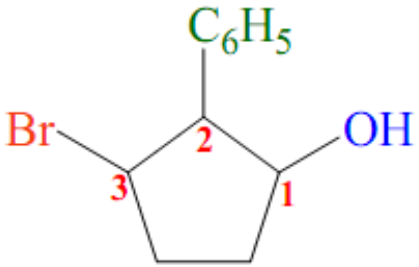
Hept-5-en-2-ol



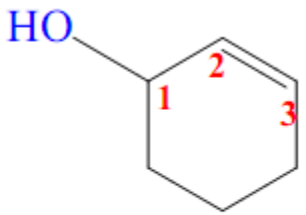
But-3-yn-1-ol



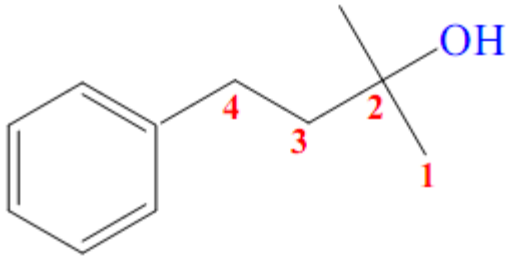
3-Ethylbut-3-en-2-ol



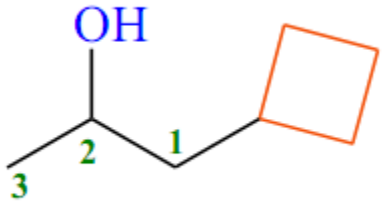
3-Bromo-2-phenyl cyclopentanol



Cyclohex-**2-en**ol

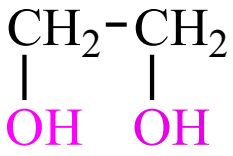


2-Methyl-4-phenyl butan-2-ol

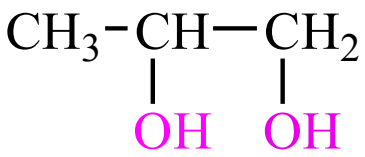


1-Cyclobutylpropan-2-ol

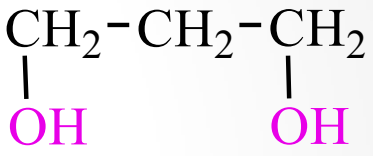
- If more than one hydroxyl group, use suffixes -diol, -triol, etc.



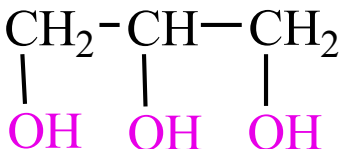
IUPAC name: 1,2-Ethanediol
Common name: Ethylene glycol



1,2-Propanediol
Propylene glycol



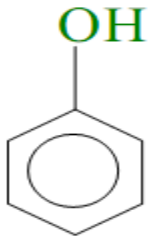
1,3-Propanediol
Trimethylene glycol



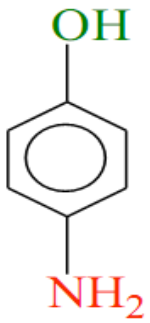
1,2,3-propanetriol
Glycerol

Nomenclature of Phenols

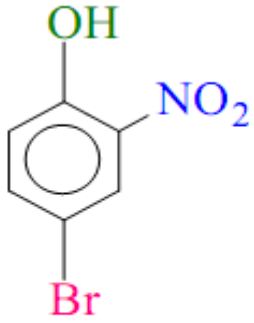
- The ortho, meta, para system is used in common names.
- While the numbering system is employed in IUPAC names and in this case numbering of the ring begins at the hydroxyl substituted carbon and proceeds in the direction of the next substituted carbon that processes the lower number.



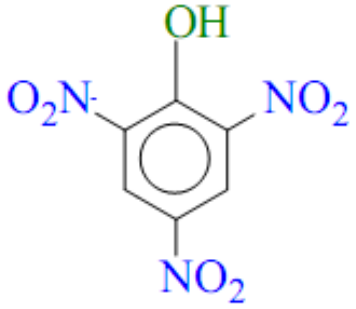
Phenol



4- aminophenol



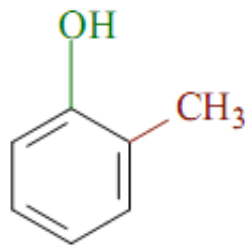
4-Bromo-2-nitrophenol



2,4,6-Trinitrophenol

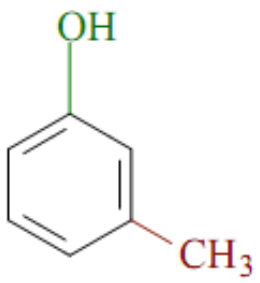
Common name: Picric acid

- Some phenols have common names as shown in the following examples:



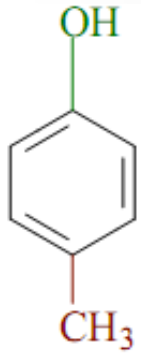
2-methylphenol

o-cresol



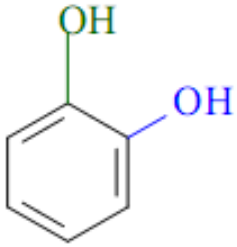
3-methylphenol

m-cresol



4-methylphenol

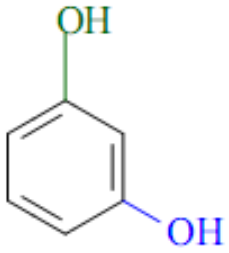
p-cresol



2-hydroxyphenol

or 1,2-Benzenediol

Catechol



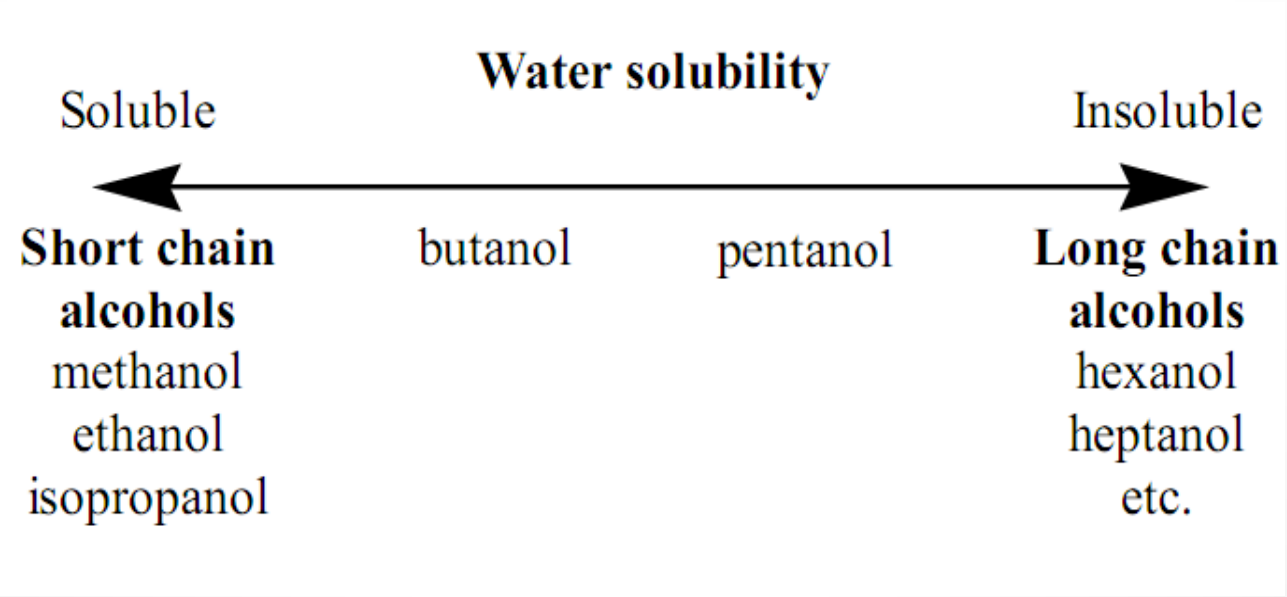
3-hydroxyphenol

Resorcinol

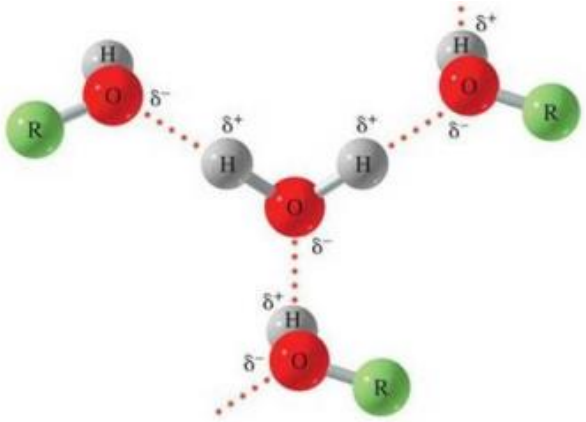
Physical Properties of Alcohols and Phenols

- Smaller straight chain alcohols are usually liquids.
- Phenols are crystalline solids or liquids.

Solubility of alcohols:



- The solubility of lower alcohols is due to existence of hydrogen bonds between water and polar -OH group of alcohol molecules.

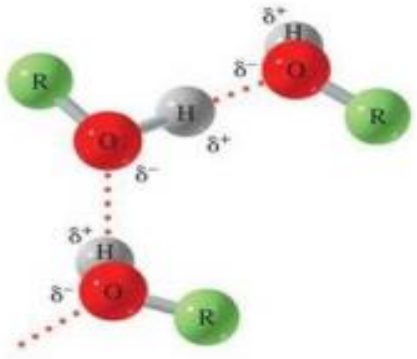


- The solubility increases with branching of chain.
- The number of hydroxyl groups increases the solubility.

- Phenols are moderately soluble in water but readily soluble in organic solvents.

Boiling points of alcohols:

- Because alcohols hydrogen bond to each other, they have higher boiling points than alkanes of the same molecular weight.
- The boiling point of alcohols increases as the molecules become larger.



$CH_3CH_2{-}OH$

Ethanol

Mol wt = 46; bp= 78°C

$CH_3CH_2CH_3$

n-propane

Mol wt = 44; bp= -42°C

- The boiling point decreases with increase in branching in alkyl group.

$CH_3CH_2\,CH_2CH_2{-}OH$

1-Butanol

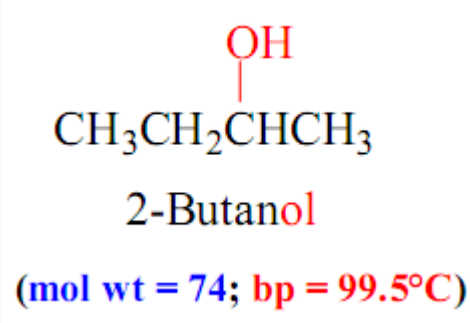
(mol wt = 74; bp = 118°C)

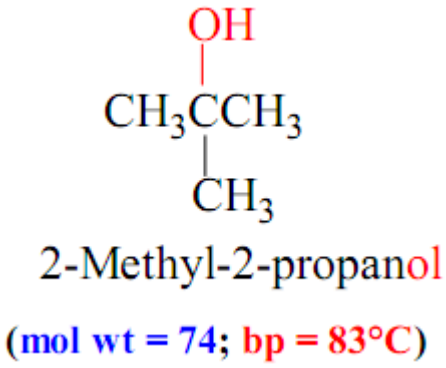
$$CH_3CH(CH_3)CH_2{-}OH$$

2-Methyl-1-propanol

(mol wt = 74; bp = 108°C)

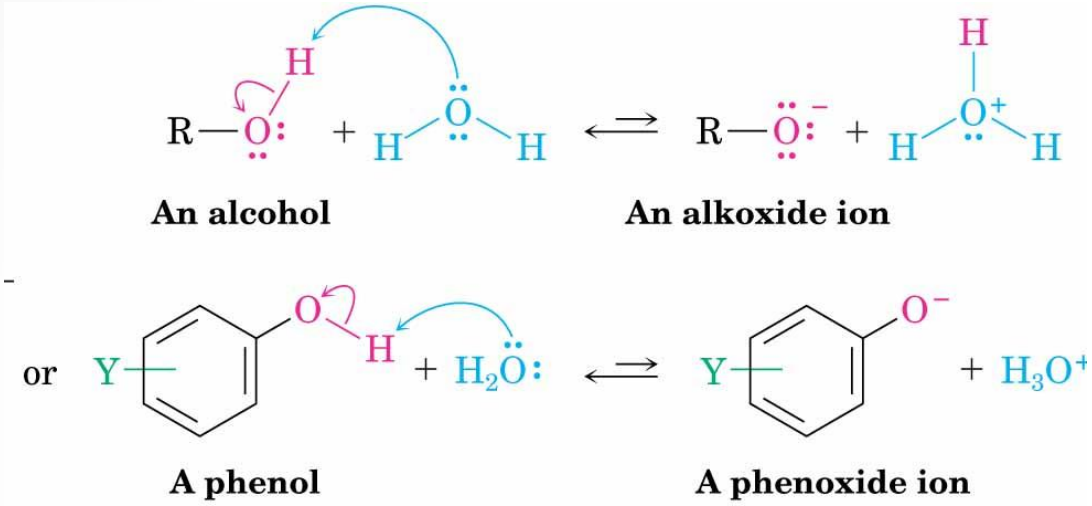
- The boiling point increases with increase of number of hydroxyl groups.
- Boiling points of 1° alcohol > 2° alcohol > 3° alcohol



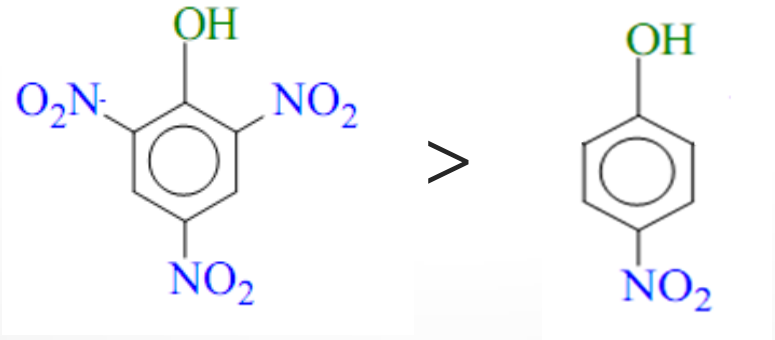


Acidities of Alcohols and Phenols:

- Alcohols and Phenols have weak acidic properties.

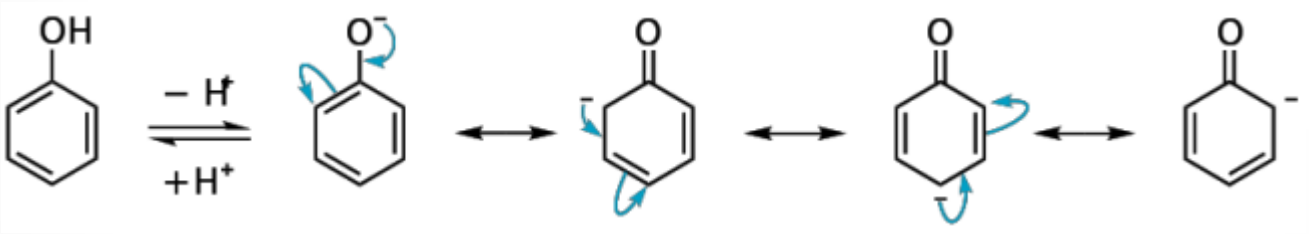


- Introduction of the electro-withdrawing groups, such as NO_2 or CN the ring increases the acidity of phenols dramatically.



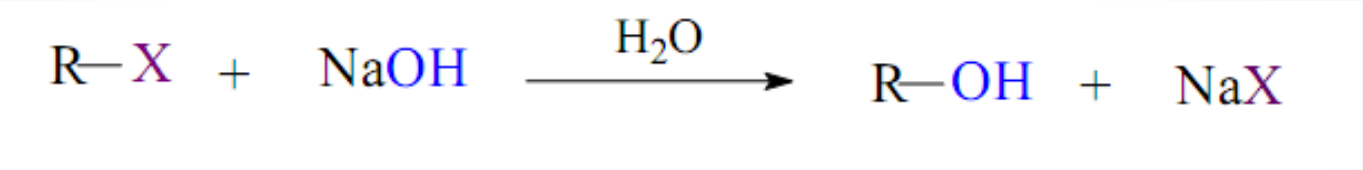
- Phenols are a stronger acids than Alcohols.
- Because the negative charge in oxygen is dispersed by resonance through the benzene ring.

Resonance structures of phenoxide anion

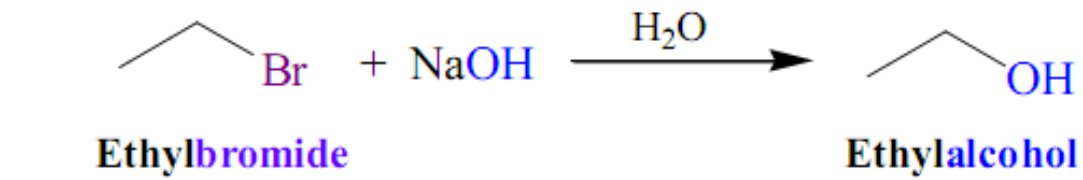


Preparation of Alcohols

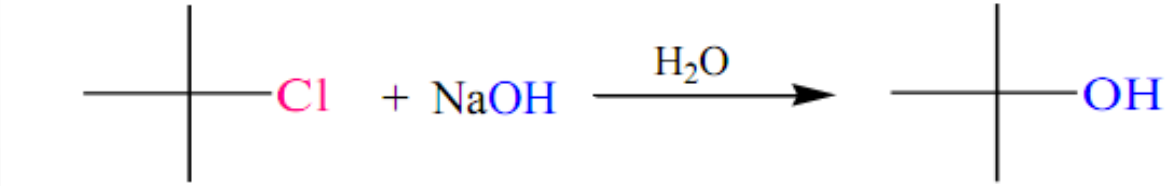
1- Hydrolysis of Alkyl halide:



Examples:



Ethylbromide **Ethylalcohol**

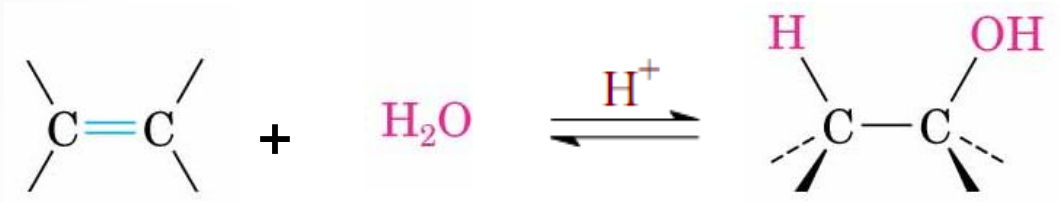


tert-Butyl chloride **tert-Butyl alcohol**

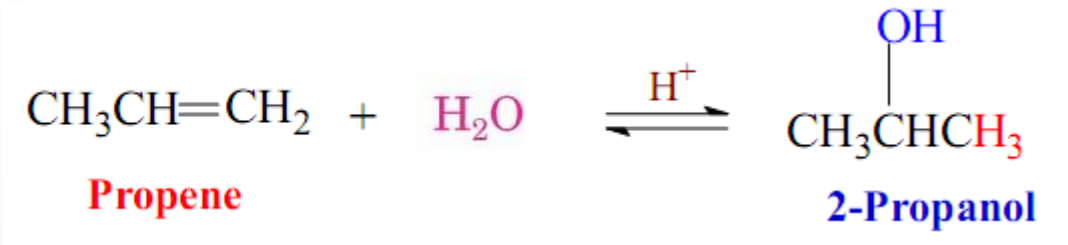
2- Hydration of Alkenes:

A- Markovnikov's Rule

Addition of water to a double bond in the presence of an acid catalysts.

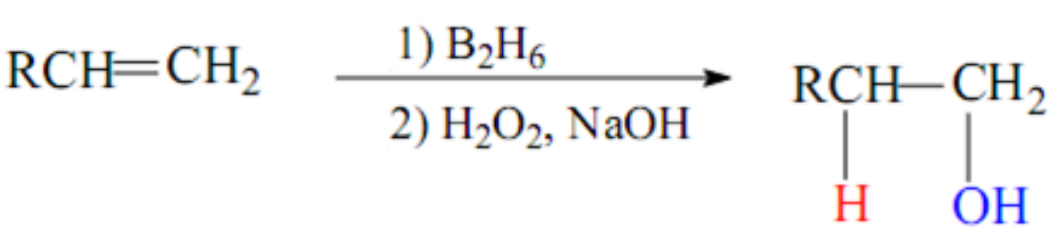


Example:

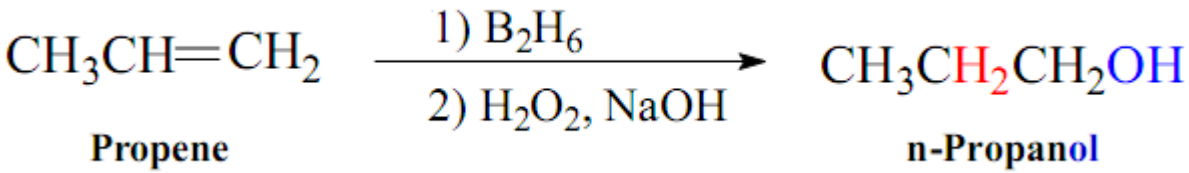


B- anti-Markovnikov's Rule

Addition of diborane B_2H_6 , followed by oxidation with alkaline hydrogen peroxide H_2O_2,NaOH.

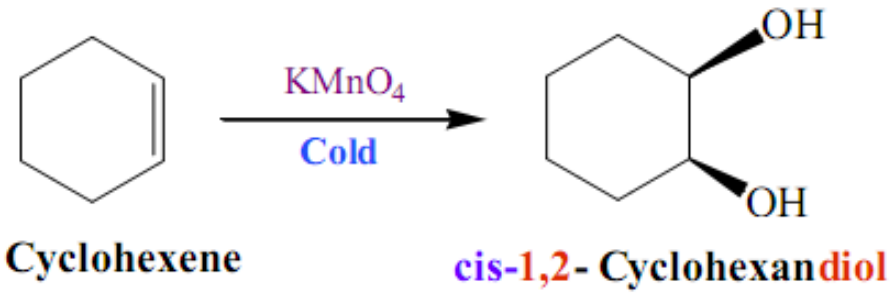


Example:

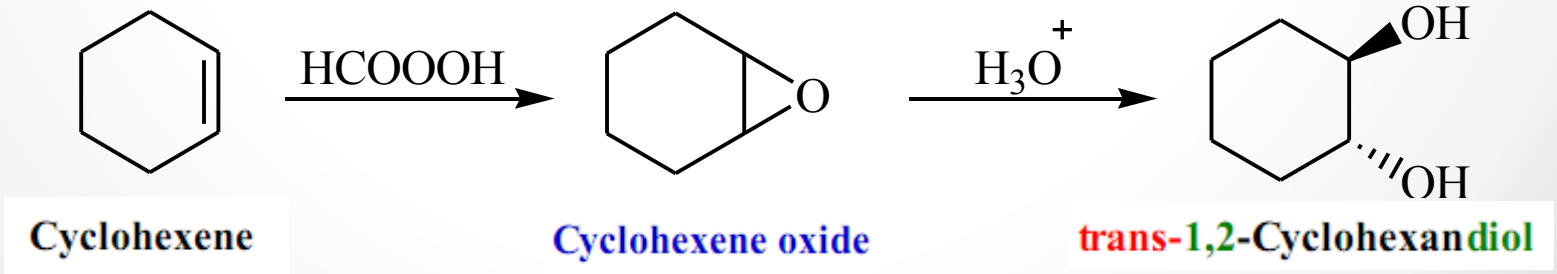


3- Oxidation of Alkenes to Vicinal Diols:

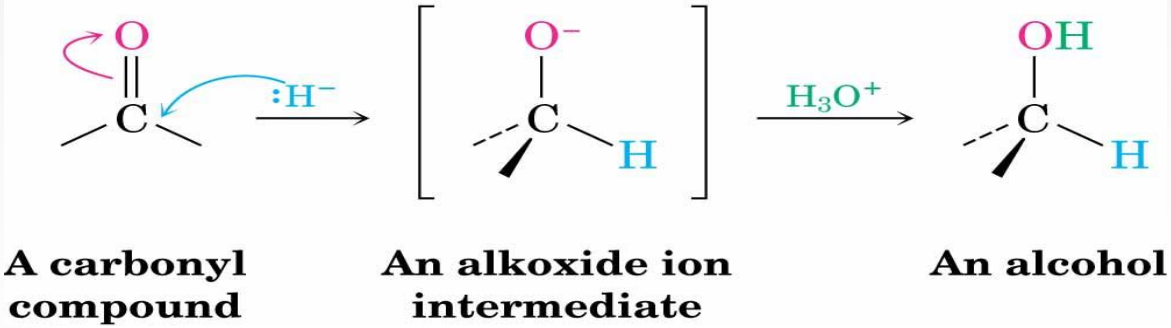
- Oxidation of Alkenes with cold Potassium permanganate $KMnO_4$ or Osmium tetroxide OsO_4 provides occurs with syn addition and provides cis vicinal diols.



- Oxidation of Alkenes with Peroxy acid HCOOOH provides occurs with anti addition and provides trans vicinal diols

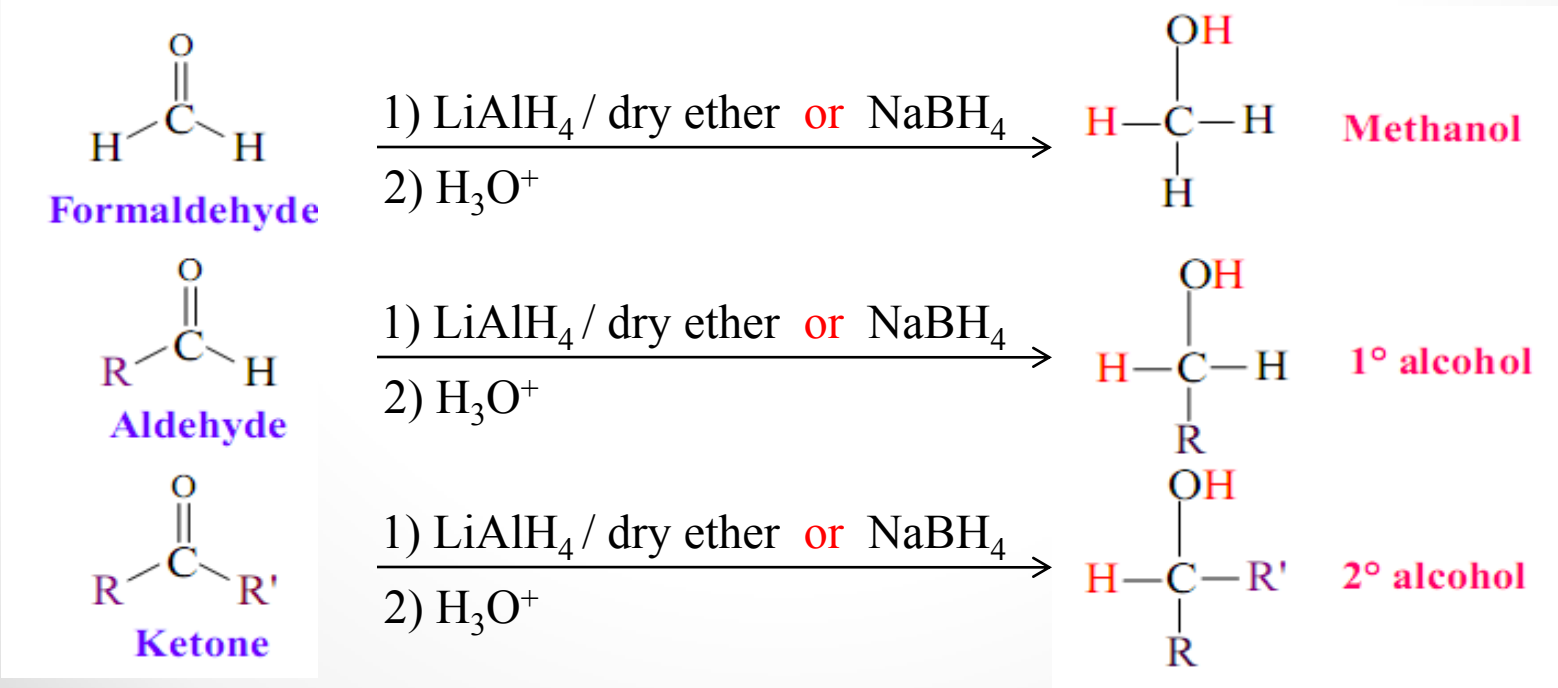


4- Reduction of Aldehydes, Ketones, Acids and Esters:



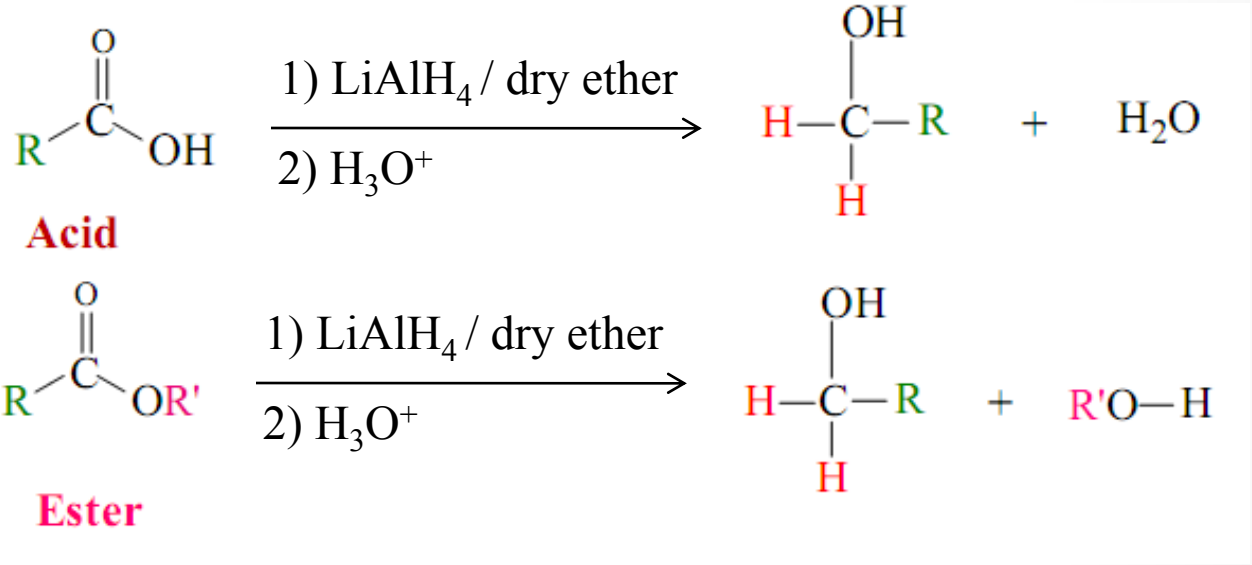
A- Reduction of Aldehydes and Ketones

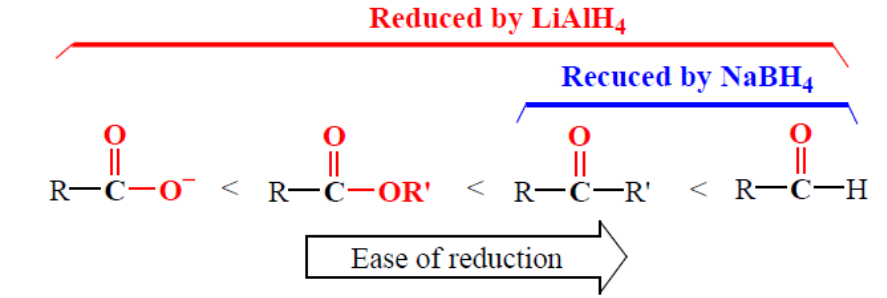
Reduction by hydride reagents, Lithium aluminium hydride $LiAlH_4$ or Sodium boro hydride $NaBH_4$



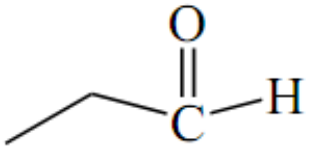
B- Reduction of Acids and Esters

- Carboxylic acids and esters are reduced to give primary alcohols.
- $LiAlH_4$ is used because $NaBH_4$ is not effective.





