South Valley University

Faculty of Education

Chemistry Department

Organic Chemistry

1st year students – Faculty of Education

Science group

Second Term 2022/2023

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9- **Chemistry of alcohols.**
10- **Chemistry of aldehydes and ketones.**
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What is pencil lead made of if it isn't lead?

Pencil lead is a mixture of graphite and clay.
Graphite is one form of the element carbon.
Other forms of carbon are diamond - the hardest naturally occurring substance on the earth, soot, charcoal and coke.

Pencils used to be made with lead, many years ago. Lead is poisonous and so sucking the end of your pencil could be quite dangerous.
We now use graphite and clay because it is safer and because we can make pencils of different hardness.

Chemistry of Living Things:

Living things are a lot like laboratories…
There's some serious chemistry going on inside.
Your body is an incredibly complex chemical machine taking in chemicals & food, and causing countless reactions to occur every second.

Biochemistry is the study of substances & processes occurring in all living organisms.

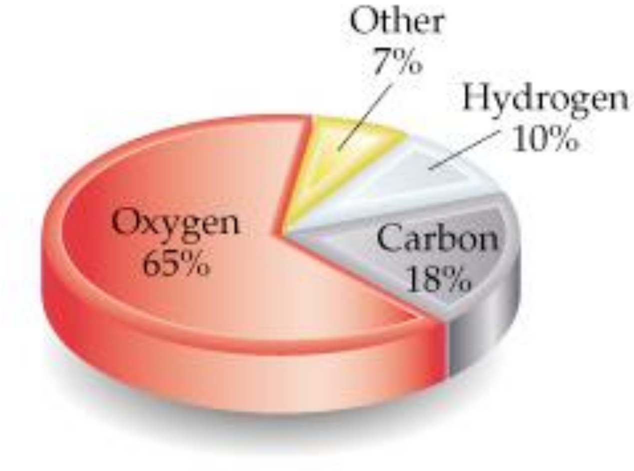
I'm made of what???

Guess how many elements your body is made up of?

25 elements make up all living things

About 97% of your body's mass is made of just 4 elements: oxygen, carbon, hydrogen, & nitrogen.

Two other major elements are phosphorous & sulfur.



Human body

Minor Elements:

Of course, other elements are also important, but they're often found in small amounts.

They may seem insignificant, but they're not.

For example, iron makes up only 0.004% of your body mass, but you can't live without it!

Major Compounds:

The human body also relies on many compounds, especially water & salt.

The human body typically consists of 60-65% water.

In other words, 2/3 of your body weight is water.

Water is important because many of our body's chemical reactions can only occur in solutions containing water.

Blood, sweat, urine… all mostly water!

Salt is also important because of how it can separate into its two ions: Na^+ and Cl^-.

Sodium ions regular the amount of water in our cells, while chlorine ions help our body digest food.

The most important element is…

Carbon

If you take away the water, the rest of the human body is 53% carbon.

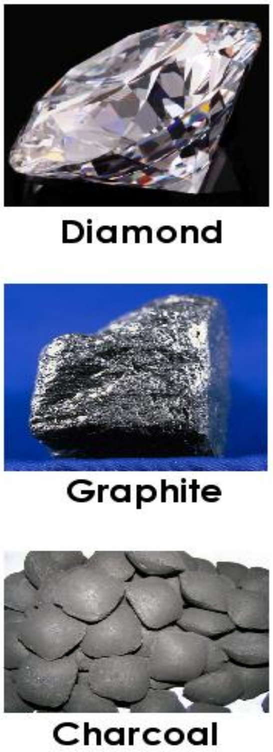
It may not be the most abundant element in living things, but it certainly is the most important. At one time, scientists thought that the chemical reactions that took place inside of living things could not occur outside of them.

The carbon molecules were so complex, scientists thought they must have been made in some unknown way. They called these carbon compounds organic compounds.

The word “organic” has lots of meanings. Eventually, scientists realized that the reactions occurring inside the body could occur outside it as well.

They also learned how important carbon is in all living things, because of its ability to <u>bond</u> with other atoms.

Forms of Carbon



Diamond

Graphite

Charcoal

Not all substances made of carbon are living. Diamonds & graphite are pure forms of carbon.

Non-organic carbon compounds, and compounds without carbon, are called <u>inorganic</u> compounds.

What is organic chemistry?

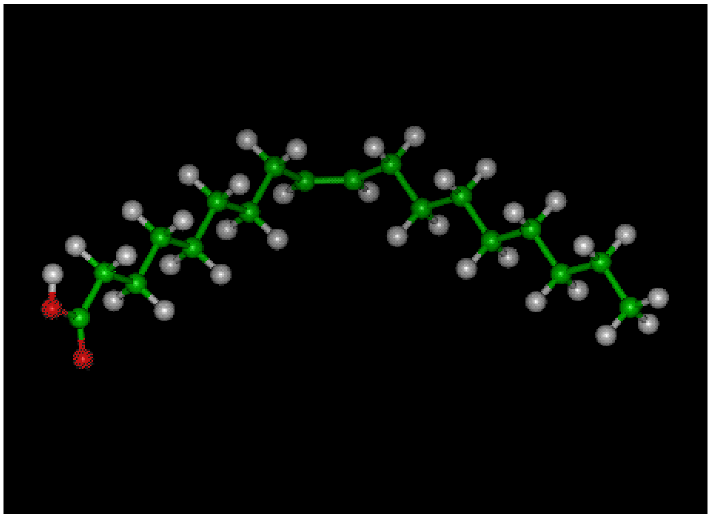
We used to describe organic chemistry as the chemistry of living things. Since the chemistry of living things is based on carbon, the chemistry of carbon compounds has come to be known as organic chemistry.

It now includes the study of carbon compounds which are not found in living things and so is an incredibly large branch of modern chemistry.

Why is life based on the element carbon?

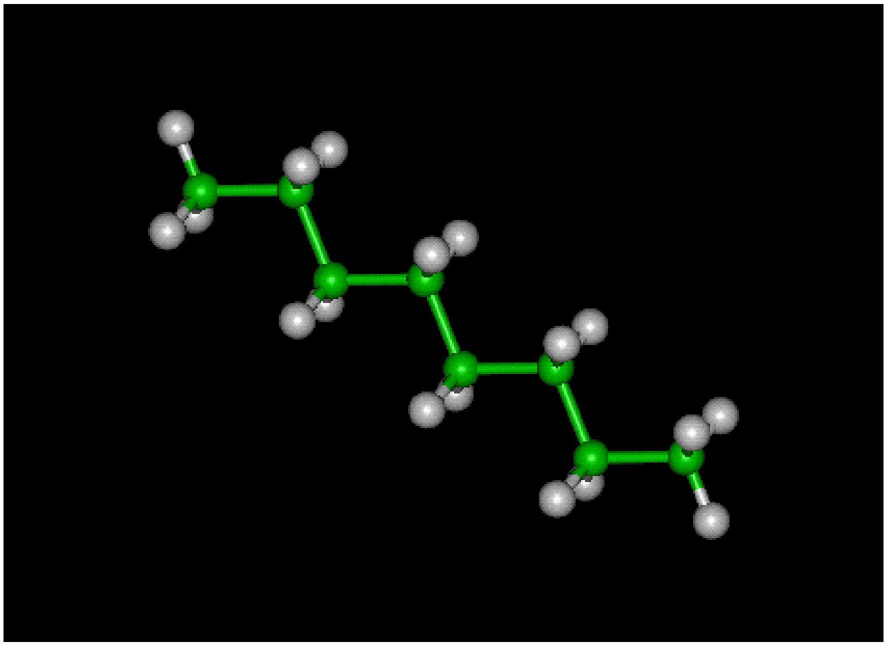
There are two important properties of carbon that make it a suitable element to form the compounds in living things:

Firstly, carbon atoms can link together to form stable chains of great length.



Carbon atoms bind strongly to each other and form very large molecules which are built around this carbon 'backbone'.

The covalent bond between two carbon atoms is strong so that the backbones are stable. In all of these compounds simple sub-units called monomers are linked together by condensation reactions.



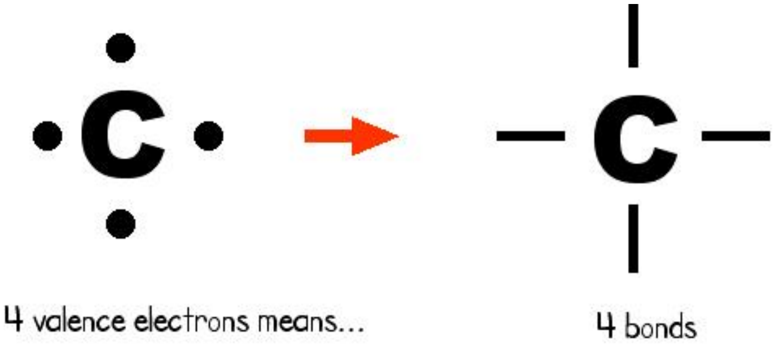
What makes carbon so special?

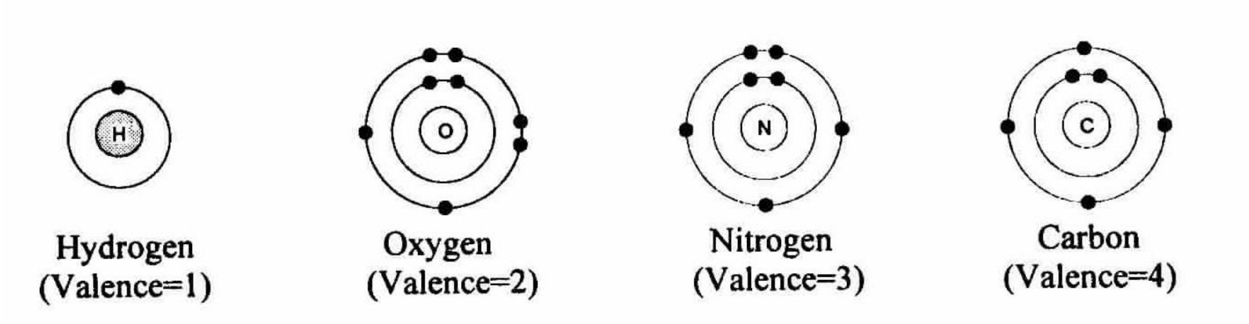
It has a "central" role in all living organisms.

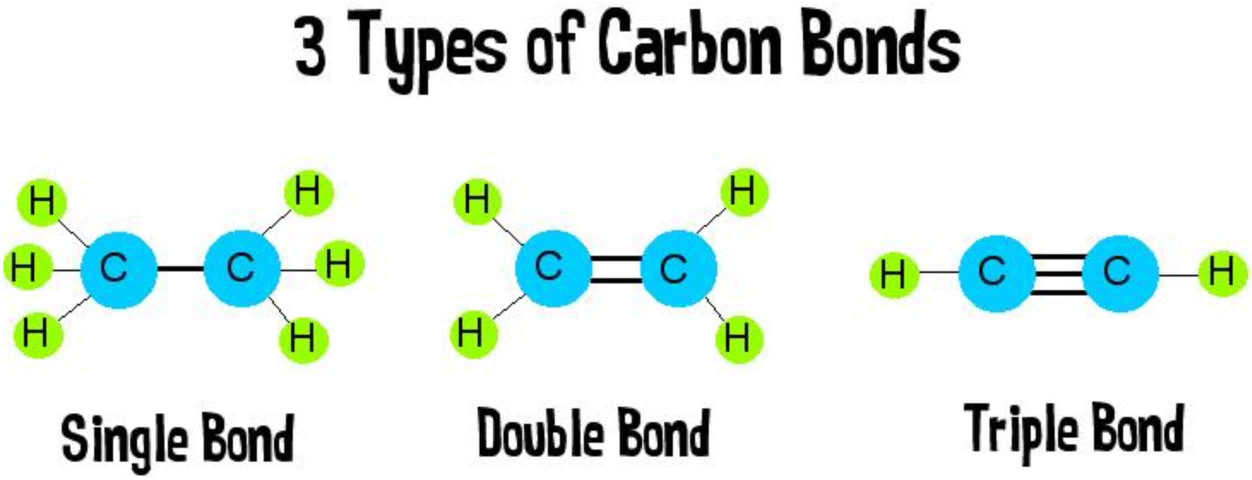
It has 4 valence electrons.

It makes 4 covalent bonds.

It can bond with any element, but really loves to bond with other carbon atoms and make long chains.



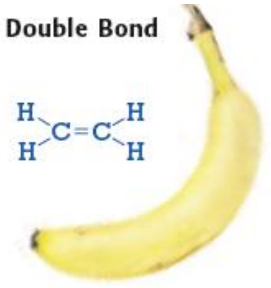



3 Types of Carbon Bonds


Single Bond

$$\begin{array}{ccccccc} & & H & H & H & & \\ H & - & C-C & & -C & - & H \\ & & H & H & H & & \end{array}$$

The **propane** in this camping stove contains only single bonds.


Double Bond

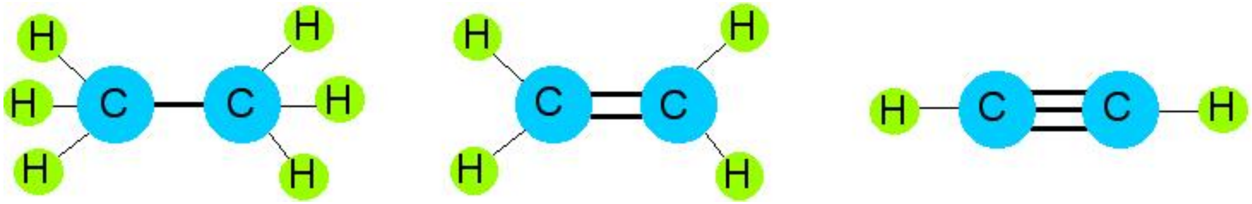
$$\begin{array}{ccc} H & & H \\ & C=C & \\ H & & H \end{array}$$

Fruits make **ethene,** which is a compound that helps ripen the fruit.

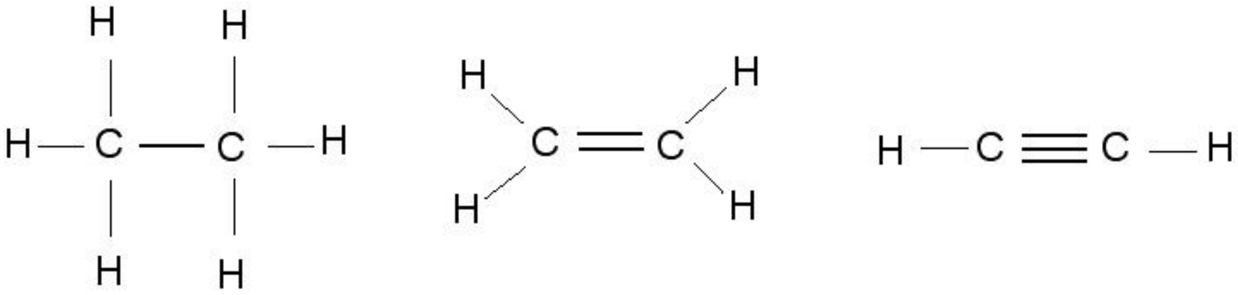

Triple Bond

H−C≡C−H

Ethyne is better known as *acetylene*. It is burned in this miner's lamp and in welding torches.



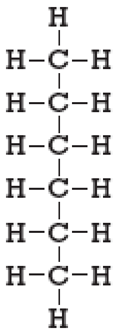
Full Structural Formulas



Simplified Structural Formulas

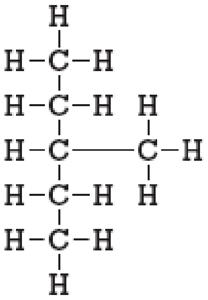
$CH_3 - CH_3$ $CH_2 = CH_2$ $CH \equiv CH$

3 Types of Carbon Backbones:



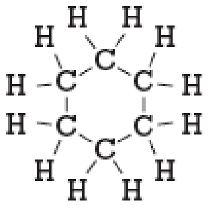
Straight chain

Carbon atoms are connected one after another.



Branched chain

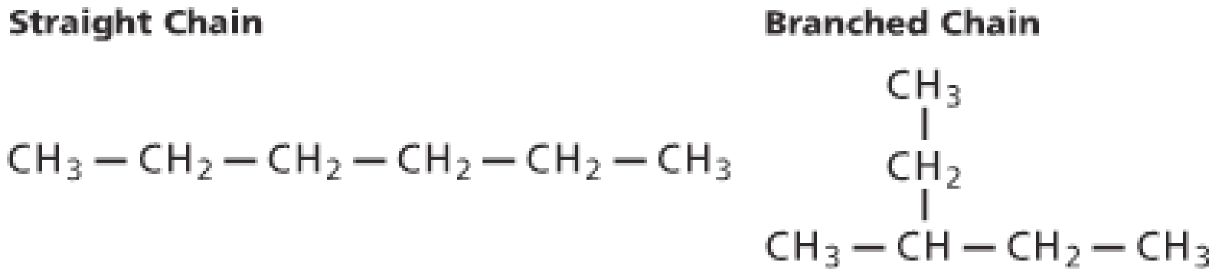
The chain of carbon atoms branches when a carbon atom bonds to more than two other carbon atoms.



Ring

The chain of carbon atoms forms a ring.

Carbon forms long chains:



$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

$$\begin{array}{c}\phantom{CH_3-{}}CH_3\phantom{{}-CH_2-CH_3}\\ \phantom{CH_3-{}}|\phantom{{}-CH_2-CH_3}\\ \phantom{CH_3-{}}CH_2\phantom{{}-CH_2-CH_3}\\ \phantom{CH_3-{}}|\phantom{{}-CH_2-CH_3}\\ CH_3-CH-CH_2-CH_3\end{array}$$

One carbon chain may contain hundreds of carbon atoms.

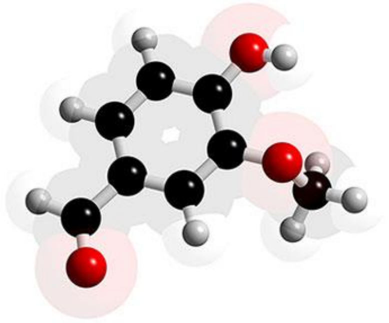
Unlike other elements, carbon atoms can bond to each other to form very long chains.

One carbon chain may contain hundreds of carbon atoms. Notice how the CH_2 units repeat.

A very large carbon-based molecule made of repeating units is called a polymer. Each unit of a polymer is called a monomer.

Polymers can be *thousands* of atoms long.

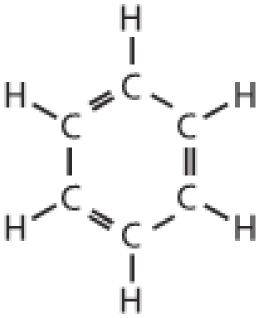
Carbon forms Rings:



Carbon-based molecules also can be shaped like rings. Most carbon rings contain 5 or 6 carbon atoms.

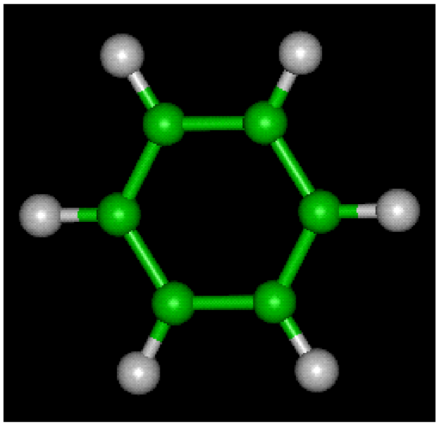
One of the most important carbon rings is benzene.

It has 6 carbons & 6 hydrogens, with alternating double bonds.



Benzene Ring

Simplified Benzene Ring



Many compounds are based on Benzene.

They often have very strong smells or aromas, so they are called aromatic compounds.

An example of one aromatic compound is a molecule called vanillin.

Guess what that smells like!

Silicon is similar to carbon. Why is there no life forms based on silicon?

Silicon is unsuitable because, although it is a valence IV element like carbon (4 electrons to share), BUT the silicon-silicon covalent bond is not strong enough for it to form long stable chains.

So, it cannot form molecules of the complexity needed to make up cells like carbon can!

Long Chain Hydrocarbons & their Names:

<u>The alkanes</u> make up a series of saturated hydrocarbons, called a <u>homologous series</u> because they have similar properties and have the same general formula:

The first four members of the series are gases at room temperature and are called:

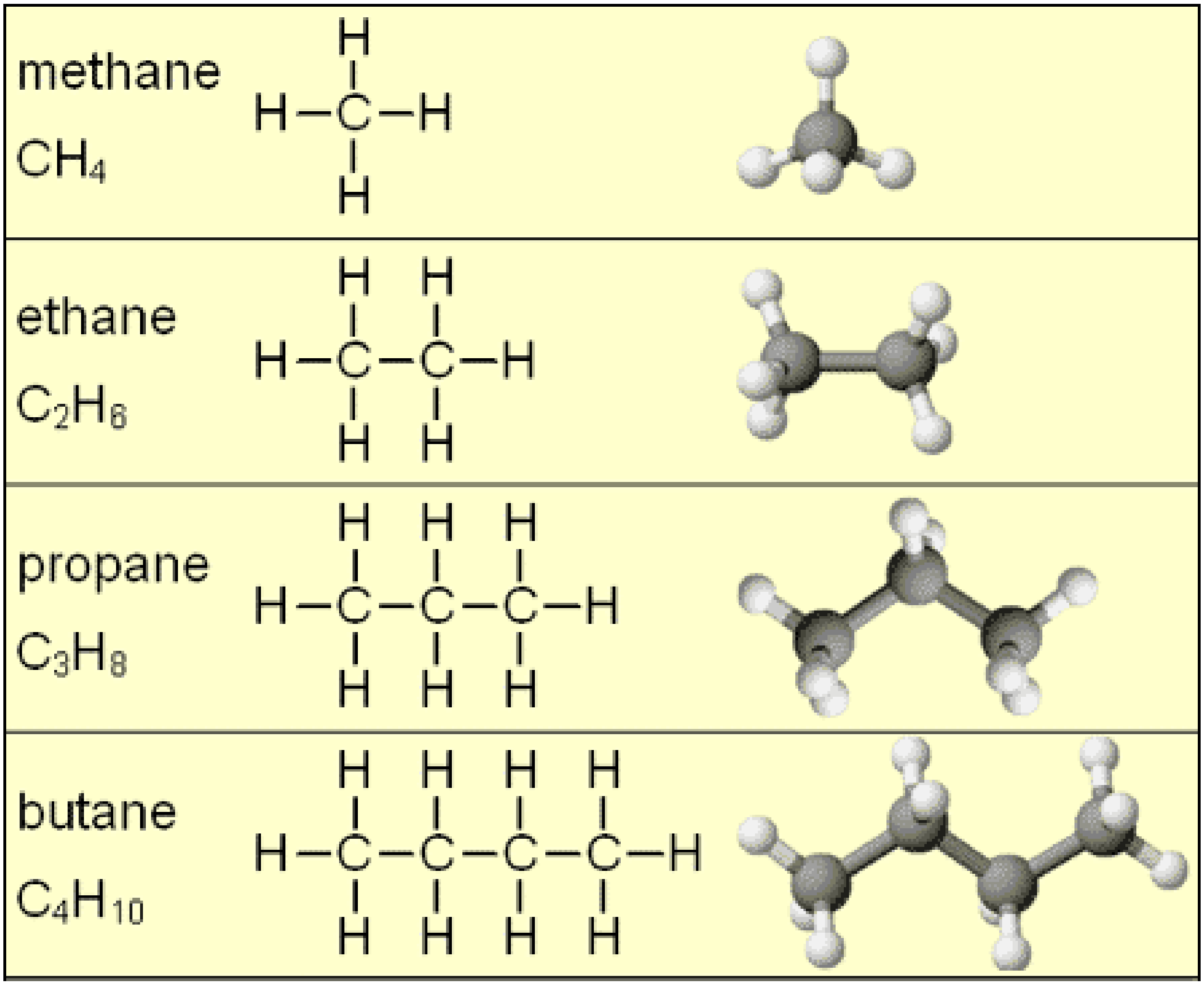
<u>methane,</u> CH_4

<u>ethane,</u> C_2H_6

<u>propane,</u> C_3H_8

<u>butane,</u> C_4H_{10}

Alkanes



Alkanes with increasing numbers of carbon atoms have names are based on the Greek word for the number of carbon atoms in the chain of each molecule.