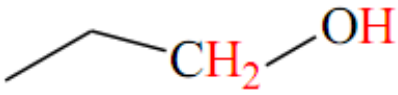
Examples:



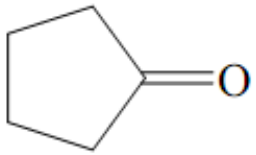
Propanal

1) $LiAlH_4$ / dry ether or $NaBH_4$

2) H_3O^+



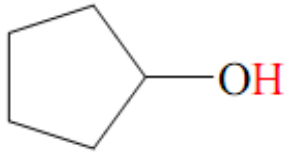
1-Propanol



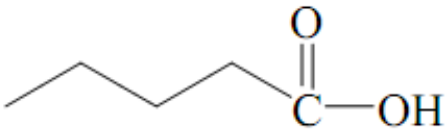
Cyclohexanone

1) $LiAlH_4$ / dry ether or $NaBH_4$

2) H_3O^+



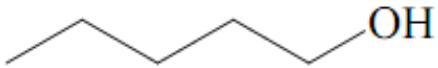
Cyclohexanol



Pentanoic acid

1) $LiAlH_4$ / dry ether

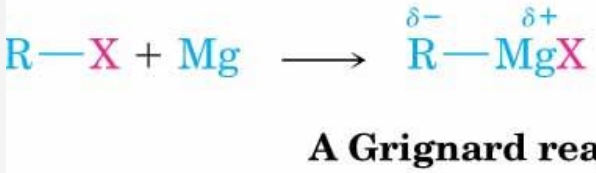
2) H_3O^+



1-Pentanol

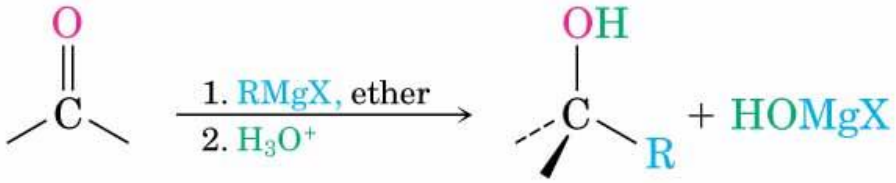
5- From Grignard reagent:

Grignard formation

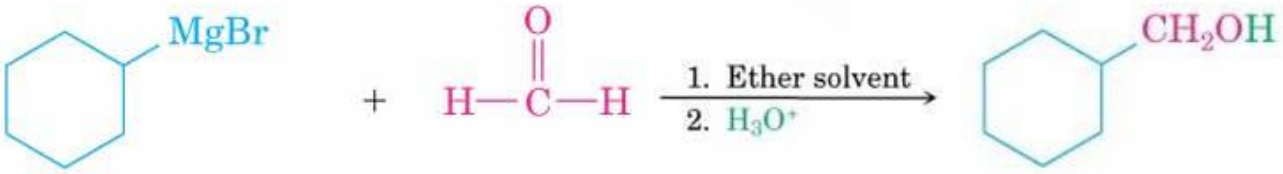


R = 1°, 2°, or 3° alkyl, aryl, or vinylic
X = Cl, Br, or I

A Grignard reagent

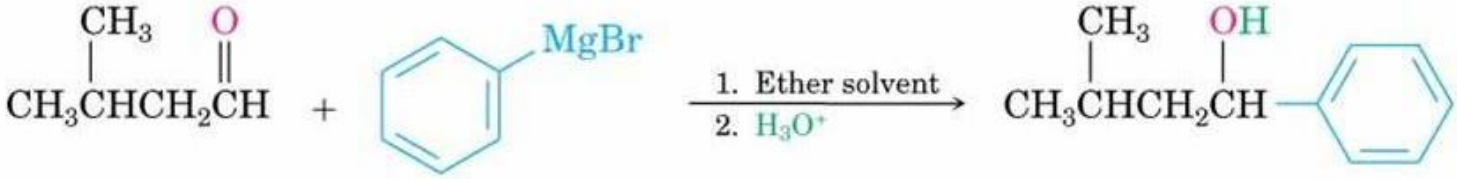


Formaldehyde reaction



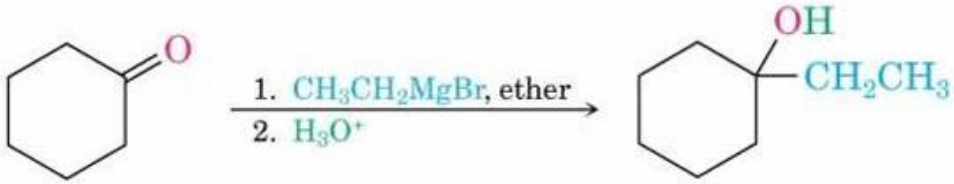
Cyclohexylmagnesium bromide + **Formaldehyde** → **Cyclohexylmethanol (a 1° alcohol)**

Aldehyde reaction



3-Methylbutanal + **Phenylmagnesium bromide** → **3-Methyl-1-phenyl-1-butanol (a 2° alcohol)**

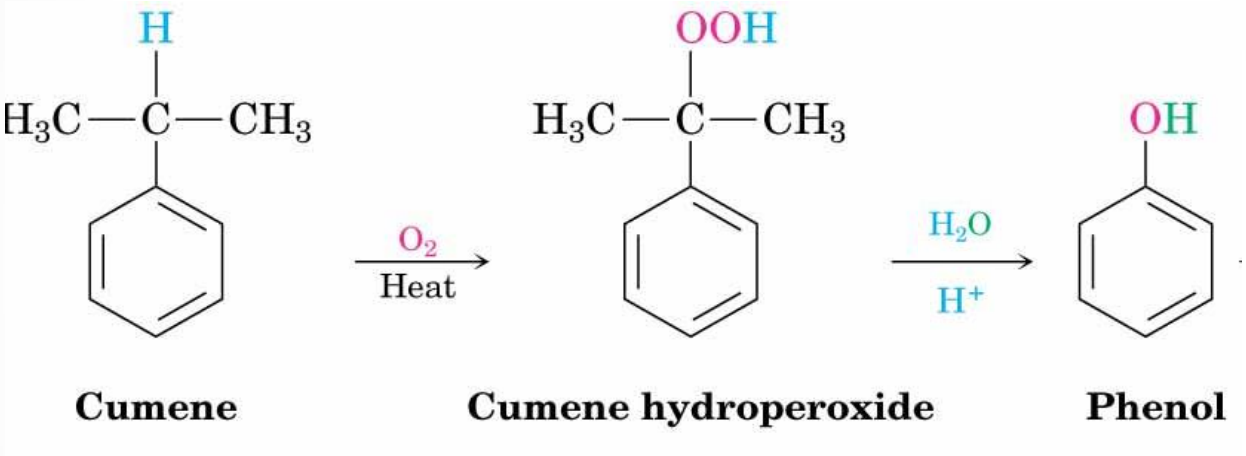
Ketone reaction



Cyclohexanone → **1-Ethylcyclohexanol (a 3° alcohol)**

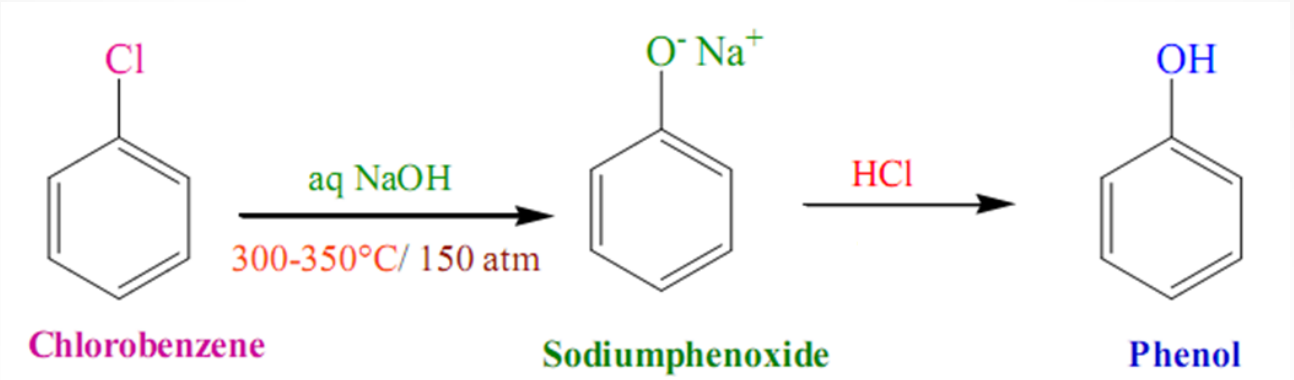
Preparation of Phenols

A- Industrial process from readily available cumene (isopropylbenzen)

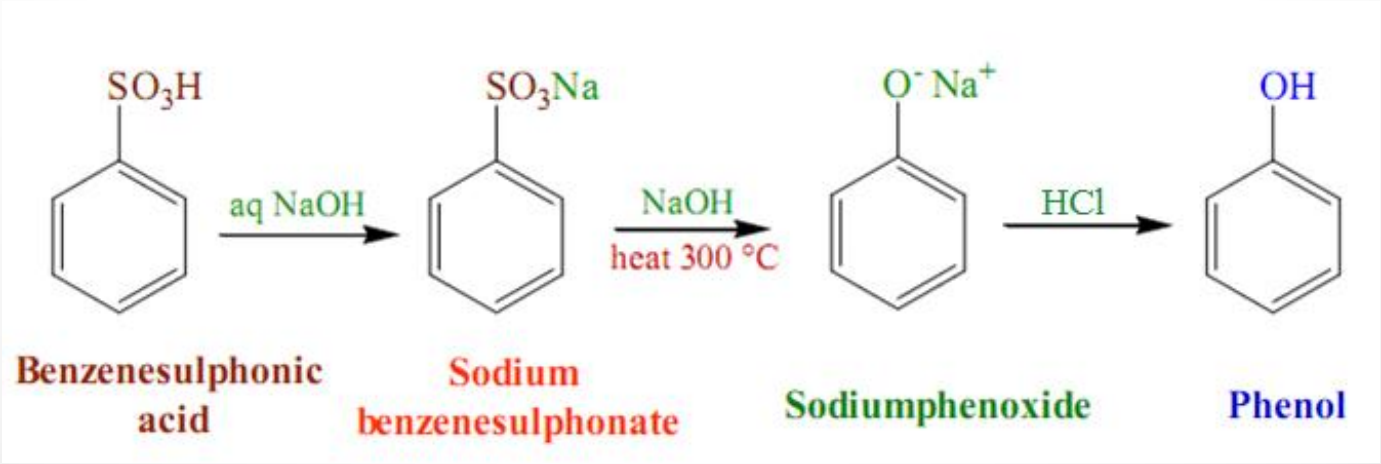


B- In the laboratory:

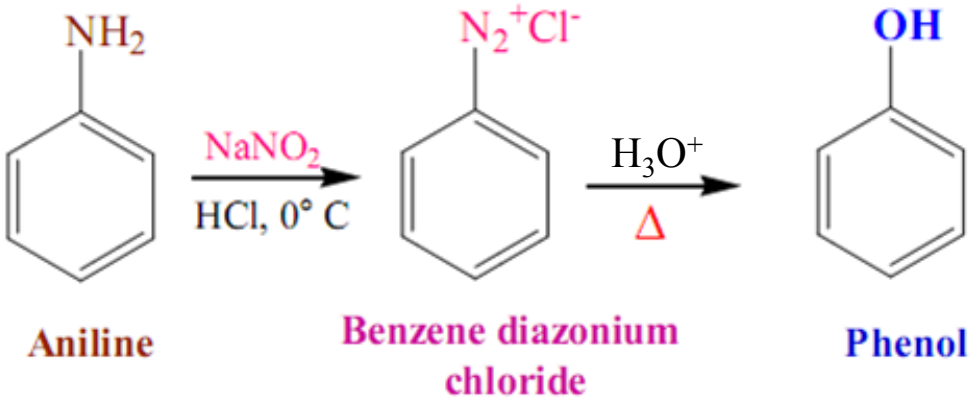
1- From Chlorobenzene



2- Alkali fusion of sulfonates

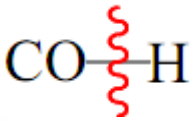


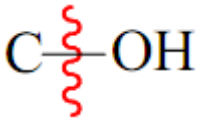
3- Hydrolysis of Diazonium salts



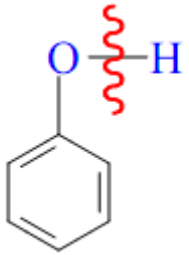
Reactions of Alcohols and Phenols

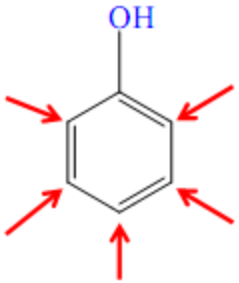
- Alcohols undergo two kinds of reactions



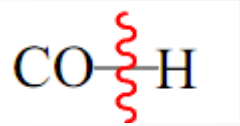


- Phenols undergo two kinds of reactions





A- Reactions involving oxygen-hydrogen bond breaking



1- Salt Formation

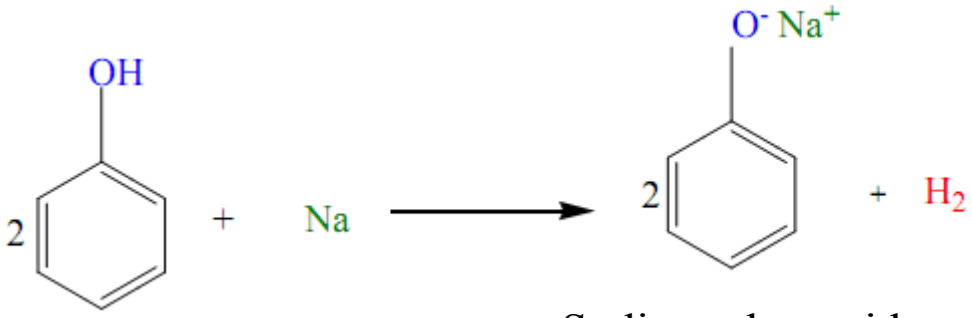
Alcohols

$$2\ R{-}O{-}H + Na \longrightarrow 2\ RONa + H_2$$

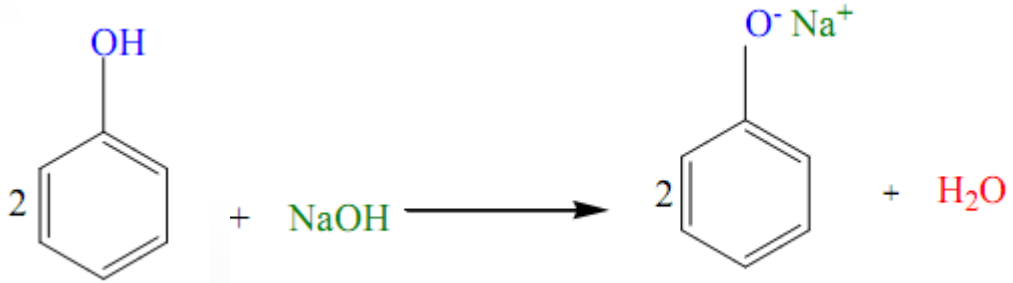
Sodium alkoxide

$$2\ R{-}O{-}H + NaOH \longrightarrow \text{No Reaction}$$

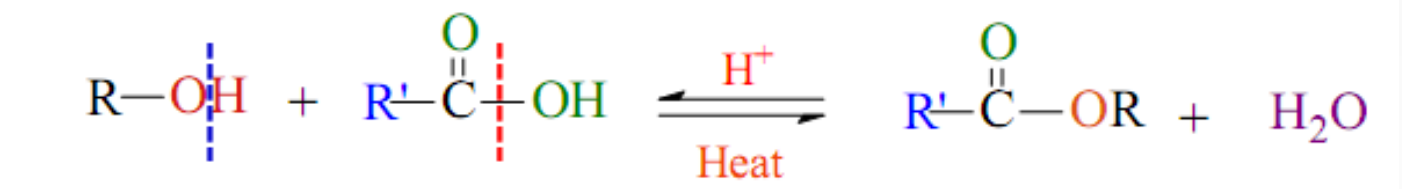
Phenols



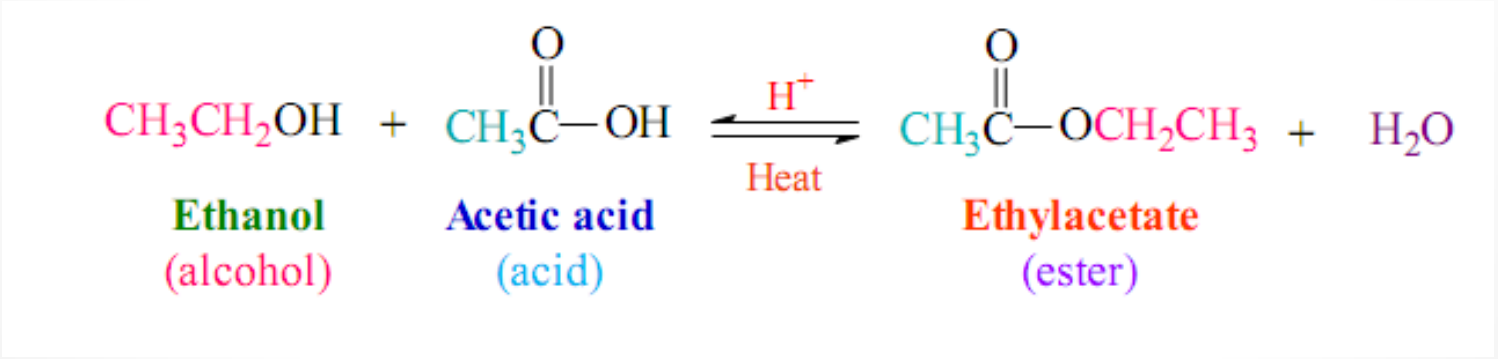
Sodium phenoxide



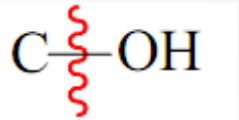
2- Reaction of Alcohols with Carboxylic acids: Ester Formation



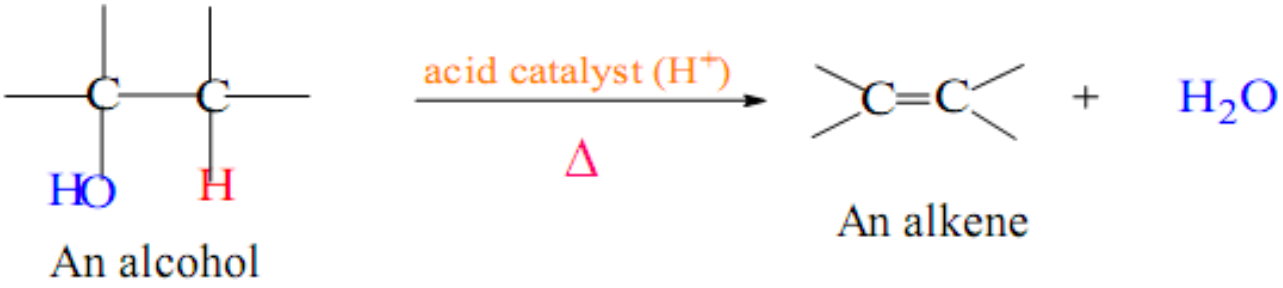
Example:



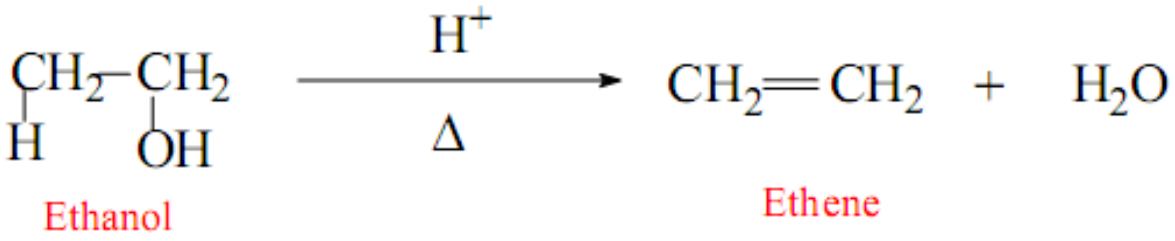
B- Reactions involving carbon-oxgen bond breaking

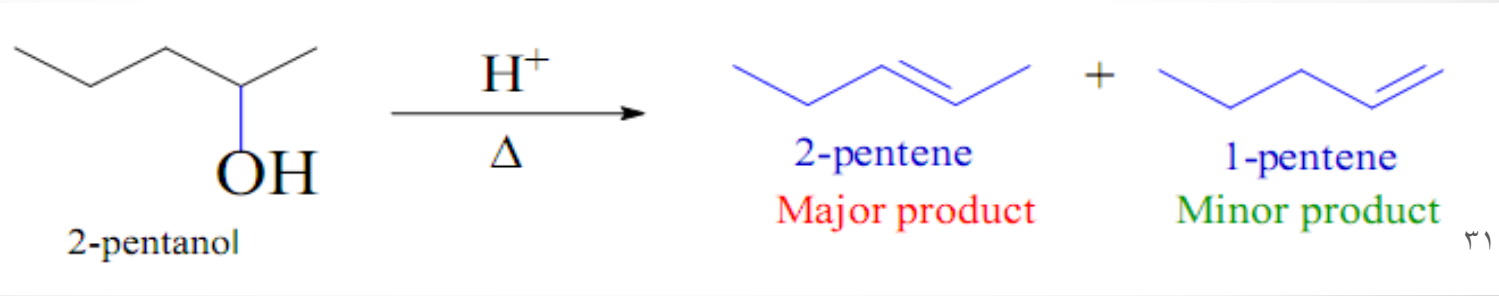


1- Dehydrations of Alcohols: Formation of Alkenes

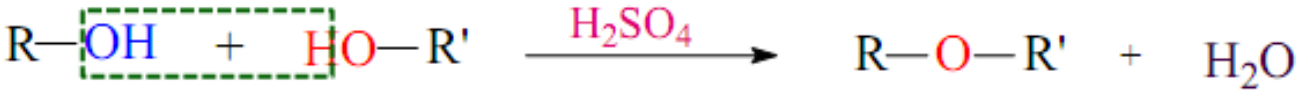


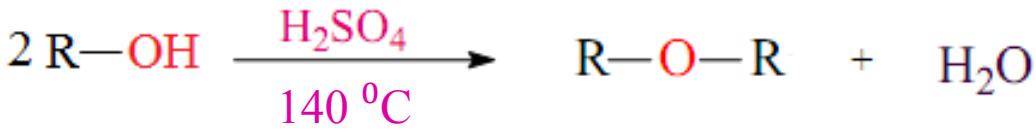
Examples:



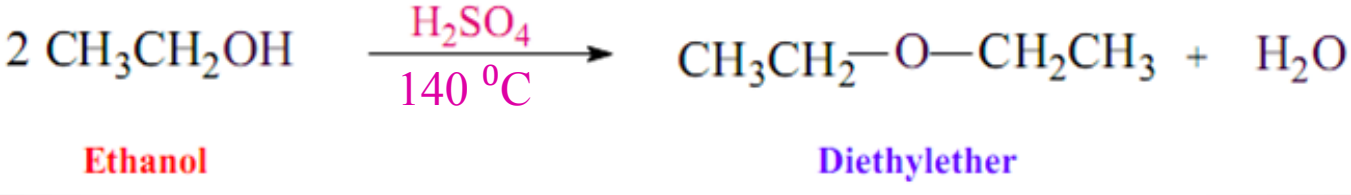


2- Dehydrations of Alcohols: Ethers Formation

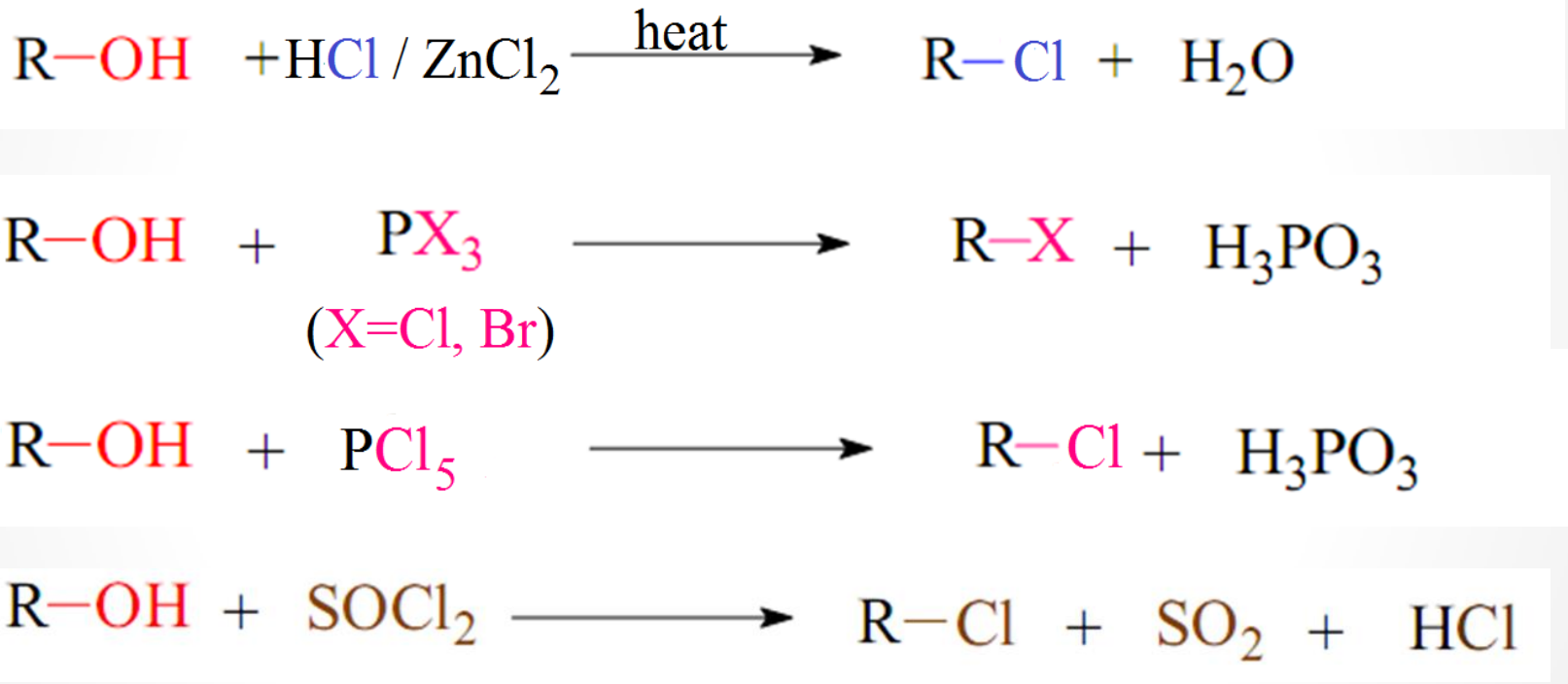




Example:



3- Replacement of the OH group by Halide: Alkyl Halides Formation



C- Oxidation of Alcohols to Carbonyl Compounds

- Oxidation of alcohols gives different products depending on the *class of alcohols that is oxidized* and on the *kind of oxidizing agent that is used*.

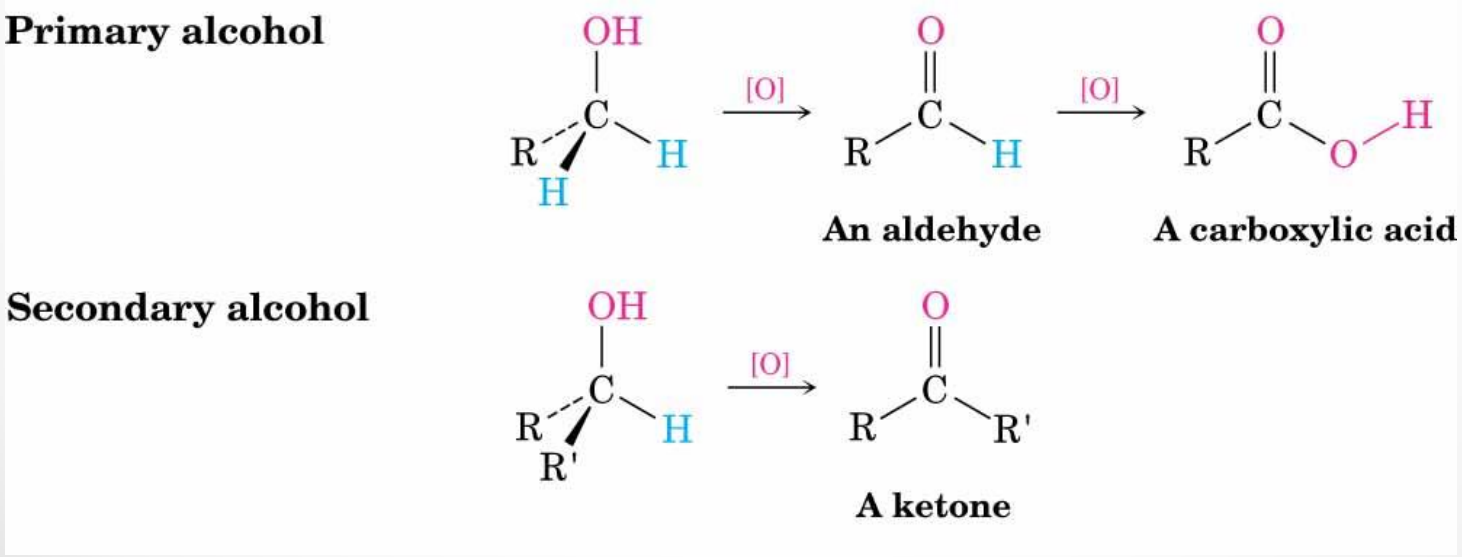
- Oxidizing agent:

  Very strong: $KMnO_4 / H^+ / \Delta$

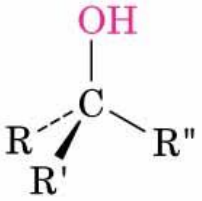
  Strong: $KMnO_4 / OH^-$ or H_2CrO_4 or $K_2Cr_2O_4 / H^+$

  Mild: CrO_3 / pyridine or Cu / 300 °C

.