So you can get, for example,

pentane (5),

hexane (6),

heptane (7)

and octane (8).

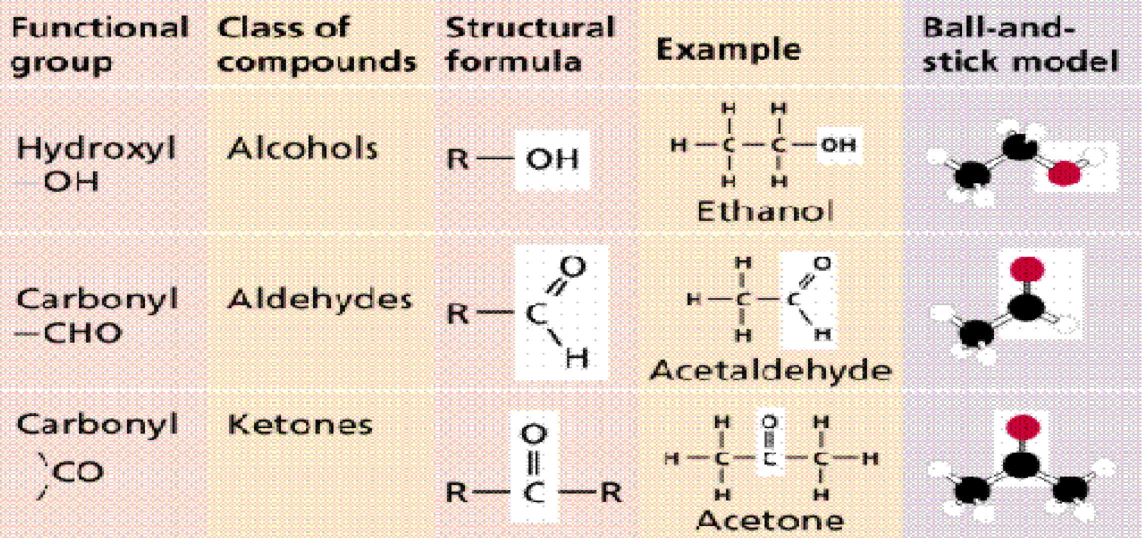
From pentane onwards, approximately the next thirty alkanes in the series are liquids.

Alkanes with even longer chains are waxy solids.

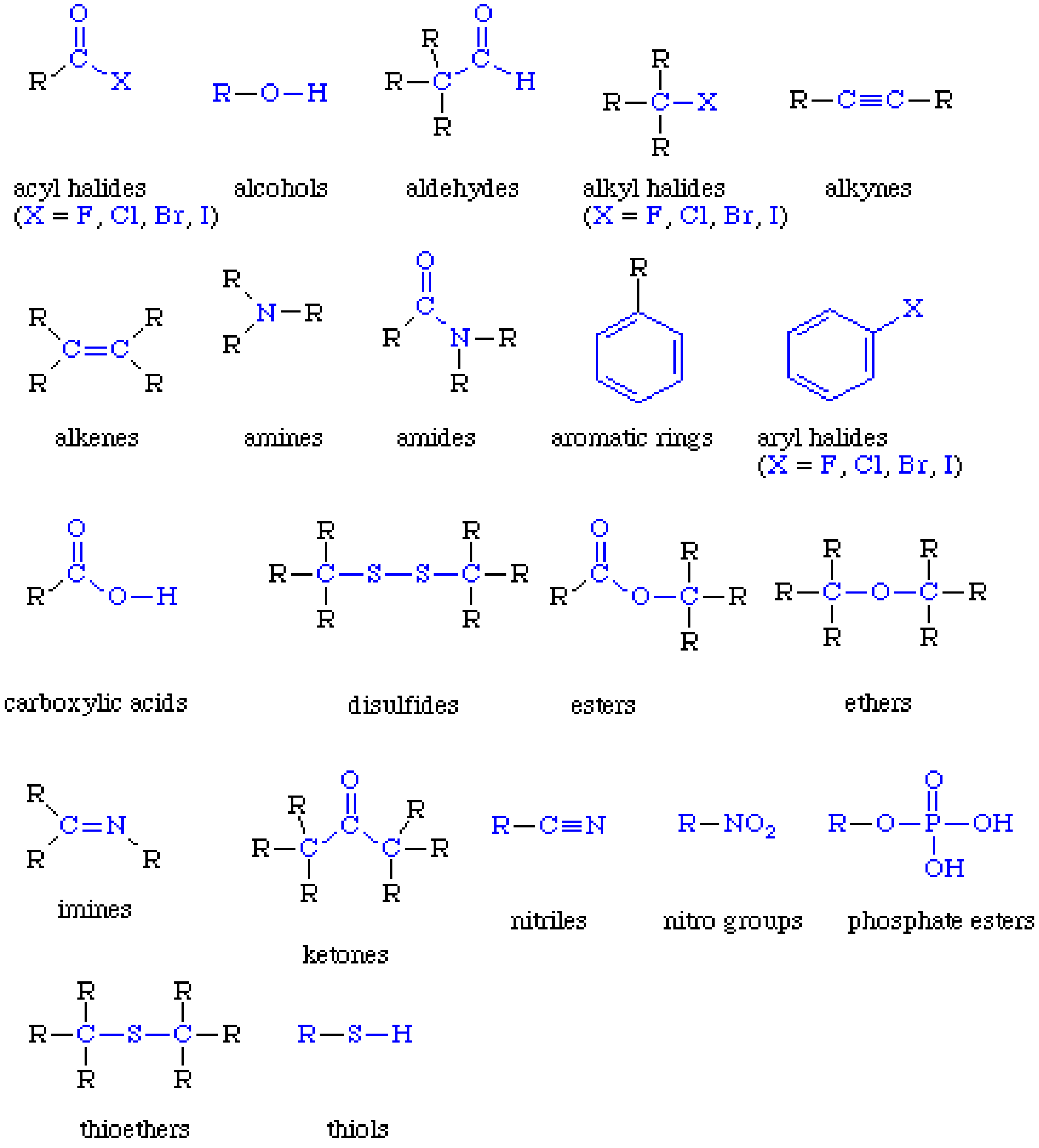
They are typical covalent compounds, insoluble in water but able to mix with each other. Alkanes burn in oxygen to produce carbon dioxide and steam.

Classification of organic compounds

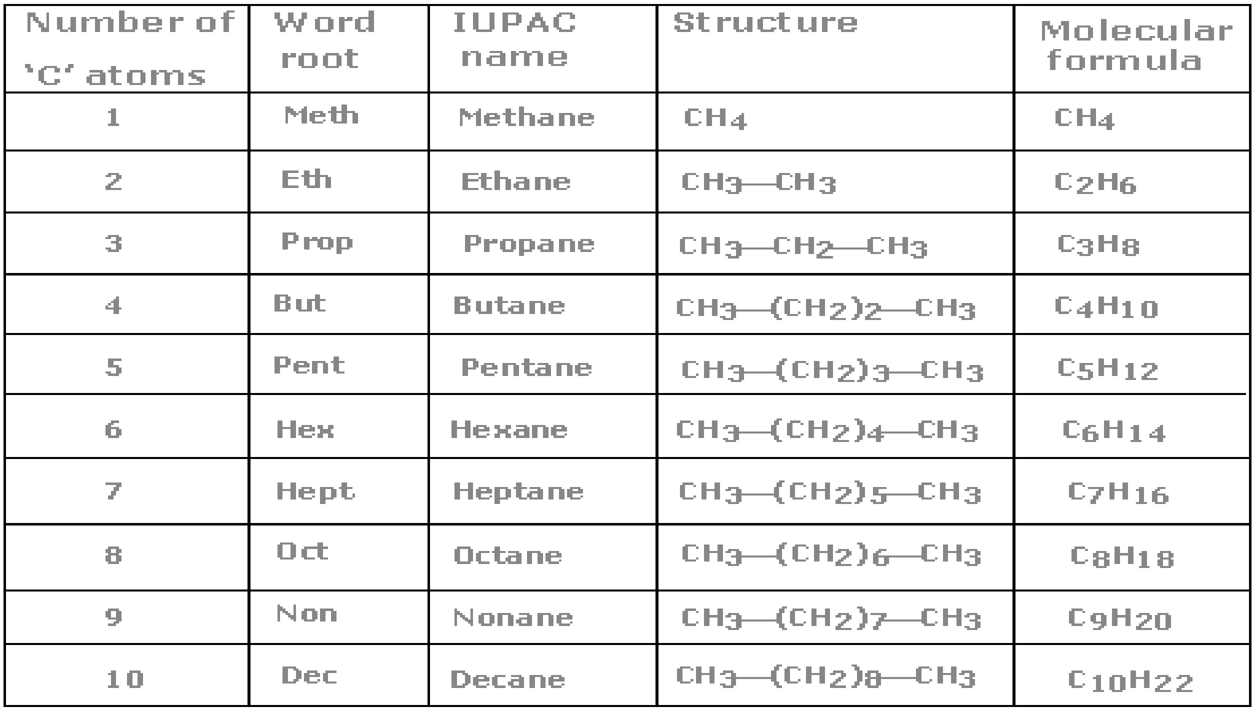
Related compounds that have the same functional group (groups of atoms found within molecules that are involved in the chemical reactions characteristic of those molecules).



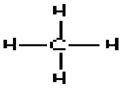
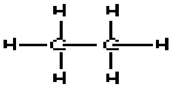
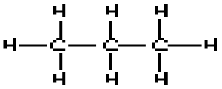
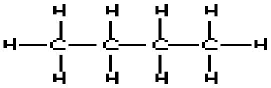
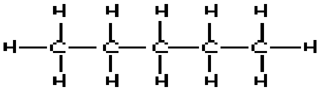
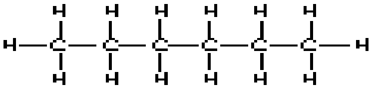
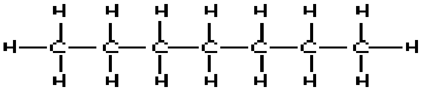
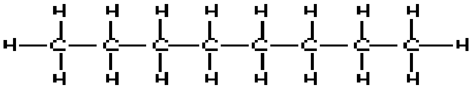
Functional group	Class of compounds	Structural formula	Example	Ball-and-stick model
Hydroxyl —OH	Alcohols	R — OH	Ethanol	
Carbonyl —CHO	Aldehydes	$R-\overset{\overset{O}{\|}}{C}-H$	Acetaldehyde	
Carbonyl ⟩CO	Ketones	$R-\overset{\overset{O}{\|}}{C}-R$	Acetone	



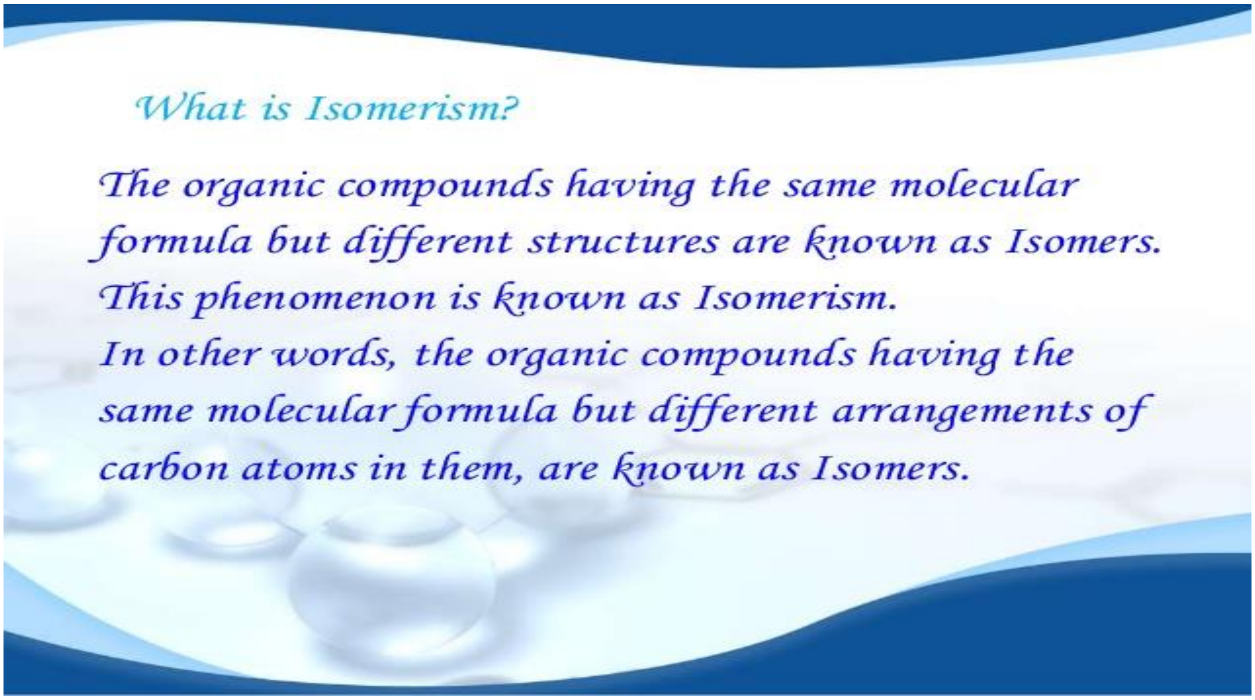
- **differ from each other by a CH_2 unit can be represented by a general formula**
  - **examples: C_nH_{2n+2} (alkanes) or C_nH_{2n} (alkenes) or…**



Number of 'C' atoms	Word root	IUPAC name	Structure	Molecular formula
1	Meth	Methane	CH_4	CH_4
2	Eth	Ethane	$CH_3—CH_3$	C_2H_6
3	Prop	Propane	$CH_3—CH_2—CH_3$	C_3H_8
4	But	Butane	$CH_3—(CH_2)_2—CH_3$	C_4H_{10}
5	Pent	Pentane	$CH_3—(CH_2)_3—CH_3$	C_5H_{12}
6	Hex	Hexane	$CH_3—(CH_2)_4—CH_3$	C_6H_{14}
7	Hept	Heptane	$CH_3—(CH_2)_5—CH_3$	C_7H_{16}
8	Oct	Octane	$CH_3—(CH_2)_6—CH_3$	C_8H_{18}
9	Non	Nonane	$CH_3—(CH_2)_7—CH_3$	C_9H_{20}
10	Dec	Decane	$CH_3—(CH_2)_8—CH_3$	$C_{10}H_{22}$

# Carbons	Name	Structure
1	methane	
2	ethane	
3	propane	
4	butane	
5	pentane	
6	hexane	
7	heptane	
8	octane	

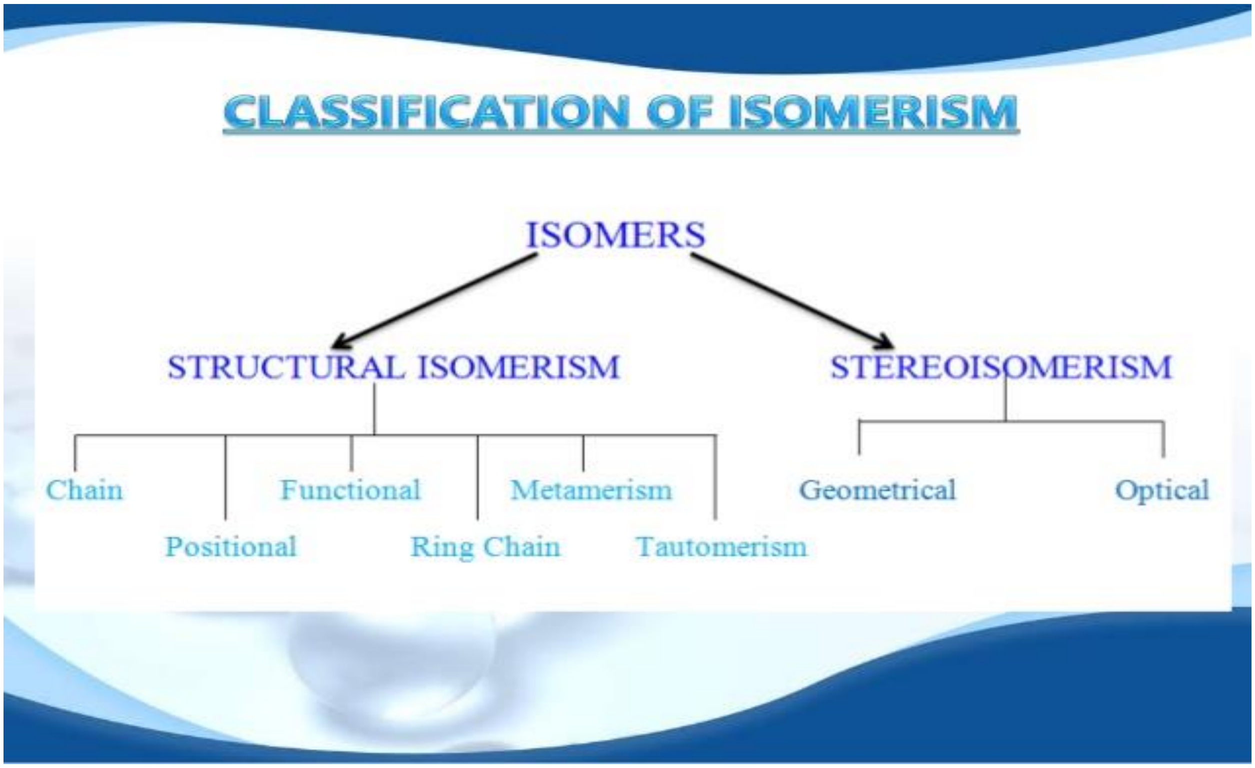
Isomerism



What is Isomerism?

The organic compounds having the same molecular formula but different structures are known as Isomers. This phenomenon is known as Isomerism.

In other words, the organic compounds having the same molecular formula but different arrangements of carbon atoms in them, are known as Isomers.



CLASSIFICATION OF ISOMERISM

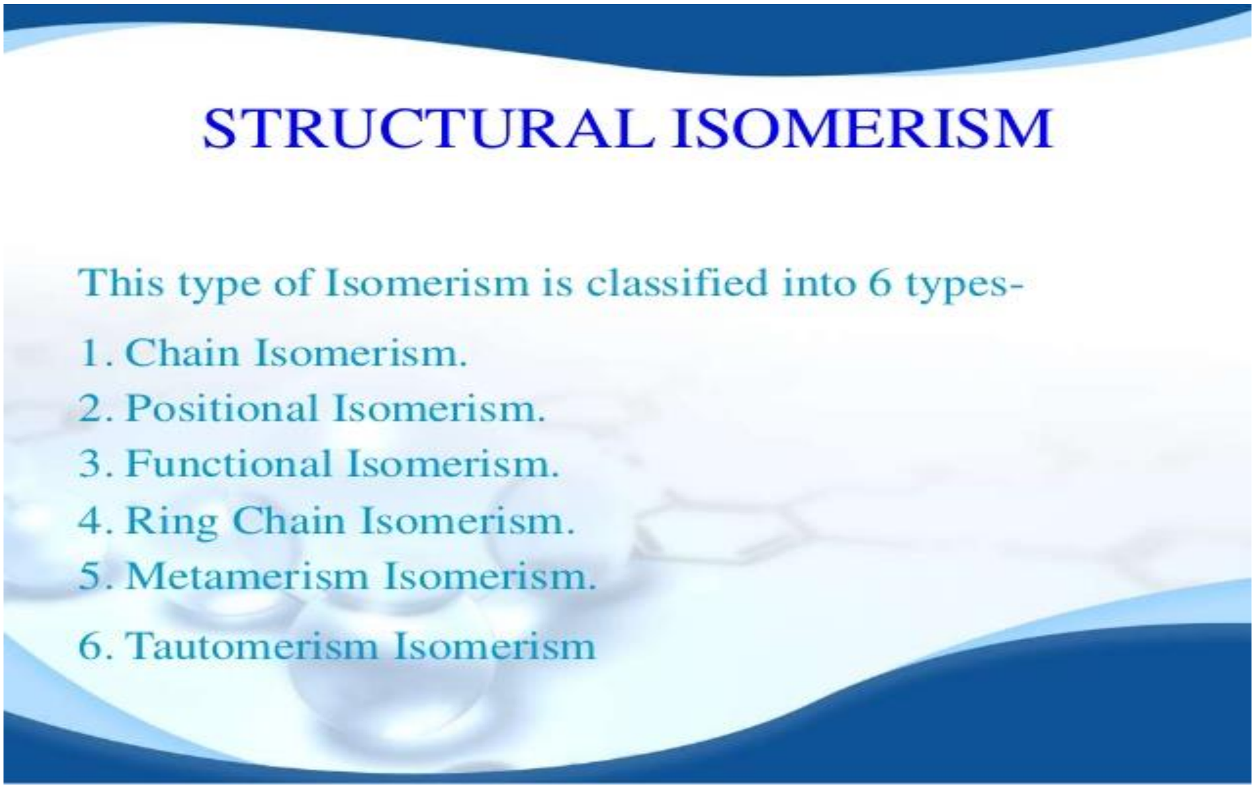
ISOMERS

STRUCTURAL ISOMERISM

- Chain
- Positional
- Functional
- Ring Chain
- Metamerism
- Tautomerism

STEREOISOMERISM

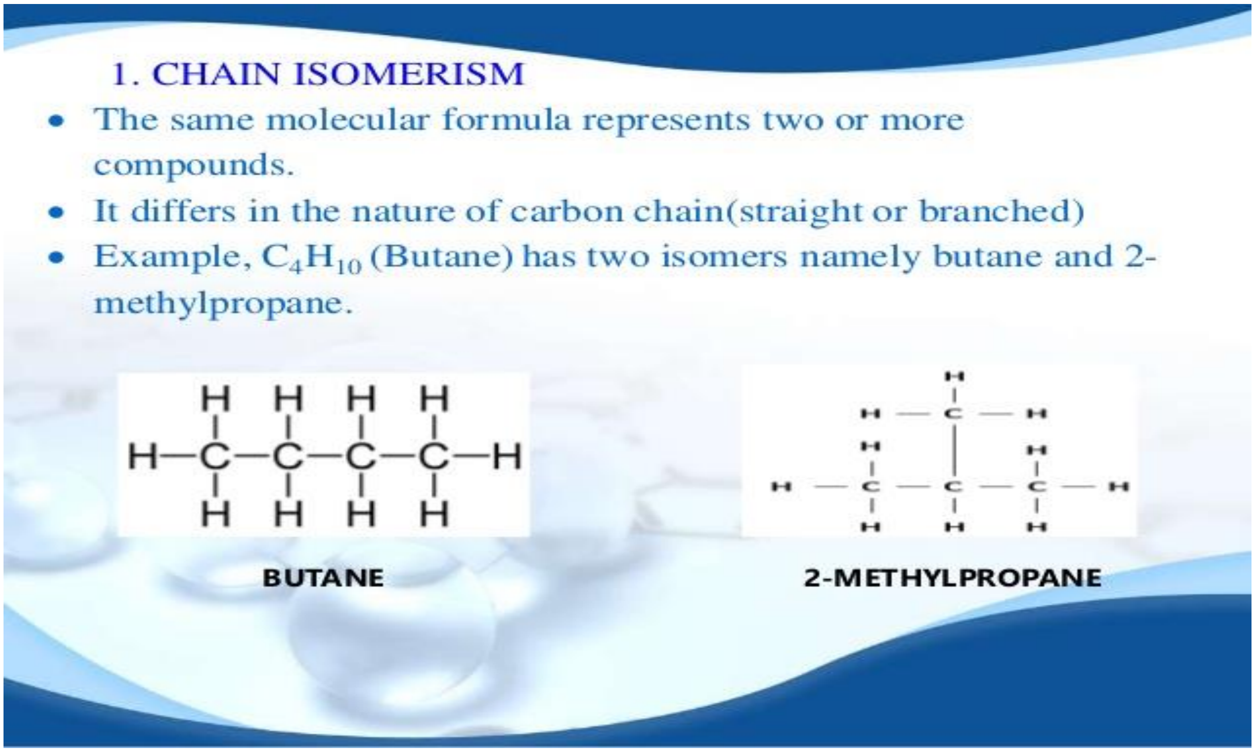
- Geometrical
- Optical



STRUCTURAL ISOMERISM

This type of Isomerism is classified into 6 types-

1. Chain Isomerism.
2. Positional Isomerism.
3. Functional Isomerism.
4. Ring Chain Isomerism.
5. Metamerism Isomerism.
6. Tautomerism Isomerism

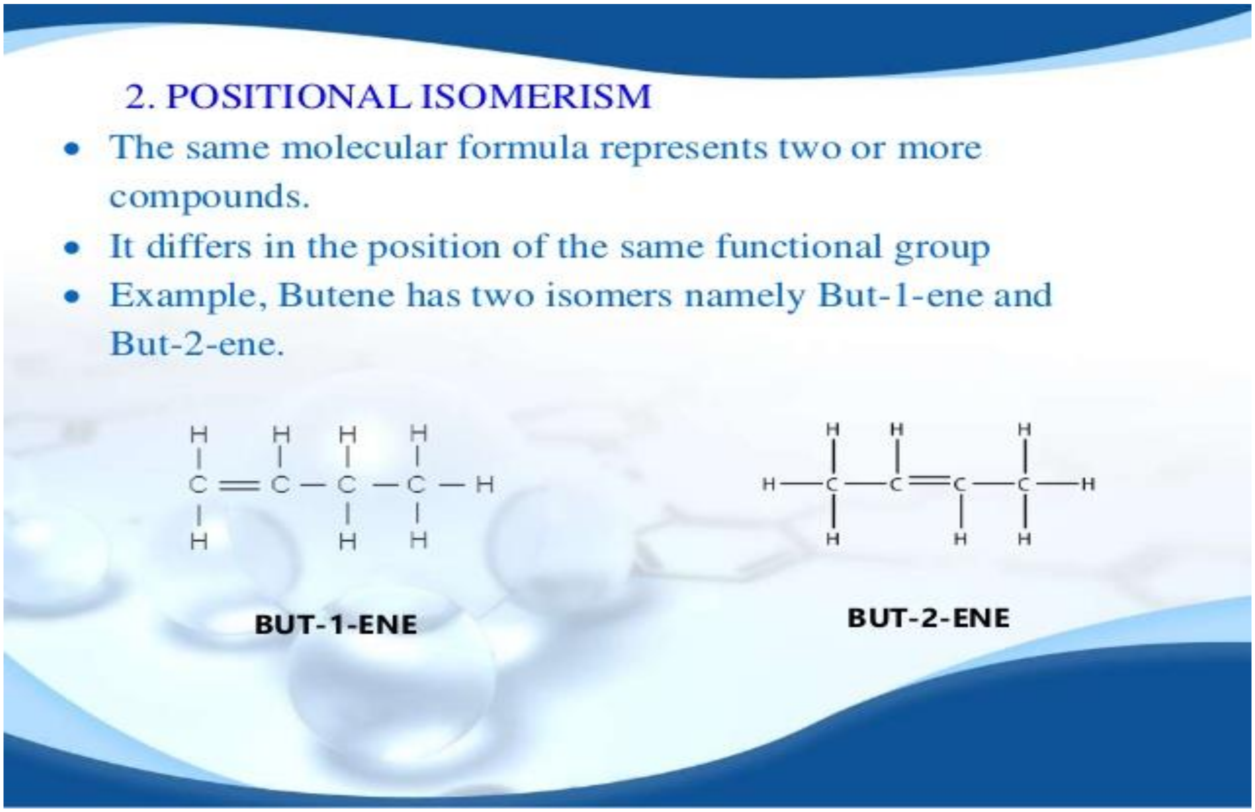


1. CHAIN ISOMERISM

- The same molecular formula represents two or more compounds.
- It differs in the nature of carbon chain(straight or branched)
- Example, C_4H_{10} (Butane) has two isomers namely butane and 2-methylpropane.

BUTANE

2-METHYLPROPANE

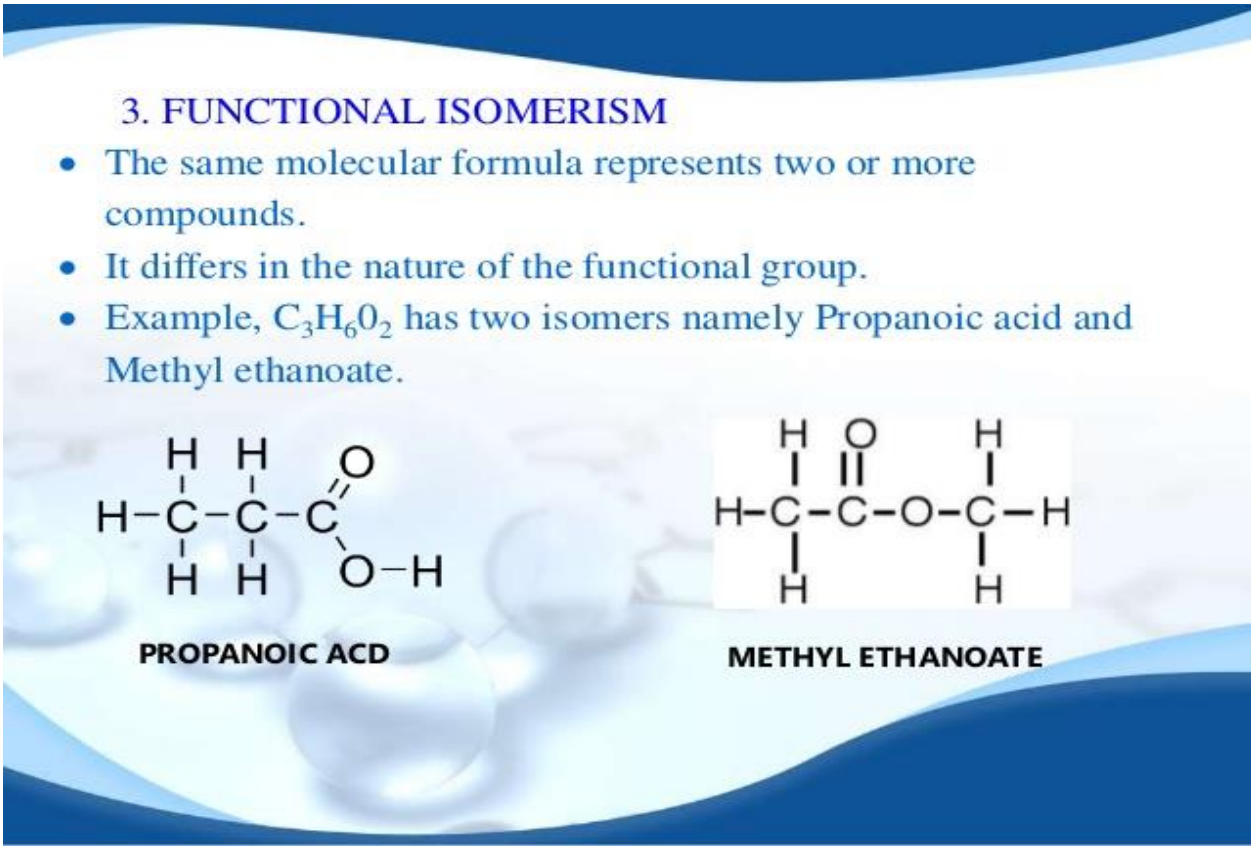


2. POSITIONAL ISOMERISM

- The same molecular formula represents two or more compounds.
- It differs in the position of the same functional group
- Example, Butene has two isomers namely But-1-ene and But-2-ene.

BUT-1-ENE

BUT-2-ENE



3. FUNCTIONAL ISOMERISM

- The same molecular formula represents two or more compounds.
- It differs in the nature of the functional group.
- Example, $C_3H_60_2$ has two isomers namely Propanoic acid and Methyl ethanoate.

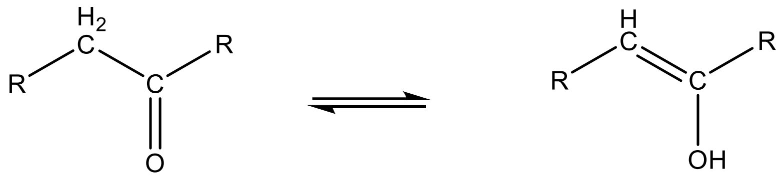
PROPANOIC ACD

METHYL ETHANOATE

Resonance versus tautomerism

Tautomerism is a type of isomerism in compounds contains carbonyl group beside methylene group.

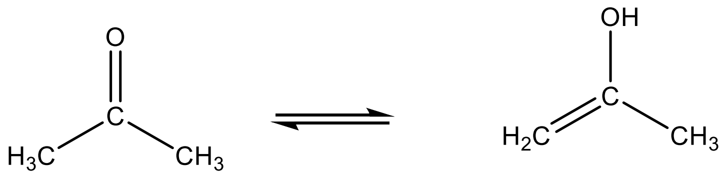
These compounds present in a balance between two forms are keto form and enol form, these forms known as tautomeric isomers (tautomerism).



keto form

enol form

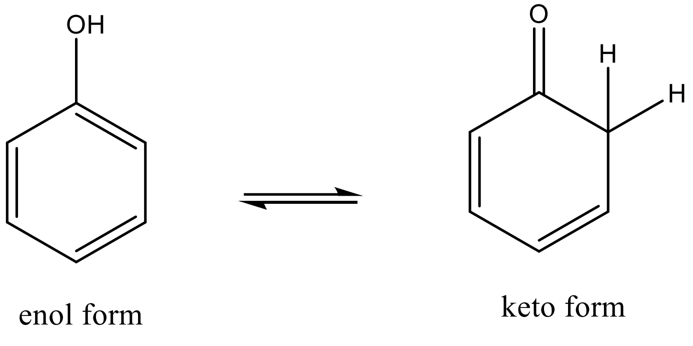
Example (1): acetone:



keto form

enol form

Example (2): phenol:



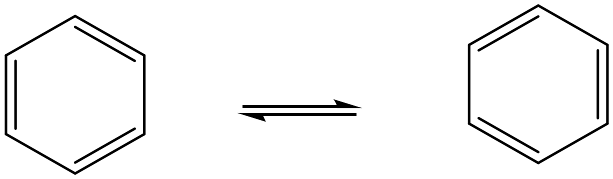
enol form

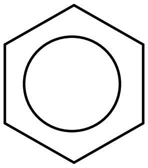
keto form

Resonance:

Is a type of isomerism present in compound in more than one form in its structural formula differs in the position of π electrons.

Example: benzene:





Naming Organic Compounds

The name of any organic compound is comprised of three portions:

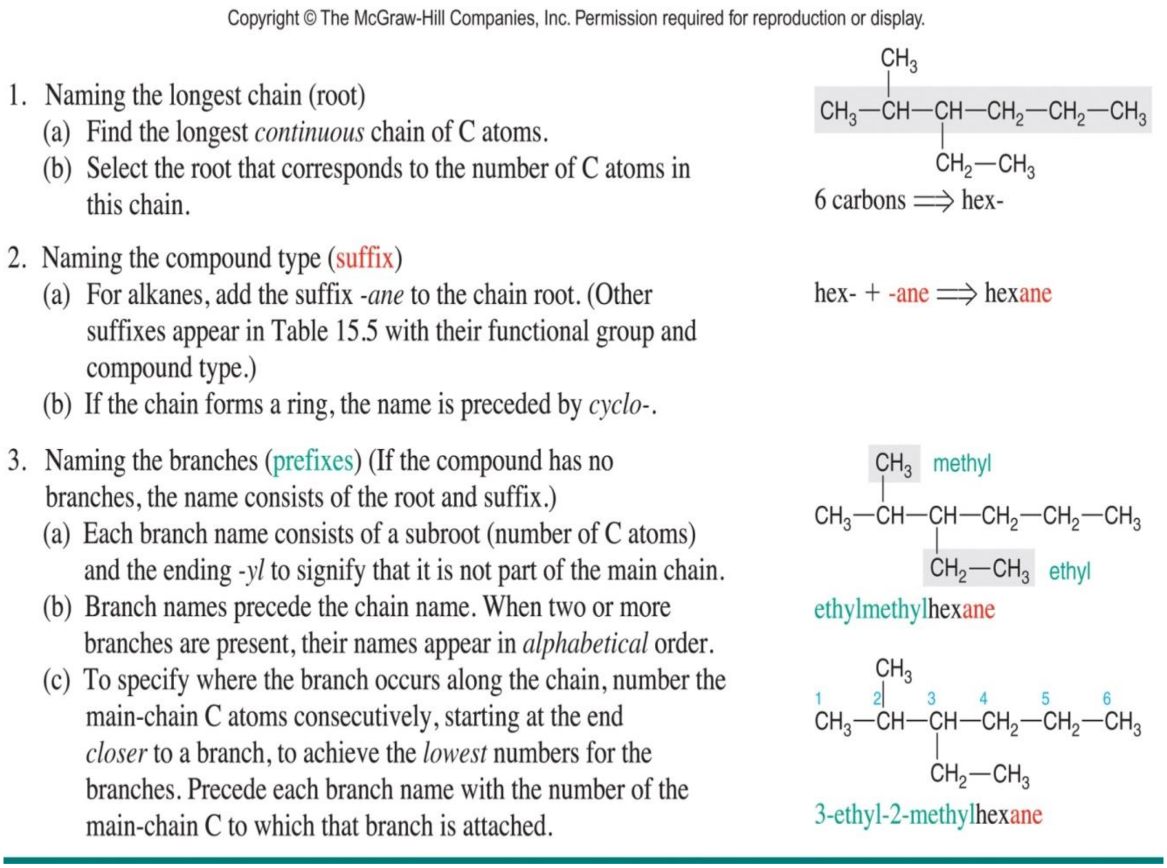
PREFIX + ROOT + SUFFIX

The *root* name of the compound is determined from the *number* of C atoms in the *longest continuous chain.* The *suffix* indicates the *type* of organic compound, and is placed after the root. The suffix for an alkane is –ane. The *prefix* identifies any groups attached to the main chain.

Numerical Roots for Carbon Chains and Branches

Roots	Number of C Atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

Rules for Naming an Organic Compound



1. Naming the longest chain (root)
   (a) Find the longest *continuous* chain of C atoms.
   (b) Select the root that corresponds to the number of C atoms in this chain.

$CH_3-\overset{CH_3}{\overset{|}{C}H}-\underset{CH_2-CH_3}{\underset{|}{C}H}-CH_2-CH_2-CH_3$

6 carbons ⟹ hex-

2. Naming the compound type (suffix)
   (a) For alkanes, add the suffix *-ane* to the chain root. (Other suffixes appear in Table 15.5 with their functional group and compound type.)
   (b) If the chain forms a ring, the name is preceded by *cyclo-*.

hex- + -ane ⟹ hexane

3. Naming the branches (prefixes) (If the compound has no branches, the name consists of the root and suffix.)
   (a) Each branch name consists of a subroot (number of C atoms) and the ending *-yl* to signify that it is not part of the main chain.
   (b) Branch names precede the chain name. When two or more branches are present, their names appear in *alphabetical* order.
   (c) To specify where the branch occurs along the chain, number the main-chain C atoms consecutively, starting at the end *closer* to a branch, to achieve the *lowest* numbers for the branches. Precede each branch name with the number of the main-chain C to which that branch is attached.

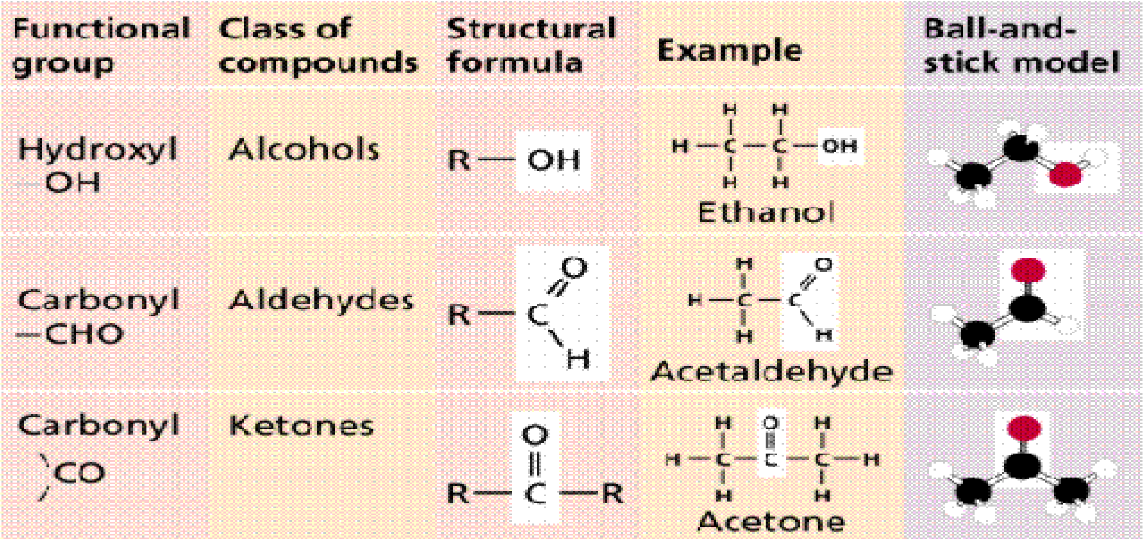
$CH_3-\overset{CH_3\ \text{methyl}}{\overset{|}{C}H}-\underset{CH_2-CH_3\ \text{ethyl}}{\underset{|}{C}H}-CH_2-CH_2-CH_3$

ethylmethylhexane

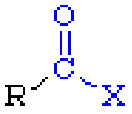
$\overset{1}{C}H_3-\overset{CH_3}{\overset{2|}{C}H}-\underset{CH_2-CH_3}{\underset{|}{\overset{3}{C}H}}-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_3$

3-ethyl-2-methylhexane

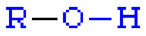
Functional groups



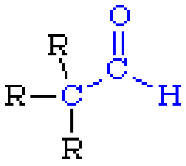
Functional group	Class of compounds	Structural formula	Example	Ball-and-stick model
Hydroxyl $-OH$	Alcohols	$R-OH$	Ethanol	
Carbonyl $-CHO$	Aldehydes	$R-C(=O)-H$	Acetaldehyde	
Carbonyl $>CO$	Ketones	$R-C(=O)-R$	Acetone	



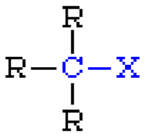
acyl halides
(X = F, Cl, Br, I)



alcohols

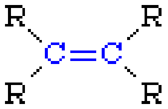


aldehydes

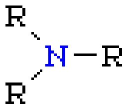


alkyl halides
(X = F, Cl, Br, I)

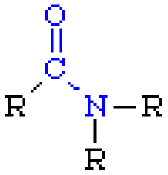
alkynes



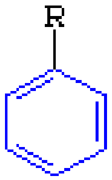
alkenes



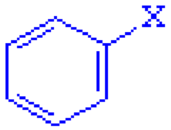
amines



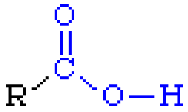
amides



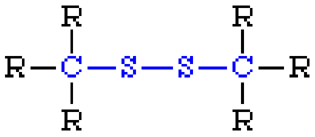
aromatic rings



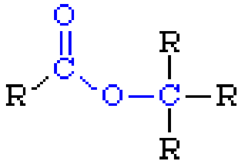
aryl halides
(X = F, Cl, Br, I)



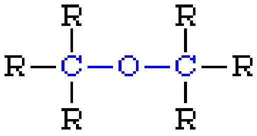
carboxylic acids



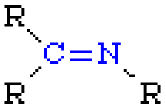
disulfides



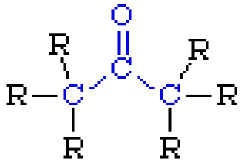
esters



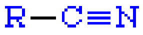
ethers



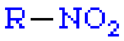
imines



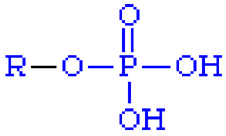
ketones



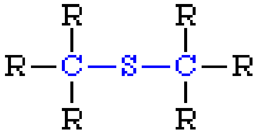
nitriles



nitro groups



phosphate esters



thioethers

thiols

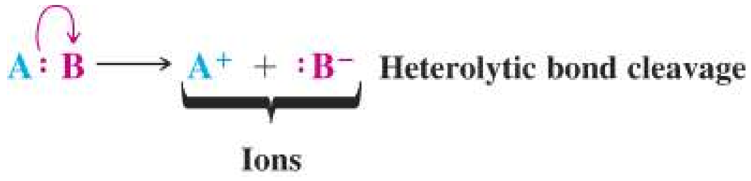
Chemical reaction (التفاعل الكيميائى)

بصفة عامة التفاعل الكيميائى فى مجمله عبارة عن كسر روابط كيميائية وتكوين روابط جديدة. ولذا يجب توضيح الكيفية التى يتم بها تكسير رابطة او تكوين رابطة أخرى.

Cleavage of Covalent Bonds (كيفية تكسير رابطة تساهمية)

a- Homolytic bond Cleavage: تكسير متماثل للرابطة

b- Heterolytic bond Cleavage: تكسير غير متماثل للرابطة



Bond making (كيفية تكوين رابطة)

a- Homogenic bond making (تكوين متماثل للرابطة)

أمثلة: تفاعلات جذور حرة

b- Heterogenic bond making (تكوين غير متماثل للرابطة)

أمثلة: تفاعلات قطبية أو قطبية نسبية

Types of Reactions and Their Mechanisms

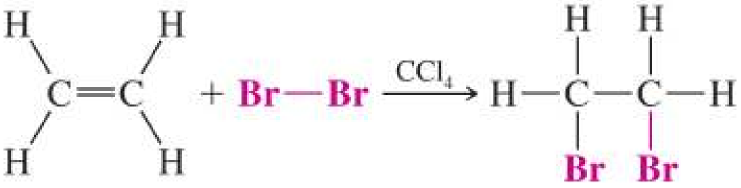
بصفة عامة يمكن تقسيم التفاعلات العضوية الى أربع أنواع من التفاعلات.