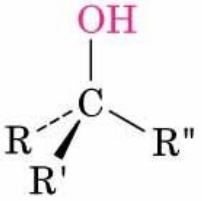
Tertiary alcohol



[O]

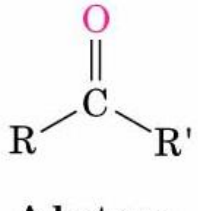
Mild or strong oxidizing

NO reaction



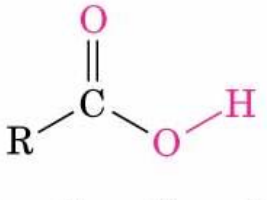
[O]

very strong oxidizing



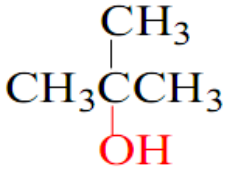
A ketone

+



A carboxylic acid

Examples:

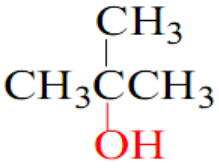


[O]

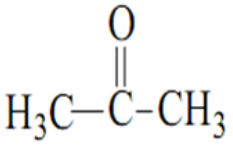
Mild or strong oxidizing

No reaction

t-butyl alcohol



$KMnO_4 / H^+ / \Delta$



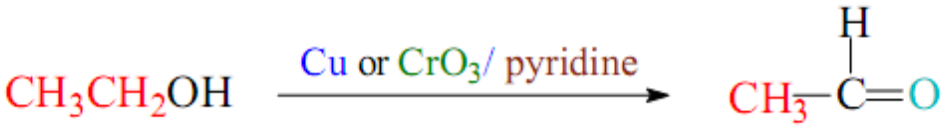
Acetone

+

HCOOH

Formic acid

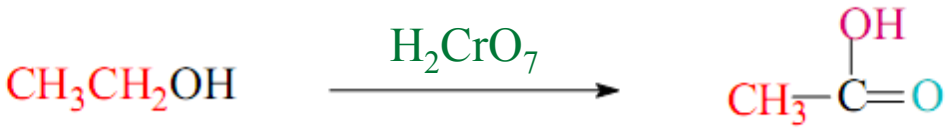
with mild oxidizing agent



Ethanol

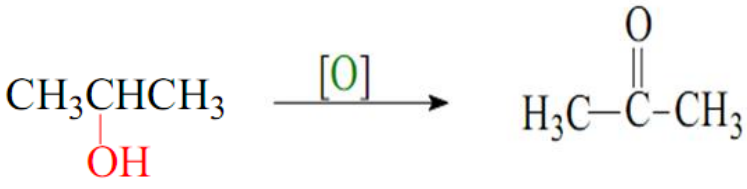
Ethanal
Acetaldehyde

with stronger oxidizing agents



Ethanol

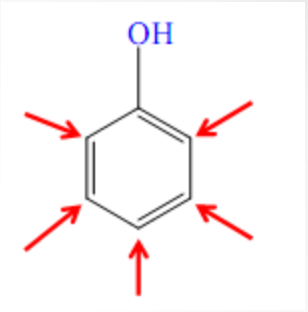
Acetic acid



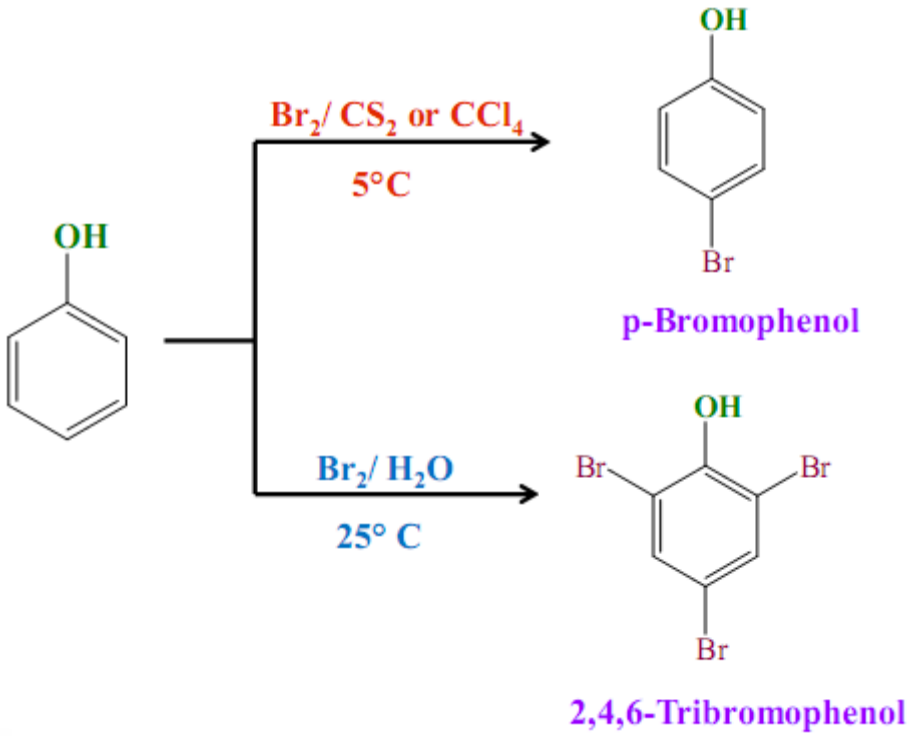
2- Propanol

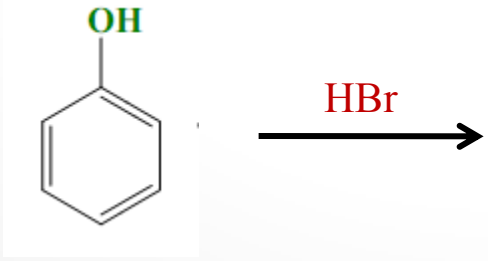
Acetone

D- Reaction of Aromatic ring of Phenols



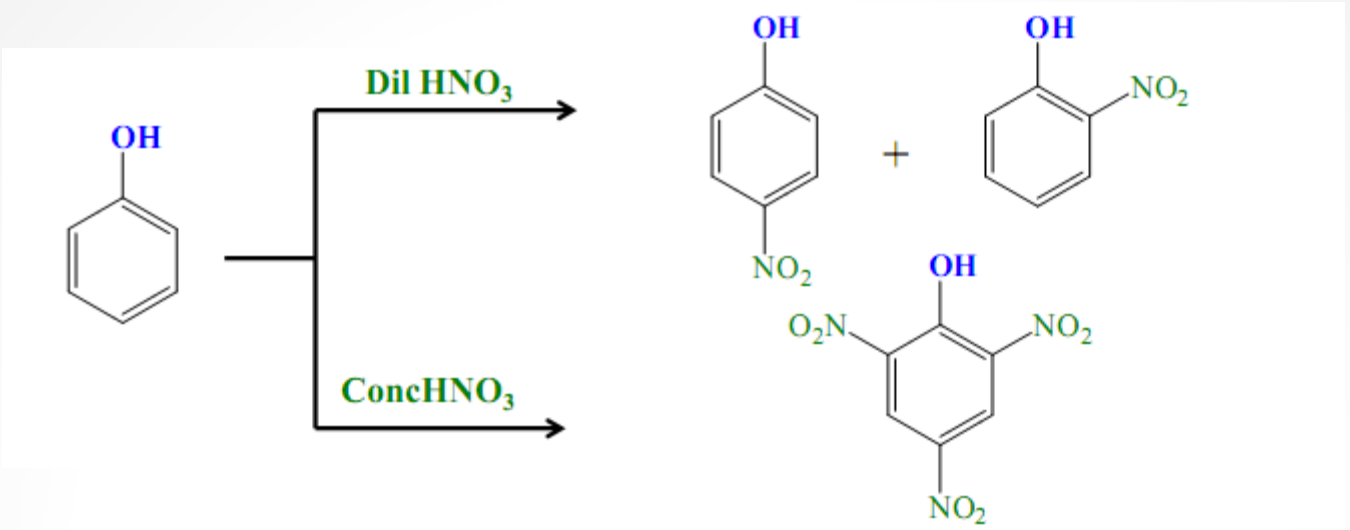
1- Halogenation



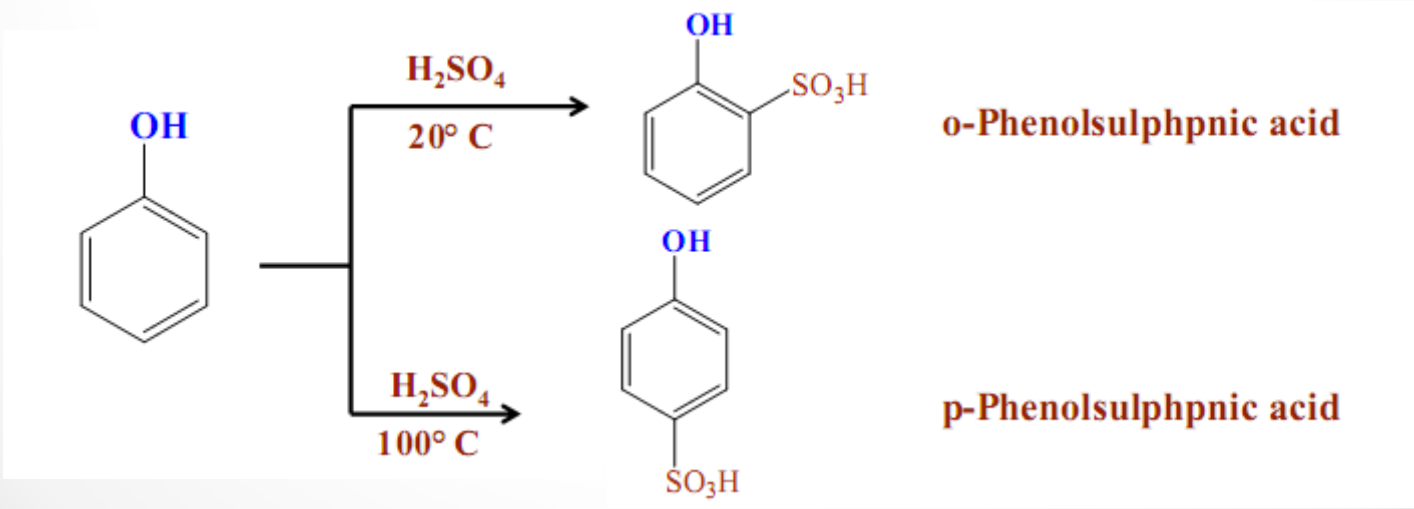


2- Nitration

At high temperature At low temperature

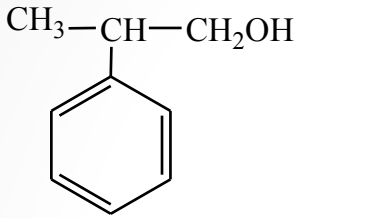


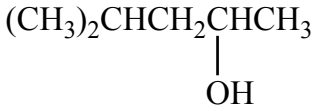
3- Sulphonation

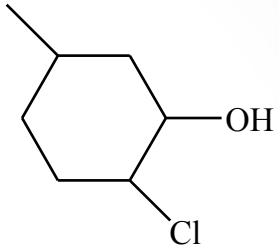


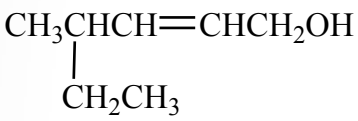
Homework

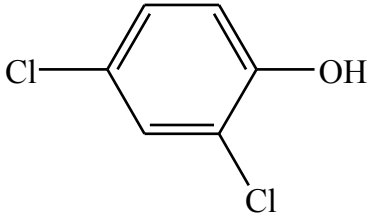
1- Name the following compounds.

a) 

b) 

c) 

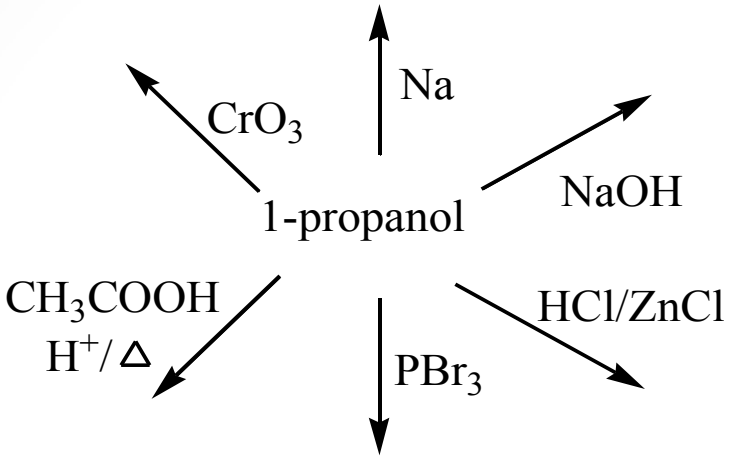
d) 

e) 

2- What is the correct IUPAC name.

a) 2-Methyl-2-penten-4-ol
b) 4-Chloro-5-phenyl-5-heptanol
c) 4-Bromocylohexanol

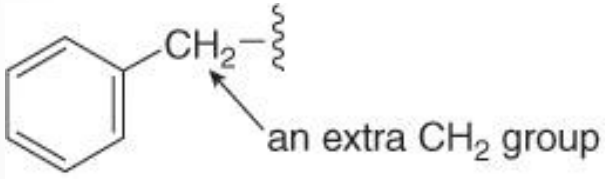
3- Complete the following reactions.



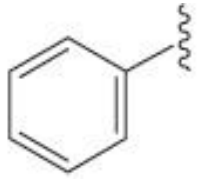
Nomenclature of Aromatic compounds

- When a benzene ring is a substituent, the term **phenyl** is used (for C_6H_5-)

  You may also see "Ph" or "ϕ" in place of "C_6H_5"
- "**Benzyl**" refers to "$C_6H_5CH_2$-"

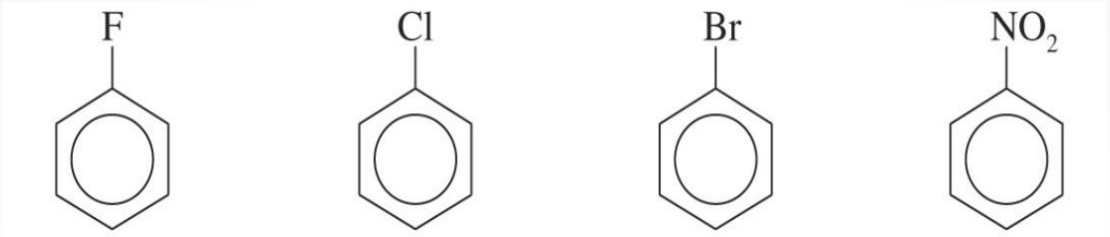


benzyl group
$C_6H_5CH_2-$



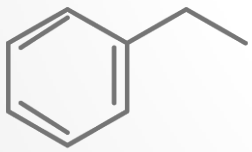
phenyl group
C_6H_5-

- Benzene is the parent name for some monosubstituted benzenes; the substituent name is added as a prefix.

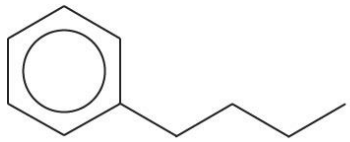


Fluorobenzene Chlorobenzene Bromobenzene Nitrobenzene

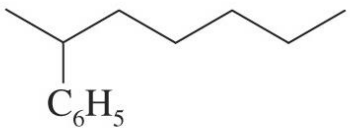
- The C_6H_5- group is called phenyl when it is a substituent
  - A hydrocarbon with a saturated chain and a benzene ring is named by choosing the larger structural unit as the parent
  - If the chain is unsaturated then it must be the parent and the benzene is then a phenyl substituent



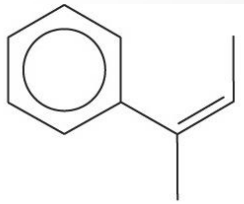
Ethylbenzene



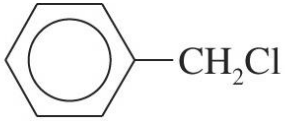
Butylbenzene



2-Phenylheptane

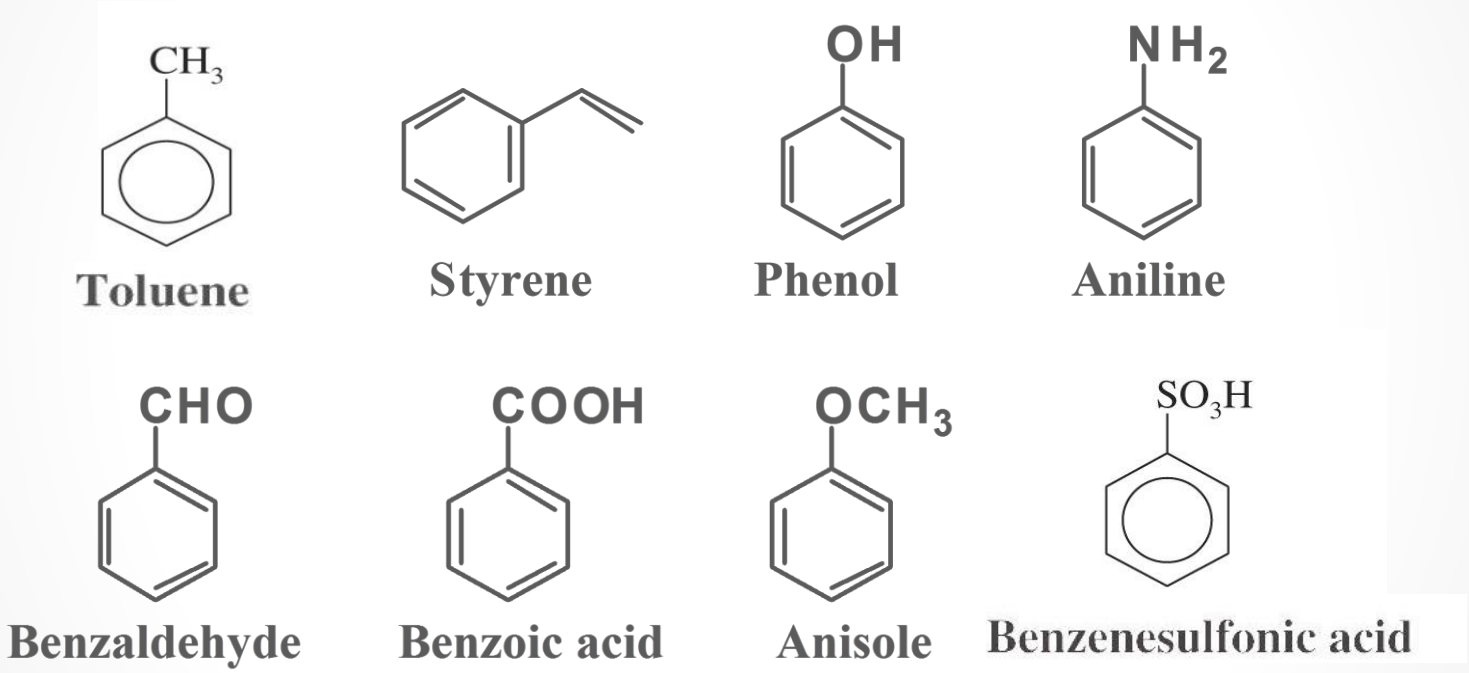


(Z)-2-Phenyl-2-butene

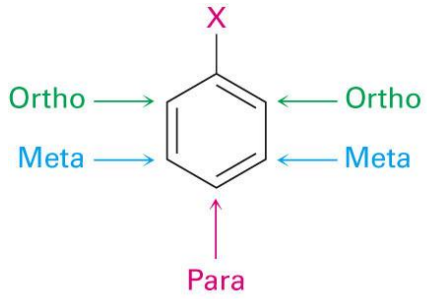


Benzyl chloride

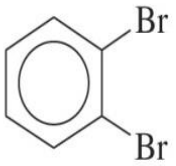
- For other monosubstituted benzenes, the presence of the substituent results in a new parent name.



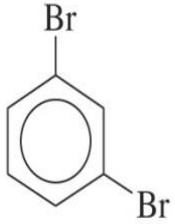
- When two substituents are present their position may be indicated by the prefixes *ortho*, *meta*, and *para* (*o*, *m* and *p*) or by the corresponding numerical positions.



- If the two groups on the benzene ring are different, alphabetize the names of the substituents preceding the word benzene.
- If one substituent is part of a common root, name the molecule as a derivative of that monosubstituted benzene.

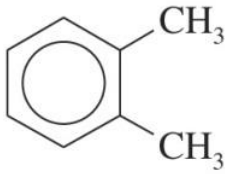


1,2-Dibromobenzene
(*o*-dibromobenzene)
ortho

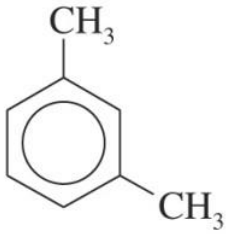


1,3-Dibromobenzene
(*m*-dibromobenzene)
meta

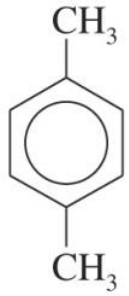
1,4-Dibromobenzene
(*p*-dibromobenzene)
para



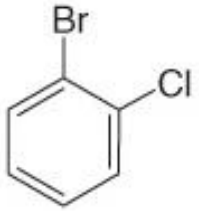
1,2-Dimethylbenzene
(*o*-xylene)



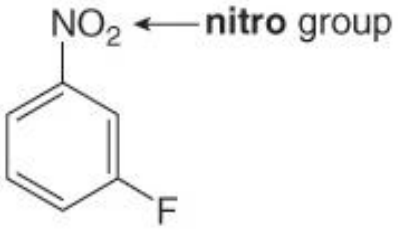
1,3-Dimethylbenzene
(*m*-xylene)



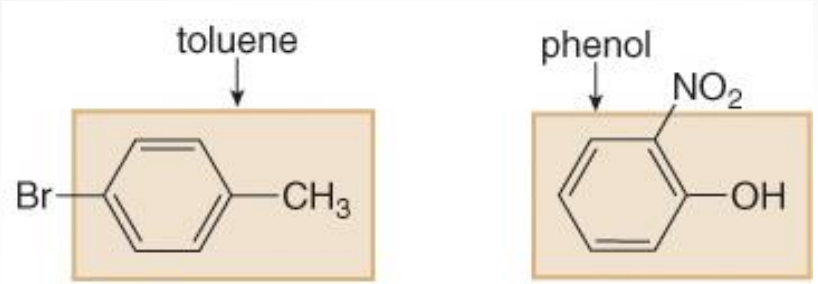
1,4-Dimethylbenzene
(*p*-xylene)



o-bromochlorobenzene

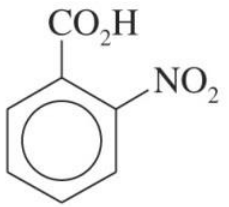


m-fluoronitrobenzene

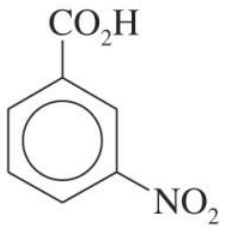


***p*-bromo**toluene

***o*-nitro**phenol



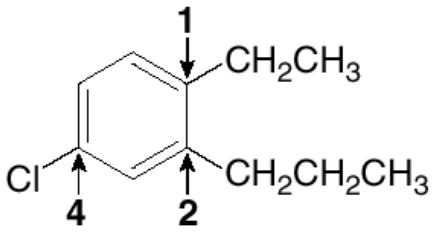
2-Nitrobenzoic acid
(*o*-nitrobenzoic acid)



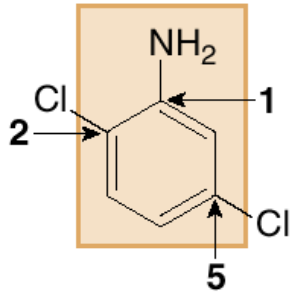
3-Nitrobenzoic acid
(*m*-nitrobenzoic acid)

4-Nitrobenzoic acid
(*p*-nitrobenzoic acid)

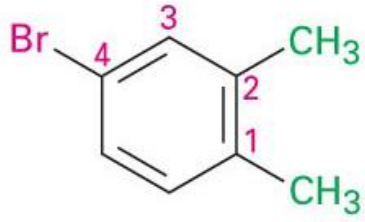
- For three or more substituents on a benzene ring:
  - Number to give the lowest possible numbers around the ring.
  - Alphabetize the substituent names.
  - When substituents are part of common roots, name the molecule as a derivative of that monosubstituted benzene. The substituent that comprises the common root is located at C1.



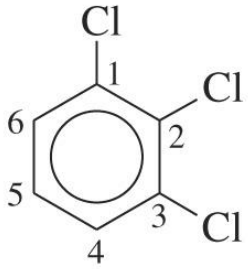
4-chloro-1-ethyl-2-propylbenzene



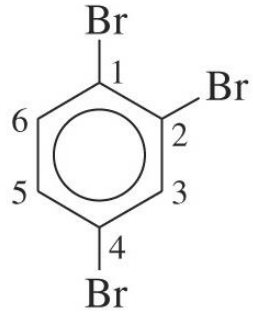
2,5-dichloroaniline



4-Bromo-1,2-dimethylbenzene

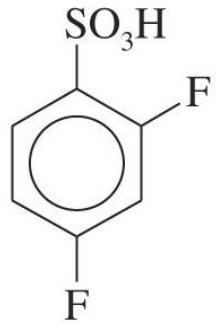


1,2,3-Trichlorobenzene

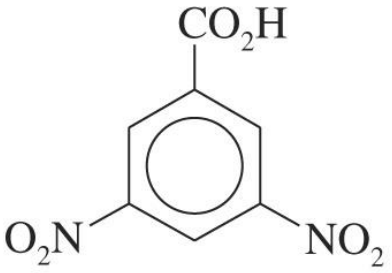


1,2,4-Tribromobenzene
(*not* 1,3,4-tribromobenzene)

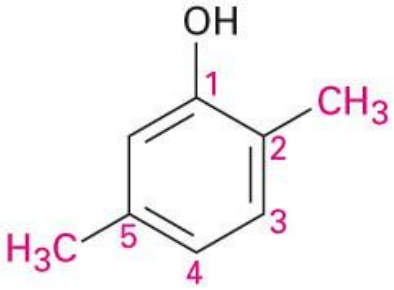
2,4,6-Trinitrotoluene (TNT)



2,4-Difluorobenzenesulfonic acid

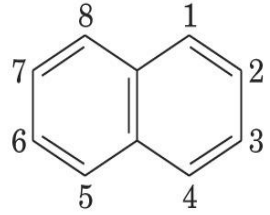


3,5-Dinitrobenzoic acid

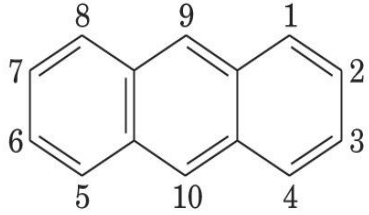


2,5-Dimethylphenol

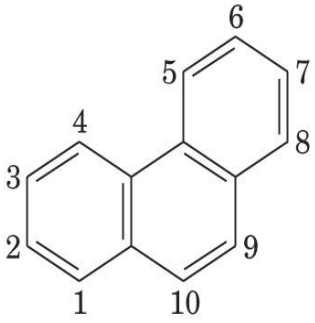
❑ Polynuclear Aromatic Hydrocarbons:



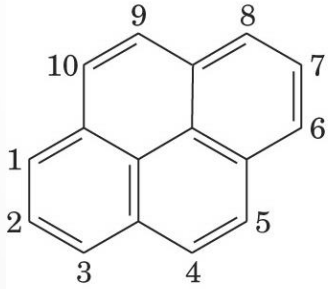
Naphthalene
$C_{10}H_8$



Anthracene
$C_{14}H_{10}$

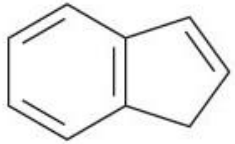


Phenanthrene
$C_{14}H_{10}$



Pyrene
$C_{16}H_{10}$

Biphenyl

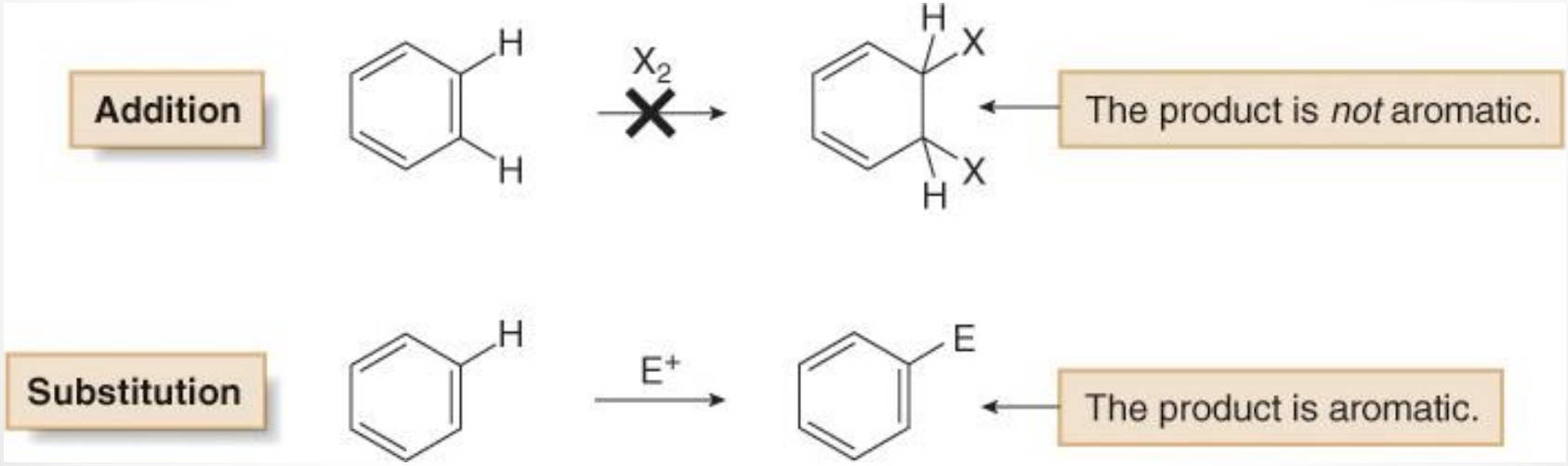


Indene

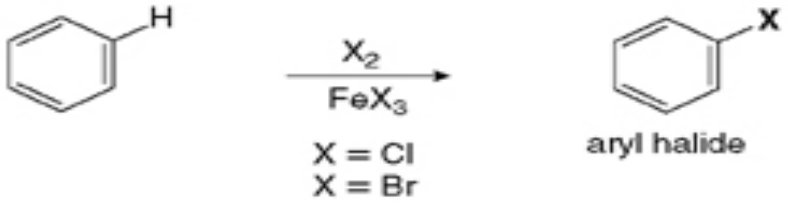
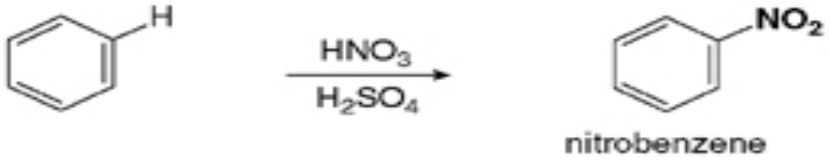
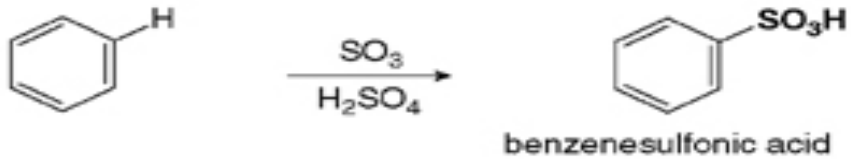
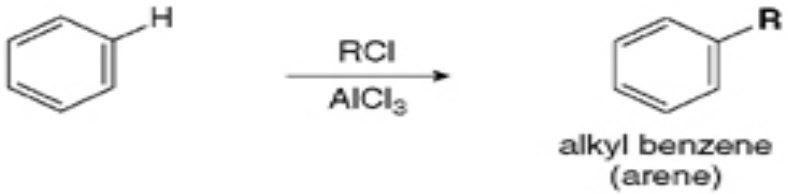
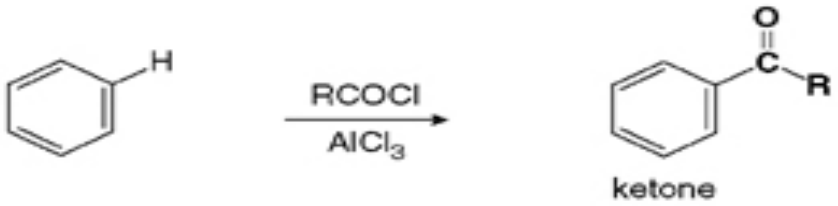
Electrophilic Aromatic Substitution

1- Specific Electrophilic Aromatic Substitution Reactions

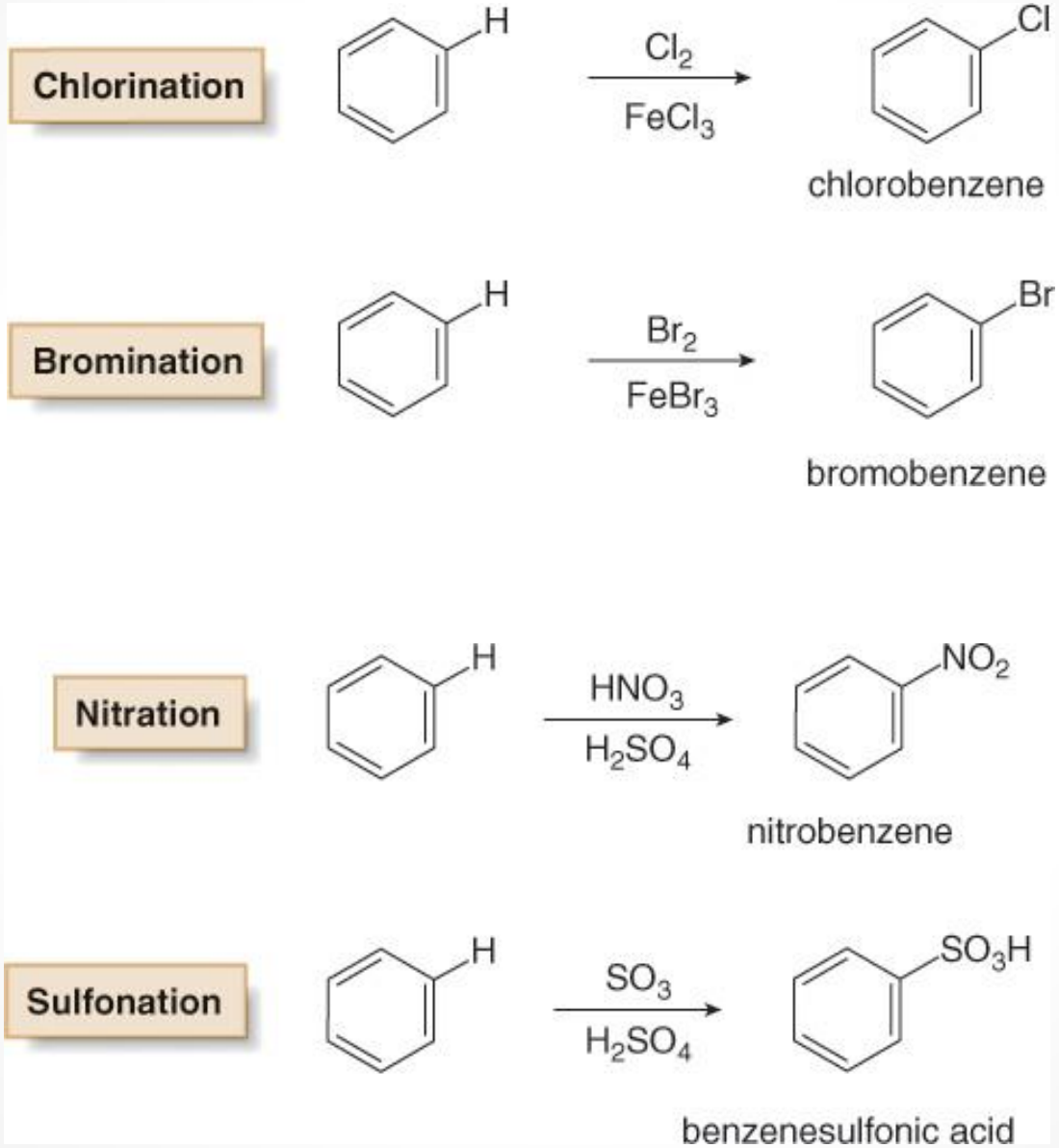
- Benzene does not undergo addition reactions like other unsaturated hydrocarbons, because addition would yield a product that is not aromatic.
- Substitution of a hydrogen keeps the aromatic ring intact.