1- Substitution reactions تفاعلات استبدال

$$H_3C{-}Cl + Na^+OH^- \xrightarrow{H_2O} H_3C{-}OH + Na^+Cl^-$$

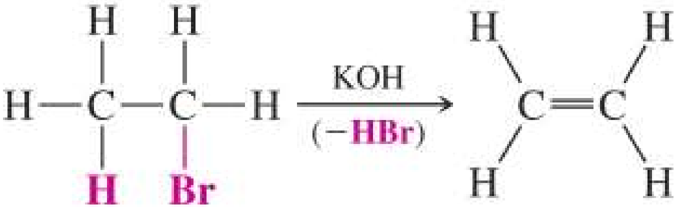
A substitution reaction

2- Addition reactions تفاعلات اضافة



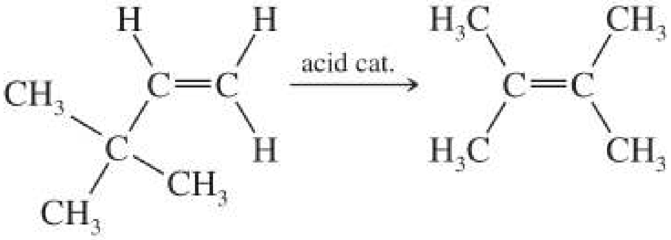
An addition reaction

3- Elimination reactions تفاعلات نزع



An elimination reaction

4- Rearrangement reactions تفاعلات اعادة ترتيب

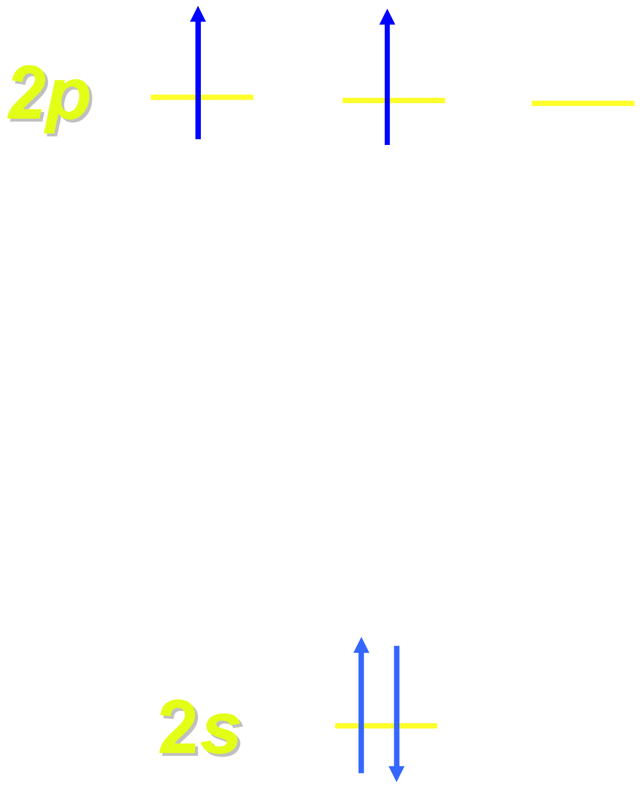


A rearrangement

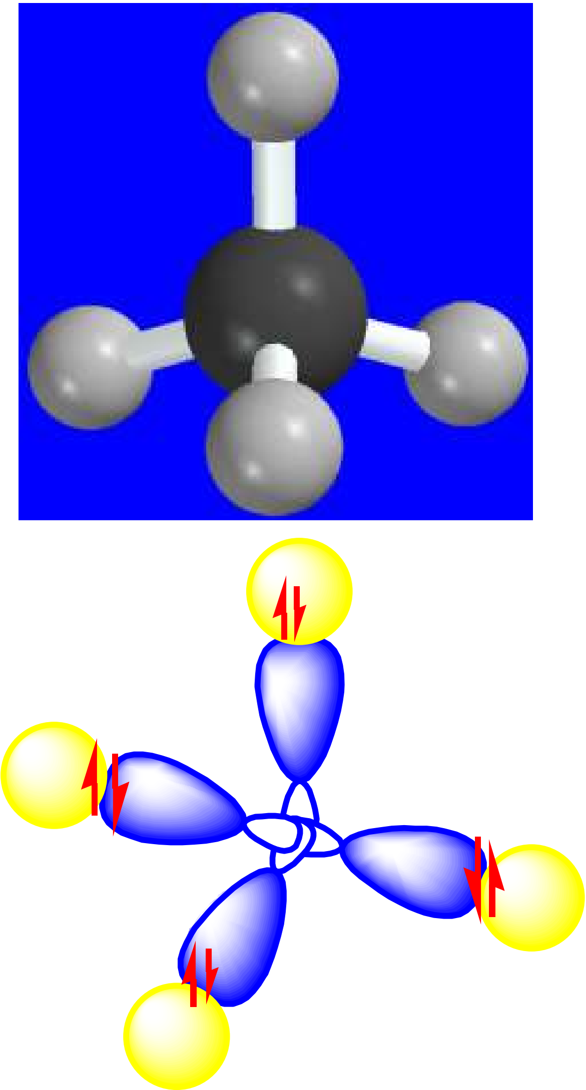
تهجين المدارات وتكوين الروابط فى الميثان، الأيثان، الأيثيلين، الأسيتيلين

التركيب الألكترونى للكربون

- فقط عدد ٢ الكترون غير مزدوج
- لذا المقدره على الأرتباط بعدد ٢ ذرة هيدروجين فقط
- هل الكربون ثنائى التكافؤ!!!!



التركيب الفراغى للميثان



- **الشكل الفراغى:** رباعى السطوح هرمى الشكل
- مقدار الزاوية = 109.5°
- طول الرابطه C—H = 110 pm
- هذا يدلل على ان الكربون رباعى التكافؤ.

وهذا يعزى الى التهجين.

مدارات مهجنه من نوع sp^3

2p

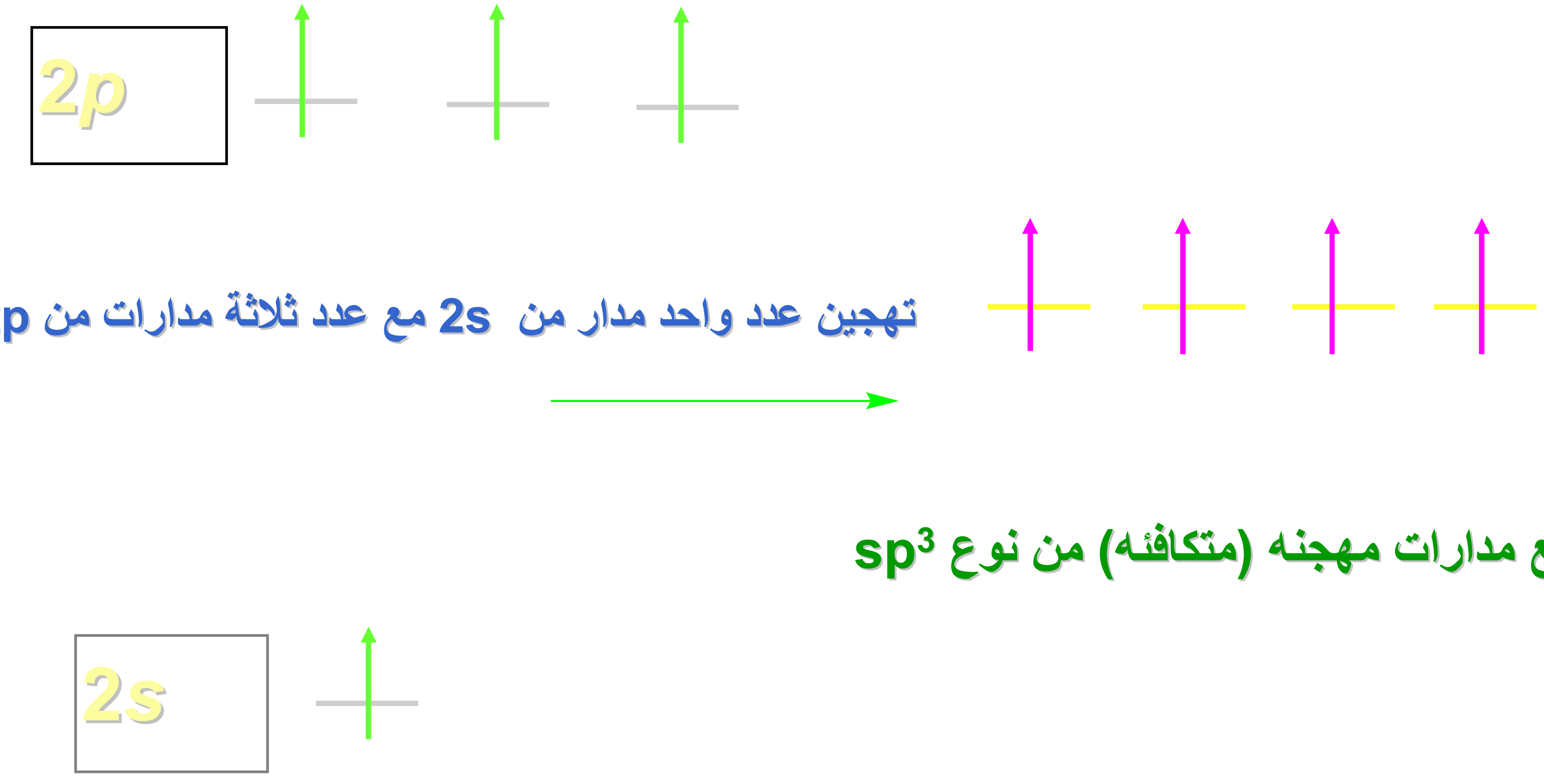
2p

اثارة الكترون من المدار 2s الى المدار 2p

2s

2s

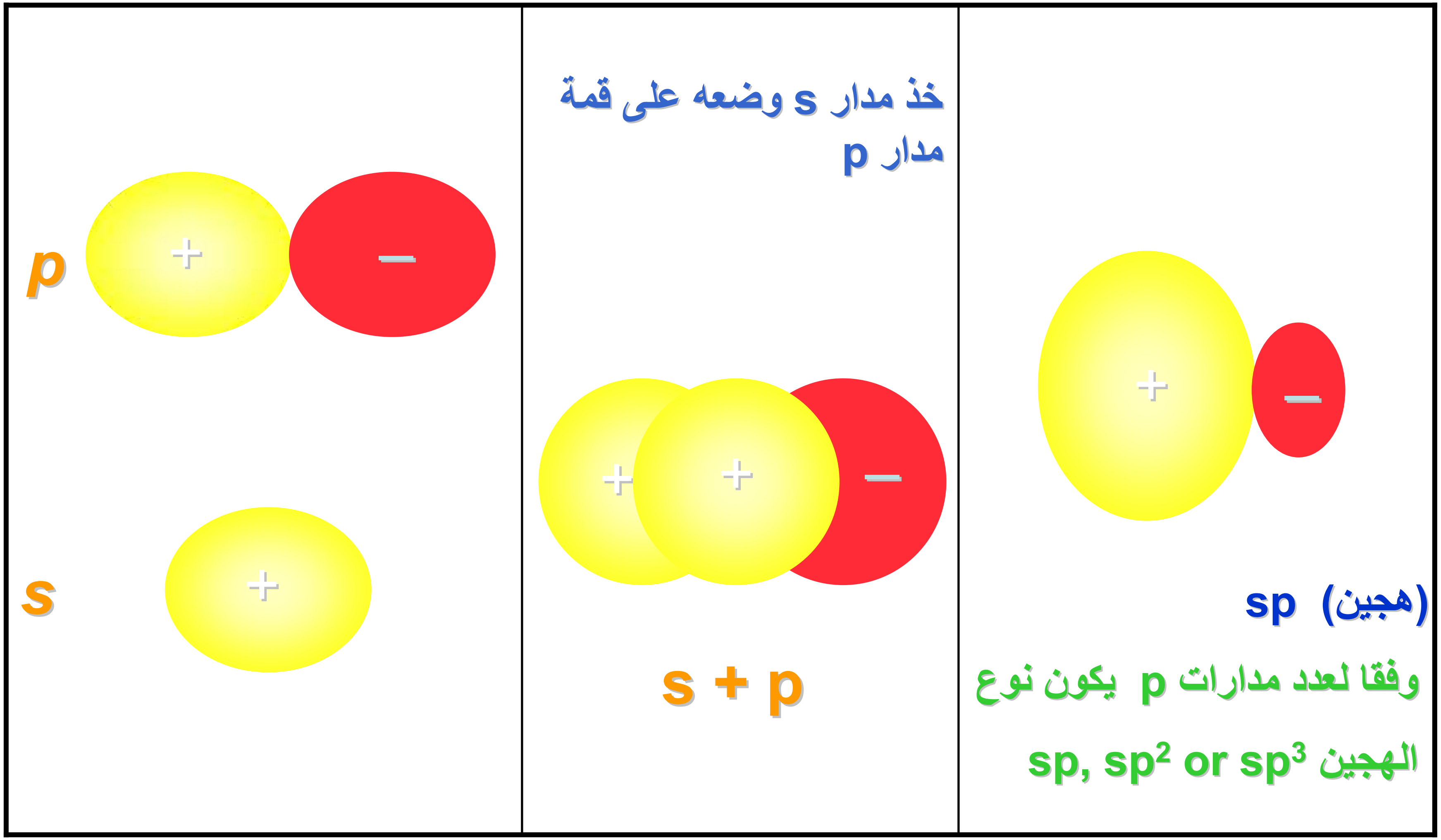
مدارات مهجنه من نوع sp^3



تهجين عدد واحد مدار من 2s مع عدد ثلاثة مدارات من 2p

الناتج: هو أربع مدارات مهجنه (متكافئه) من نوع sp^3

شكل المدارات المهجنه من نوع sp^3



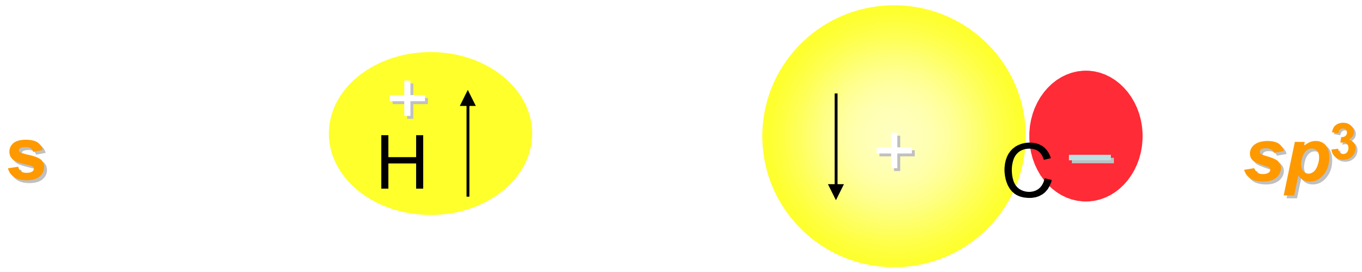
خذ مدار s وضعه على قمة مدار p

(هجين) sp

وفقا لعدد مدارات p يكون نوع الهجين sp, sp^2 or sp^3

الرابطة سيجما C—H

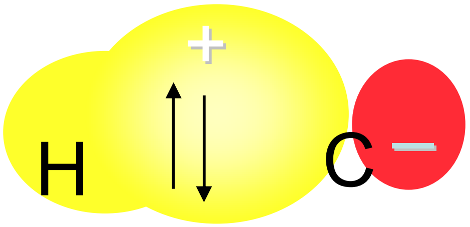
- تداخل مدار نصف ممتلىء من s مع مدار نصف ممتلىء من هجين sp^3



يعطى:

H—C σ bond

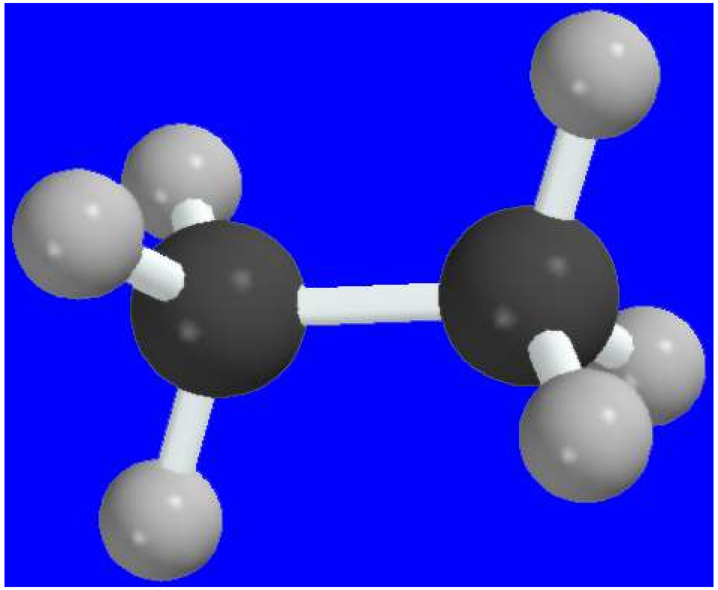
هجين من نوع $s\text{-}sp^3$



التركيب الفراغى للأيثان

C_2H_6

CH_3CH_3

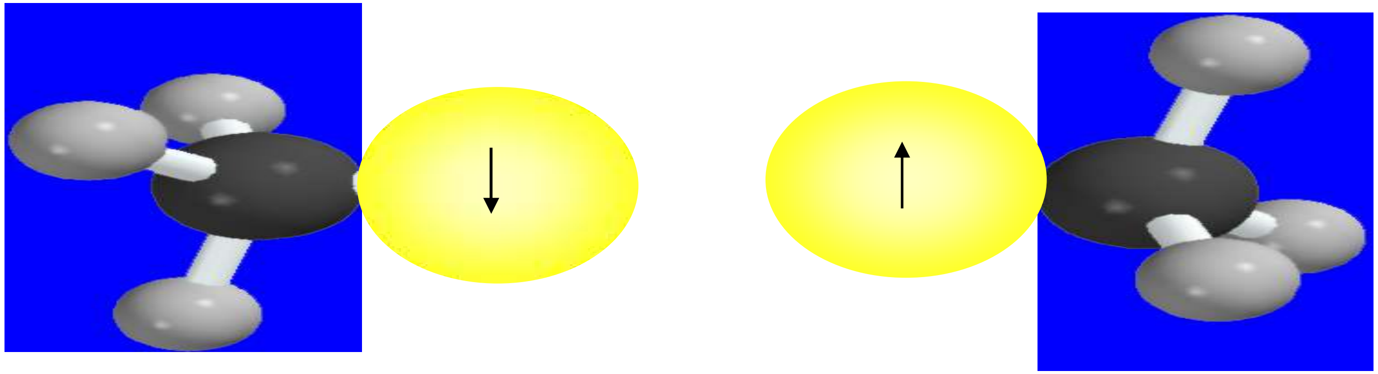


- **الشكل الفراغى:** رباعى السطوح هرمى الشكل عند ذرات الكربون

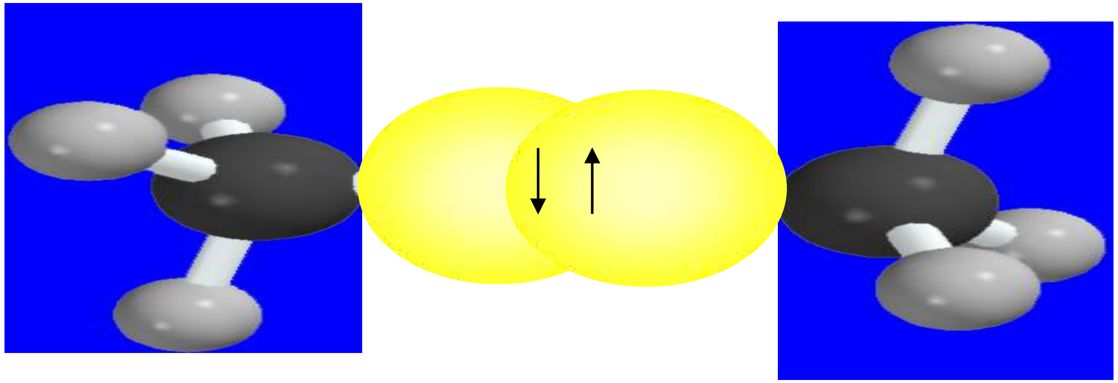
C—H طول الرابطه = 110 pm

C—C طول الرابطه = 153 pm

الرابطة سيجما C-C



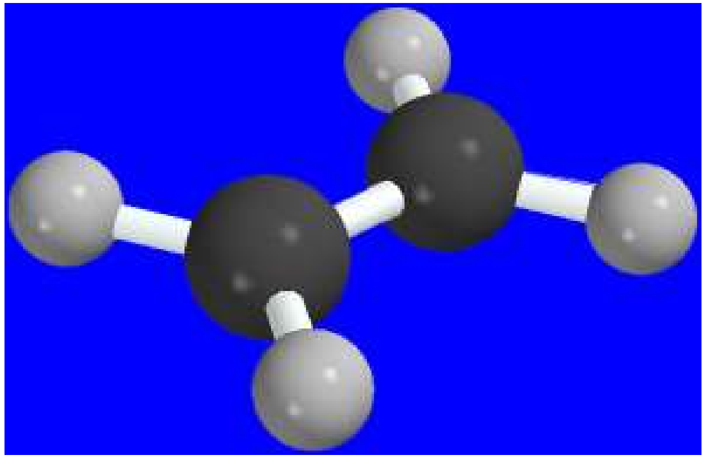
C—C σ bond, sp^3-sp^3 هجين من نوع



التركيب الفراغى للأيثيلين

C_2H_4

$H_2C{=}CH_2$



مستو الشكل

120° تقارب : زوايا الرابطة

أطوال الروابط :
C-H = 110 pm
C=C = 134 pm

هجين من نوع sp^2

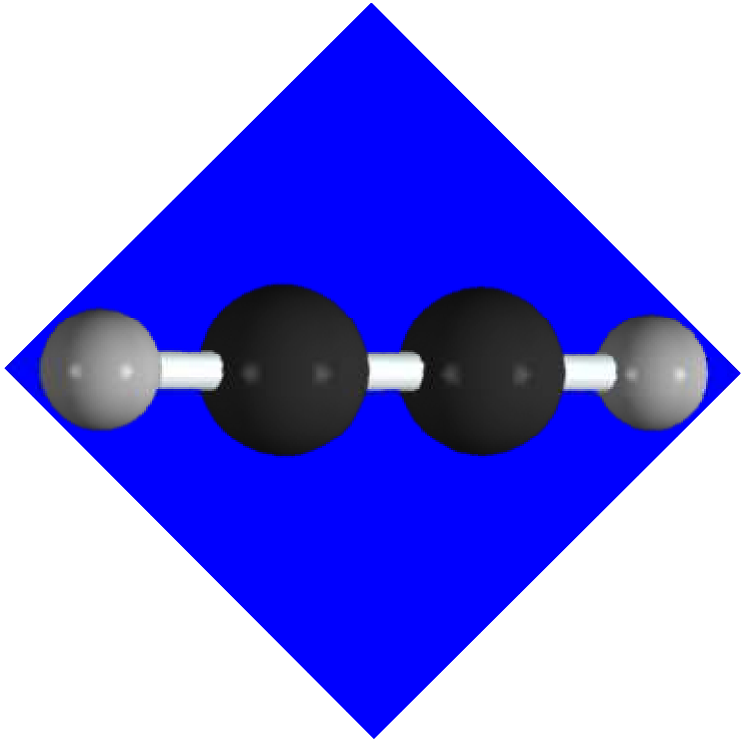
الناتج: هو ثلاث مدارات مهجنه (متكافئه) من نوع sp^2

بالأضافه الى عدد واحد مدار p لم يدخل فى التهجين (حيث
انه مشترك فى تكوين عدد واحد رابطة ثنائه من نوع π)

التركيب الفراغى للأسيتيلين

C_2H_2

$HC\equiv CH$



خطى الشكل

زوايا الرابطة: 180°

أطوال الروابط: C—H = 106 pm

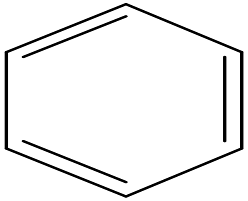
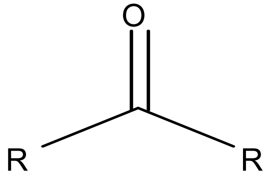
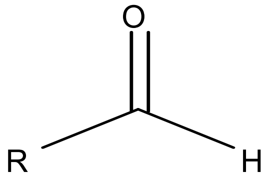
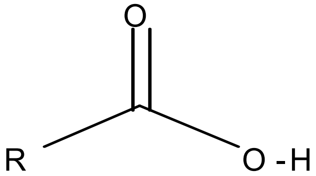
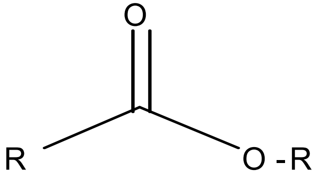
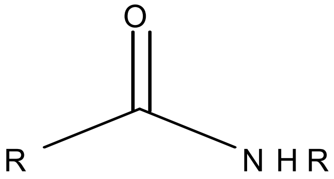
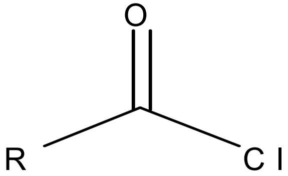
C≡C = 120 pm

هجين من نوع sp

الناتج: هو عدد ٢ مدار مهجن (متكافئه) من نوع sp

بالأضافه الى عدد ٢ مدار p لم يدخلا فى التهجين (حيث انهم
مشتركين فى تكوين عدد ٢ رابطة ثنائه من نوع π)

Common Functional Groups (المجموعات الفعاله)

$R-H$	alkane
$RHC=CHR$	alkene
$R-C\equiv C-R$	alkyne
	aromatic
$R-O-H$	alcohol
$R-O-R$	ether
	ketone
	aldehyde
	carboxylic acid
	ester
	amide
	acid chloride
$R-NH_2$	amine
$RHC=NH$	imine
$R-C\equiv N$	nitrile

26

HYDROCARBONS

You have studied in the previous lesson that hydrocarbons are the compounds containing carbon and hydrogen. You also know that they are classified as aliphatic, alicyclic and aromatic hydrocarbons. They constitute a very important class of organic compounds and are widely used as fuels, lubricants and dry cleaning agents. They are also used as important ingredients in medicines and in dyes. Petroleum and coal are the major sources of various types of hydrocarbons. The products obtained from fractional distillation of petroleum and destructive distillation of coal are used almost in every sphere of life. Hydrocarbons are considered to be the parent organic compounds, from which other organic compounds can be derived by replacing one or more hydrogen atoms with different functional groups. In this lesson, you will study about the preparation, important physical and chemical properties of hydrocarbons.

Objectives

After reading this lesson, you will be able to :

- list different methods of preparation of alkanes;
- explain the reasons for variation in physical properties of alkanes;
- describe different chemical properties of alkanes;
- list different methods of preparation of alkenes;
- explain the physical properties of alkenes;
- describe the chemical properties of alkenes;
- list different methods of preparation of alkynes;
- explain physical and chemical properties of alkynes;
- discuss the cause of greater reactivity of alkenes and alkynes over alkanes;
- distinguish alkanes, alkenes and alkynes;
- list various fractions obtained by destructive distillation of coal;
- explain the stability of various organic compounds using resonance;

- describe methods of preparation, physical properties and chemical properties of benzene, and
- list various uses of hydrocarbons.

26.1 Alkanes (Paraffins)

Alkanes are saturated hydrocarbons. They are very less reactive towards various reagents; hence, they are also referred to as *paraffins* (*parum* means little, *affins* means affinity).

26.1.1 Methods of Preparation

Some important methods of preparation of alkanes are as follows:

1. **From Haloalkanes (Alkyl Halides):** Monohaloalkanes can be converted to alkanes by following three methods :

   a) **By reduction of haloalkanes:** The replacement of halogen atom of haloalkanes with hydrogen is called the reduction and can be carried out by the following reagents :

   (i) Zinc and dilute HCl

$$\underset{\textbf{Bromomethane}}{CH_3Br} + Zn + 2\,HCl \longrightarrow \underset{\textbf{Methane}}{CH_4} + ZnCl_2 + HBr$$

   (ii) HI in the presence of red phosphorus

$$\underset{\textbf{Iodoethane}}{C_2H_5I} + HI \xrightarrow[\text{423 K}]{\text{red phosphorus}} \underset{\textbf{Methane}}{C_2H_6} \quad ZnCl_2 \quad HBr$$

   (iii) Catalytic reduction

$$\underset{\textbf{Chloromethane}}{CH_3Cl} + H_2 \xrightarrow{\text{Pt (catalyst)}} \underset{\textbf{Methane}}{CH_4} \quad HCl$$

   b) **By using Grignard's Reagent :** A Grignard reagent is a compund of the type RMgX which is prepared by reacting a haloalkane with magnesium metal in the presence of dry ether.

$$\underset{\textbf{Bromoethane}}{C_2H_5Br + Mg} \xrightarrow{\text{dry ether}} \underset{\textbf{Ethyl Magnesium Bromide}}{C_2H_5MgBr}$$

   The Grignard's reagents are used to prepare various compounds like hydrocarbons, ethers, alcohols and carboxylic acids. It reacts with the compounds containing active hydrogen and forms alkanes. An easily replaceable hydrogen atom present in the compounds is called *active hydrogen*. An active hydrogen is present in (i) alcohols and (ii) water and (iii) acids.

$$CH_3MgBr + C_2H_5OH \rightarrow CH_4 + Mg(OC_2H_5)Br$$

$$C_2H_5MgBr + H_2O \rightarrow C_2H_6 + Mg(OH)Br$$

   c) **By Wurtz Reaction :** In this reaction, an alkyl halide reacts with sodium metal in the presence of dry ether and forms the higher alkanes.

$$\underset{\textbf{Bromoethane}}{CH_3 - Br + 2\,Na + Br - CH_3} \xrightarrow{\text{dry ether}} \underset{\textbf{Ethane}}{CH_3 - CH_3} + 2\,NaBr$$

2. **From Unsaturated Hydrocarbons :** The unsaturated hydrocarbons (i.e. alkenes and alkynes) can be converted to alkanes by the addition of hydrogen in the presence of a catalyst like nickel, platinum or palladium.

$$CH_2 = CH_2 + H_2 \xrightarrow[573\,K]{\text{Ni or Pt}} CH_3 - CH_3$$

$$CH \equiv CH + 2H_2 \xrightarrow[573\,K]{\text{Ni or Pt}} CH_3 - CH_3$$

This reaction is also called **hydrogenation** and is used to prepare vegetable ghee from edible oils (by converting unsaturated fats to saturated ones.)

3. **From Alcohols, Aldehydes and Ketones :** Alcohols, aldehydes and ketones on reduction with HI, in presence of red phosphorus, give alkanes.The general reactions are as shown below.

$$\underset{\textbf{Alcohol}}{ROH} + 2HI \xrightarrow{\text{red P / 423K}} \underset{\textbf{Alkane}}{RH} + I_2 + H_2O$$

$$\underset{\textbf{Aldehyde}}{RCHO} + 4HI \xrightarrow{\text{red P / 423K}} \underset{\textbf{Alkane}}{RCH_3} + 2\,I_2 + H_2O$$

$$\underset{\textbf{Ketone}}{RCOR'} + 4HI \xrightarrow{\text{red P / 423K}} \underset{\textbf{Alkane}}{RCH_2R'} + 2\,I_2 + H_2O$$

4. **From Carboxylic Acids :** Carboxylic acids can produce alkanes in a number of ways as shown below :

i) Heating with soda lime : $RCOONa + NaOH \xrightarrow[\Delta]{CaO} RH + Na_2CO_3$

In this reaction, an alkane with one carbon less than those present in the parent carboxylic acid is obtained.

ii) By Reduction of carboxylic acid:

$$RCOOH + 6\,HI \xrightarrow{\text{red P / 423 K}} RCH_3 + 3\,I_2 + 2H_2O$$

Here, an alkane with same number of carbon atoms as in the starting carboxylic acid is obtained.

iii) Kolbe's Electrolysis: Sodium or potassium salt of a carboxylic acid, on electrolysis, gives a higher alkane. The reaction takes place as follows.

$$\underset{\textbf{Sodium salt of carboxylic acid}}{RCOONa} \xrightarrow{\text{electrolysis}} \underset{\textbf{Anion}}{RCOO^-} + \underset{\textbf{Cation}}{Na^+}$$

At Anode :

$$RCOO^- \longrightarrow RCOO^\bullet + e^-$$

$$RCOO^\bullet \longrightarrow R^\bullet + CO_2$$

$$R^\bullet + R^\bullet \longrightarrow R-R$$

Thus, ethane can be obtained by the electrolysis of sodium ethonate.

$$\underset{\textbf{Sodium ethanote}}{2\,CH_3COONa} \longrightarrow \underset{\textbf{Ethane (at anode)}}{CH_3-CH_3}$$

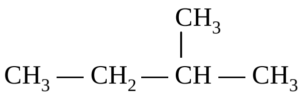
Note that the alkanes with even number of carbon atoms can easily be prepared by this method.

26.1.2 Physical Properties of Alkanes

Physical State: The physical state of alkanes depends upon the intermolecular forces of attraction present between molecules which in turn, depend upon the surface area of the molecules. *As the molecular mass of the alkanes increases, their surface area also increases, which in turn, increases the intermolecular forces of attraction, and accordingly, the physical state of alkanes changes from gaseous to liquid, and then to solid.* The alkanes containing 1 to 4 carbon atoms are gases, whereas those containing 5 to 17 carbon atoms are liquids, and the still higher ones are solids. In the case of isomeric alkanes, the straight chain alkanes will have maximum surface area, and hence, stronger intermolecular force of attraction. As the branching increases, surface area decreases. Hence the intermolecular forces of attraction decrease. Let us consider the isomers of pentane (C_5H_{12}).

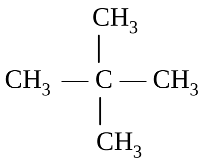
$$CH_3-CH_2-CH_2-CH_2-CH_3$$

***n*-Pentane**



$$CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

2-Methylbutane
(Isopentane)



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

2,2-Dimethylpropane
(Neopentane)

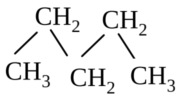
Amongst these three isomeric compounds, neopentane will have the weakest intermolecular forces of attraction due to the smallest surface area of its molecules.

Density: *The density of alkanes increases with the increase in molecular mass which increases with the increase in the number of carbon atoms.* All alkanes are lighter than water i.e. their density is less than 1.0 g/cm^3. The maximum density in the case of alkanes is 0.89 g cm^3. The lower density of alkanes than water is due to the absence of strong intermolecular attractions in alkanes.

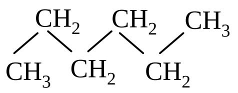
Boiling Point: *The boiling points of alkanes also increase with the increase in the molecular mass.* In straight chain alkanes, the increase in boiling points due to the increase in surface area of the molecules. Branching in a chain reduces the surface area and therefore, decreases the boiling point of alkanes. Thus, in the above example, isopentane and neopantane have a lower boiling point than pentane.

Melting Point: Similar to the boiling points, the melting points of alkanes also increase with the increase in their molecular mass, but there is no regular variation in melting point. The melting points of alkanes depend not only upon the size and shape of the molecules, but also on the arrangement (i.e. the packing) of the molecules in the crystal lattice.

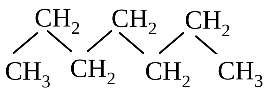
In alkanes, each carbon atom is sp^3 hybridized which results in a bond angle of $109^0 28'$. In straight chain hydrocarbons the carbon atoms are arranged in a zig-zag way in the chain. If the molecule contains an odd number of carbon atoms, then the two terminal methyl groups lie on the same side. So the interaction between the alkane molecules, with odd number of carbon atoms, is less than the molecule with even number of carbon atoms, in which terminal methyl groups lie on the opposite sides.



***n*-Pentane**
(Carbon atoms = 5, m.p.142 K)



***n*-Hexane**
(Carbon atoms =6, m.p. = 179 K)



***n*-Heptane**
(carbon atoms = 7, m.p. = 183 K)

In the above structures, we find that alkanes containing even number of carbon atoms are more symmertical and can be more closely packed as compared with alkanes containing odd number of carbon atoms and can be more closely packed. Van der Waal's force of attraction is stronger, due to which they have higher melting points. *Therefore, the alkanes with odd number of carbon atoms have lower melting point than those having even number of carbon atoms.*

26.1.3 Chemical Properties of Alkanes

1. Halogenation reactions: The chemical reactions in which a hydrogen atom of an alkane is replaced by a halogen atom are known as *halogenation*. Alkanes react with chlorine in the following way.

$$\underset{\textbf{Methane}}{CH_4} + Cl_2 \xrightarrow[-HCl]{\text{Diffused Sunlight}} \underset{\textbf{Chloromethane}}{CH_3Cl}$$

$$CH_3Cl + Cl_2 \xrightarrow[-HCl]{} \underset{\textbf{Dichloromethane}}{CH_2Cl_2}$$

$$CH_2Cl_2 + Cl_2 \xrightarrow[-HCl]{} \underset{\textbf{Trichloromethane}}{CHCl_3}$$

$$CHCl_3 + Cl_2 \xrightarrow[-HCl]{} \underset{\textbf{Tetrachloromethane}}{CCl_4}$$

Chlorination of methane takes place via the **free radical mechanism**. When the reaction mixture is exposed to sunlight, chlorine molecules absorb energy from sunlight and get converted to free radicals i.e. chlorine atoms with an unpaired electron $(\dot{C}l)$. The chlorine radicals then combine with methane and form methyl radical $[\dot{C}H_3]$. The methyl radical further reacts with chlorine molecule and produces chloromethane. This reaction continuously takes place till it is stopped or the reactants completely react to form the products. The free radical mechanism involves the following three steps.

(i) **Chain Initiation Step:** It involves the formation of free radicals.

$$Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet} \qquad (h\nu = \text{energy of light})$$

(ii) **Chain Propagation Step :** The free radicals give rise to the formation of more free radicals as is shown in the following reaction.

$$CH_4 + \dot{C}l \longrightarrow \dot{C}H_3 + HCl$$

$$\dot{C}H_3 + Cl_2 \longrightarrow CH_3Cl + \dot{C}l$$

(iii) **Chain Termination Step :** In this step, free radicals combine with one another and the further reaction stops.

$$\dot{C}H_3 + \dot{C}l \longrightarrow CH_3Cl$$

$$\dot{C}l + \dot{C}l \longrightarrow Cl_2$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3 - CH_3$$

The reactivity of halogens is in the order of $F_2 > Cl_2 > Br_2 > I_2$.

2. **Oxidation:** Alkanes undergo oxidation (combustion) in excess of oxygen and produce carbon dioxide and water. This reaction is highly exothermic in nature.For example :

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O \; + \; 890 \text{ KJ mol}^{-1}$$

If the combustion is carried out in the presence of an insufficient supply of air or O_2, then *incomplete combustion takes place forming carbon monoxide* instead of carbon dioxide.

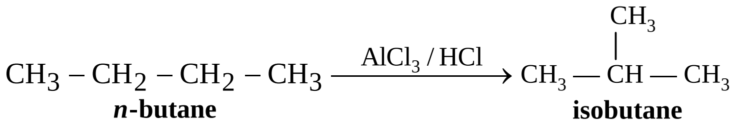
$$2C_2H_6 + 5O_2 \xrightarrow{\text{heat}} 4CO + 6H_2O$$

3. **Cracking or Pyrolysis:** At very high temperature and in the absence of air, the alkanes break apart into smaller fragments. For example,

$$CH_3 - CH_2 - CH_3 \xrightarrow{873\text{ K}} CH_3CH = CH_2 + H_2$$

or $$CH_2 = CH_2 + CH_4$$

4. **Isomerisation :** *n*-Alkanes, in the presence of aluminium halide and HCl, are converted to their branched isomers.



$$\underset{\textbf{\textit{n}-butane}}{CH_3 - CH_2 - CH_2 - CH_3} \xrightarrow{AlCl_3\,/\,HCl} \underset{\textbf{isobutane}}{CH_3 - \overset{\overset{\large CH_3}{|}}{C}H - CH_3}$$

26.1.4 Uses of Alkanes

Alkanes are used as fuel gases, solvents, drycleaning agents, lubricants and in ointments (paraffin wax). Methane is used for illuminating and domestic fuel and also for the production of other organic compounds such as haloalkanes, methanol, formaldehyde and acetylene. Propane is used as a fuel, refrigerant and as raw material in the petrochemical industry. Butane and its isomer–isobutane, are the major constituents of LPG .

Intext Questions 26.1

1. List four important uses of hydrocarbons.

   ....

2. What is Grignard's reagent in a molecule?

   ....

3. What is an active hydrogen in a molecule?

   ....

4. What makes the physical properties of various hydrocarbons different?

   ....

5. Name two alkanes which are gases and two alkanes which are liquids at room temperature.

   ....

6. Name three isomers of pentane.

   ....

7. Which one has higher b.p. *n*-butane or *n*-pentane? Explain.

   ....

8. Write the balanced chemical equation for the complete combustion of propane.

   ....

26.2 Alkenes

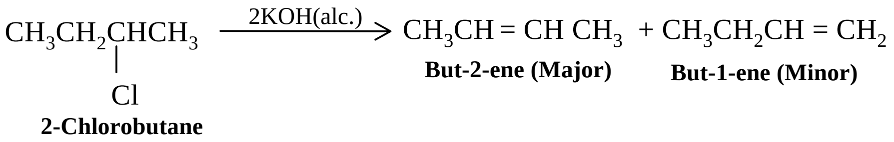
These are unsaturated hydrocarbons containing at least one double bond between two carbon atoms. The hydrocarbons of this class are also called **olefines** (*olefiant* = oil forming).

26.2.1 Methods of Preparation

In the laboratory, alkenes are generally prepared either from haloalkanes (alkyl halides) or alcohols.

1. From Haloalkanes: Halaoalkanes are converted to alkenes by dehydrohalogenation. The process of removal of halogen acid like HCl, HBr or HI from the adjacent carbon atoms of alkyl halides, when reacted with alcoholic solution of potassium hydroxide, is called *dehydrohalogenation*.

$$\underset{\textbf{Chloroethane}}{CH_3 — CH_2 — Cl} + KOH(alc.) \rightarrow \underset{\textbf{Ethene}}{CH_2 = CH_2} + KCl + H_2O$$



$$CH_3CH_2\underset{\underset{Cl}{|}}{C}HCH_3 \xrightarrow{2KOH(alc.)} CH_3CH=CH\,CH_3 + CH_3CH_2CH=CH_2$$

2-Chlorobutane **But-2-ene (Major)** **But-1-ene (Minor)**

The major product is formed according to the Saytzeff's Rule.

Saytzeff's Rule : ***It states that when an alkyl halide reacts with alcoholic solution of potassium hydroxide and if two alkenes are possible, then the one which is more substituted, will be the major product.*** In the above example, but-2-ene is the major product because it contains two alkyl groups attached to the –C=C– group.

2. From Alcohols : Alkenes can be prepared from alcohols by dehydration in the presence of a suitable dehydrating agent such as (i) Al_2O_3 or (ii) concentrated H_2SO_4.

$$CH_3-CH_2-OH \xrightarrow[623-633K]{Al_2O_3} CH_2=CH_2+H_2O$$

Ethanol **Ethene**

$$CH_3-CH_2-OH \xrightarrow[433K]{conc.\ H_2SO_4} CH_2=CH_2+H_2O$$

Ethanol **Ethene**

In the dehydration of higher alcohols, the major product obtained is according to the Saytzeff's Rule.

26.2.2 Physical Properties of Alkenes

Some important physical properties of alkanes are as follows:

Physical State : Unbranched alkenes containing upto four carbon atoms are gases and containing five to sixteen carbon atoms are liquids while those with more than 16 carbon atoms are solids.

Boiling Points : The boiling points of alkenes increase with molecular mass as is shown in Table 26.1.

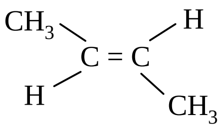
Table 26.1 : Boiling points of Alkenes

Alkene	Ethene	Propene	But-1-ene	Pent-1-ene	Hex-1-ene
b.p. (K)	169	226	267	303	337

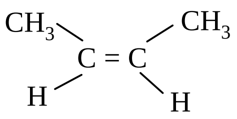
The increase in boiling point can be attributed to the van der Waals forces which increases with number of carbon atoms of the alkene. The branched chain alkenes have lower boiling points than those of straight chain isomers.

Melting Point : In alkenes, there is increase in the melting point with the increase in molecular mass. In the case of isomeric alkenes, the ***cis*** and ***trans*** isomers have different melting points.

For example



***trans*-But-2-ene**
(m.p. 167 K)



***cis*-But-2-ene**
(m.p. = 134 K)

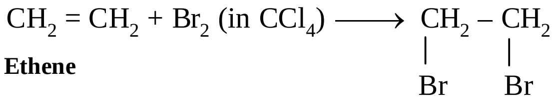
26.2.3 Chemical Properties of Alkenes

1. **Addition Reactions :** The chemical reactions in which a molecule adds to another molecule are called an *addition reaction*. These reactions are characteristic of unsaturated compounds like alkenes and alkynes. The following reactions illustrate the addition reactions of alkenes.

(i) **Addition of Hydrogen :** Addition of hydrogen to unsaturated hydrocarbons takes place in the presence of a catalyst like Ni, Pt or Pd.

$$\underset{\textbf{Ethene}}{CH_2 = CH_2} + H_2 \xrightarrow[573K]{Ni\ (Pt\ or\ Pd)} \underset{\textbf{Ethane}}{CH_3 - CH_3}$$

(ii) **Addition of Halogens :** Halogens on addition to alkenes, form 1,2-dihaloalkanes.



$$\underset{\textbf{Ethene}}{CH_2 = CH_2} + Br_2\ (\text{in } CCl_4) \longrightarrow \begin{array}{cc} CH_2 - & CH_2 \\ | & | \\ Br & Br \end{array}$$

1, 2-Dibromoethane

As a result of this addition reaction, the reddish-brown colour of Br_2 gets discharged. This reaction is also used as test for unsaturation in hydrocarbons.