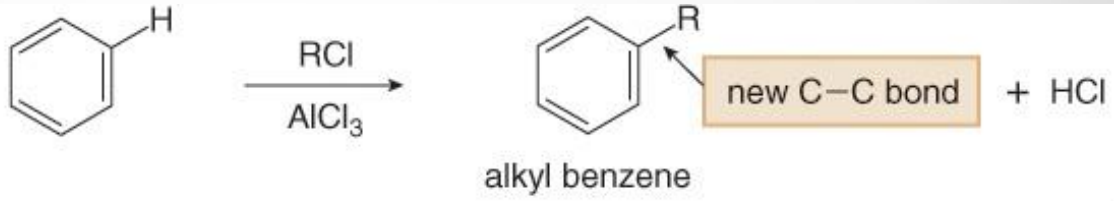
Halogenation, Alkylation, Nitration, and Sulfonation are the typical electrophilic aromatic substitution reactions.

Reaction	Electrophile
[1] Halogenation—Replacement of H by X (Cl or Br)	
	$E^+ = Cl^+$ or Br^+
[2] Nitration—Replacement of H by NO_2	
	$E^+ = \overset{+}{N}O_2$
[3] Sulfonation—Replacement of H by SO_3H	
	$E^+ = \overset{+}{S}O_3H$
[4] Friedel–Crafts alkylation—Replacement of H by R	
	$E^+ = R^+$
[5] Friedel–Crafts acylation—Replacement of H by RCO	
	$E^+ = R\overset{+}{C}O$

Examples:

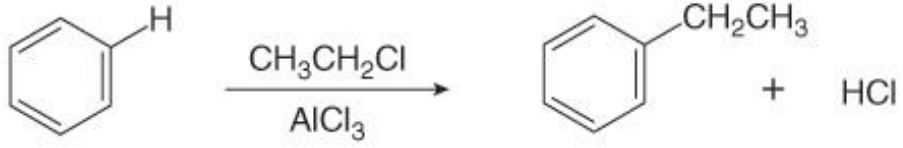

Chlorination
H
Cl_2
$FeCl_3$
Cl
chlorobenzene
Bromination
H
Br_2
$FeBr_3$
Br
bromobenzene
Nitration
H
HNO_3
H_2SO_4
NO_2
nitrobenzene
Sulfonation
H
SO_3
H_2SO_4
SO_3H
benzenesulfonic acid

Friedel–Crafts alkylation—General reaction

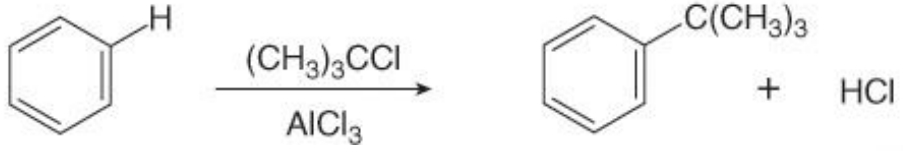


Examples

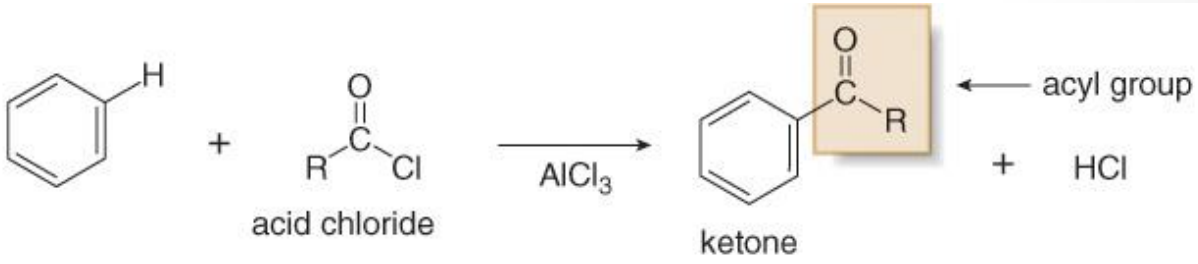
[1]



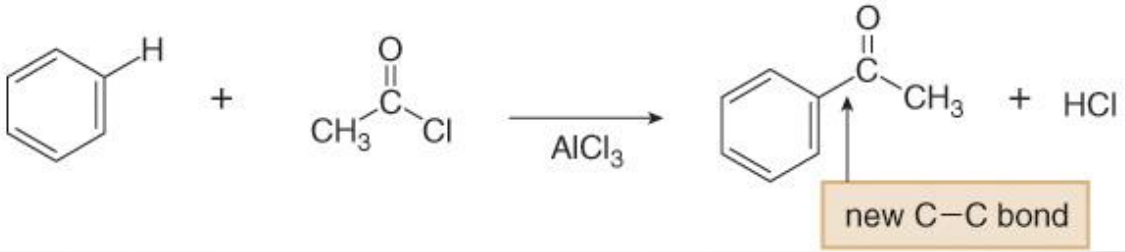
[2]



Friedel–Crafts acylation—General reaction

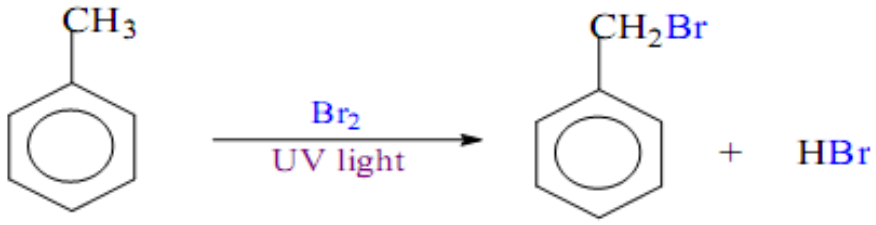


Example



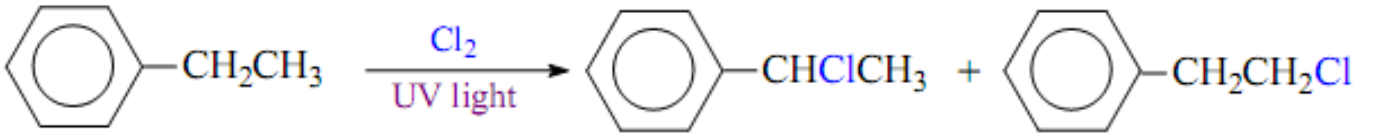
2- Side-Chain Reactions of Aromatic Compounds

A) Halogenation of an Alkyl Side-Chain



Toluene

BenzylBromide



Ethylbenzene

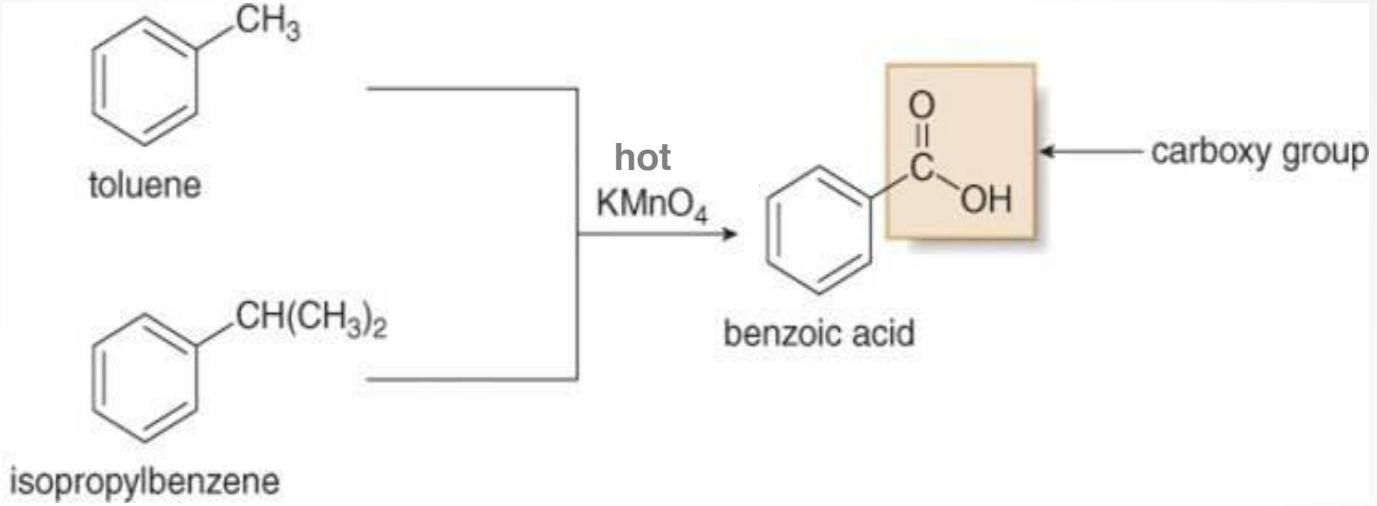
1-Chloro-1-phenylethane

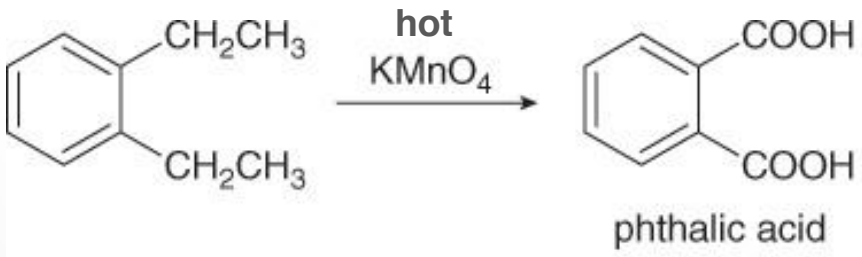
Major product

1-Chloro-2-phenylethane

Minor product

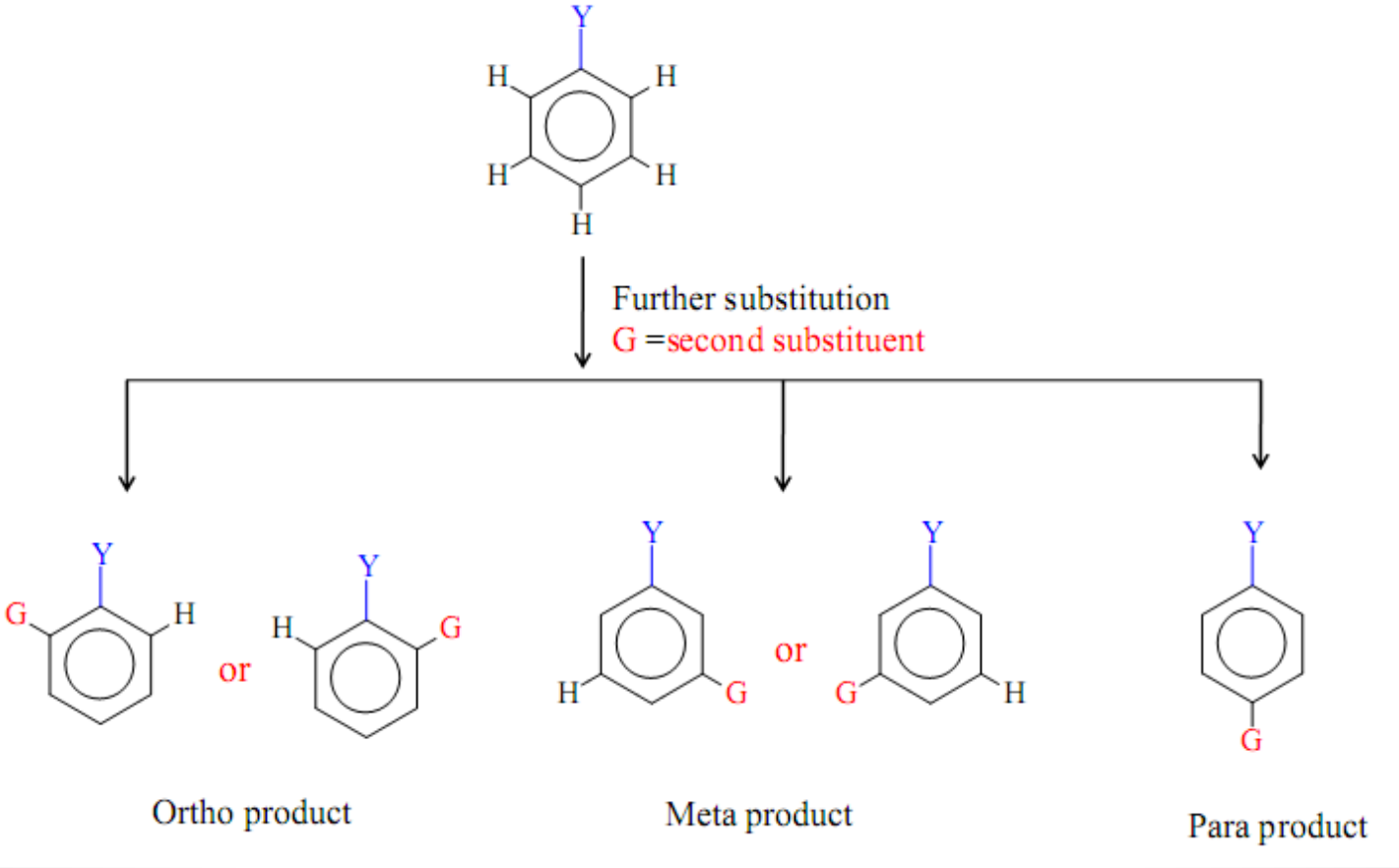
B) Oxidation of an Alkyl Side-Chain





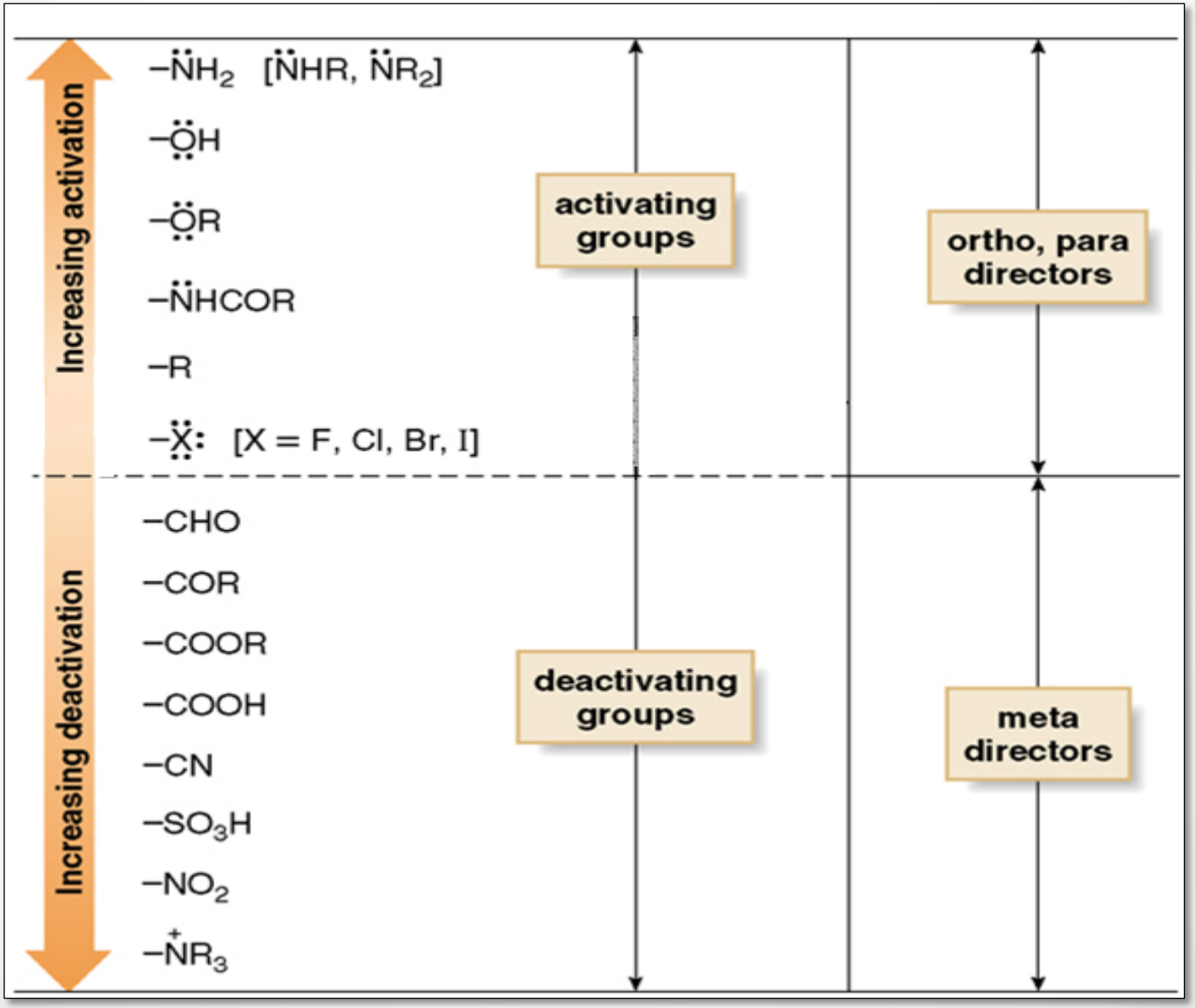
Disubstituted Benzenes: Orientation

The monpsubstituted benzene C_6H_5—Y, has **5 replaceable hydrogens.**

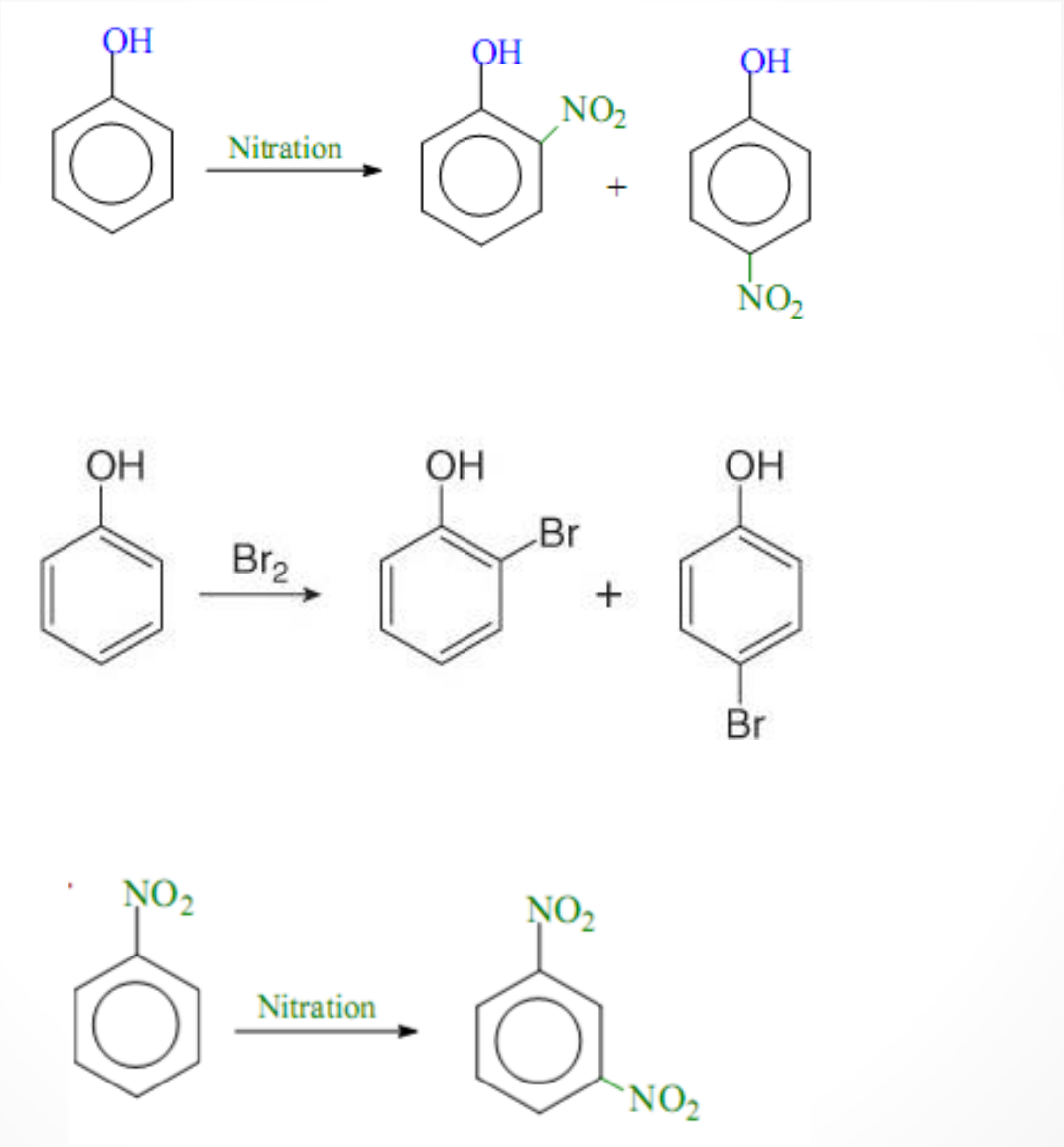


Product ratio conclusion:
40% ortho, 40% meta, 20% para

Orientation and Reactivity Effects of Substitutions Y in Electrophilic Aromatic Substitution

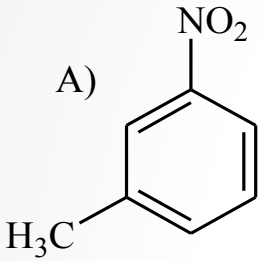


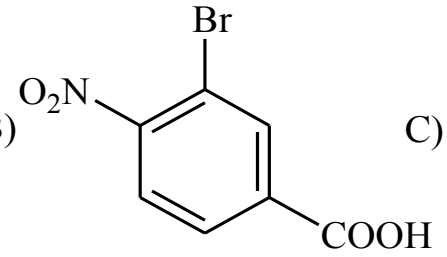
Examples:

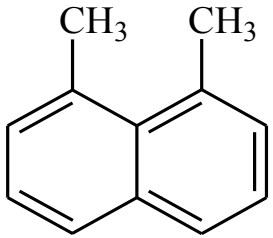

OH
Nitration
OH
NO2
+
OH
NO2
OH
Br2
OH
Br
+
OH
Br
NO2
Nitration
NO2
NO2

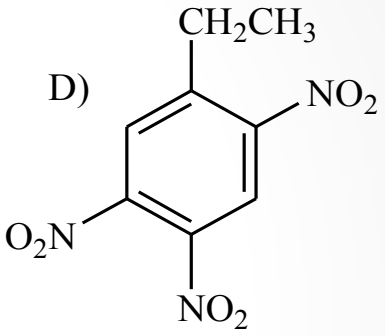
Homework

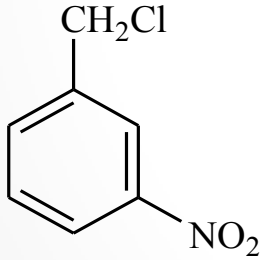
1- Name the following compounds.

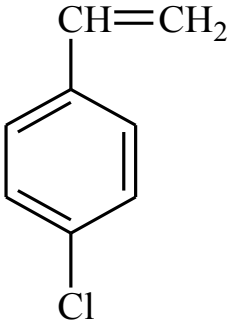
A) 

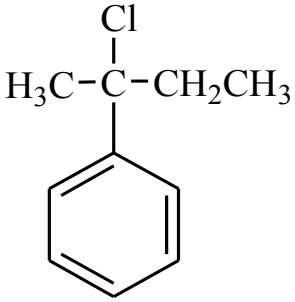
B) 

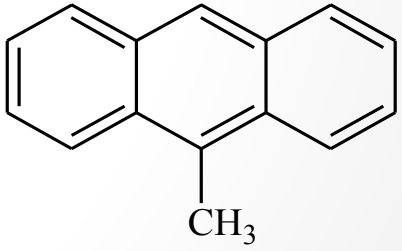
C) 

D) 

E) 

F) 

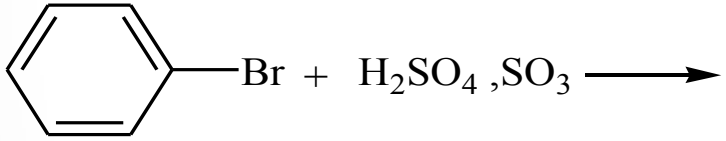
G) 

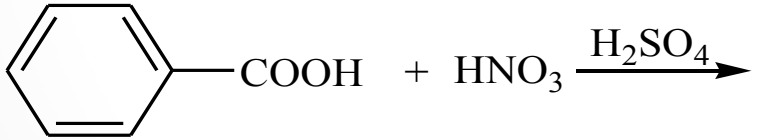
H) 

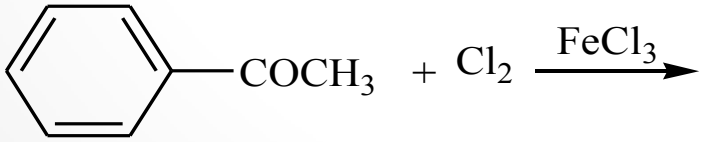
2- Write the structures of the following compounds.

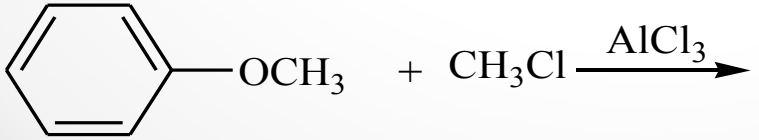
A) *p*-Nitroethylbenzene
B) 2,2-Dimethyl-1-phenylbutane
C) *o*-Ehtylaniline
D) 1,5-Dimethylnaphthalene
E) 9-Bromoanthracene
F) 2,4-Dinitroflurorbenzene
G) 2-Benzyl-3-nitro-5-bromophenol

3- Complete the following reactions.

A) 

B) 

C) 

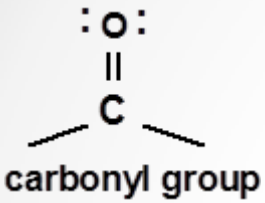
D) 

Chem. 108

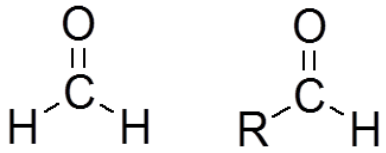
Aldehydes and Ketones

Chapter 9

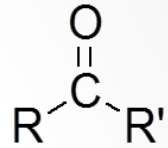
Aldehydes and ketones are simple compounds which contain a carbonyl group (a carbon-oxygen double bond).



aldehyde

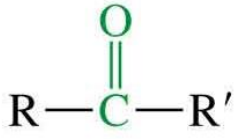
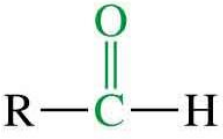
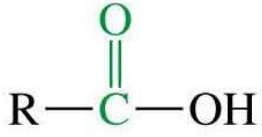
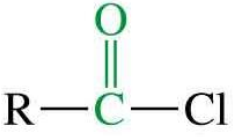
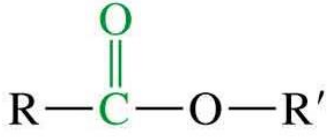
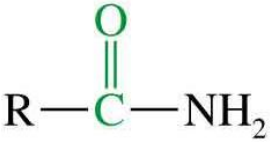


ketone



R can be Ar

Some Common Classes Carbonyl Compounds

Class	General Formula	Class	General Formula
ketones		aldehydes	
carboxylic acids		acid chlorides	
esters		amides	

Aldehydes

RCHO or RCH=O

Nomenclature

Common Names

- Use the common name of the carboxylic acids.
- Drop *-ic acid* and add *-aldehyde*.
  - 1 C: formic acid → formaldehyde
  - 2 C's: acetic acid → acetaldehyde
  - 3 C's: propionic acid → propionaldehyde
  - 4 C's: butyric acid → butyraldehyde.