(iii) **Addition of Halogen Acids (HX) :** When halogen acids are added to alkenes , hydrogen adds to one carbon atom whereas halogen atom adds to the second carbon atom of the double bond.

$$\underset{\textbf{Ethene}}{CH_2 = CH_2} \quad + \quad HBr \longrightarrow \underset{\textbf{Bromoethane}}{CH_3 - CH_2 - Br}$$

In case of unsymmetrical alkenes (which contain unequal number of H-atoms attached to the carbon atoms of the double bonds), the addition of HX takes place according to the **Markownikoff's rule. This rule states that in the addition of halogen acids to unsymmetrical alkenes, the halogen of HX goes to that carbon atom of C = C bond which already has less H-atoms attached to it.** In other words, hydrogen atom of HX goes to the carbon atom with more number of H-atoms attached to it.

$$\underset{\textbf{Propene}}{CH_3CH = CH_2} + HBr \longrightarrow \underset{\textbf{2-Bromopropane}}{CH_3CHBr\ CH_3}$$

If the addition of HBr is carried out in the presence of peroxides such as benzoyl peroxide, then the reaction takes place contrary to Markownikoff's rule. This is also known as **Anti Markownikoff's addition** or **peroxide effect**.

$$\underset{\textbf{Propene}}{CH_3CH = CH_2} + HBr \xrightarrow{\text{benzoyl peroxide}} \underset{\textbf{1 – Bromopropane}}{CH_3CH_2 - CH_2 - Br}$$

(iv) **Addition of Water :** Addition of water takes place in the presence of mineral acids like H_2SO_4.

$$CH_2 = CH_2 + H_2O \xrightarrow[\text{Heat}]{H_2SO_4} CH_3 - CH_2 - OH$$

Ethene **Ethanol**

(v) Addition of H_2SO_4

$$CH_2 = CH_2 + \text{conc. } H_2SO_4 \longrightarrow CH_3 - CH_2 - HSO_4$$

Ethene **Ethyl hydrogen sulphate**

(vi) Addition Polymerization : The process in which many molecules of an alkene add together to form a larger molecule is called **addition polymerization.**

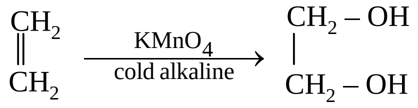
$$n\,(CH_2{=}CH_2) \xrightarrow[\text{heat, pressure}]{} \left(CH_2 - CH_2 \right)_n$$

Ethene **Polyethene**

2. **Oxidation :** The oxidation of alkenes can be done by using different oxidizing agents like $KMnO_4$, oxygen and ozone.

(i) Oxidation with $KMnO_4$

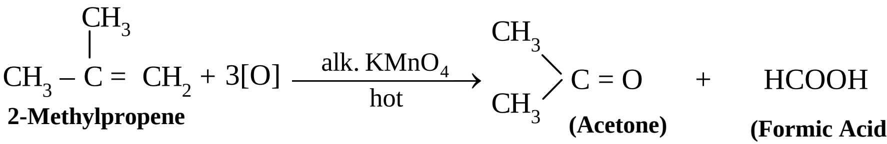
Alkenes are unsaturated hydrocarbons having Pi (®)-bond(s) between the carbon atoms, so they are easily oxidized by cold dilute alkaline solution of $KMnO_4$.



$$\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} \xrightarrow[\text{cold alkaline}]{KMnO_4} \begin{array}{l} CH_2 - OH \\ | \\ CH_2 - OH \end{array}$$

Ethene **Ethanediol**

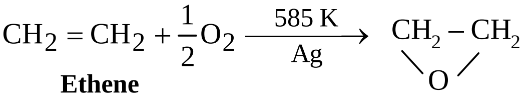
When an alkaline solution of $KMnO_4$ (Baeyer's Reagent) is added to an alkene, the purple colour of $KMnO_4$ gets discharged. This reaction is used to test unsaturation in hydrocarbons. On treatment with hot alkaline $KMnO_4$ the alkene gets oxidized to ketones or further to acids depending upon its structure. This happens due to the breaking of carbon-carbon double bond.



$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2 + 3[O] \xrightarrow[\text{hot}]{\text{alk. } KMnO_4} \begin{array}{l} CH_3 \\ CH_3 \end{array}\!\!\rangle C = O \quad + \quad HCOOH$$

2-Methylpropene **(Acetone) Propanone** **(Formic Acid) Methanoic acid**

(ii) Oxidation with Oxygen : Ethene on oxidation with oxygen in the presence of silver (Ag) gives epoxyethane. The reaction is shown below:



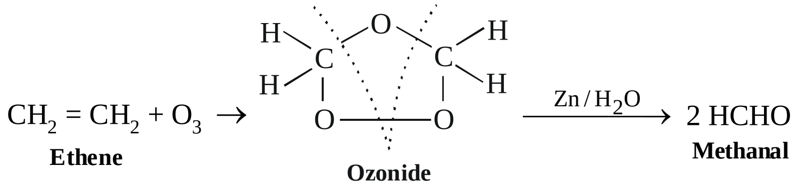
$$CH_2 = CH_2 + \frac{1}{2}O_2 \xrightarrow[\text{Ag}]{585\text{ K}} CH_2 - CH_2 \text{ (bridged by O)}$$

Ethene **Epoxyethane**

(iii) Combustion : The oxidation reaction, in which carbon dioxide and water are formed along with the liberation of heat and light, is called **combustion.**

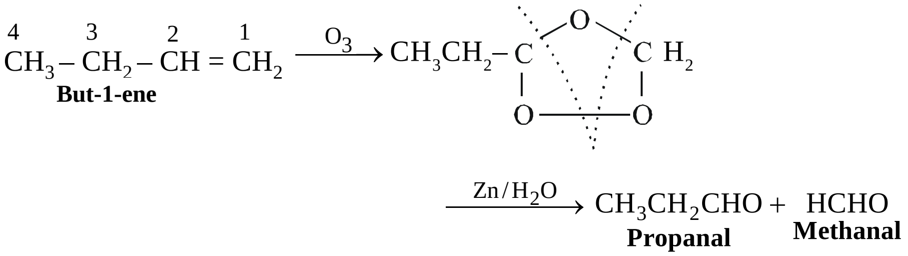
$$CH_2 = CH_2 + 3\,O_2 \xrightarrow{\text{heat}} 2\,CO_2 + 2\,H_2O \qquad \Delta H = -1411 \text{ KJ mol}^{-1}$$

(iv) Oxidation with Ozone : Ozone adds to the alkene forming ozonide. The ozonide when further reacted with water in the presence of zinc dust, forms aldehydes or ketones, or both.

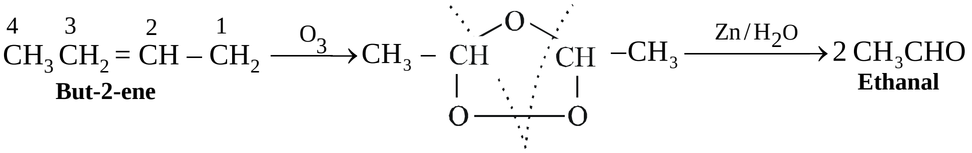


This process of addition of ozone to an unsaturated hydrocarbon followed by hydrolysis is called **ozonolysis.**

Ozonolysis can be used for the determination of the position of double bonds in alkenes by analysing the products formed i.e. aldehydes and ketones. This is explained below.



When but-1-ene is oxidized with ozone and the ozonide formed is hydrolysed, we get one mole of propanal and one mole of methanal, showing that the double bond is between carbon atom 1 and 2. Whereas but-2-ene on oxidation with ozone, followed by hydrolysis, gives two moles of ethanal, showing that the double bond is present between carbon atoms 2 and 3 as shown below.



26.2.4 Uses of Alkenes

Ethene is used for making mustard gas, which is a poisonous gas used in warfare. It is also used for artificial ripening of fruits, as a general anaesthetic and for producing other useful materials such as polythene, ethanal, ethylene glycol (antifreeze), ethylene oxide (fumigant) etc.

Intext Questions 26.2

1. Which one has higher boiling point*: cis* but-2-ene or *trans* but-2-ene?

....

2. Name the products formed when ethene is oxidized with cold alkaline solution of $KMnO_4$.

....

3. Write the conditions for hydrogenation of alkenes.

   ....

4. What happens when ethene reacts with oxygen at 575 K in presence of Ag?

   ....

26.3 Alkynes

These are also unsaturated hydrocarbons which contain atleast one triple bond between two carbon atoms. Some examples are as follows :

$$\underset{\textbf{Ethyne}}{CH \equiv CH},\quad \underset{\textbf{Propyne}}{CH_3 - C \equiv CH},\quad \underset{\textbf{But-2-yne}}{CH_3 - C \equiv C - CH_3}$$

26.3.1 Preparation of Ethyne (Acetylene):

Some important methods for preparation of ethyne are explained below.

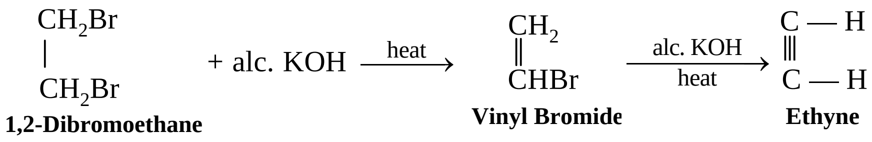
1. From Calcium Carbide: Ethyne can be prepared in the laboratory, as well as on a large scale, by the action of water on calcium carbide.

$$\underset{\textbf{Calcium carbide}}{CaC_2} + \underset{\textbf{Water}}{2\,H_2O} \longrightarrow \underset{\textbf{Ethyne}}{H - C \equiv C - H} + Ca(OH)_2$$

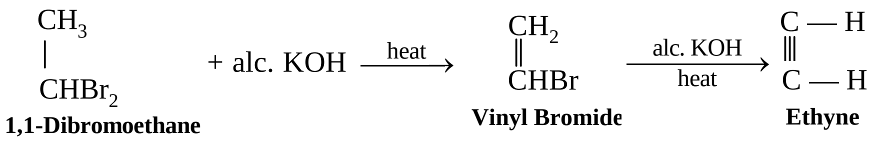
Ethyne prepared by this method generally contains the impurities of hydrogen sulphide and phosphine due to the impurities of calcium sulphide and calcium phosphide in calcium carbide.

2. Preparation of Ethyne from Dihaloalkanes

Ethyne can be prepared by refluxing *geminal* dihaloalkanes (having both halogens attached to the same carbon atom) or *vicinal* dihaloalkanes (having halogen atoms attached to the adjacent carbon atoms) with alcoholic solution of KOH.



$$\underset{\textbf{1,2-Dibromoethane}}{\begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array}} + \text{alc. KOH} \xrightarrow{\text{heat}} \underset{\textbf{Vinyl Bromide}}{\begin{array}{l} CH_2 \\ \| \\ CHBr \end{array}} \xrightarrow[\text{heat}]{\text{alc. KOH}} \underset{\textbf{Ethyne}}{\begin{array}{l} C - H \\ ||| \\ C - H \end{array}}$$



$$\underset{\textbf{1,1-Dibromoethane}}{\begin{array}{l} CH_3 \\ | \\ CHBr_2 \end{array}} + \text{alc. KOH} \xrightarrow{\text{heat}} \underset{\textbf{Vinyl Bromide}}{\begin{array}{l} CH_2 \\ \| \\ CHBr \end{array}} \xrightarrow[\text{heat}]{\text{alc. KOH}} \underset{\textbf{Ethyne}}{\begin{array}{l} C - H \\ ||| \\ C - H \end{array}}$$

3. Preparation of higher alkynes : Higher alkynes can be prepared by the reaction of alkynides of lower alkynes with primary alkyl halides.

$$R - C \equiv CH + Na \xrightarrow{\text{liq. } NH_3} R - C \equiv C^{-}Na^{+}$$

$$R - C \equiv C^{-}Na^{+} + CH_3I \longrightarrow R - C \equiv C - CH_3 + NaI$$

26.3.2 Physical Properties of Alkynes

1. First three members of alkynes are gases, the next eight members are liquids and members having more than twelve carbon atoms are solids.
2. They are colourless and odourless, except ethyne which has a garlic odour.
3. The melting points, boiling points and densities of alkynes increase with the increasing molar mass. In alkynes, there are π(pi)-electrons due to which these molecules are slightly polar. So charge separation takes place in alkynes, and hence dipoles are formed. The presence of dipoles increases the inter molecular force of attraction, and hence the boiling points of alkynes are higher than those of the corresponding alkanes.
4. Alkynes are very slightly soluble in water and soluble in acetone.

26.3.3 Chemical Properties of Alkynes

1. Addition Reactions : Some of the addition reactions of alkynes are as follows.

(i) Addition of Hydrogen : Addition of hydrogen to alkynes takes place in the presence of a catalyst like Ni, Pt or Pd.

$$CH \equiv CH + H_2 \xrightarrow[573\ K]{\text{Ni or Pt or Pd}} CH_2 = CH_2 \xrightarrow{H_2 + \text{Ni or Pt or Pd}} CH_3 - CH_3$$

(ii) Addition of Halogens : When halogens are added to alkynes, they form 1,2-dihaloalkenes and 1,1,2,2-tetrahaloalkanes.

$$\underset{\textbf{Ethyne}}{CH \equiv CH} \xrightarrow{Br_2 \text{ in } CCl_4} \underset{\textbf{1,2-Dibromoethene}}{CHBr = CHBr} \xrightarrow{Br_2 \text{ in } CCl_4} \underset{\textbf{1,1,2,2-Tetrabromoethane}}{CHBr_2 - CHBr_2}$$

(iii) Addition of Halogen Acids (HX) : Addition of HBr to ethyne is as follows :

$$\underset{\textbf{Ethyne}}{CH \equiv CH} \xrightarrow{HBr} \underset{\textbf{Bromoethene}}{CH_2 = CHBr} \xrightarrow{HBr} \underset{\textbf{1,1–Dibromoethane}}{CH_3 - CHBr_2}$$

(iv) Addition of Water : Addition of water takes place in the presence of mineral acids like H_2SO_4 and in the presence of Hg^{2+} as the catalyst.

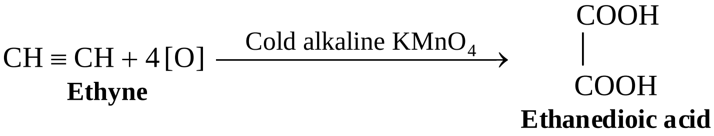
$$\underset{\textbf{Ethyne}}{CH \equiv CH + H_2O} \xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4} \underset{\substack{\textbf{Vinyl Alcohol}\\ \textbf{(Unstable)}}}{[CH_2 = CHOH]} \xrightleftharpoons{\text{Rearrangement}} \underset{\textbf{Ethanal}}{CH_3CHO}$$

(v) Addition of H_2SO_4: Conc. H_2SO_4 adds to ethyne as shown below.

$$CH \equiv CH \xrightarrow{\text{conc. } H_2SO_4} \underset{\textbf{Vinyl hydrogen sulphate}}{CH_2 = CHHSO_4} \xrightarrow{H_2SO_4} \underset{\textbf{Ethylidene hydrogen sulphate}}{CH_3 - CH\ (HSO_4)_2}$$

2. Oxidation : Alkynes undergo oxidation with oxygen, $KMnO_4$ and ozone.

(i) **Oxidation with $KMnO_4$**



$$\underset{\textbf{Ethyne}}{CH \equiv CH + 4[O]} \xrightarrow{\text{Cold alkaline } KMnO_4} \underset{\textbf{Ethanedioic acid}}{\begin{array}{c} COOH \\ | \\ COOH \end{array}}$$

The colour of alkaline solution of $KMnO_4$ is discharged on reaction with alkynes. Alkynes on heating with alkaline $KMnO_4$ give carboxylic acids.

$$R - C \equiv C - R' \xrightarrow[\text{heat}]{KMnO_4 + KOH} RCOOH + R'COOH$$

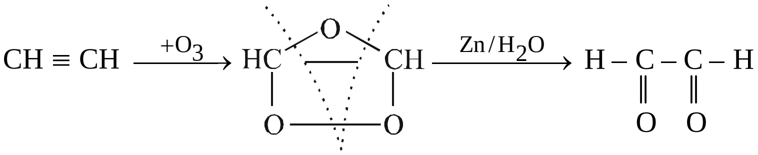
However, ethyne, on similar treatment, gives carbon dioxide and water.

$$CH \equiv CH + 4\,[O] \xrightarrow[\text{heat}]{KMnO_4 + KOH} (COOH)_2 \xrightarrow[\text{Heat}]{[O]} 2\,CO_2 + H_2O$$

Combustion : Combustion of ethyne in excess of oxygen or air gives carbon dioxide and water as shown below :

$$2\,C_2H_2 + 5\,O_2 \xrightarrow{\text{heat}} 4\,CO_2 + 2\,H_2O \quad \Delta H = -1300 \text{ KJ mol}^{-1}$$

Ozonolysis : On ozonolysis, alkynes give dicarbonyl compounds at the position of C≡C without breaking the chain of carbon atoms as shown below :



3. **Formation of Acetylides :** Ethyne forms precipitates of copper and silver acetylides when passed through ammonical solution of cuprous chloride and ammonical silver nitrate, respectively.

$$CH \equiv CH + 2Cu(NH_3)_2 \longrightarrow \underset{\textbf{Cuprous acetylide (red)}}{CuC \equiv CCu} + 2\,NH_4^+ + 2\,NH_3$$

$$CH \equiv CH + 2Ag(NH_3)_2 \longrightarrow \underset{\textbf{Silver acetylide (white)}}{AgC \equiv CAg} + 2\,NH_4^+ + 2\,NH_3$$

26.3.4 Acidic Nature of Ethyne

The acidic nature of hydrocarbons can be determined with the help of the percentage (%) of *s*-character of the hydrocarbon. The greater the percentage of *s*-character of a hydrocarbon, the more will be its acidic nature.

Table 26.2 : % *s*-Character of hyrid orbitals in Hydrocarbons

Hydrocarbon	Type of hybridization	(%) s-character
Alkanes	sp^3	25%
Alkenes	sp^2	33.3%
Alkynes	sp	50%

As alkynes have 50% *s*- character, they are the most acidic in nature. An *sp*-hybridized carbon atom is more electronegative than sp^2 or sp^3 carbon atoms. Due to greater electronegativity of *sp* hybridized carbon atom in ethyne, hydrogen atom is less tightly held by the carbon and hence, it can be removed as a proton (H^+) by a strong base like sodium metal and sodamide. **The following reactions of ethyne with sodium and sodamide confirm its acidic nature.** In these reactions, disodium acetylide is formed.

$$\underset{\textbf{Ethyne (Acetylene)}}{H-C\equiv C-H} + 2\,Na \xrightarrow{\text{Heat}} \underset{\textbf{Disodium Acetylide}}{Na-C\equiv C-Na} + H_2$$

$$\underset{\textbf{Ethyne}}{H-C\equiv C-H} + \underset{\textbf{Sodamide}}{2\,NaNH_2} \xrightarrow{\text{Heat}} \underset{\textbf{Disodium Acetylide}}{Na-C\equiv C-Na} + 2\,NH_3$$

26.3.5 Uses of Alkynes

Ethyne (acetylene) is used for producing oxyacetylene flame (2800ºC) which is used for for welding and cutting of iron and steel. It is also used for artificial ripening of fruits and vegetables. It also finds use in the production of a number of other organic compounds such as ethanal, ethanoic acid, ethanol, synthetic rubbers and synthetic fibre *orlon*.

26.3.6 Distinction Between Alkanes, Alkenes and Alkynes

The folloiwng table shows different tests for distinction between alkanes, alkenes and alkynes :

Table 26.3 : Tests for identification of alkanes, alkenes and alkynes

S.No	Test	Alkanes	Alkenes	Alkynes
1.	Add bromine dissolved in carbon tetrachloride.	No change	Reddish brown colour of Br_2 is discharged	Reddish brown colour of Br_2 is discharged
2.	Add alkaline solution of $KMnO_4$ (Baeyer's reagent)	No change	Purple colour of $KMnO_4$ is discharged	Purple colour of $KMnO_4$ is discharged
3.	Add ammonical solution of silver nitrate	No change	No change	White ppt. of silver acetylide is formed
4.	Add ammonical solution of cuprous chloride (Cu_2Cl_2)	No change	No change	Red ppt. of cuprous acetylide is formed

Intext Questions 26.3

1. How is ethyne prepared from calcium carbide?

   ....

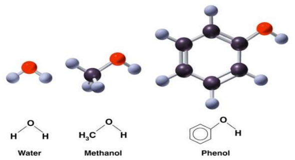
2. Give one reaction to confirm the acidic nature of ethyne.

   ....

Alcohols, Phenols and Ethers

- **Alcohols, phenols and ethers** may be viewed as organic *derivatives of water*.
- **Alcohols** **and** **phenols** have a common functional group, *the hydroxyl group, -OH*.

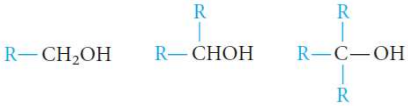
H-O-H	**R-O-H**	**Ar-O-H**	**R-O-R**	**R-O-Ar**	**Ar-O-Ar**
Water	**Alcohol**	**Phenol**	**Ether**		



- **Alcohols** are compounds whose molecules have a hydroxyl group attached to a *saturated* carbon atom.
- **Phenols** are compounds that have a hydroxyl group attached directly to a ***benzene ring .***
- **Ethers** are compounds whose molecules have an oxygen atom bonded to two carbon atom.

Classification of Alcohols and Ethers

- **Alcohols** are classified as primary (1°), secondary (2°), or tertiary (3°), depending on whether one, two, or three organic groups are connected to the hydroxyl-bearing carbon atom.



primary (1°) secondary (2°) tertiary (3°)

  - ***Methyl alcohol****, which is not strictly covered by this classification, is usually grouped with the primary alcohols.*

- **Ethers are classified as**
  - **Symmetrical ethers;**

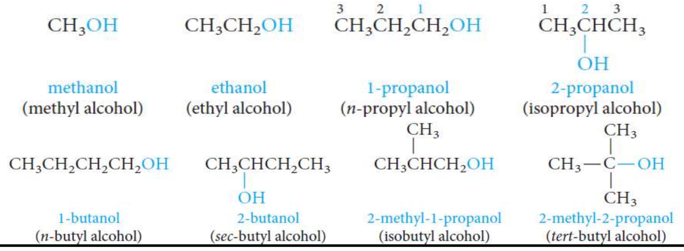
    When the organic groups attached to the oxygen are identical.
  - **Unsymmetrical ethers** (*mixed ethers*);

    When the organic groups attached to the oxygen are different.

Nomenclature of Alcohols

- The **common names** for the simplest alcohols consist of alkyl group attached to the hydroxyl function followed by the word alcohol: Alkyl *alcohol* .
- In the **IUPAC system**, alcohols are named according to the following rules.
  1. Select the longest continuous carbon chain that *contains the* -OH *group*.

     Drop the –e ending of the parent alkane and replace it by the suffix *-ol: Alkanol*
  2. When isomers are possible, the chain is numbered so as to give the functional group (-OH) the *lowest possible number*.



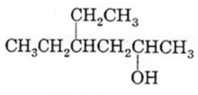
methanol (methyl alcohol); ethanol (ethyl alcohol); 1-propanol (*n*-propyl alcohol); 2-propanol (isopropyl alcohol)

1-butanol (*n*-butyl alcohol); 2-butanol (*sec*-butyl alcohol); 2-methyl-1-propanol (isobutyl alcohol); 2-methyl-2-propanol (*tert*-butyl alcohol)

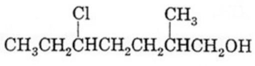
Nomenclature of Alcohols

3. When alkyl side chains or other groups are present; they are named alphabetically and their positions are indicated by a number.

The position of the functional group (-OH) is always given the lowest possible number at the end of the name.

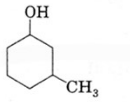

$CH_3CH_2\overset{CH_2CH_3}{C}HCH_2\underset{OH}{C}HCH_3$

4-Ethyl-2-hexanol
(*not* 3-Ethyl-5-hexanol)

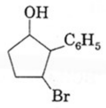

$CH_3CH_2\overset{Cl}{C}HCH_2CH_2\overset{CH_3}{C}HCH_2OH$

5-Chloro-2-methyl-1-heptanol
(*not* 3-Chloro-6-methyl-7-heptanol)

For cyclic alcohols, numbering always starts from the carbon bearing the -OH group.



3-Methylcyclohexanol
(*not* 1-Methyl-3-cyclohexanol)



3-Bromo-2-phenylcyclopentanol
(*not* 1-Bromo-2-phenyl-3-cyclopentanol)

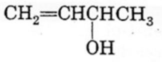
Nomenclature of Alcohols

4. With Unsaturated Alcohols; If a molecule contains both an -OH group and a C=C or C-C triple bond, the -OH group takes preference before the double or triple bonds in getting the lower number.

The name should include (if possible) both the hydroxyl and the unsaturated groups, even if this does not make the longest chain the parent hydrocarbon.

$CH_2{=}CHCH_2OH$

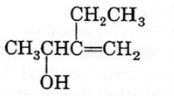
2-propen-1-ol
(allyl alcohol)


$CH_2{=}CH\underset{OH}{C}HCH_3$

3-Buten-2-ol
(*not* 1-Buten-3-ol)

$HC{\equiv}CCH_2CH_2OH$

3-Butyn-1-ol
(*not* 1-Butyn-4-ol)

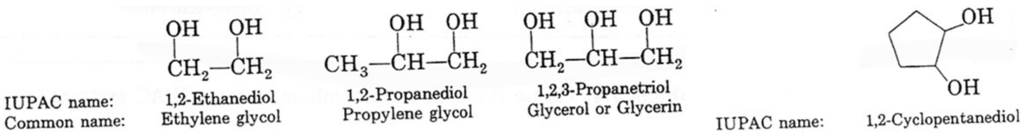

$CH_3\underset{OH}{C}H\overset{CH_2CH_3}{C}{=}CH_2$

3-Ethyl-3-buten-2-ol
(longest chain including C=C)

Nomenclature of Alcohols

○ Alcohols with More Than One Hydroxyl Group

- Compounds with two adjacent alcohol groups are called *glycols*.
  The most important example is ethylene glycol.
- Compounds with more than two hydroxyl groups are also known, and several, such as glycerol and sorbitol, are important commercial chemicals.

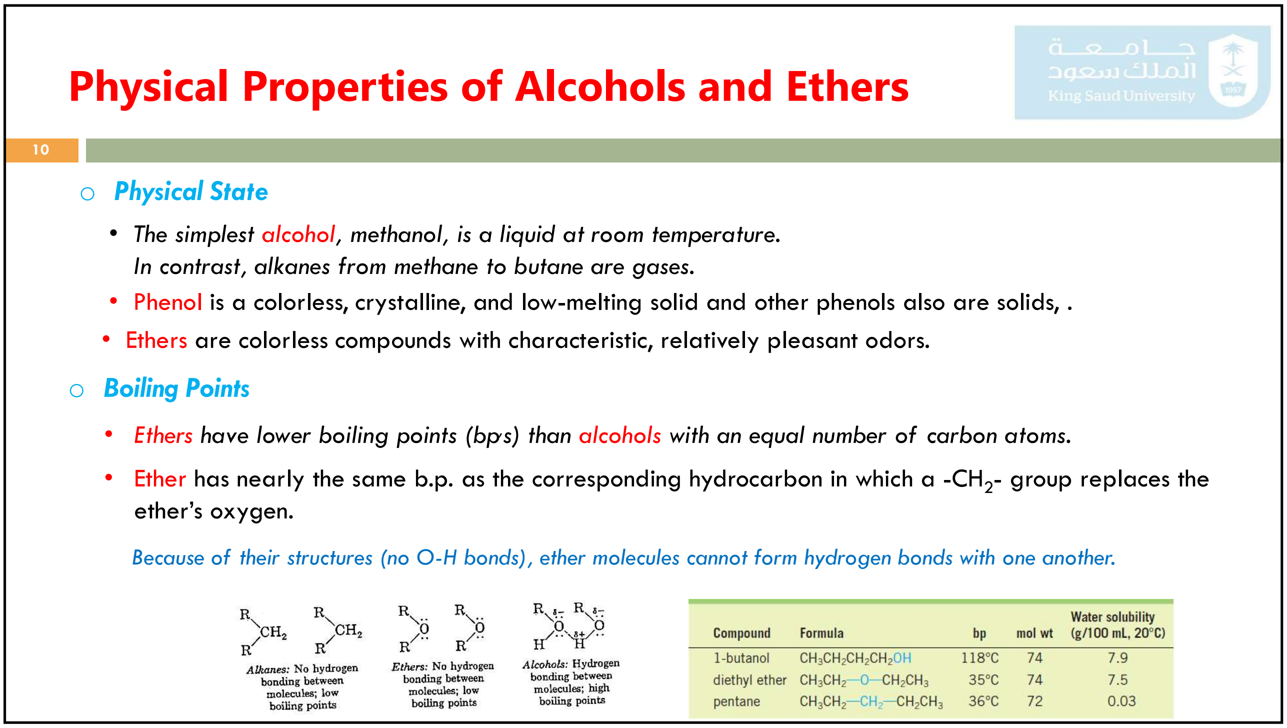


$\overset{OH}{\overset{|}{CH_2}}-\overset{OH}{\overset{|}{CH_2}}$ $CH_3-\overset{OH}{\overset{|}{CH}}-\overset{OH}{\overset{|}{CH_2}}$ $\overset{OH}{\overset{|}{CH_2}}-\overset{OH}{\overset{|}{CH}}-\overset{OH}{\overset{|}{CH_2}}$

IUPAC name: 1,2-Ethanediol 1,2-Propanediol 1,2,3-Propanetriol IUPAC name: 1,2-Cyclopentanediol

Common name: Ethylene glycol Propylene glycol Glycerol or Glycerin

- *Ethylene glycol is used as the "permanent" antifreeze in automobile radiators and as a raw material in the manufacture of Dacron.*
- *Ethylene glycol is completely miscible with water.*
- *Glycerol is a syrupy, colorless, water-soluble, high-boiling liquid with a distinctly sweet taste. Its soothing qualities make it useful in shaving and toilet soaps and in cough drops and syrups.*



Physical Properties of Alcohols and Ethers

○ ***Physical State***

- *The simplest alcohol, methanol, is a liquid at room temperature.*
  In contrast, alkanes from methane to butane are gases.
- Phenol is a colorless, crystalline, and low-melting solid and other phenols also are solids, .
- Ethers are colorless compounds with characteristic, relatively pleasant odors.

○ ***Boiling Points***

- *Ethers have lower boiling points (bp's) than alcohols with an equal number of carbon atoms.*
- Ether has nearly the same b.p. as the corresponding hydrocarbon in which a -CH_2- group replaces the ether's oxygen.

Because of their structures (no O-H bonds), ether molecules cannot form hydrogen bonds with one another.

Alkanes: No hydrogen bonding between molecules; low boiling points

Ethers: No hydrogen bonding between molecules; low boiling points

Alcohols: Hydrogen bonding between molecules; high boiling points

Compound	Formula	bp	mol wt	Water solubility (g/100 mL, 20°C)
1-butanol	$CH_3CH_2CH_2CH_2OH$	118°C	74	7.9
diethyl ether	$CH_3CH_2—O—CH_2CH_3$	35°C	74	7.5
pentane	$CH_3CH_2—CH_2—CH_2CH_3$	36°C	72	0.03

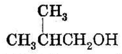
Physical Properties of Alcohols and Ethers

○ *Boiling Points*

- *Series of normal alcohols; The boiling points increase with increasing molecular weights.*
- *A comparison of boiling points among isomeric alcohols; The boiling points decrease as the number of alkyl branches from the carbinol group increases.*

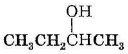
$CH_3CH_2CH_2CH_2OH$

1-Butanol
(mol wt = 74; bp = 118°C)



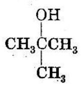
$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2OH$

2-Methyl-1-propanol
(mol wt = 74; bp = 108°C)



$CH_3CH_2\overset{\overset{\displaystyle OH}{|}}{C}HCH_3$

2-Butanol
(mol wt = 74; bp = 99.5°C)



$CH_3\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_3$

2-Methyl-2-propanol
(mol wt = 74; bp = 83°C)

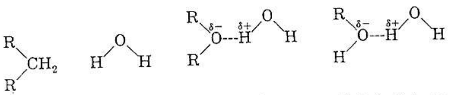
- Phenol and most other phenols have high boiling points.

Physical Properties of Alcohols and Ethers

○ *Solubility*

- *The lower alcohols are completely miscible with water.*
- *As the number of carbons in the alcohol increases, the solubility in water decreases.*
- Low-molecular-weight ethers, such as dimethyl ether, are quite soluble in water.

Ether molecules can form hydrogen bonds to water.



Alkanes: No hydrogen bonding with water; insoluble

Ethers: Hydrogen bonding with water; soluble

Alcohols: Hydrogen bonding with water; soluble

Structure	Name	Mol.wt.	Bp (° C)	Solubility in H_2O At 20 °C
$CH_3CH_2CH_3$	propane	44	−42	insoluble
CH_3OCH_3	methyl ether	46	−24	soluble
CH_3CH_2OH	ethanol	46	78	soluble
$CH_3CH_2CH_2CH_3$	*n*-butane	58	−0.5	insoluble
$CH_3CH_2OCH_3$	ethyl methyl ether	60	8	soluble
$CH_3CH_2CH_2OH$	1-propanol	60	97	soluble
$CH_3(CH_2)_3CH_3$	*n*-pentane	72	35	insoluble
$CH_3CH_2OCH_2CH_3$	ethyl ether	74	36	7.5 g/100 g
$CH_3(CH_2)_2CH_2OH$	1-butanol	74	118	7.9 g/100 g
$CH_3(CH_2)_5CH_3$	*n*-heptane	100	98	insoluble
$CH_3(CH_2)_2O(CH_2)_2CH_3$	*n*-propyl ether	102	91	0.2 g/100 g
$CH_3(CH_2)_4CH_2OH$	1-hexanol	102	157	0.6 g/100 g

- Phenol and most other phenols are slightly soluble in water .

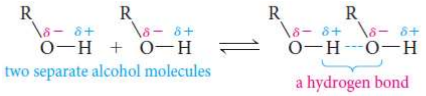
Hydrogen Bonding in Alcohols and Ethers

- The **boiling points** (bp's) of alcohols are much higher than those of ethers or hydrocarbons with similar molecular weights.

	CH_3CH_2OH	CH_3OCH_3	$CH_3CH_2CH_3$
mol wt	46	46	44
bp	+78.5°C	−24°C	−42°C

Why? Because alcohols form *hydrogen bonds* with one another.

The O-H bond is polarized by the high electronegativity of the oxygen atom and places a partial positive charge on the hydrogen atom and a partial negative charge on the oxygen atom.

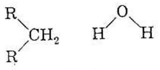


Two or more alcohol molecules thus become loosely bonded to one another through hydrogen bonds.

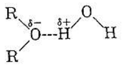
- Consequently, alcohols have relatively high boiling points because they must supply enough heat to break the hydrogen bonds before each molecule.
- Hydrogen bonds are weaker than ordinary covalent bonds.

Hydrogen Bonding in Alcohols and Ethers

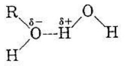
- The lower molecular-weight alcohols and ethers can form H-bond with water molecules.
- This accounts for the complete miscibility of the lower alcohols and ethers with water.



Alkanes: No hydrogen bonding with water; insoluble



Ethers: Hydrogen bonding with water; soluble



Alcohols: Hydrogen bonding with water; soluble

- However, as the organic chain lengthens and the alcohol becomes relatively more hydrocarbon like, its water solubility decreases.

Table 7.1 Boiling Point and Water Solubility of Some Alcohols

Name	Formula	bp, °C	Solubility in H_2O g/100 g at 20°C
methanol	CH_3OH	65	completely miscible
ethanol	CH_3CH_2OH	78.5	completely miscible
1-propanol	$CH_3CH_2CH_2OH$	97	completely miscible
1-butanol	$CH_3CH_2CH_2CH_2OH$	117.7	7.9
1-pentanol	$CH_3CH_2CH_2CH_2CH_2OH$	137.9	2.7
1-hexanol	$CH_3CH_2CH_2CH_2CH_2CH_2OH$	155.8	0.59

The Acidity of Alcohols and Phenols

- **Like water, alcohols and phenols are weak acids.**

  The hydroxyl group can act as a proton donor, and dissociation occurs in a manner similar to that for water

$$\mathrm{RO{-}\mathbf{H}} + \mathrm{Base} \longrightarrow \mathrm{RO{:}^{-}} + \mathrm{Base{-}\mathbf{H}}$$

Alcohol
as acid

Alkoxide ion
(conjugate base
of alcohol)

$$\mathrm{ArO{-}\mathbf{H}} + \mathrm{Base} \longrightarrow \mathrm{ArO{:}^{-}} + \mathrm{Base{-}\mathbf{H}}$$

Phenol
as acid

Phenoxide ion
(conjugate base
of phenol)

The Acidity of Alcohols and Phenols

- **Alkoxides**, the conjugate bases of alcohols, can be prepared by the reaction of an alcohol with sodium or potassium metal.

$$\underset{\text{alcohol}}{2\,\ddot{\underset{..}{\mathrm{RO}}}\!-\!\mathrm{H}} + 2\,\mathrm{K} \longrightarrow \underset{\text{potassium alkoxide}}{2\,\ddot{\underset{..}{\mathrm{RO}}}{:}^-\ \mathrm{K}^+} + \mathrm{H}_2$$

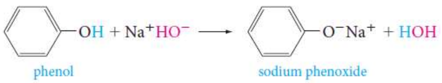
- Treatment of alcohols with sodium hydroxide does not convert them to their alkoxides.

This is because alkoxides are stronger bases than hydroxide ion, so the reaction goes in the reverse direction.

Since alcohols are weaker acids than water, it is not possible to form the salt of an alcohol in aqueous alkaline solutions.

- Treatment of phenols with sodium hydroxide converts them to phenoxide ions.

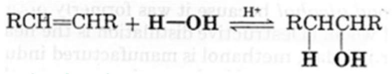
$$\mathrm{ROH} + \mathrm{Na^+HO^-} \not\rightleftarrows \mathrm{RO^-Na^+} + \mathrm{H_2O}$$



Preparation of Alcohols

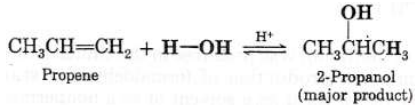
1. Hydration of Alkenes

a. Addition of water to a double bond in the presence of an *acid catalyst, H^+*.



$$RCH{=}CHR + H{-}OH \underset{}{\overset{H^+}{\rightleftharpoons}} \underset{\substack{| \quad\ | \\ H \quad OH}}{RCHCHR}$$

b. The addition follows *Markovnikov's rule*.

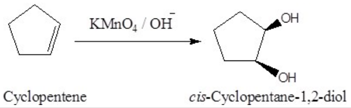


$$CH_3CH{=}CH_2 + H{-}OH \overset{H^+}{\rightleftharpoons} CH_3\overset{\substack{OH \\ |}}{C}HCH_3$$

c. *It is not possible to prepare primary alcohols* except Ethanol.

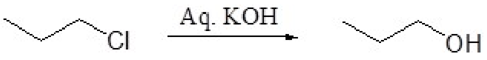
2. Oxidation of Cycloalkenes

Alkenes react with alkaline potassium permanganate to form glycols.



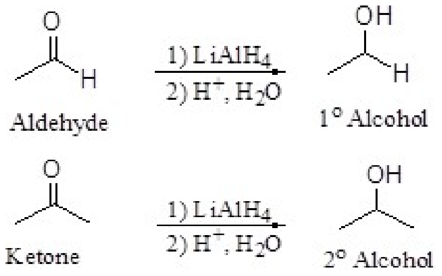
Preparation of Alcohols

○ *Nucleophilic Substitution of Alkyl Halide*



○ *Reduction of Ketones, and Aldehydes*

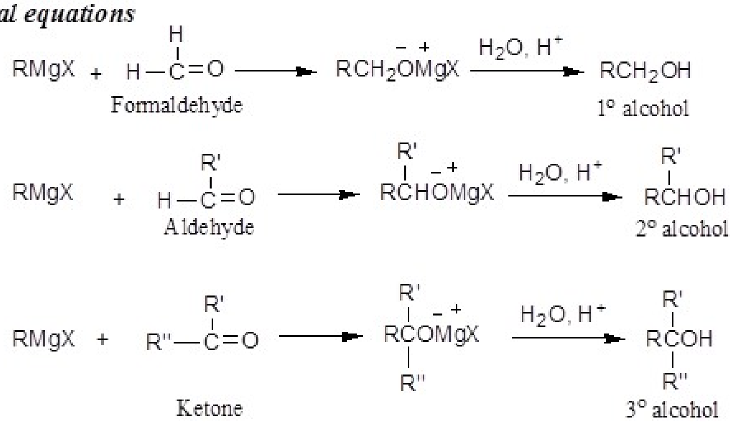
Aldehydes and ketones are easily reduced to primary and secondary alcohols, respectively.



Preparation of Alcohols

○ *Addition of Grignard's Reagent to Aldehydes and Ketones*

General equations



$$RMgX + \underset{\text{Formaldehyde}}{H-\overset{H}{\overset{|}{C}}=O} \longrightarrow RCH_2\overset{-}{O}\overset{+}{Mg}X \xrightarrow{H_2O,\ H^+} \underset{1^\circ\text{ alcohol}}{RCH_2OH}$$

$$RMgX + \underset{\text{Aldehyde}}{H-\overset{R'}{\overset{|}{C}}=O} \longrightarrow R\overset{R'}{\overset{|}{C}}H\overset{-}{O}\overset{+}{Mg}X \xrightarrow{H_2O,\ H^+} \underset{2^\circ\text{ alcohol}}{R\overset{R'}{\overset{|}{C}}HOH}$$

$$RMgX + \underset{\text{Ketone}}{R''-\overset{R'}{\overset{|}{C}}=O} \longrightarrow R\underset{R''}{\underset{|}{\overset{R'}{\overset{|}{C}}}}\overset{-}{O}\overset{+}{Mg}X \xrightarrow{H_2O,\ H^+} \underset{3^\circ\text{ alcohol}}{R\underset{R''}{\underset{|}{\overset{R'}{\overset{|}{C}}}}OH}$$

Reactions of Alcohols, Phenols and Ethers

- **Alcohols** undergo two kinds of reactions:
  - Those that involve the breaking of the oxygen-hydrogen bond (CO-H).
  - Those that involve the rupture of the carbon-oxygen bond (C-OH).
- **Phenols** do not participate in reactions where the C-OH bond is broken.
- **Ethers** are quite stable compounds.
  - The ether linkage does not react with bases, reducing agents, oxidizing agents, or active metals.
  - *Ethers react only under strongly acidic conditions.*

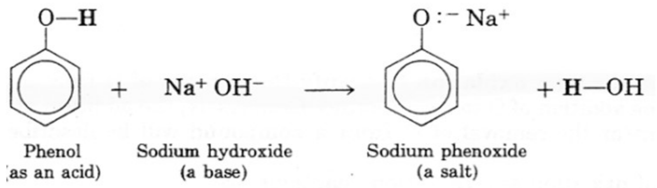
Reactions of Alcohols

A) Those that involve the breaking of the oxygen-hydrogen bond (CO-H).

1) Reactions of Alcohols and Phenols as Acids: Salt Formation.

$$\mathrm{R{-}OH} + \mathrm{Na^+\,OH^-} \longrightarrow \text{No reaction}$$

$$\underset{\text{Methanol}}{2\,\mathrm{CH_3O{-}\mathbf{H}}} + 2\,\mathrm{Na} \longrightarrow \underset{\text{Sodium methoxide}}{2\,\mathrm{CH_3O{:}^-\,Na^+}} + \mathbf{H_2}\uparrow$$



Reactions of Alcohols

A) Those that involve the rupture of the carbon-oxygen bond (C-OH).

1) Nucleophilic Substitution Reaction; The Reaction of Alcohols with Hydrogen Halides: Alkyl Halides

Alcohols react with hydrogen halides (HCl, HBr and HI) to give alkyl halides.

$$\underset{\text{alcohol}}{\mathrm{R{-}OH}} + \mathrm{H{-}X} \longrightarrow \underset{\text{alkyl halide}}{\mathrm{R{-}X}} + \mathrm{H{-}OH}$$

2) Dehydration of Alcohols: Formation of Alkenes

Alcohols can be dehydrated by heating them with strong acid.

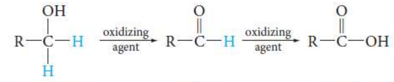
$$\underset{\text{ethanol}}{\mathrm{H{-}CH_2CH_2{-}OH}} \xrightarrow{\mathrm{H^+,\ 180^\circ C}} \underset{\text{ethylene}}{\mathrm{CH_2{=}CH_2}} + \mathrm{H{-}OH}$$

Reactions of Alcohols

B) Oxidation Reactions

Alcohols with at least one hydrogen attached to the hydroxyl-bearing carbon can be oxidized to carbonyl compounds.

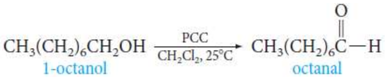
- **Primary alcohols** give aldehydes, which may be further oxidized to carboxylic acids.



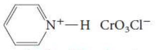
$$\mathrm{R{-}CH(OH){-}H} \xrightarrow[\text{agent}]{\text{oxidizing}} \mathrm{R{-}C({=}O){-}H} \xrightarrow[\text{agent}]{\text{oxidizing}} \mathrm{R{-}C({=}O){-}OH}$$

primary alcohol　aldehyde　carboxylic acid

  - **Primary alcohols**, oxidation can be stopped at aldehyde stage by special reagents, such as "pyridinium chlorochromate (PCC)".



$$\underset{\text{1-octanol}}{\mathrm{CH_3(CH_2)_6CH_2OH}} \xrightarrow[\mathrm{CH_2Cl_2,\ 25^\circ C}]{\mathrm{PCC}} \underset{\text{octanal}}{\mathrm{CH_3(CH_2)_6C({=}O){-}H}}$$

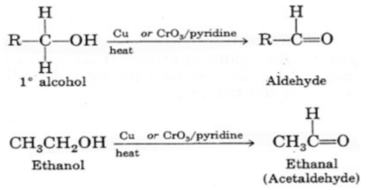


pyridinium chlorochromate (PCC)

Reactions of Alcohols

B) Oxidation Reactions

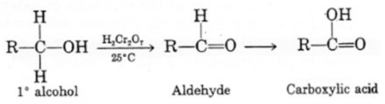
- **Primary alcohols** yield aldehydes when treated with *mild oxidizing agents* such as hot metallic copper or CrO_3 in pyridine.



$$R-\overset{H}{\underset{H}{C}}-OH \xrightarrow[heat]{Cu\ \ or\ CrO_3/pyridine} R-\overset{H}{C}=O$$

$$CH_3CH_2OH \xrightarrow[heat]{Cu\ \ or\ CrO_3/pyridine} CH_3\overset{H}{C}=O$$

- **Primary alcohols;** when treated with *stronger oxidizing agents*, such as chromic acid, $H_2Cr_2O_7$, or neutral potassium permanganate, $KMnO_4$, the intermediate aldehydes formed initially are oxidized further to carboxylic acids.