Structure	IUPAC name	Common name	Structure	IUPAC	Common name
HCO_2H	methanoic acid	**formic acid**	HCHO	methanal	**formaldehyde**
CH_3CO_2H	ethanoic acid	**acetic acid**	CH_3CHO	ethanal	**acetaldehyde**
$CH_3CH_2CO_2H$	propanoic acid	**propionic acid**	CH_3CH_2CHO	propanal	**propionaldehyde**
$CH_3(CH_2)_2CO_2H$	butanoic acid	**butyric acid**	$CH_3(CH_2)_2CHO$	butanal	**butyraldehyde**
$CH_3(CH_2)_3CO_2H$	pentanoic acid	**valeric acid**	$CH_3(CH_2)_3CHO$	pentanal	**valeraldehyde**
$CH_3(CH_2)_4CO_2H$	hexanoic acid	**caproic acid**	$CH_3(CH_2)_4CHO$	hexanal	**caproaldehyde**

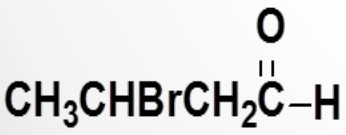
- Substituents locations are given using Greek letters

(α, β, γ, δ) beginning with the carbon next to the carbonyl carbon.

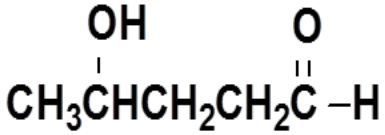
5 4 3 2 1

C—C—C—C—C=O

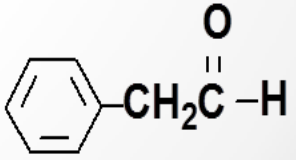
δ γ β α



β-bromobutyraldehyde



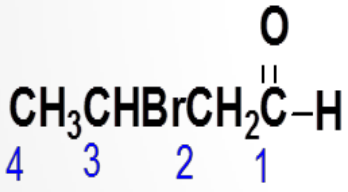
γ-hydroxyvaleraldehyde



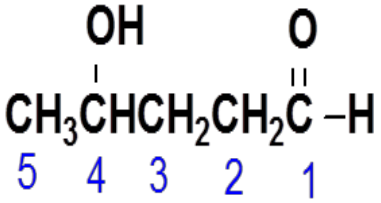
α-phenylacetaldehyde

IUPAC System

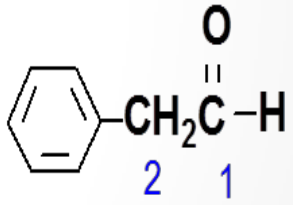
- Select the longest carbon chain containing the carbonyl carbon.
- The **-e** ending of the parent alkane name is replaced by the suffix **-al**.
- The carbonyl carbon is always numbered "1." (It is not necessary to include the number in the name.)



3-bromobutanal



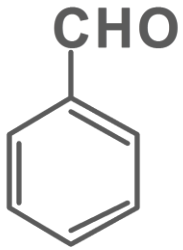
4-hydroxypentanal



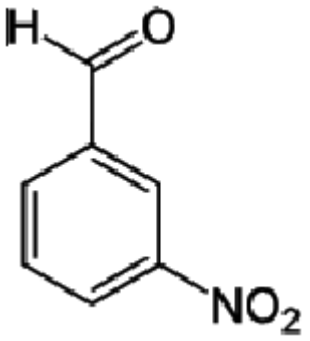
2-phenylethanal

- Aromatic aldehydes are usually designated as derivatives of the simplest aromatic aldehyde,

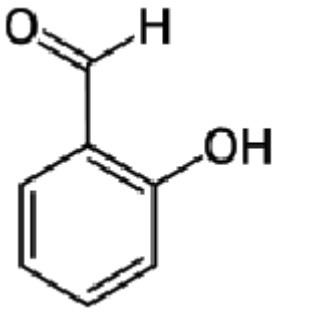
Benzaldehyde



Benzaldehyde



m-Nitrobenzaldehyde
3-Nitrobenzaldehyde



Salicylaldehyde
(*o*-Hydroxybenzaldehyde)
2-Hydroxybenzaldehyde

Ketones

RCOR’ (R and R’=alkyl or aryl)

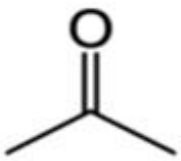
Nomenclature

Common Names

The common name for a ketone is constructed by adding ketone to the names of the two alkyl groups on the C=O double bond, listed in alphabetical order.

IUPAC System

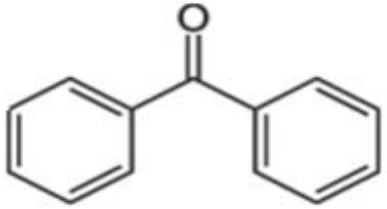
- Select the longest carbon chain containing the carbonyl carbon.
- The -e ending of the parent alkane name is replaced by the suffix -one.
- The chain is numbered in such a way as give the lowest number to the C=O group.



Dimethylketone

acetone

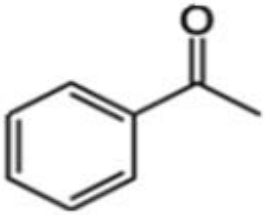
2-Propanone



Diphenylketone

Benzophenone

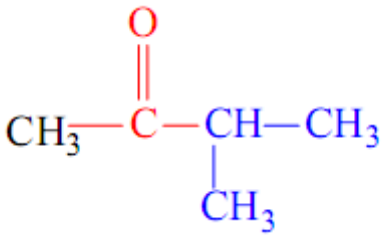
diphenylmethanone



Methylphenylketone

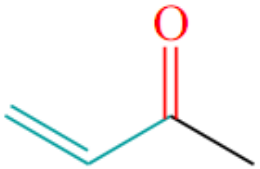
acetophenone

1-Phenyl-2-ethanone



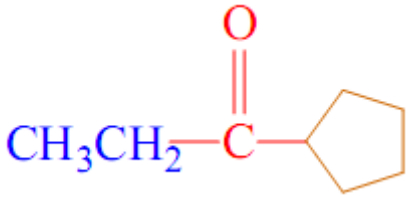
isopropyl methyl ketone

3-Methylbutan-2-one



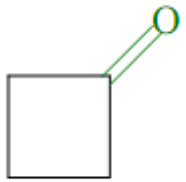
Methyl vinyl ketone

3-buten-2-one



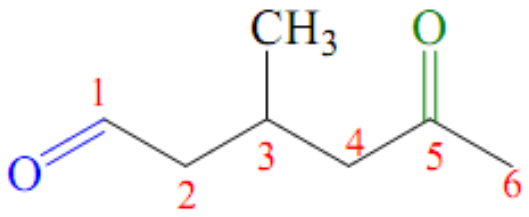
Cyclopentyl ethyl ketone

1-Cyclopentyl-1-propanone

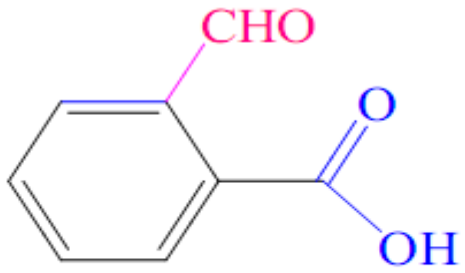


Cyclobutanone

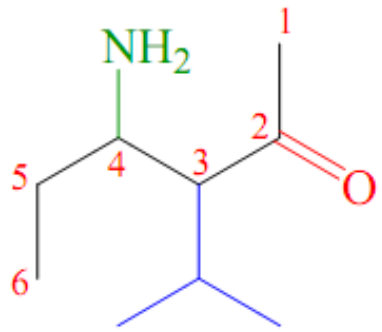
- On a molecule with a higher priority functional group, C=O is *oxo-* and -CHO is *formyl.*
- Aldehyde priority is higher than ketone
- Carboxylic acid priority is higher than aldehyde



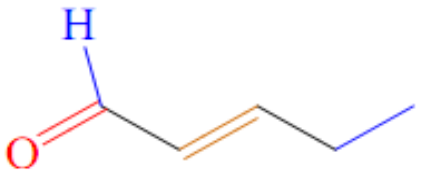
3-Methyl-5-oxohexanal



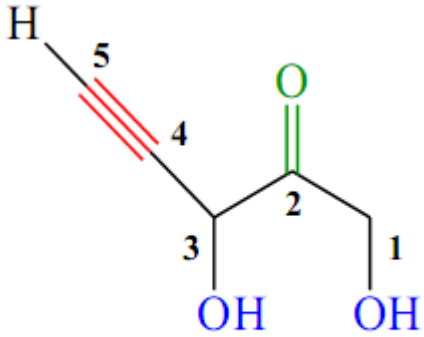
2- formyl benzoic acid



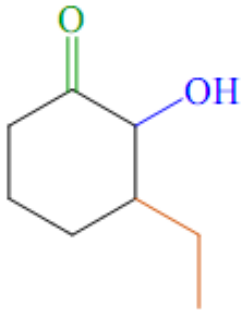
4-amino-3-isopropyl-2-hexanone



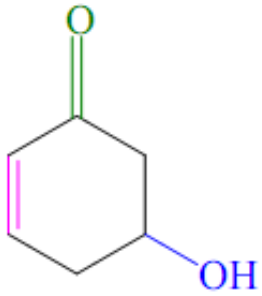
2-pentenal



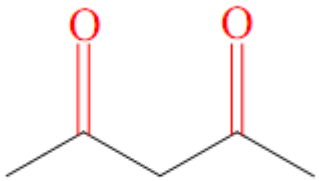
1,3- dihydroxypent-4-yn-2-one



3-Ethyl-2-hydroxycyclohexanone

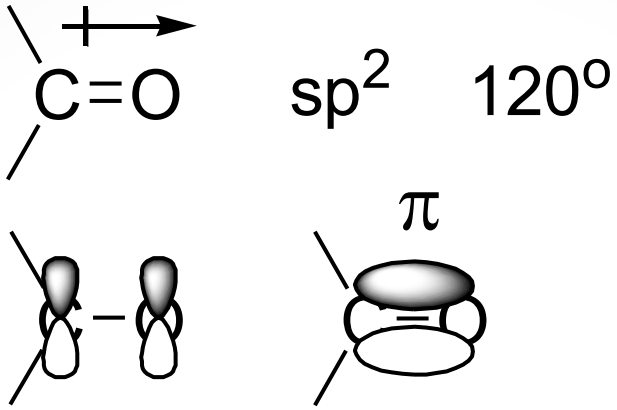


5-hydroxy-2-cyclohexenone

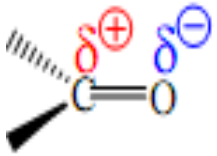


2,4-pentadione

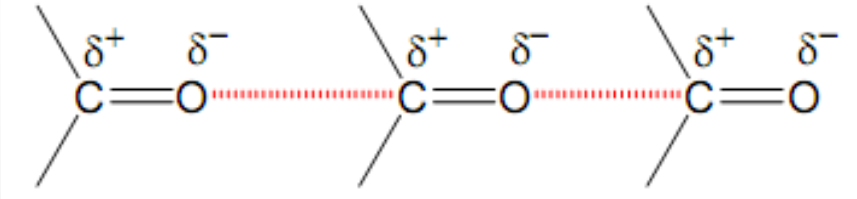
Physical Properties of Aldehydes and Ketones



Carbonyl compounds are polar, containing a dipole along the carbon-oxygen double bond.

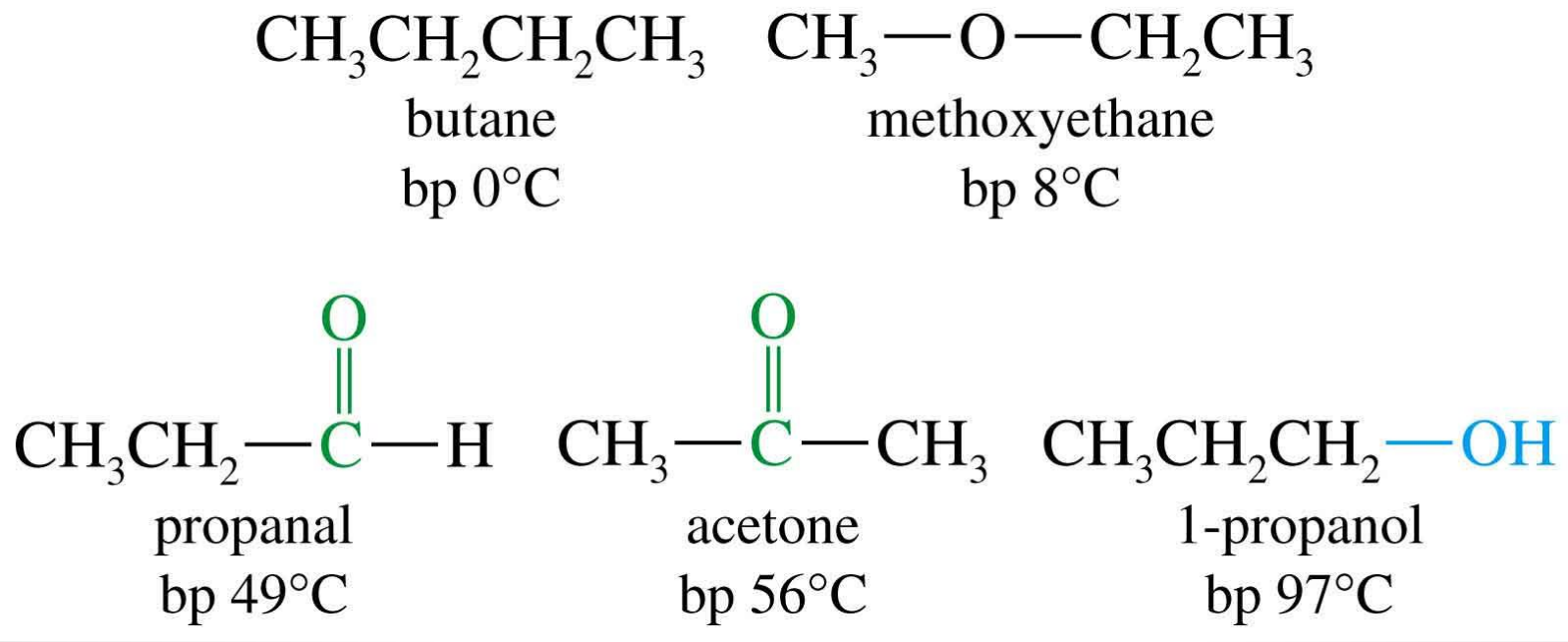


This creates weak attractive forces between carbonyl compounds, but these attractions are not as strong as those that result from hydrogen-bonding.



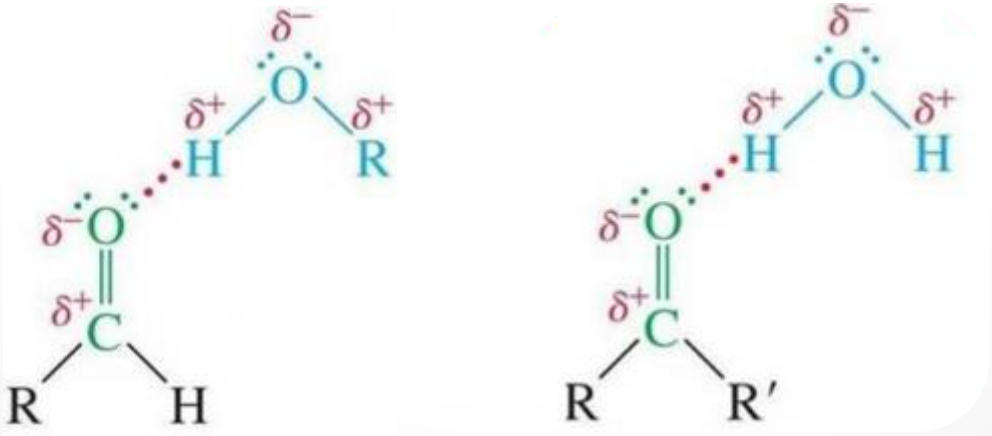
1. Boiling Points

More polar, so higher boiling point than comparable alkane or ether. Cannot H-bond to each other, so lower boiling point than comparable alcohol.



2. Solubility in water

- Carbonyl compounds can not hydrogen-bond to each other, but they can hydrogen-bond to water through the carbonyl oxygen.
- The lower aldehydes and ketones are soluble in water because they form hydrogen bonds with water.
- Aldehydes and ketones with more than six carbons are essentialy insoluble in water.
- The higher aldehydes and ketones are soluble in organic solvents such as; benzene, ether, and carbontetrachlorid.



Preparation of Aldehydes and Ketones

1- Oxidation of Alcohols

- Oxidation of alcohols gives different products depending on the *class of alcohols that is oxidized* and on the *kind of oxidizing agent that is used.*

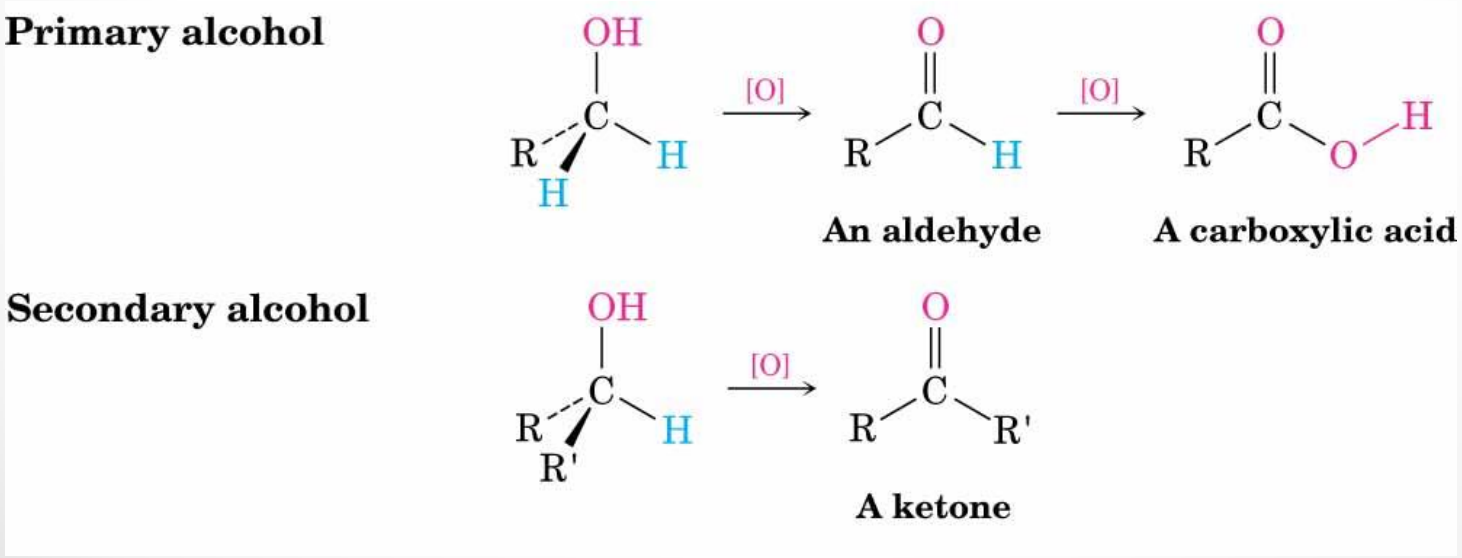
- Oxidizing agent:

  Very strong: $KMnO_4 / H^+ / \Delta$

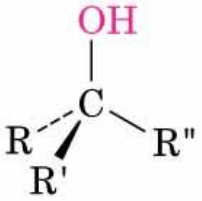
  Strong: $KMnO_4 / OH^-$ or H_2CrO_4 or $K_2Cr_2O_4 / H^+$

  Mild: CrO_3 / pyridine or Cu / 300 °C

.



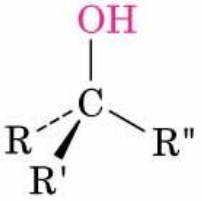
Tertiary alcohol



[O]

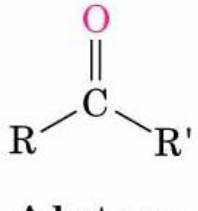
Mild or strong oxidizing

NO reaction



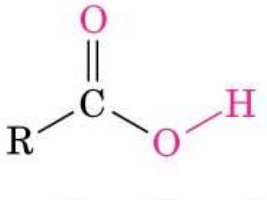
[O]

very strong oxidizing



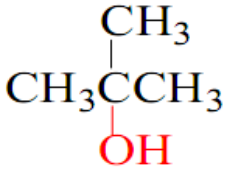
A ketone

+



A carboxylic acid

Examples:

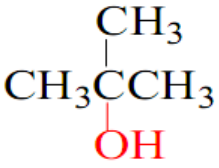


[O]

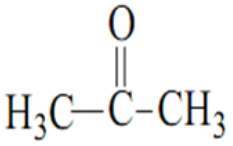
Mild or strong oxidizing

No reaction

t-butyl alcohol



$KMnO_4 / H^+ / \Delta$



Acetone

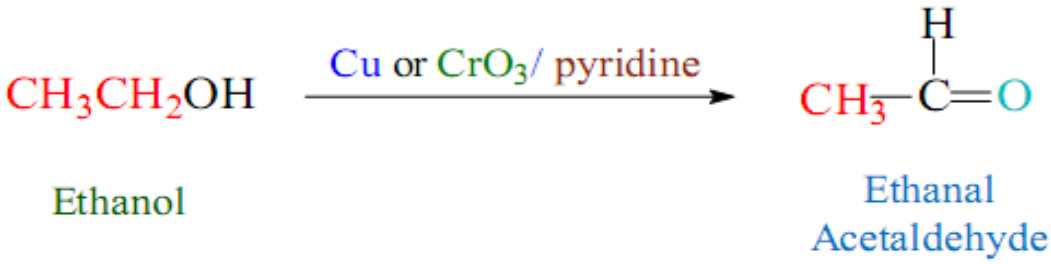
+

HCOOH

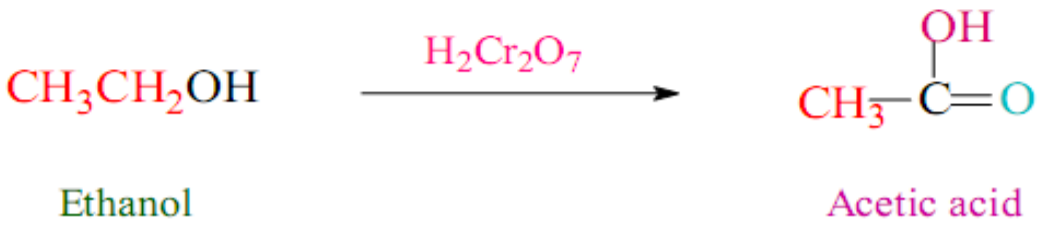
Formic acid

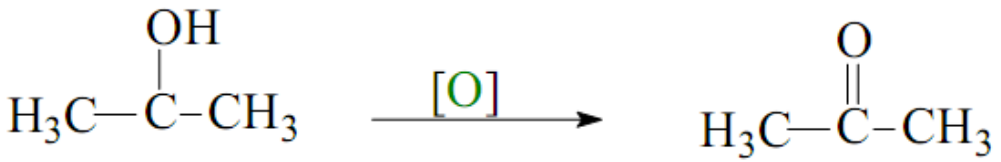
Examples:

with mild oxidizing agent



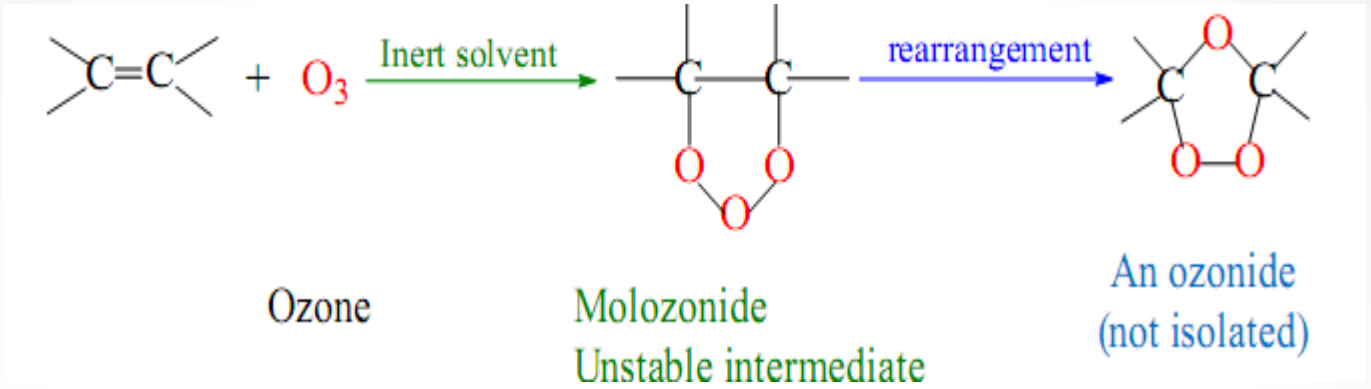
with stronger oxidizing agents

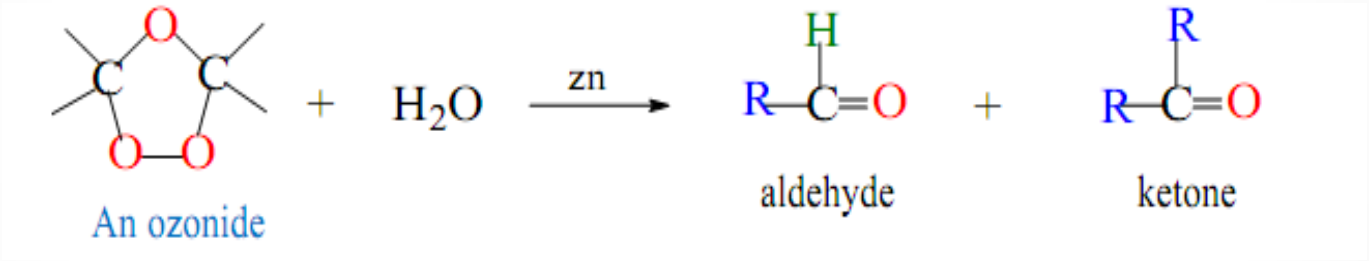




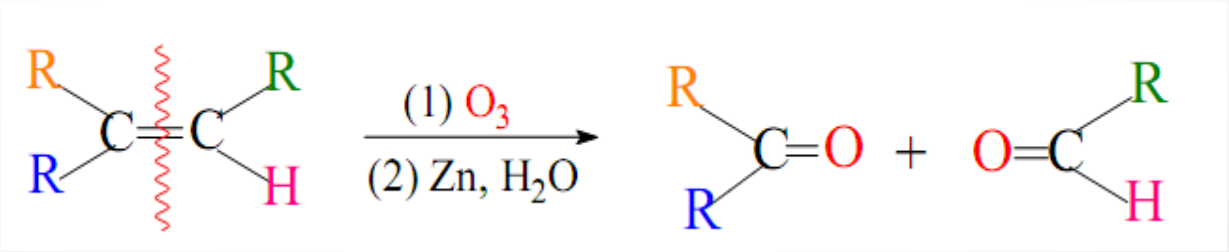
2- Ozonolysis of alkenes

Oxidation of alkenes by ozone O_3

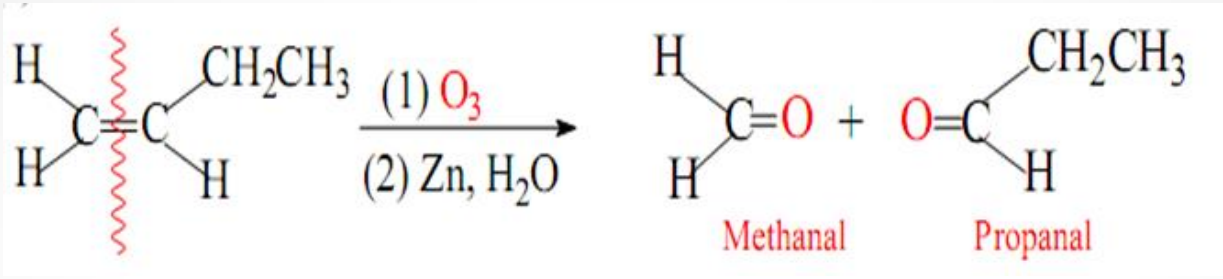


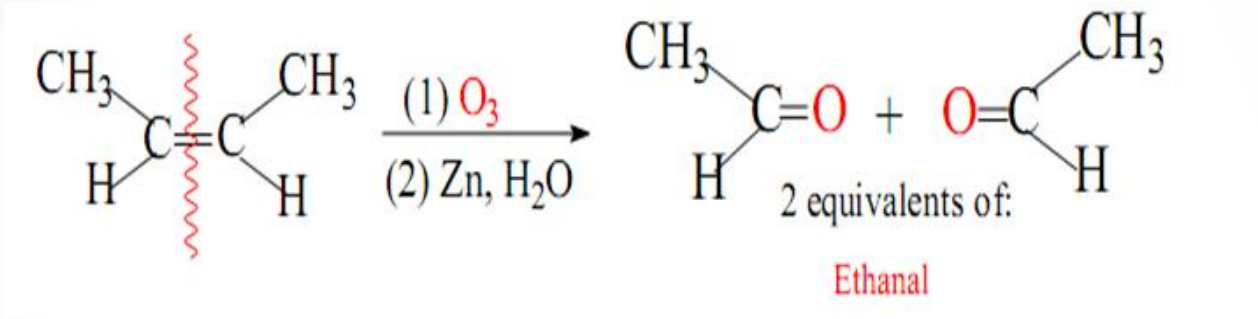


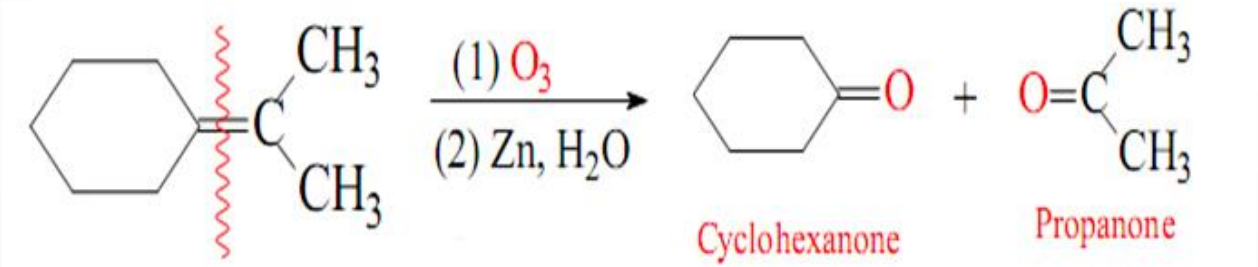
The ozonolysis reaction can be summarized by the following equation:

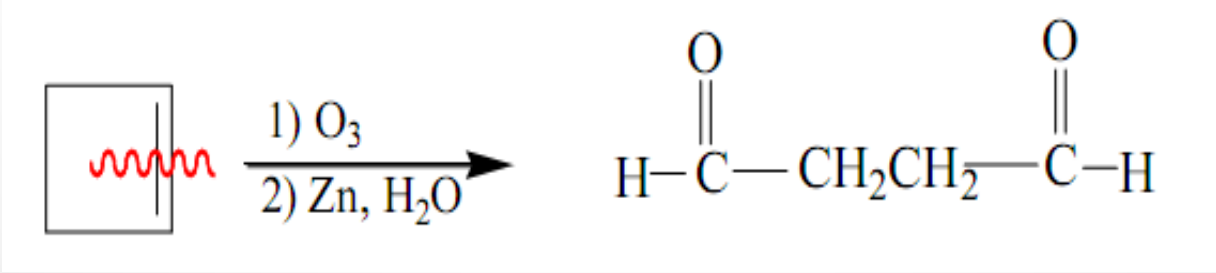


Examples:

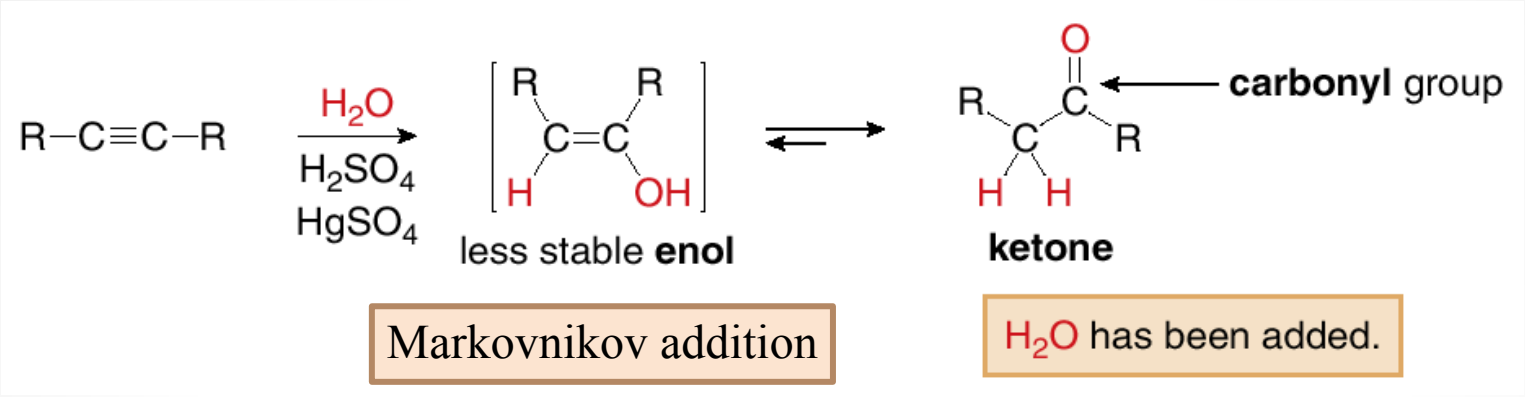

(1) O_3
(2) Zn, H_2O
Methanal
Propanal

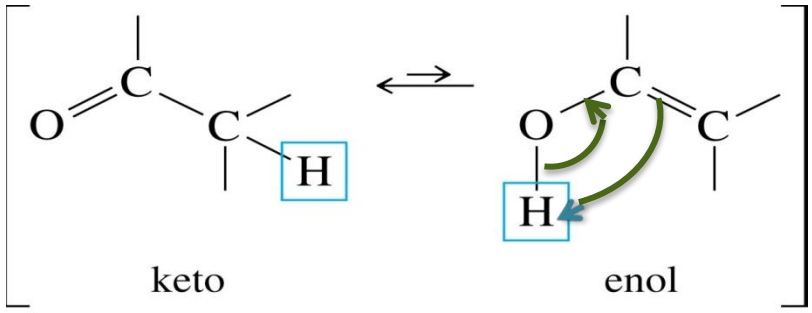

(1) O_3
(2) Zn, H_2O
2 equivalents of:
Ethanal


(1) O_3
(2) Zn, H_2O
Cyclohexanone
Propanone


1) O_3
2) Zn, H_2O

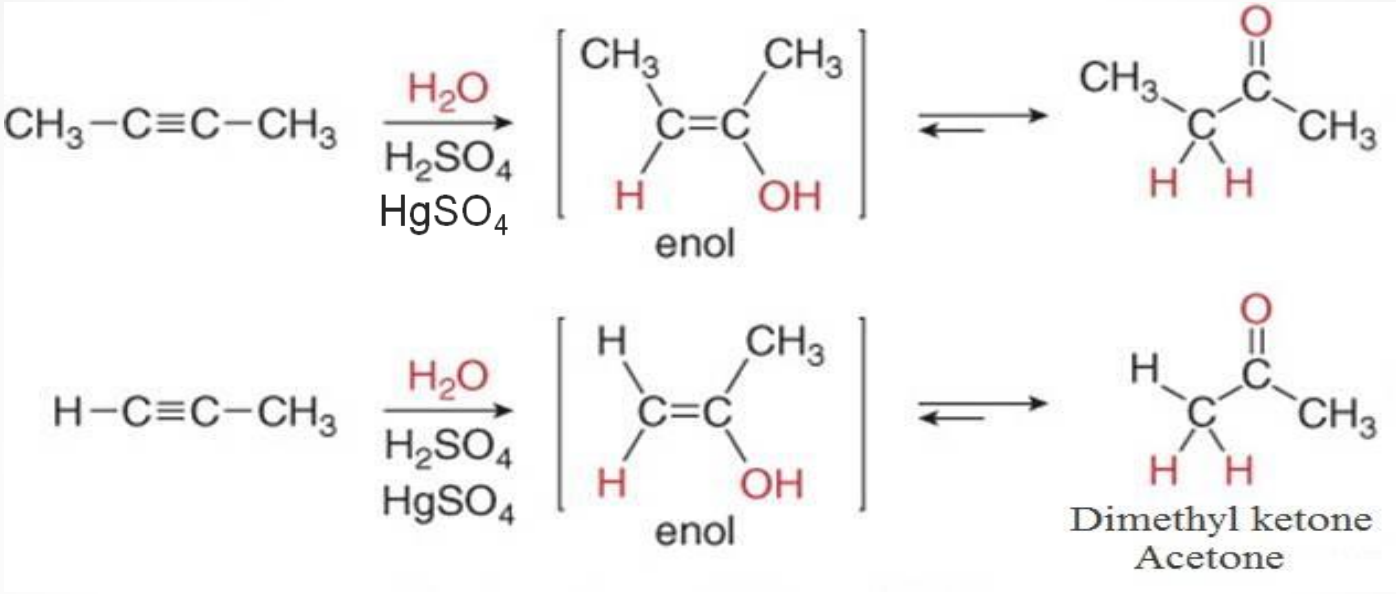
3.Hydration of alkynes: Addition of water

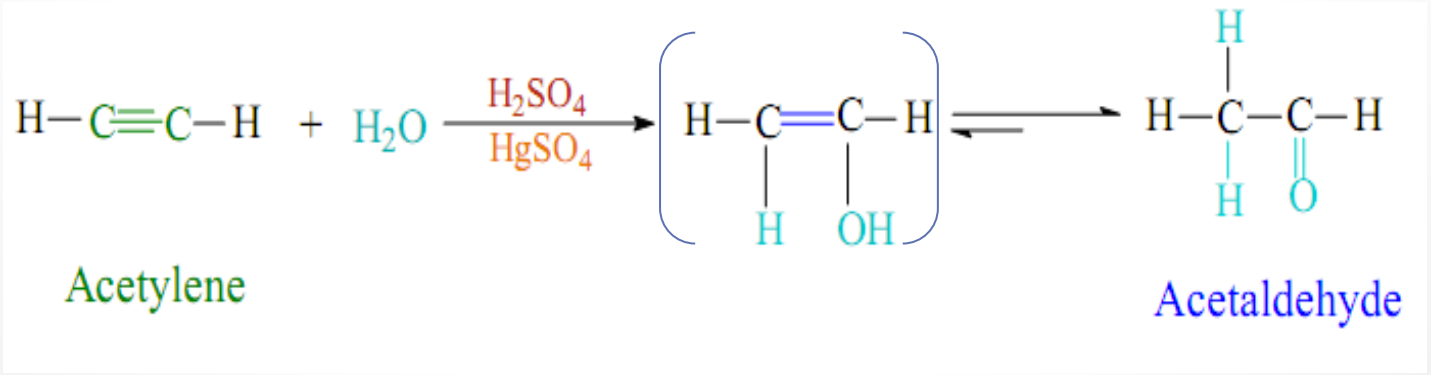




keto–enol tautomerism

Examples:

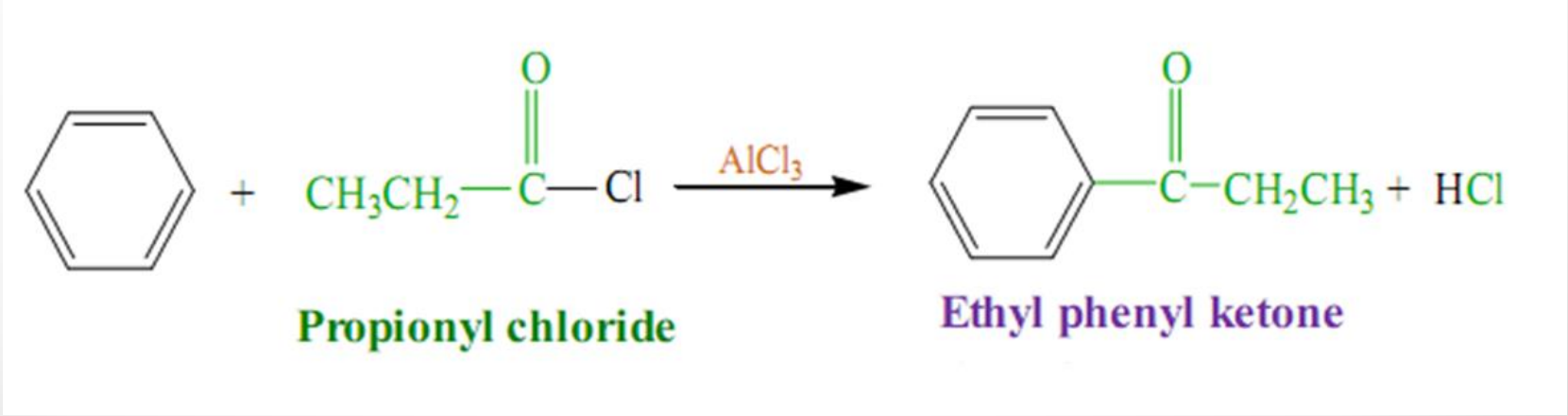

CH3–C≡C–CH3
H2O
H2SO4
HgSO4
CH3
CH3
C=C
H
OH
enol
O
CH3
C
CH3
H
H
H–C≡C–CH3
H2O
H2SO4
HgSO4
H
CH3
C=C
H
OH
enol
O
H
C
CH3
H
H
Dimethyl ketone
Acetone


H–C≡C–H + H2O
H2SO4
HgSO4
H–C=C–H
H
OH
H
H–C–C–H
H
O
Acetylene
Acetaldehyde

4- Friedel-Crafts acylation

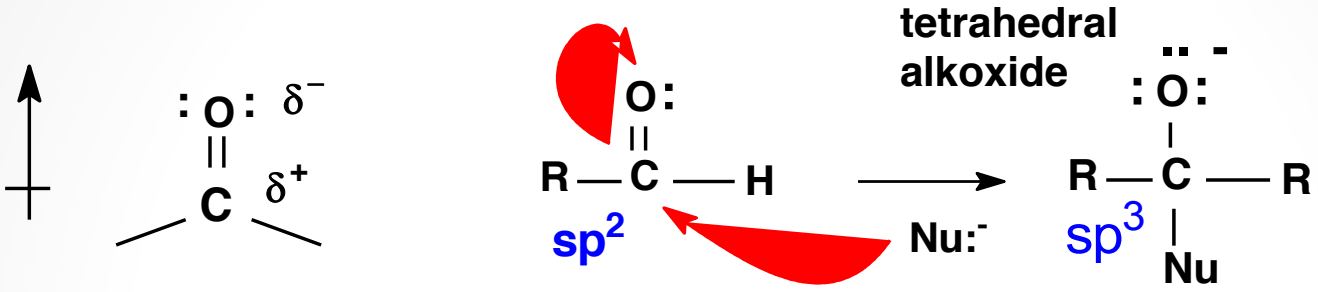
The reaction involves treatment of an aromatic ring with an acylchloride in the presence of $AlCl_3$, which acts as a catalyst.

Example:

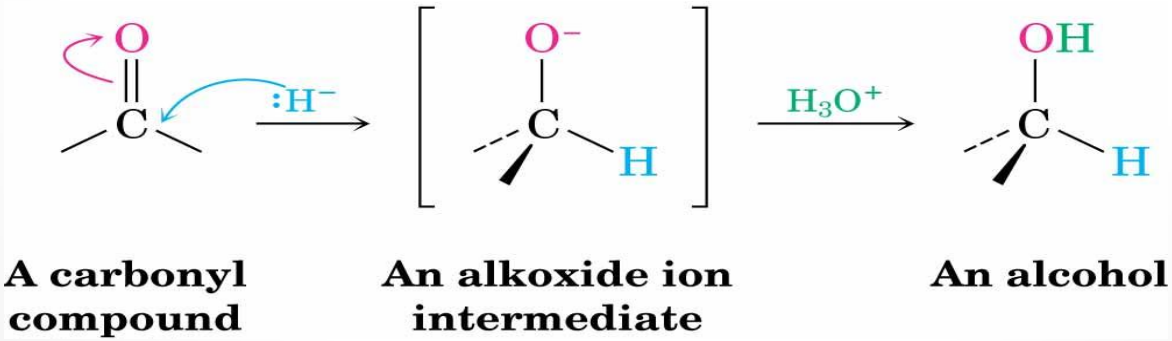


Reactions of Aldehydes and Ketones

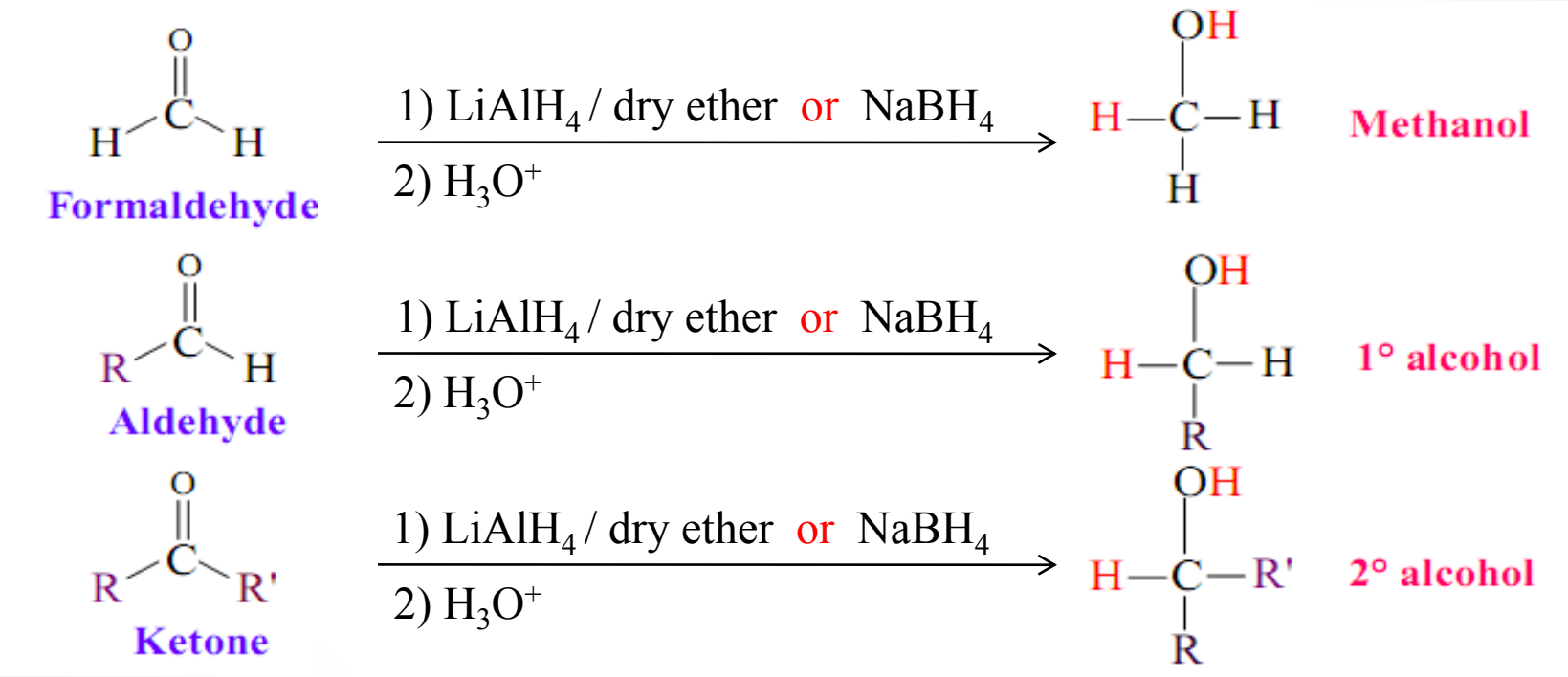
Nucleophilic Addition Reaction to the carbon-oxygen double bond.



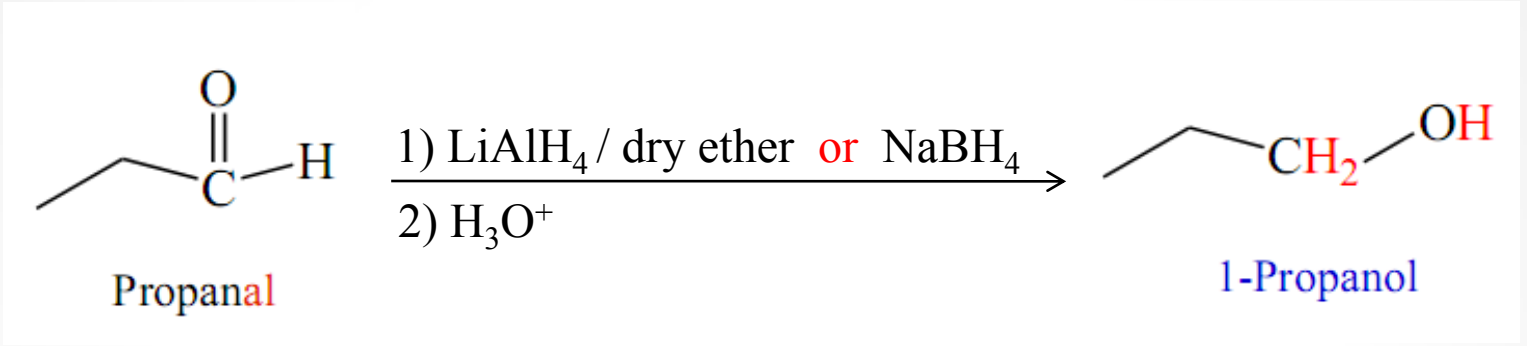
1. Addition of metal hydrides: Formation of alcohols.

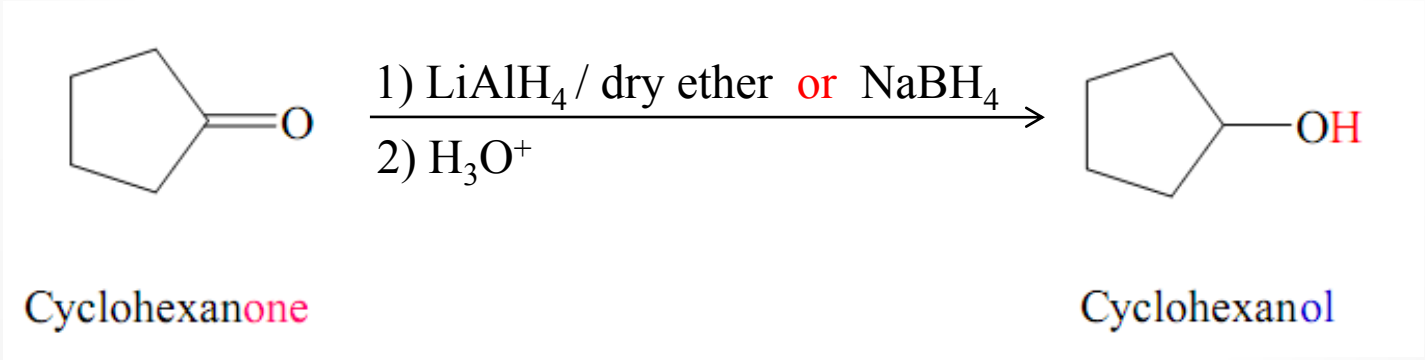


Reduction by hydride reagents, Lithium aluminium hydride $LiAlH_4$ or Sodium boron hydride $NaBH_4$.

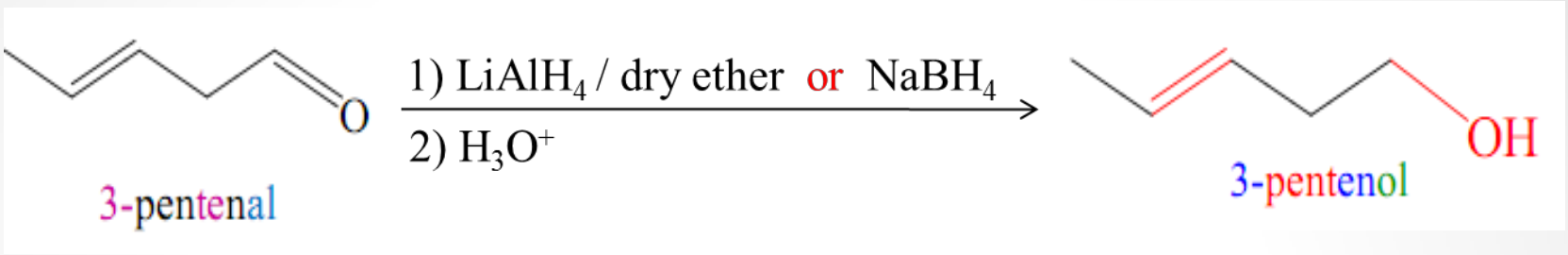


Examples:

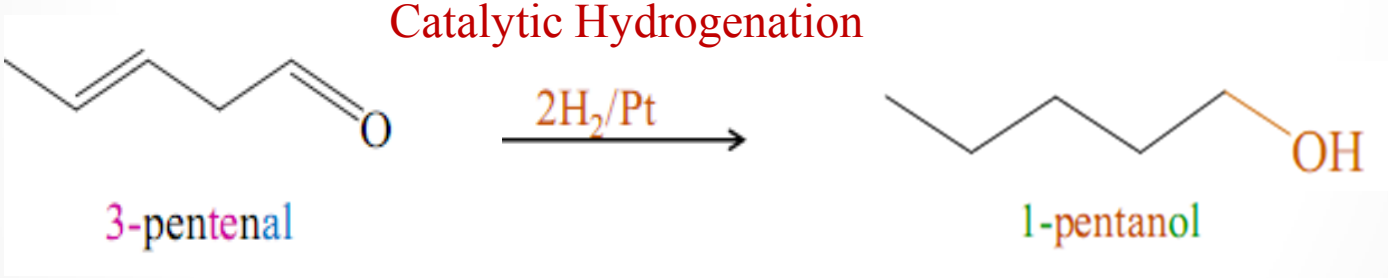

O
C
H
1) LiAlH4 / dry ether or NaBH4
2) H3O+
CH2
OH
Propanal
1-Propanol


O
1) LiAlH4 / dry ether or NaBH4
2) H3O+
OH
Cyclohexanone
Cyclohexanol

Examples:



Catalytic Hydrogenation

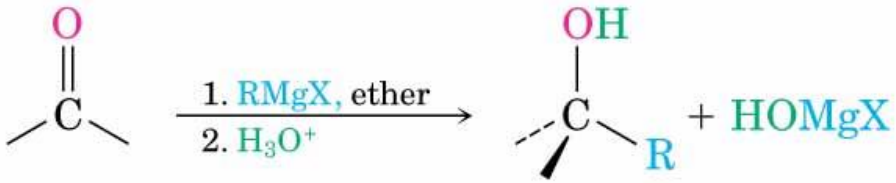


2. Addition of Grignard Reagents : Formation of alcohols.

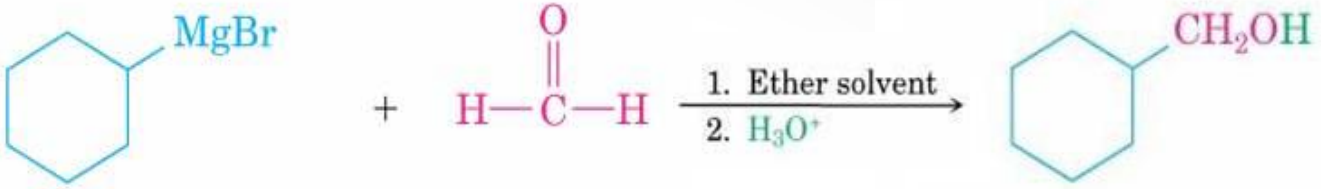
Grignard formation

R = 1°, 2°, or 3° alkyl, aryl, or vinylic
X = Cl, Br, or I

A Grignard reagent

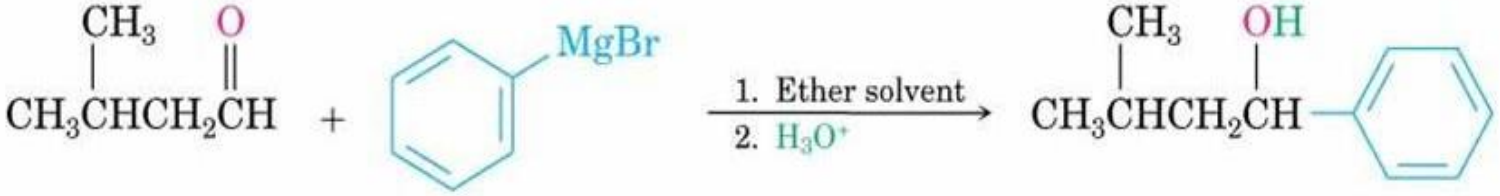


Formaldehyde reaction



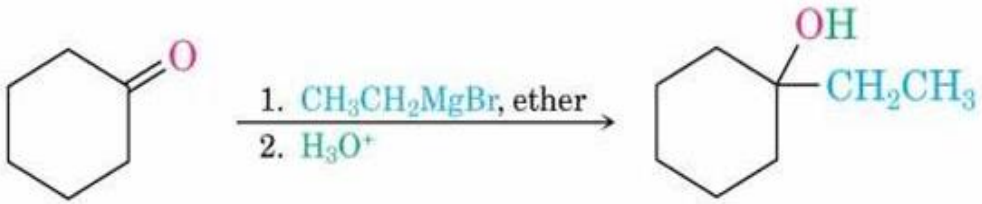
Cyclohexylmagnesium bromide + **Formaldehyde** → **Cyclohexylmethanol (a 1° alcohol)**

Aldehyde reaction



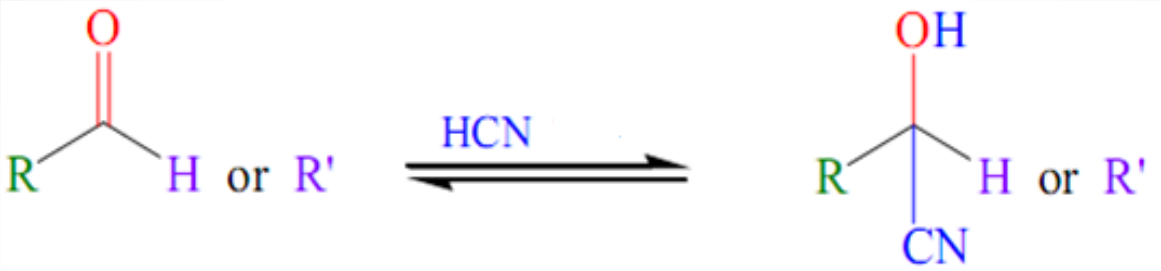
3-Methylbutanal + **Phenylmagnesium bromide** → **3-Methyl-1-phenyl-1-butanol (a 2° alcohol)**

Ketone reaction



Cyclohexanone → **1-Ethylcyclohexanol (a 3° alcohol)**

3. Addition of Hydrogen cyanide: Formation of cyanohydrin.



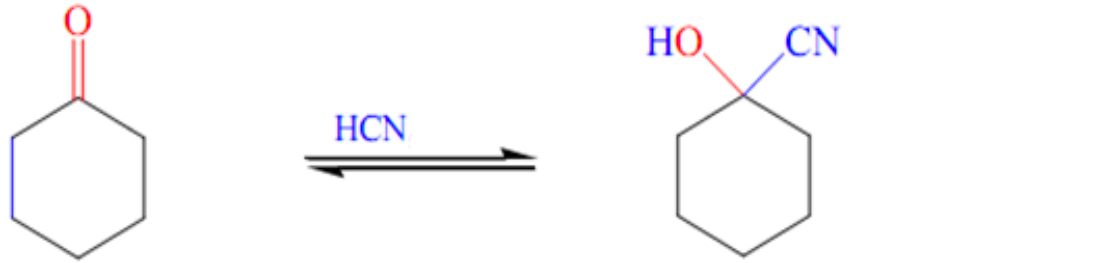
aldehydes or ketones

Cyanohydrin

Examples:

Benzaldehyde

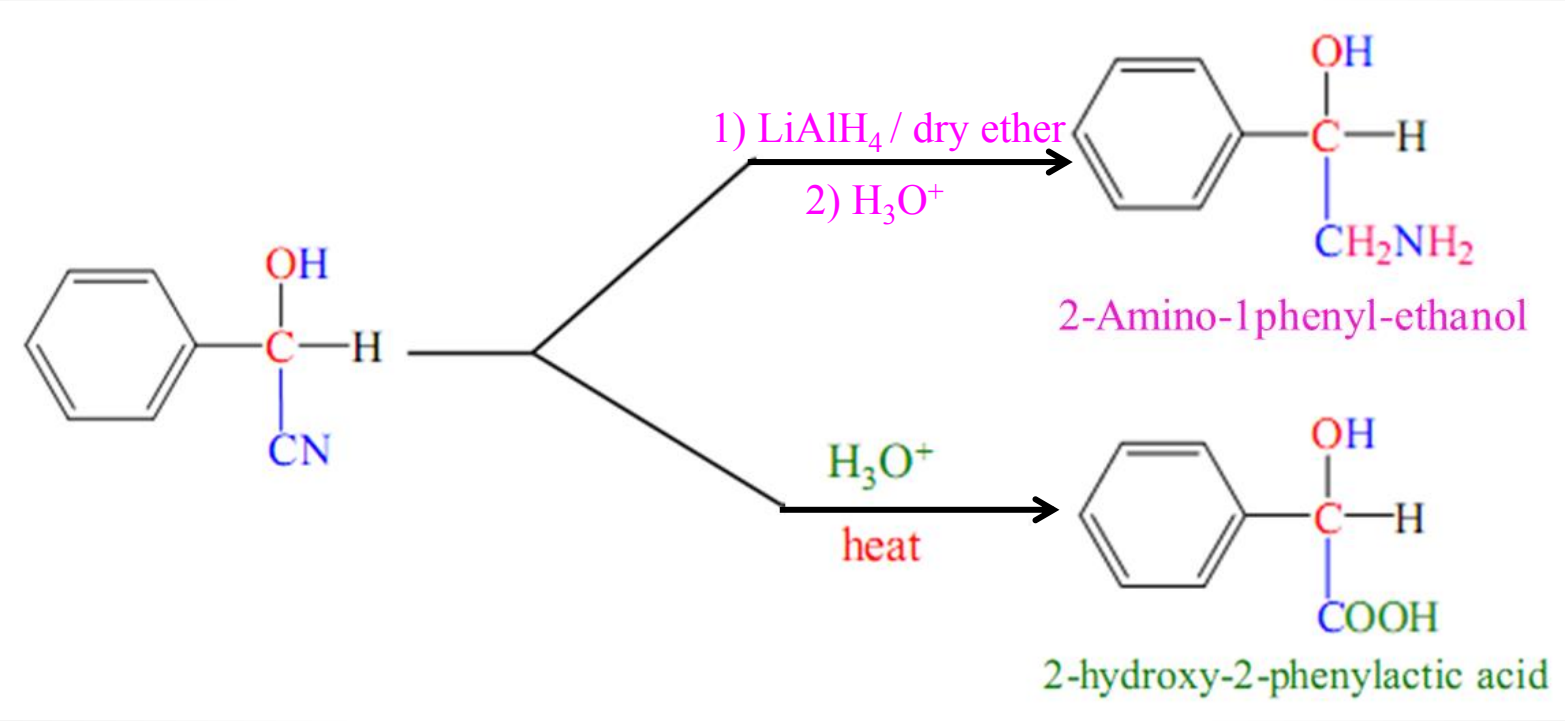
Benzaldehyde cyanohydrin



Cyclohexanone

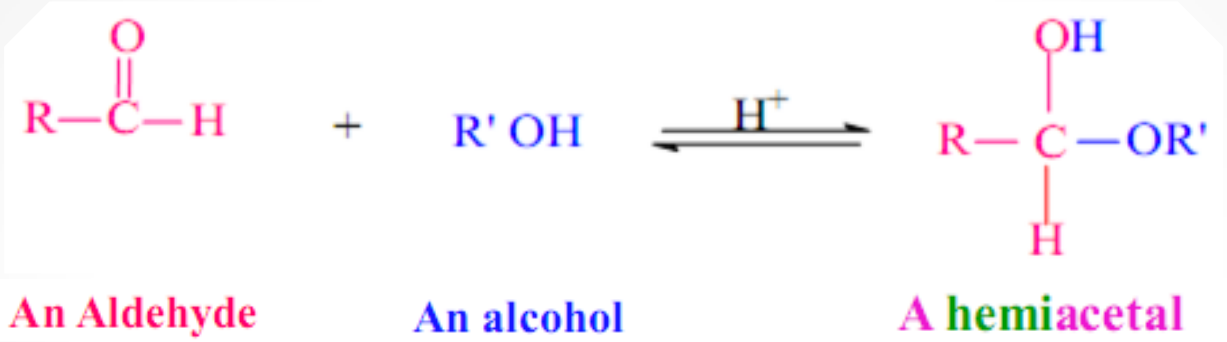
Cyclohexanone cyanohydrin

Cyanohydrins are very useful because the CN group can be converted to other functional groups.

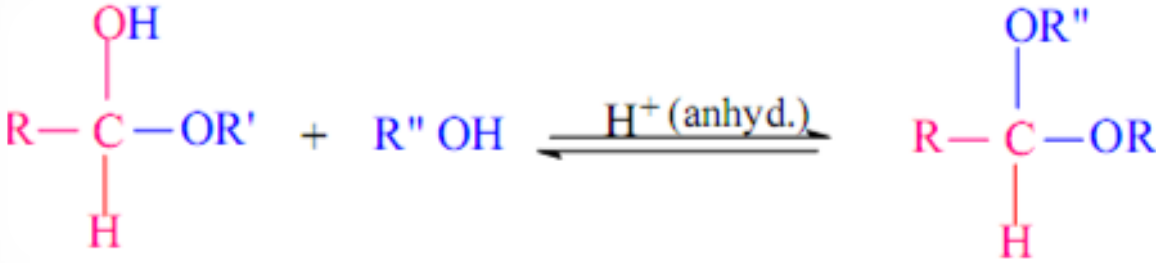


4- Nucleophilic Addition of Alcohols:

A) Formation of Hemiacetals and Acetals

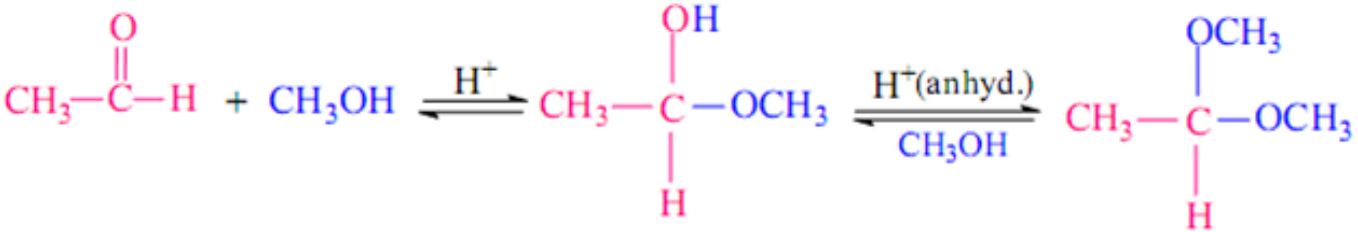


An Aldehyde **An alcohol** **A hemiacetal**



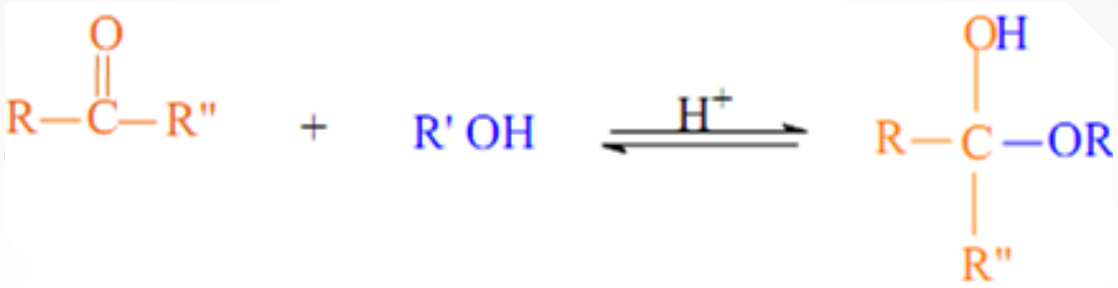
A hemiacetal **An alcohol** **Acetal**

Example:

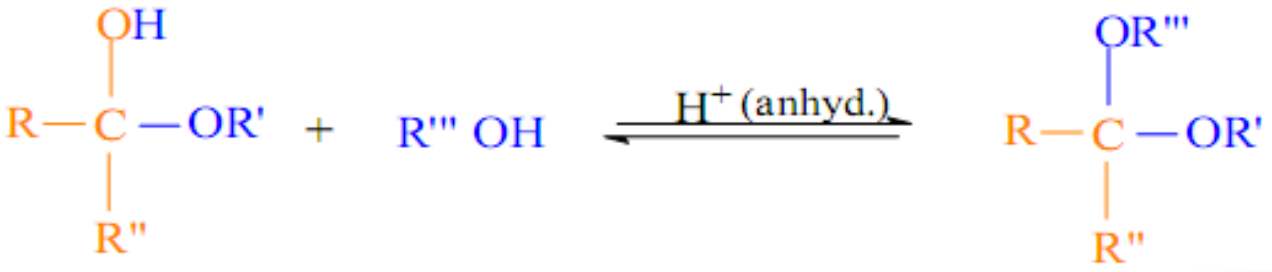


Ethanal **Methanol** **1-Methoxyethanol (A hemiacetal)** **1,1-Dimethoxyethane (An acetal)**

B) Formation of Hemiketals and Ketals

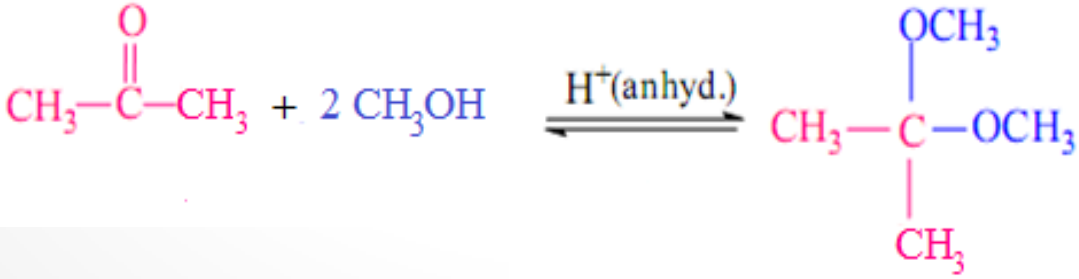


A Ketone **An alcohol** **A hemiketal**



A hemiketal **An alcohol** **ketal**

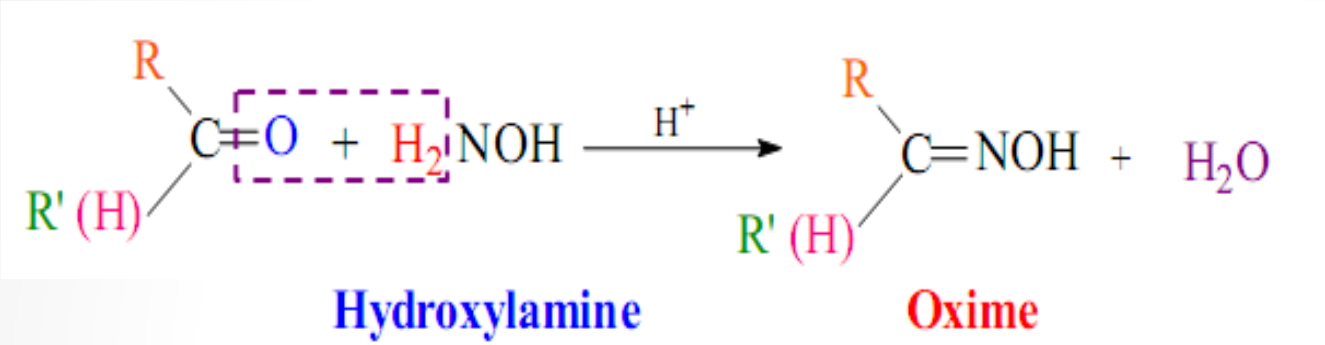
Example:



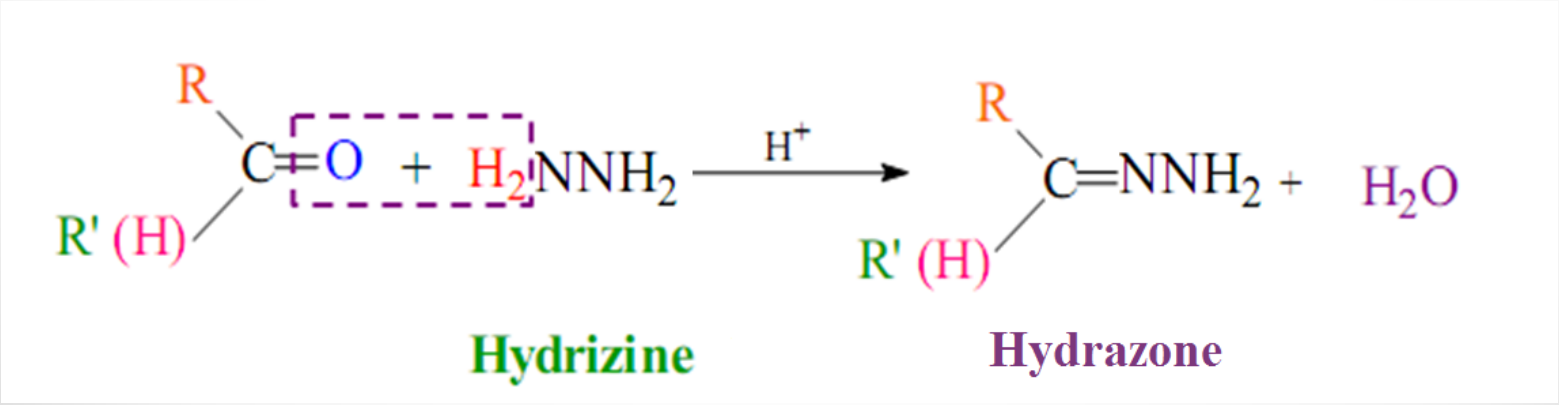
ketal

5- Addition of Ammonia and Ammonia Derivatives

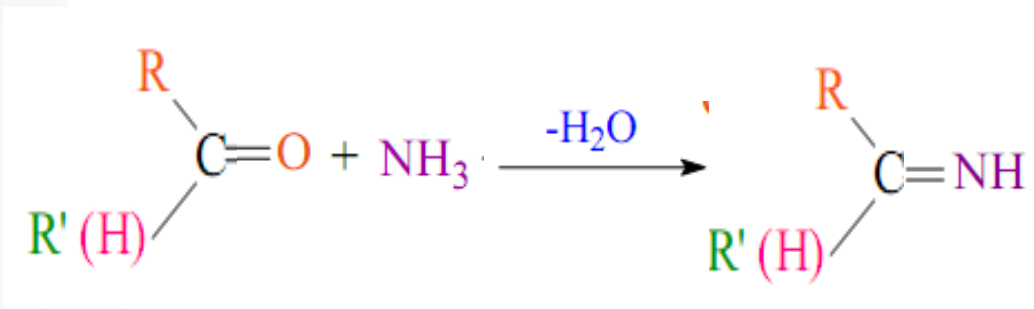
A) The Reaction with Hydroxylamine



B) The Reaction with Hydrazine



C) The Reaction with Ammonia NH_3



Imine

Introduction to Organic Chemistry

Course Number and Symbol:

108 Chem

Credit hours: (3+1)

What is Organic Chemistry?

Organic chemistry is defined as the study of carbons/ hydrogen containing compounds and their derivatives (containing other elements such as O, X and N).

Importance of Organic Compounds

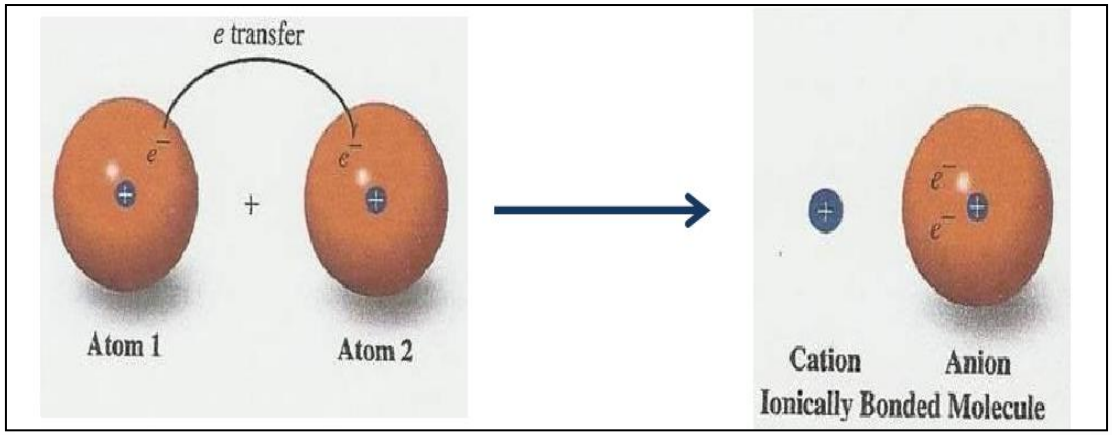
- The chemical substances that make up our bodies; are organic.
    1. DNA: the giant molecules that contain all the genetic information for a given species.
    2. proteins: blood, muscle, and skin.
    3. Enzymes: catalyze the reactions that occur in our bodies.
- Petroleum: furnish the energy that sustains life.
- Polymers: Cloths, cars, plastic, kitchen appliances.
- Medicine.

Chemical Bonds

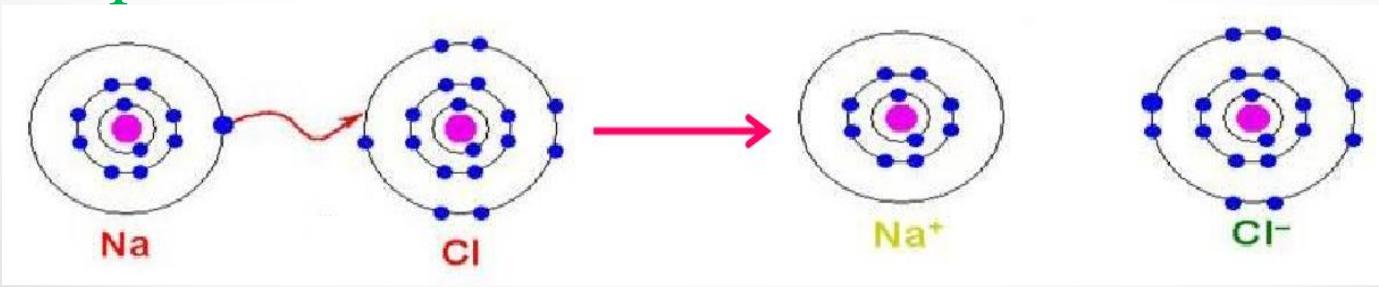
✓ When two atoms with large different electronegativity values:

1) Ionic Bonding

- **Ionic bonds form** from the electrostatic attraction between oppositely charged ions.
- Atoms **become ionic** by **losing** or **gaining** electrons from the atom it is bonding with.



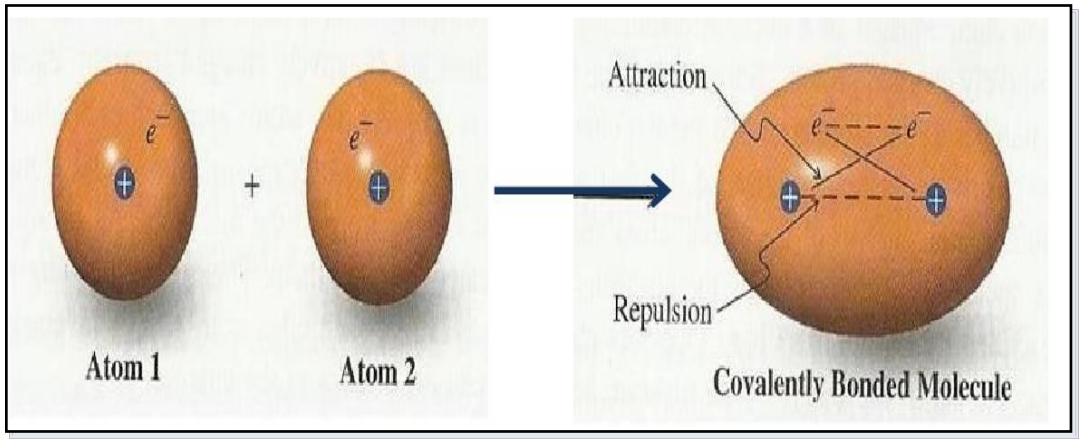
Example: NaCl



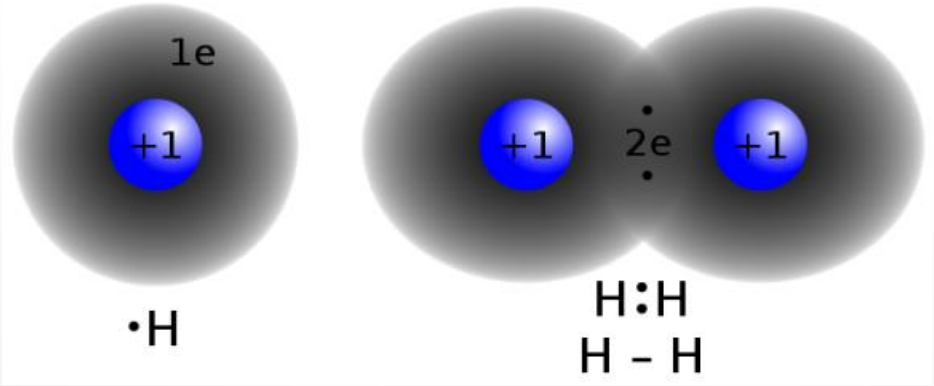
✓ When two atoms with similar electronegativity values:

1) Covalent Bonding

A **covalent bond** is a form of chemical bonding that is characterized by the sharing of pairs of electrons between atoms



Example: H_2

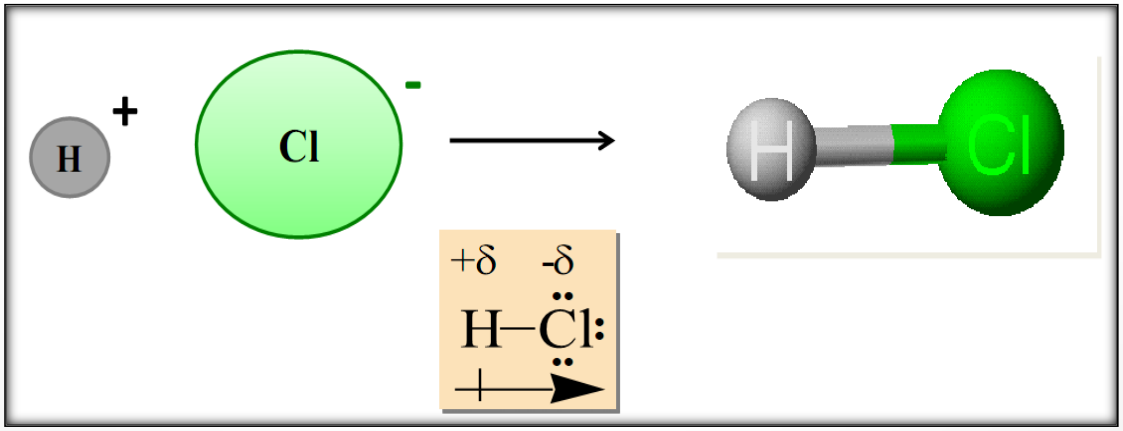


✓ When two atoms with different electronegativity values:

1) Polar Covalent Bonding

- A polar covalent bond is one in which one atom has a **greater attraction** for the electrons than the other atom.
- The electron cloud in a σ-bond between two unlike atoms is not uniform and is slightly **displaced towards** the more electronegative of the two atoms.

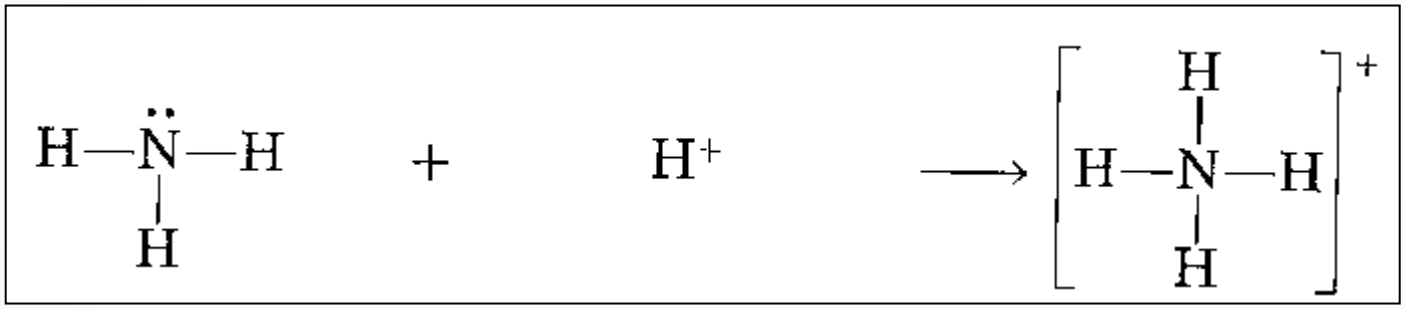
Example: HCl



2) Coordinate Covalent Bonding

There are molecules in which one atom supplies **both** electrons to another atom in the formation of covalent bond.

Example: Ammonium ion NH_4^+



How Many Bonds to an Atoms?

Covalence Numbers of Typical Elements in Organic Compounds

Element	Number of Valence electrons	Number of electrons in filled valence shell	Covalent number
H	1	2	1
C	4	8	4
N	5	8	3
O	6	8	2
F, Cl, Br, I (halogens)	7	8	1

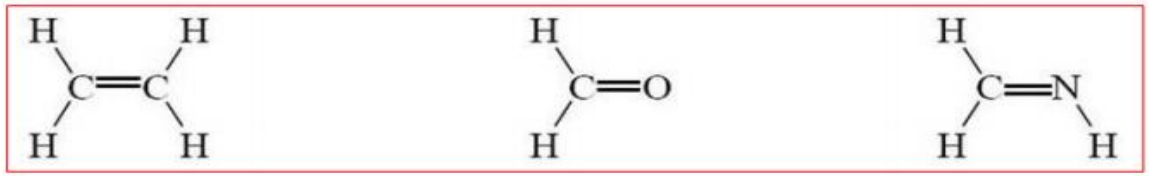
The Uniqueness of Carbon:

$$C_{6}^{12}$$

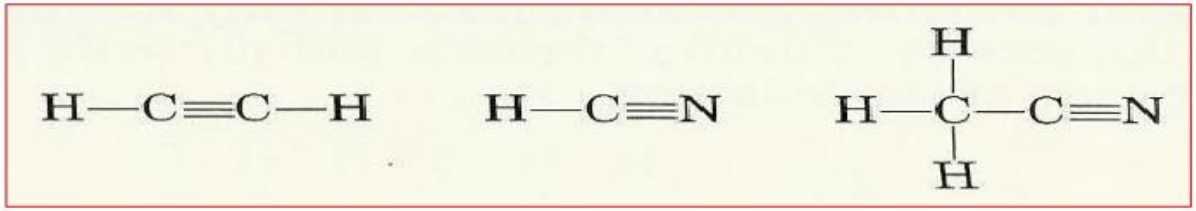
- Carbon is unique among the elements for its ability to bond with itself to form compounds of various sizes and shapes as well as to bond with many other elements

- Carbon atom can form multiple bonds, long chains, side chains and cyclic chains.

Examples:

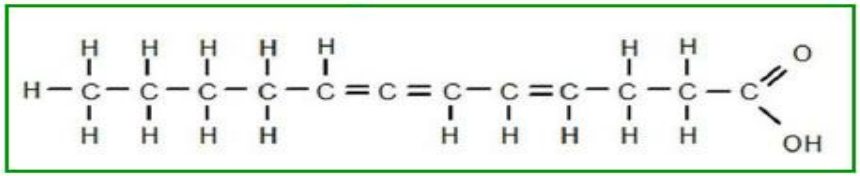


Ethylene Formaldehyde Formaldimine

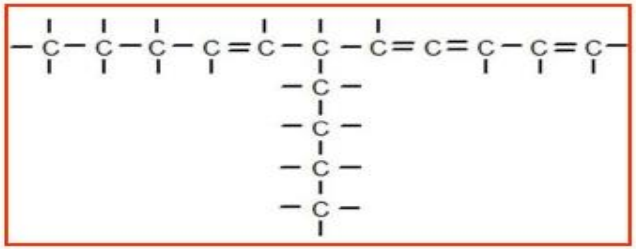


Acetylene Hydrogen cyanide Acetonitrile

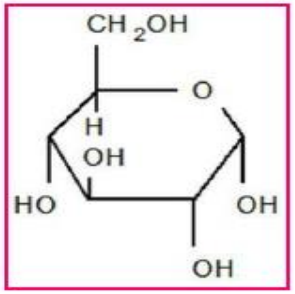
2-long chains



3-side chains



4-cyclic chains



Formula and Diagrams:

1- Molecular Formula

Examples:

The molecular formula of alkyne

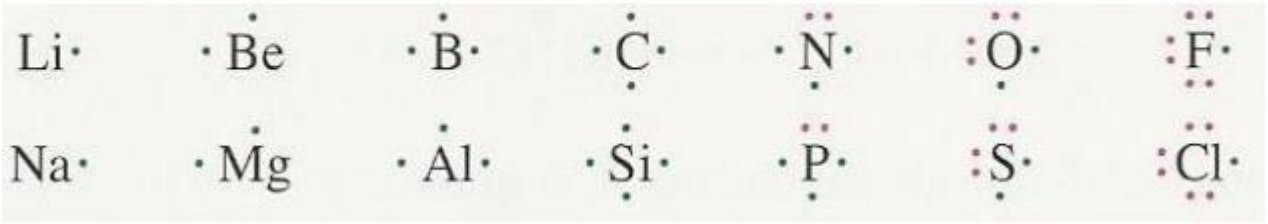
$$C_nH_{2n-2}$$

The molecular formula of carboxylic acids

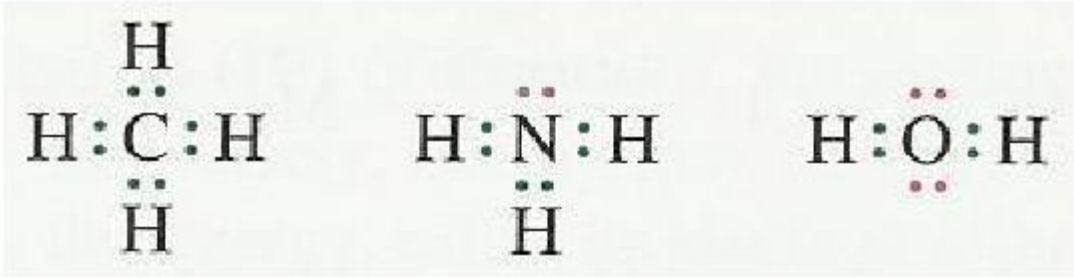
$$C_nH_{2n}O_2$$

2- Electron Dot Diagrams (Lewis structure)

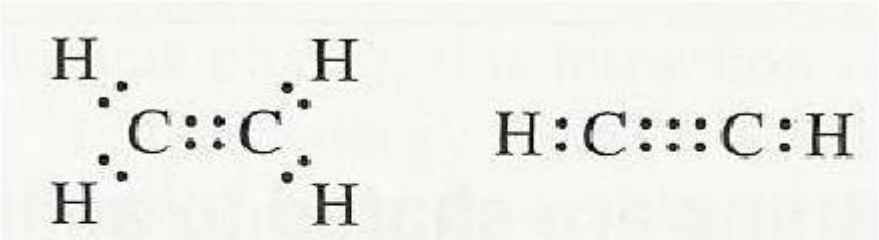
Electron valance as electron dots



Examples



Methane Ammonia Water



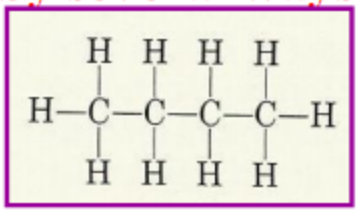
Ethene (Ethylene) Ethyne (Acetylene)

3- Structural Formula

The structure formula can be expressed by several ways

Structural Formula

- **Expanded structural formula**



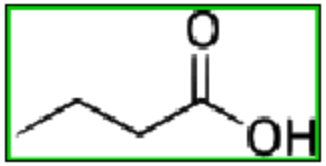
- **condensed formula**
  - **Partially**

$CH_3—CH_2—CH_2—CH_3$

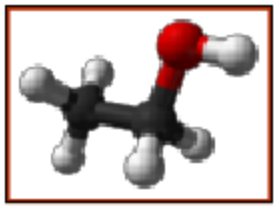
  - **Fully**

$CH_3CH_2CH_2CH_3$ *or* $CH_3(CH_2)_2CH_3$

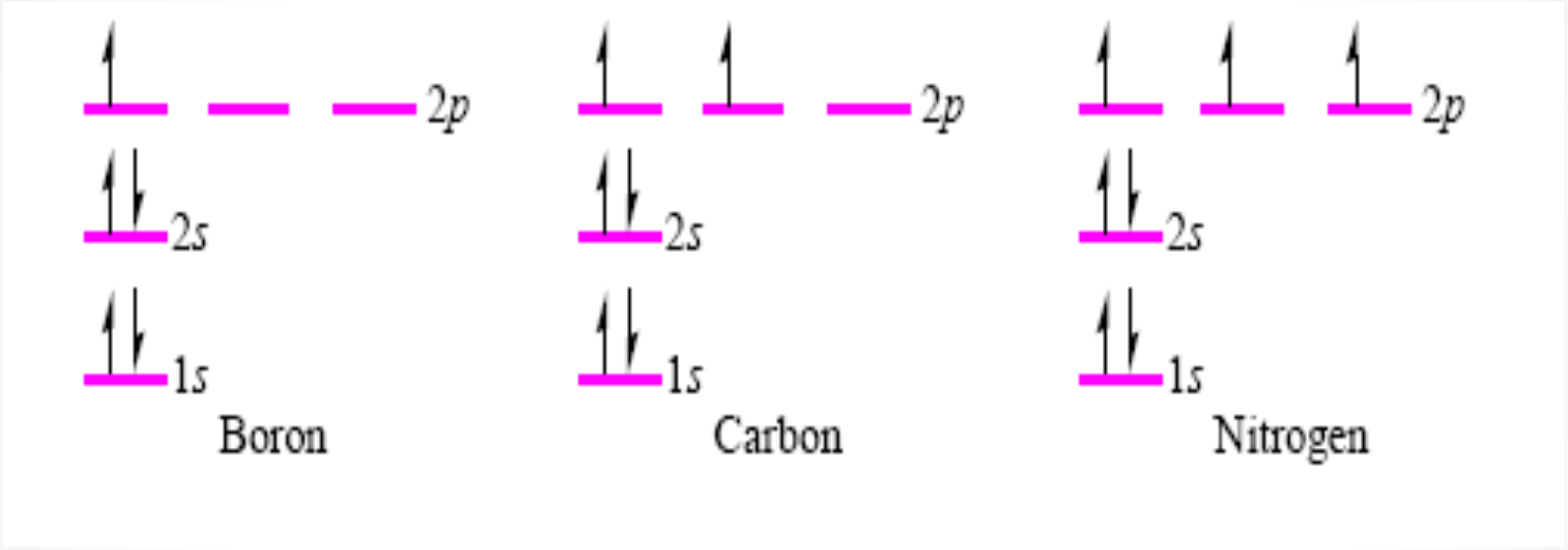
- **Bond line formula (skeltel formula)**



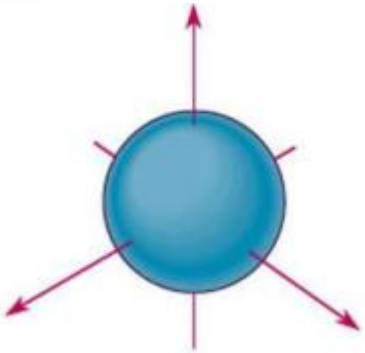
- **Ball-stick model**



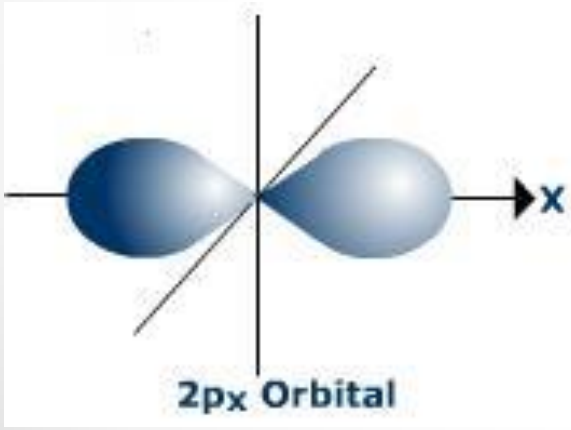
Atomic Orbitals and their Shapes

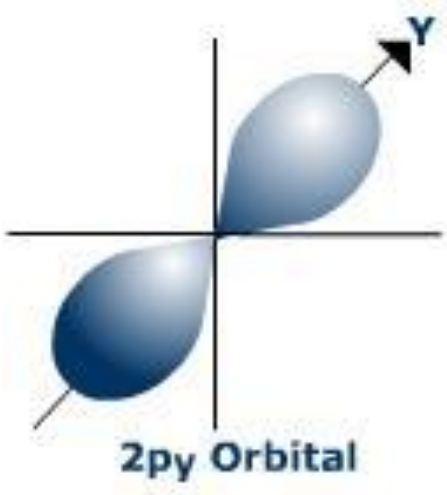


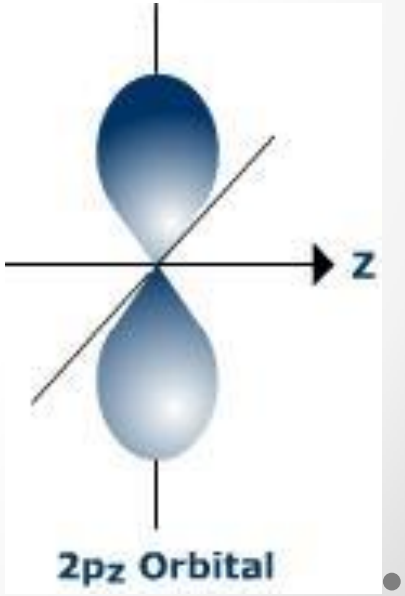
S-Orbital



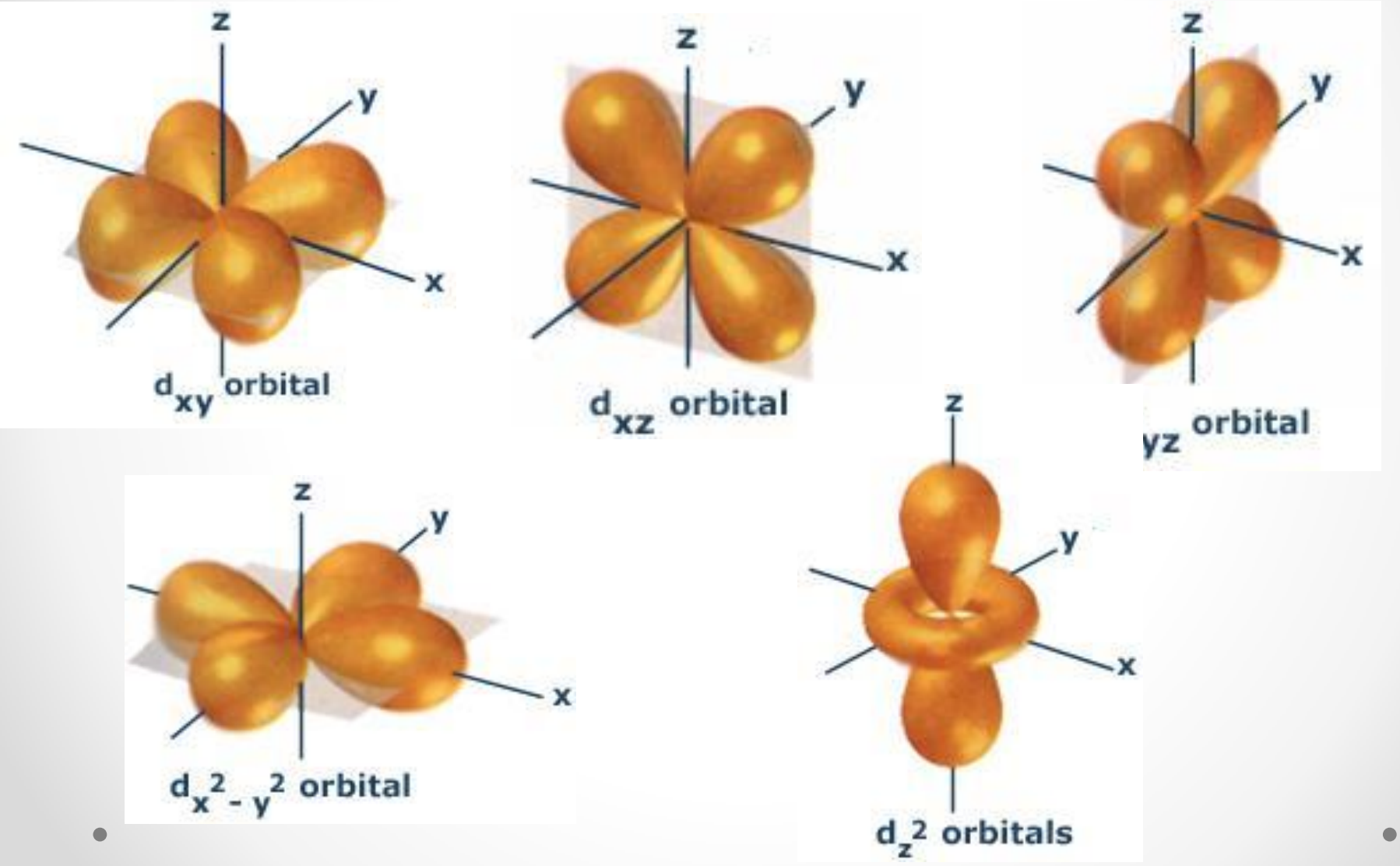
P-Orbital







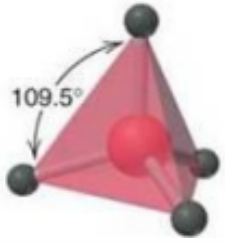
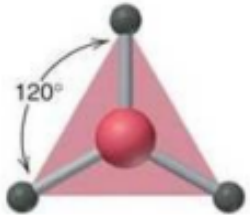
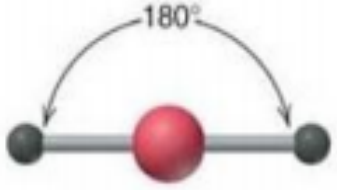
d-Orbital


z
y
x
d_{xy} orbital
z
y
x
d_{xz} orbital
z
y
x
yz orbital
z
y
x
$d_{x^2-y^2}$ orbital
z
y
x
d_{z^2} orbitals

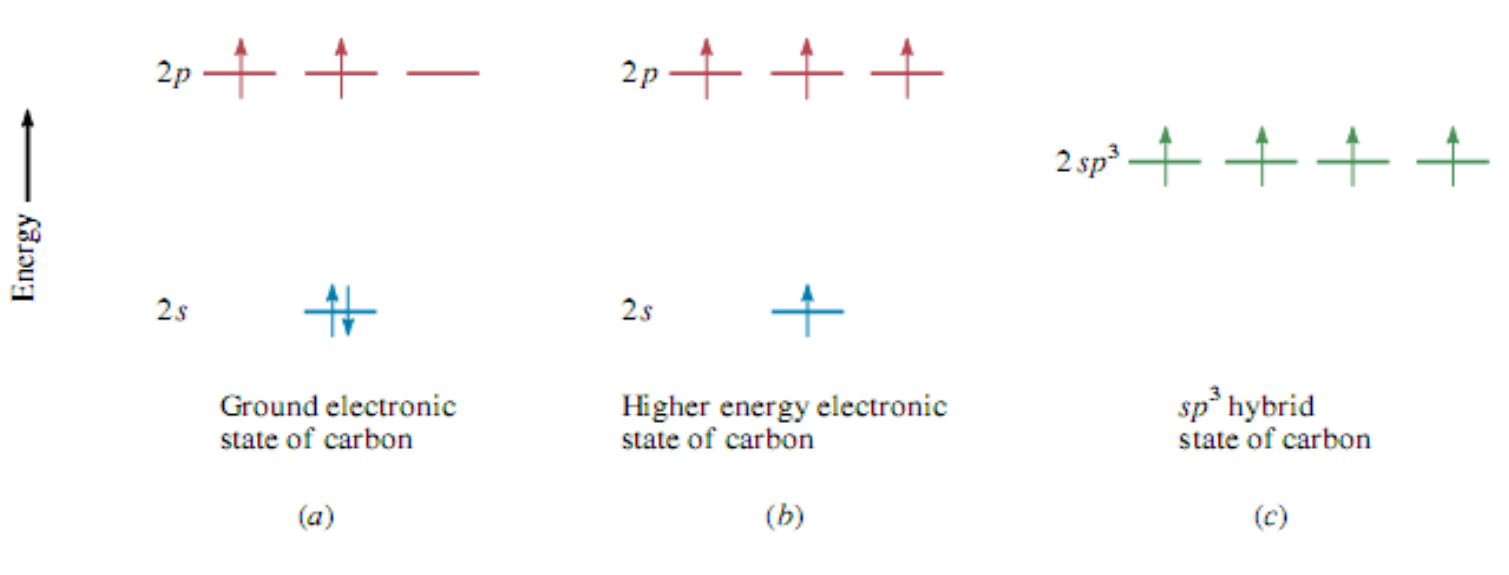
Molecular Orbital

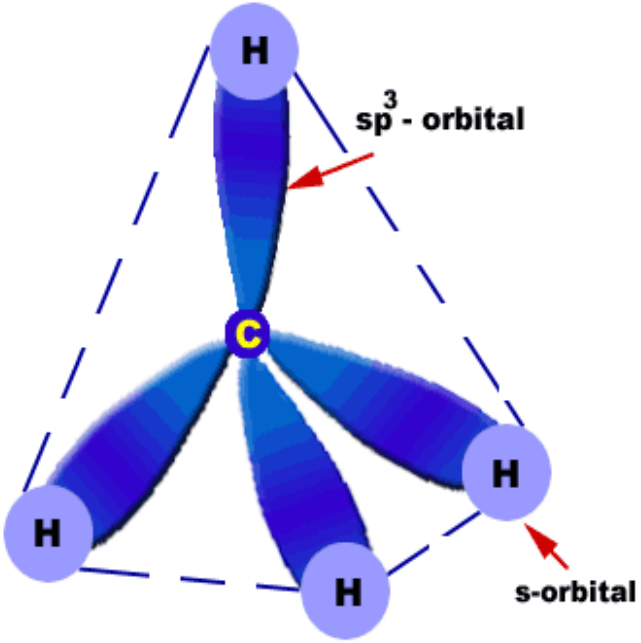
A molecular orbital is formed when two atomic orbitals overlap to generate a bond.

Types of Hybridization

sp^3	Tetrahedral	
sp^2	Trigonal Planar	
sp	Linear	

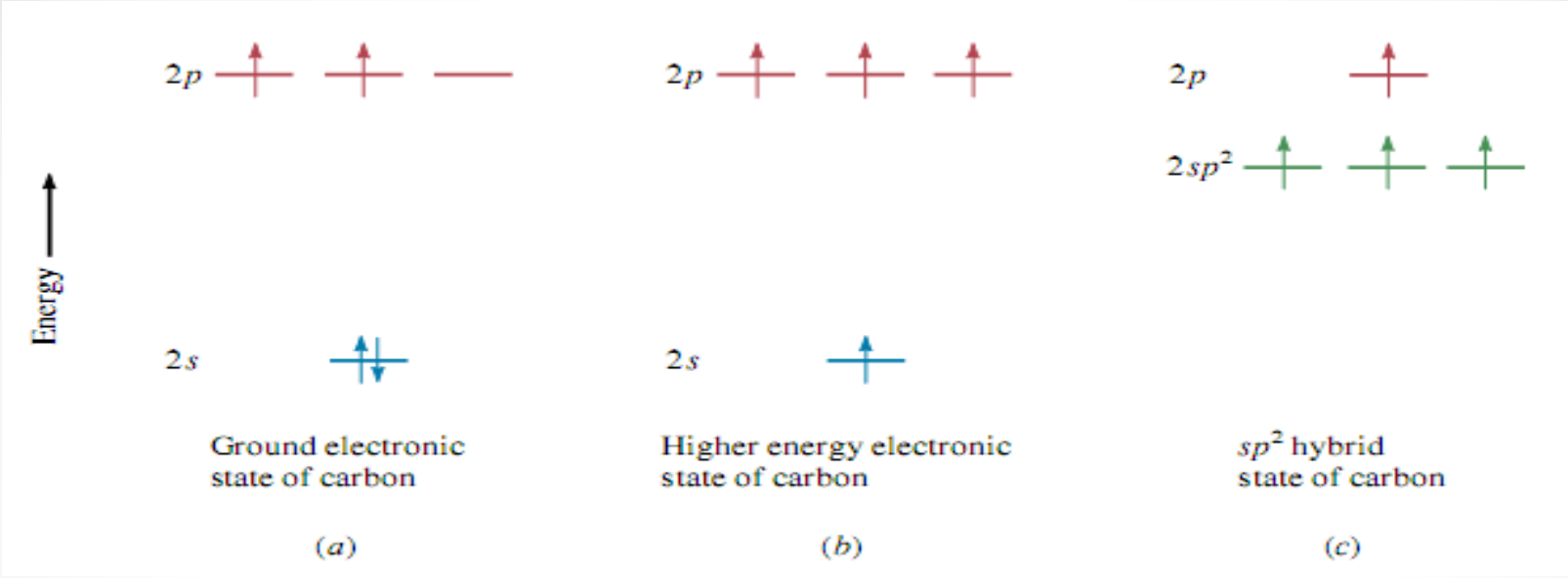
sp^3 hybridization in Methane

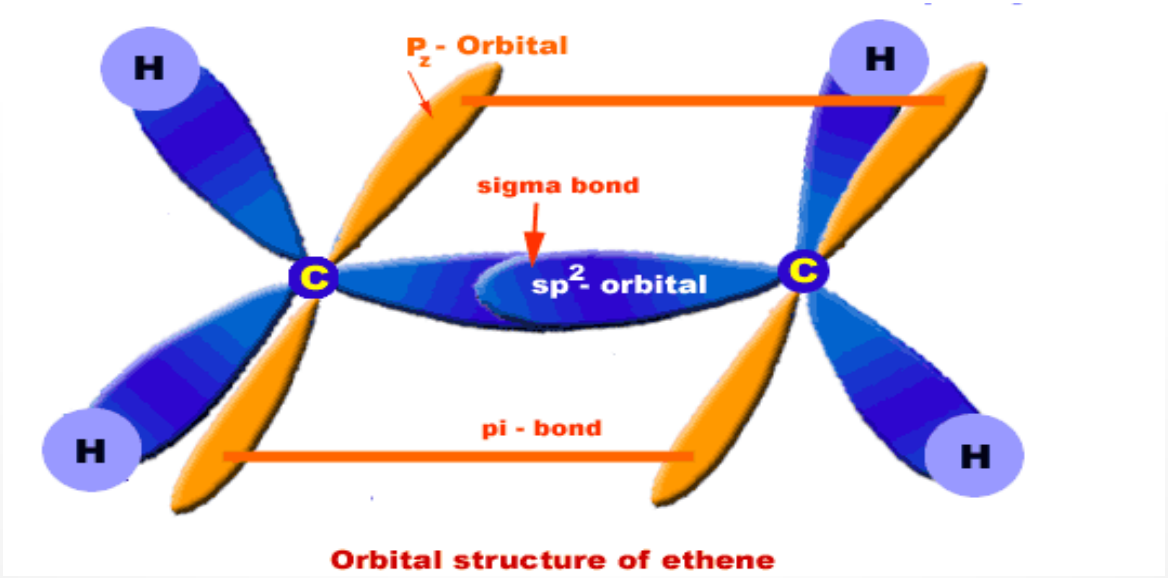




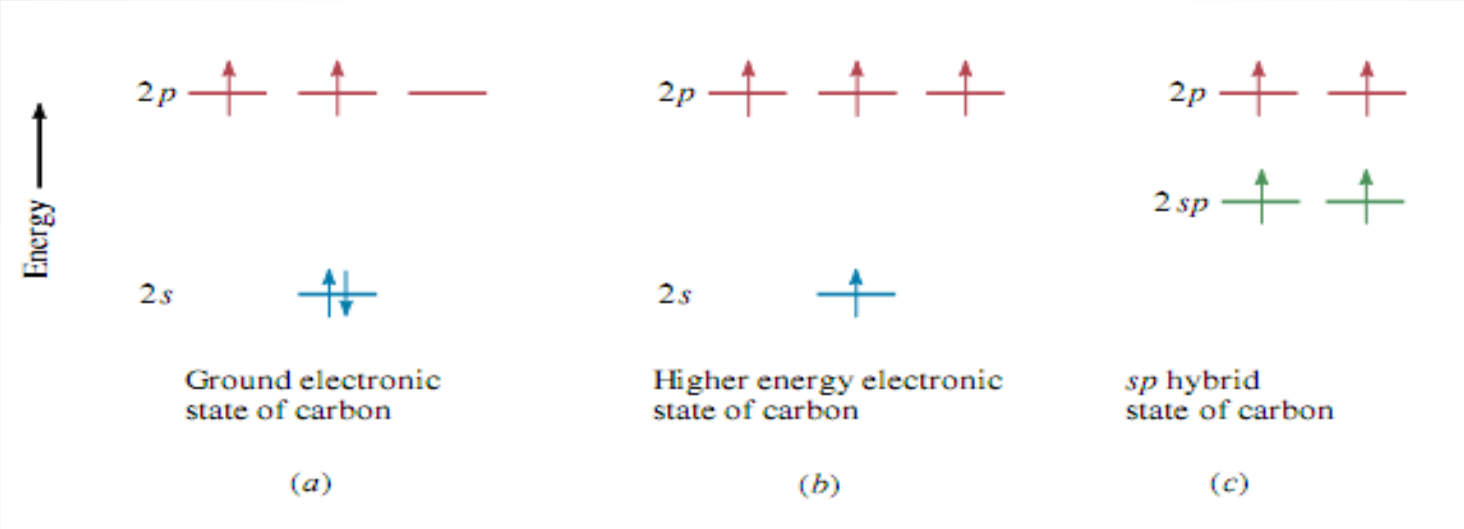
Orbital structure of methane

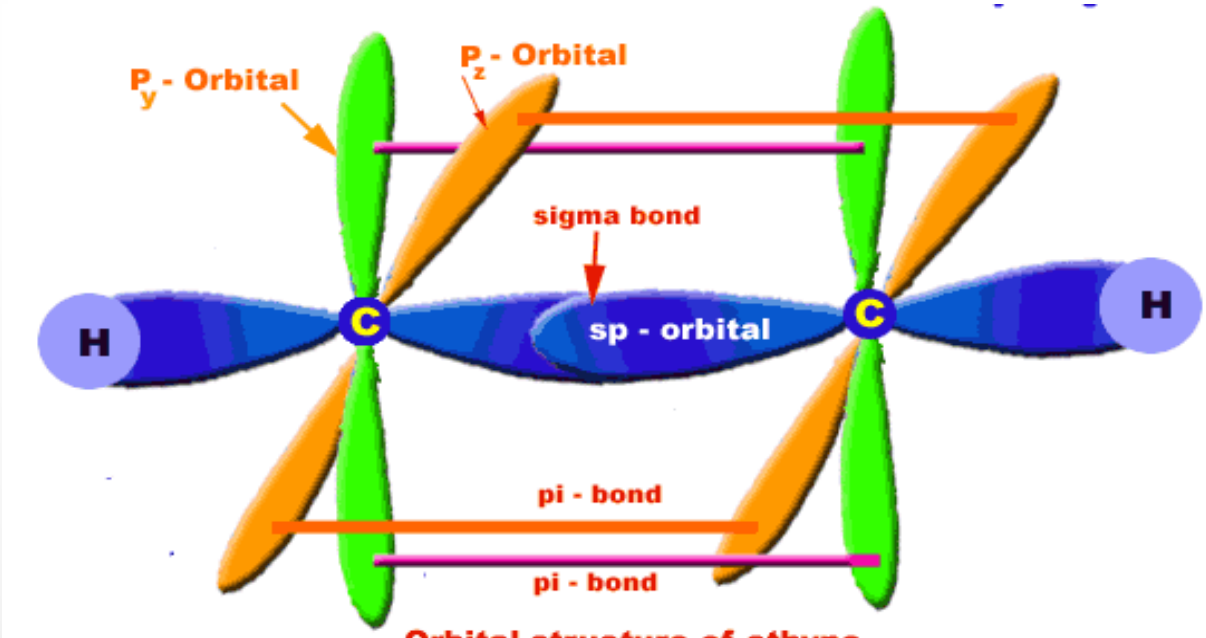
sp^2 hybridization in Ethene



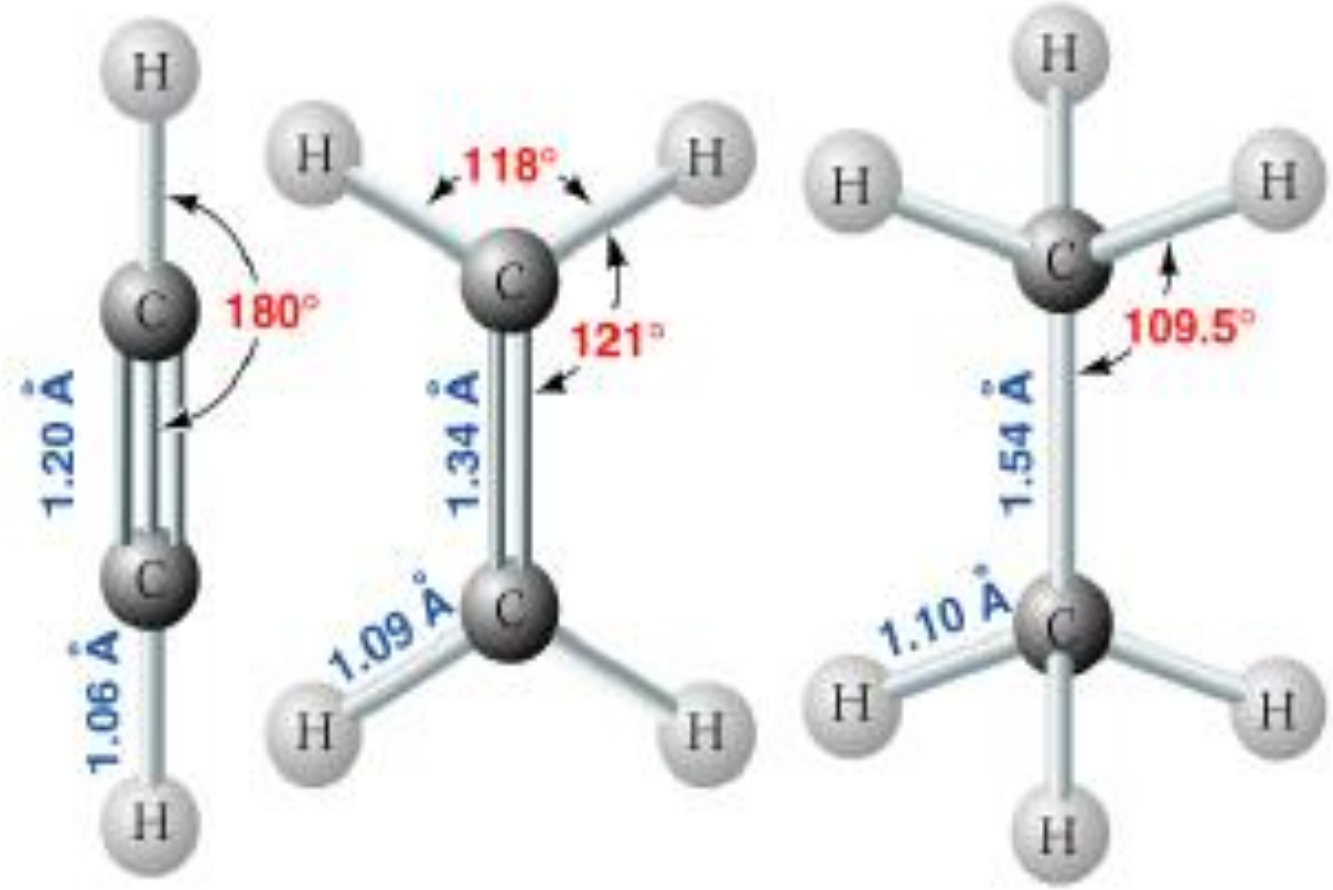


sp hybridization in Ethyne





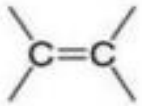
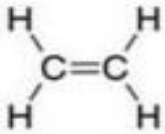
Bond lengths of Ethyne, Ethene, and Ethane



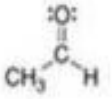
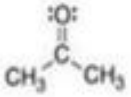
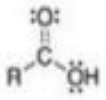
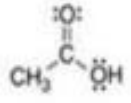
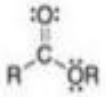
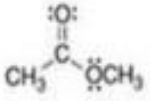
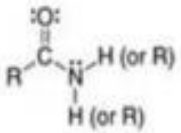
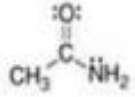
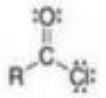
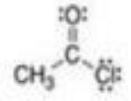
Functional Groups

Functional groups – special groups of reactive atoms that carry out chemical reactions in many organic compounds.

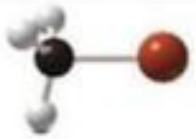
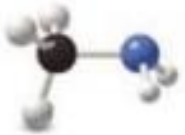
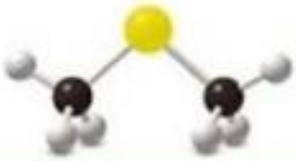
Hydrocarbons

Type of compound	General structure	Example	Functional group
Alkane	R—H	CH_3CH_3	– –
Alkene			double bond
Alkyne	—C≡C—	H—C≡C—H	triple bond
Aromatic compound			phenyl group

Compounds containing C=O

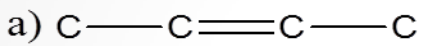
Type of compound	General structure	Example	3-D structure	Functional group
Aldehyde				C=O carbonyl group
Ketone				C=O carbonyl group
Carboxylic acid				−COOH carboxy group
Ester				−COOR
Amide				$-CONH_2$, −CONHR, or $-CONR_2$
Acid chloride				−COCl

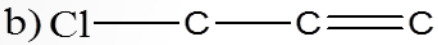
Compounds containing C-Z σ bonds

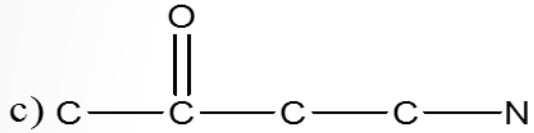
Type of compound	General structure	Example	3-D structure	Functional group
Alkyl halide	R–X: (X = F, Cl, Br, I)	CH_3–Br:		–X halo group
Alcohol	R–OH	CH_3–OH		–OH hydroxy group
Ether	R–O–R	CH_3–O–CH_3		–OR alkoxy group
Amine	R–NH_2 or R_2NH or R_3N	CH_3–NH_2		–NH_2 amino group
Thiol	R–SH	CH_3–SH		–SH mercapto group
Sulfide	R–S–R	CH_3–S–CH_3		–SR alkylthio group

Homework – 1

1- Given the skeletal structure, and assuming that only hydrogen atoms are missing, draw the correct expanded structural formula, condensed structural, and molecular formula for each of the following.

a) 

b) 

c) 

2- Draw the structural formula for the following:

C_2H_6 C_2H_4 C_2H_2 C_6H_6

3- a) One alcohol and one ether correspond to C_2H_6O. Draw their structures.
b) One carboxylic acid and one ester correspond to $C_2H_4O_2$. Draw their structures.
c) One aldehyde and one ketone correspond to C_3H_6O. Draw their structures.