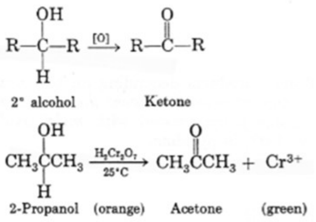


$$R-\overset{H}{\underset{H}{C}}-OH \xrightarrow[25°C]{H_2Cr_2O_7} R-\overset{H}{C}=O \longrightarrow R-\overset{OH}{C}=O$$

Reactions of Alcohols

B) Oxidation Reactions

- **Secondary alcohols**, when treated with *any of the oxidizing agents* mentioned previously, yield ketones.



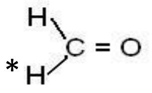
$$R-\overset{OH}{\underset{H}{C}}-R \xrightarrow{[O]} R-\overset{O}{\overset{\|}{C}}-R$$

$$CH_3\overset{OH}{\underset{H}{C}}CH_3 \xrightarrow[25°C]{H_2Cr_2O_7} CH_3\overset{O}{\overset{\|}{C}}CH_3 + Cr^{3+}$$

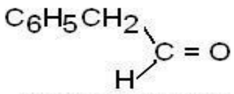
- **Tertiary alcohols**, having no hydrogen atom on hydroxyl-bearing carbon, *do not undergo oxidation*.

ALDEHYDES AND KETONES

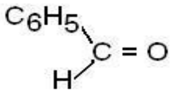
- In aldehydes, the carbonyl group is linked to either two hydrogen atom or one hydrogen atom and one carbon containing group such as alkyl, aryl or aralkyl group Examples



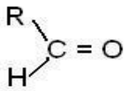
formaldehyde



phenyl acetaldehyde

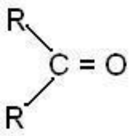


benzaldehyde

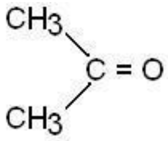


aldehyde

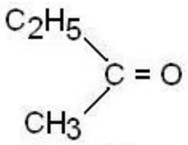
- In ketones, the carbonyl group is linked to two carbon containing groups which may be same or different alkyl, aryl group. If two R and R' groups are same, the ketone is called simple or symmetrical ketone and if R and R' are different, then ketone is known as mixed or an unsymmetrical ketone.



ketone



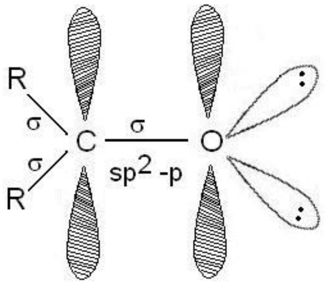
dimethyl ketone
(simple ketone)

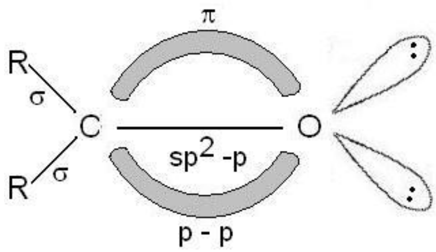


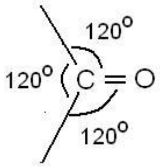
ethyl methyl ketone
(mixed ketone)

STRUCTURE

- Carbonyl carbon of both aldehyde and ketones is sp^2 – hybridised, One of the three sp^2 hybridised orbital get involved in σ- bond formation with half –filled p-orbital of oxygen atom whereas rest of the two are consumed in σ-bond formation with hydrogen and carbon depending on the structure of aldehyde or ketone.
- Unhybridised p-orbital of carbonyl carbon form π-bond with another half-filled p-orbital of oxygen atom by sideways overlapping.





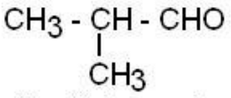


ISOMERISM IN ALDEHYDES AND KETONES

(a) Chain isomerism: Aldehydes (with 4 or more carbon atoms) and ketone (with 5 or more carbon atoms) show chain isomerism. Example

i) C_4H_8O

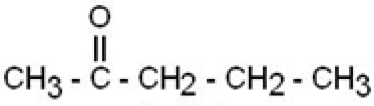
CH_3-CH_2-CH_2-CHO (butanal)



$CH_3-\underset{\underset{CH_3}{|}}{CH}-CHO$

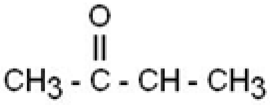
2-methylpropanal

ii) $C_5H_{10}O$



$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$

pentan-2-one

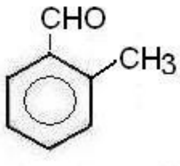


$CH_3-\overset{\overset{O}{\|}}{C}-CH-CH_3$

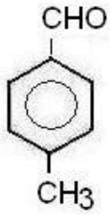
3-methylbutan-2-one

(b) Position isomerism: aliphatic aldehydes do not show position isomerism, because –CHO group is always present at the end of carbon chain.
Aromatic aldehyde show position isomerism. Example

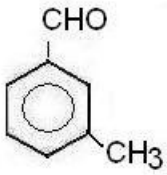
(c) Metamerism: Higher ketones show metamerism due to presence of different alkyl groups attached to the same functional group
$C_5H_{10}O$



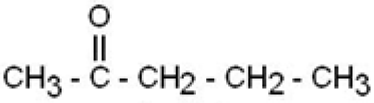
2-methylbenzaldehyde or
o - tolualdehyde



4-methylbenzaldehyde
or p-tolualdehyde

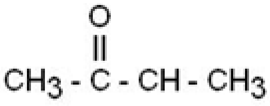


3-methylbenzaldehyde
or m-tolualdehyde



$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$

pentan-2-one



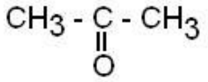
$CH_3-\overset{\overset{O}{\|}}{C}-CH-CH_3$

3-methylbutan-2-one

(d) Functional isomerism : Aldehydes and ketones show functional isomerism in them. In addition, they are also related to alcohols, ethers and other cyclic compounds. Example
C_3H_6O

ALDEHYDES AND KETONE

CH_3CH_2CHO propanal



$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ propanone

$CH_2{=}CH-CH_2-OH$ Prop-2-en-1-ol

$CH_2 = CH-OCH_3$ methoxy ethene

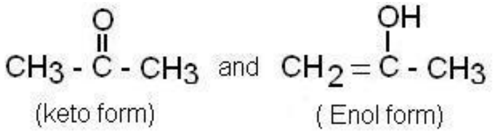
(e) Tautomerism : Aldehydes and ketones also show tautomerism

(I) C_2H_4O

$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H$ and $CH_2=\overset{\overset{\displaystyle OH}{|}}{CH}$

acetaldehyde vinyl alcohol

(II) C_3H_6O



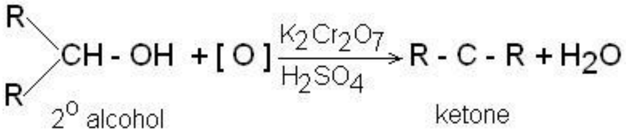
$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ and $CH_2=\overset{\overset{\displaystyle OH}{|}}{C}-CH_3$

(keto form) (Enol form)

GENERAL METHODS OF PREPARATION OF ALDEHYDES AND KETONES

1. From alcohol
   (i) Oxidation of alcohol

$$R-CH_2-OH+[O]\xrightarrow[H_2SO_4]{K_2Cr_2O_7}R\text{-}CHO+H_2O$$



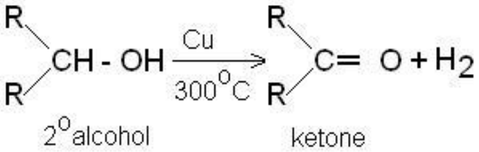
- Since the oxidizing agent used in the above reactions is a strong oxidizing agent, it oxidizes aldehydes and ketone further to carboxylic acids
- To prevent further oxidation, a mild oxidizing agent such as pyridinium chlorochromate (pcc), $CrO_3.C_5H_5N{\cdot}HCl$ or $CrO_3NH^+CrO_3Cl^-$ are used Collin's reagent [$(C_5H_5N)_2\cdot CrO_3$] can also used.

$$\underset{1^o\ \text{alcohol}}{R-CH_2OH}\xrightarrow[\text{collin's reagent}]{\text{pcc,}}\underset{\text{aldehyde}}{RCHO}$$

(ii) Catalytic dehydrogenation of alcohols

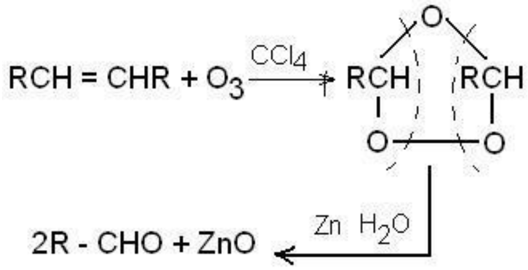
$$\underset{1^o\ \text{alcohol}}{RCH_2OH}\xrightarrow[300^oC]{Cu}\underset{\text{Aldehyde}}{RCHO}+H_2$$

ALDEHYDES AND KETONE



$$R_2CH-OH \xrightarrow[300^oC]{Cu} R_2C=O + H_2$$

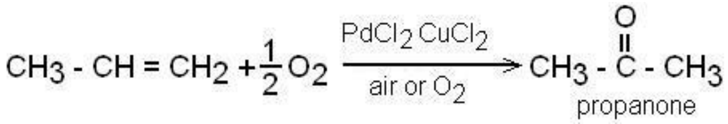
2. From alkenes
   (i) Reductive ozonolysis of alkenes.



$$RCH=CHR + O_3 \xrightarrow{CCl_4} \text{ozonide} \xrightarrow{Zn\ H_2O} 2R-CHO + ZnO$$

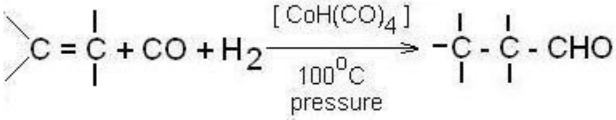
   (ii) Wacker process.

$$CH_2=CH_2 + \frac{1}{2}O_2 \xrightarrow[\text{air or } O_2]{PdCl_2\ CuCl_2} CH_3-CHO$$



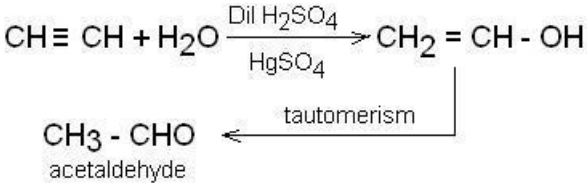
$$CH_3-CH=CH_2 + \frac{1}{2}O_2 \xrightarrow[\text{air or } O_2]{PdCl_2\ CuCl_2} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

   (iii) OXO process [Carbonylation / Hydroformylation]

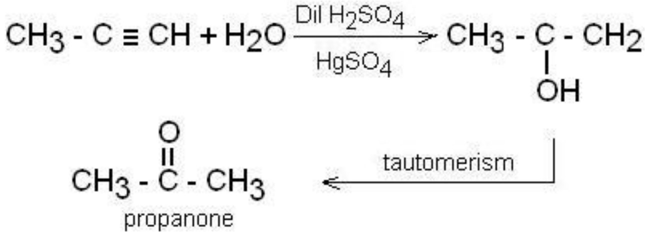


$$>C=\overset{|}{\underset{|}{C}} + CO + H_2 \xrightarrow[\substack{100^oC\\ \text{pressure}}]{[CoH(CO)_4]} -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-CHO$$

3. From alkynes

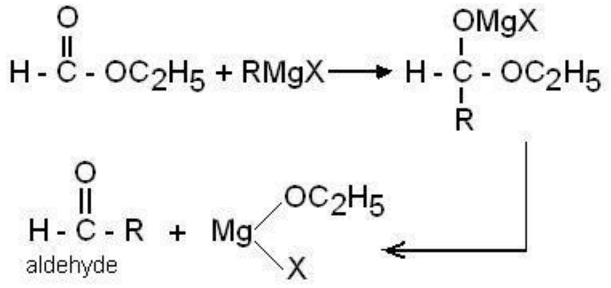


$$CH\equiv CH + H_2O \xrightarrow[HgSO_4]{Dil\ H_2SO_4} CH_2=CH-OH \xrightarrow{\text{tautomerism}} CH_3-CHO$$

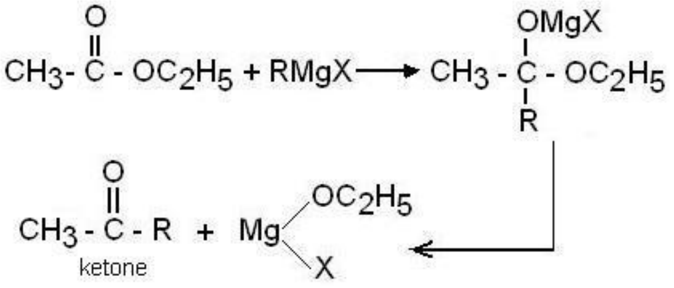


$$CH_3-C\equiv CH + H_2O \xrightarrow[HgSO_4]{Dil\ H_2SO_4} CH_3-\underset{OH}{\underset{|}{C}}-CH_2 \xrightarrow{\text{tautomerism}} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

4. From Grignard reagent
   (1) By addition to ester

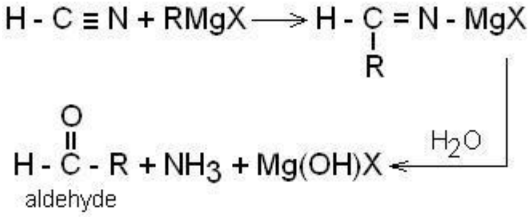


$$H-\overset{O}{\overset{\|}{C}}-OC_2H_5 + RMgX \longrightarrow H-\underset{R}{\overset{OMgX}{C}}-OC_2H_5 \longrightarrow \underset{\text{aldehyde}}{H-\overset{O}{\overset{\|}{C}}-R} + Mg\begin{matrix}OC_2H_5\\X\end{matrix}$$

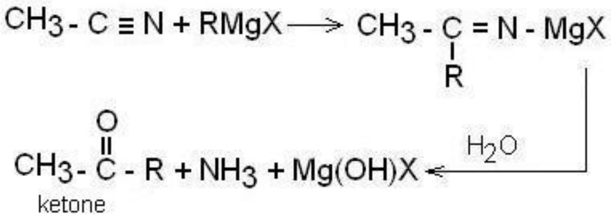


$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + RMgX \longrightarrow CH_3-\underset{R}{\overset{OMgX}{C}}-OC_2H_5 \longrightarrow \underset{\text{ketone}}{CH_3-\overset{O}{\overset{\|}{C}}-R} + Mg\begin{matrix}OC_2H_5\\X\end{matrix}$$

(iii) By addition to nitriles



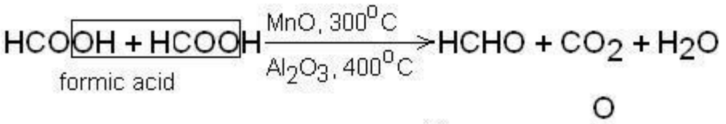
$$H-C\equiv N + RMgX \longrightarrow H-\underset{R}{C}=N-MgX \xrightarrow{H_2O} \underset{\text{aldehyde}}{H-\overset{O}{\overset{\|}{C}}-R} + NH_3 + Mg(OH)X$$



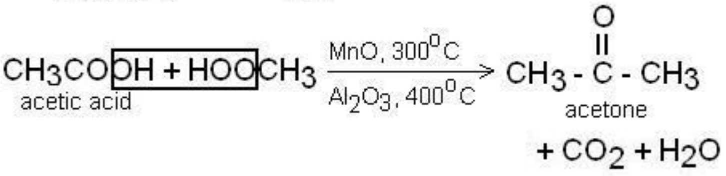
$$CH_3-C\equiv N + RMgX \longrightarrow CH_3-\underset{R}{C}=N-MgX \xrightarrow{H_2O} \underset{\text{ketone}}{CH_3-\overset{O}{\overset{\|}{C}}-R} + NH_3 + Mg(OH)X$$

5. From carboxylic acids

(i) Catalytic decomposition of carboxylic acid.

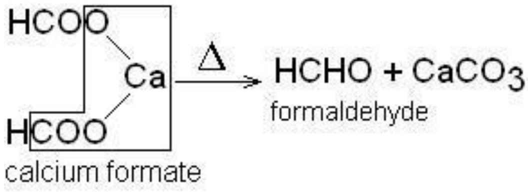


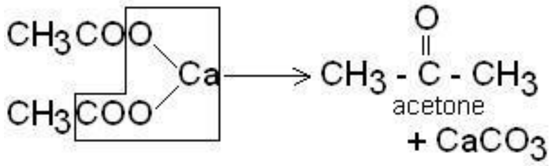
$$\underset{\text{formic acid}}{HCO\boxed{OH + HCOO}H} \xrightarrow[Al_2O_3,\ 400^0C]{MnO,\ 300^0C} HCHO + CO_2 + H_2O$$



$$\underset{\text{acetic acid}}{CH_3CO\boxed{OH + HOO}CH_3} \xrightarrow[Al_2O_3,\ 400^0C]{MnO,\ 300^0C} \underset{\text{acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} + CO_2 + H_2O$$

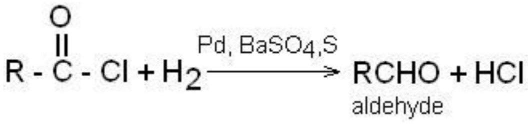
(ii) From calcium salt of carboxylic acids





6. From derivatives of carboxylic acids

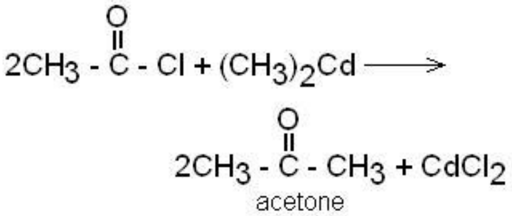
(i) Reduction of acid chlorides (Rosenmund's reaction)



$$R - \overset{\overset{O}{\|}}{C} - Cl + H_2 \xrightarrow{Pd,\ BaSO_4, S} \underset{\text{aldehyde}}{RCHO} + HCl$$

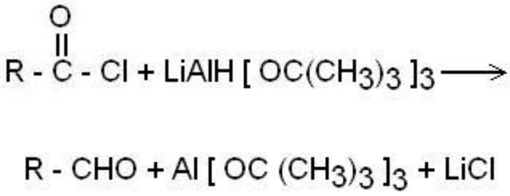
- Above reaction is known as Rosenmund's reduction and is applicable for preparation of aldehydes
- $BaSO_4$, sulphur act as poison for Pd catalyst and prevents reduction of RCHO into RCH_2OH

(ii) Reduction of acid chloride with dialkyl cadmium.



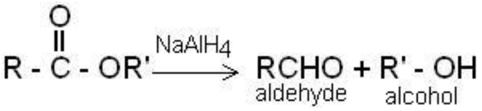
$$2CH_3 - \overset{\overset{O}{\|}}{C} - Cl + (CH_3)_2Cd \longrightarrow$$
$$\underset{\text{acetone}}{2CH_3 - \overset{\overset{O}{\|}}{C} - CH_3} + CdCl_2$$

Reduction of acid chloride into ester can also be carried out by lithium tri--butoxy aluminium hydride, $LiAlH[OC(CH_3)_3]$



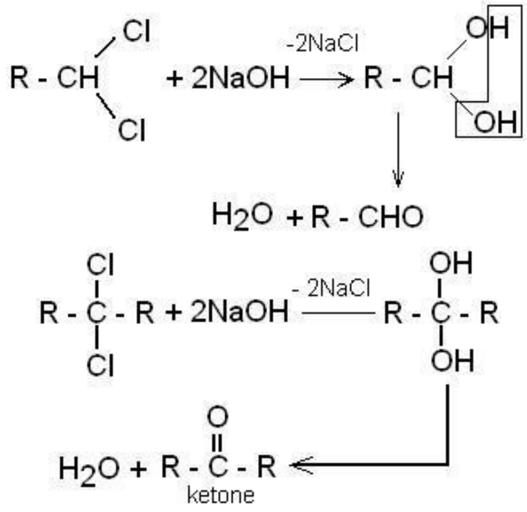
$$R - \overset{\overset{O}{\|}}{C} - Cl + LiAlH\,[\,OC(CH_3)_3\,]_3 \longrightarrow$$
$$R - CHO + Al\,[\,OC\,(CH_3)_3\,]_3 + LiCl$$

(iii) Reduction of esters

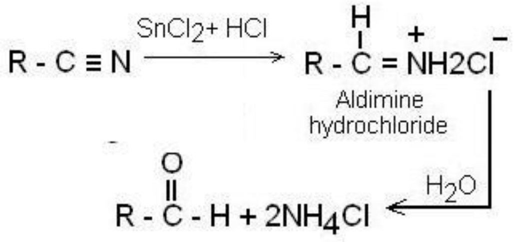


$$R - \overset{\overset{O}{\|}}{C} - OR' \xrightarrow{NaAlH_4} \underset{\text{aldehyde}}{RCHO} + \underset{\text{alcohol}}{R' - OH}$$

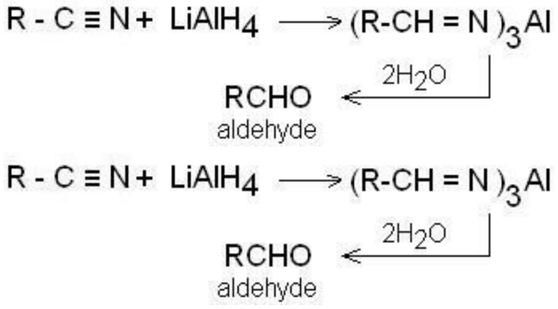
7. From gem-dihalides by hydrolysis



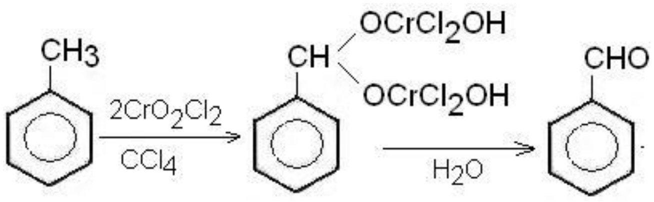
8. From nitriles by reduction
   (i) Stephen’s reduction.



   (ii) Reduction with $LiAlH_4$

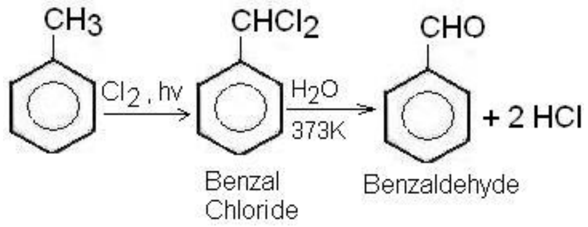


9. Preparation of aromatic carbonyl compounds.
   (i)

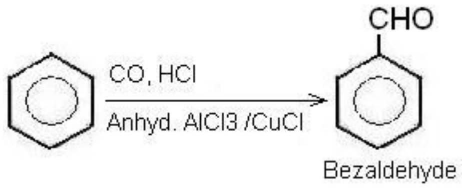


This is known as Etard reaction

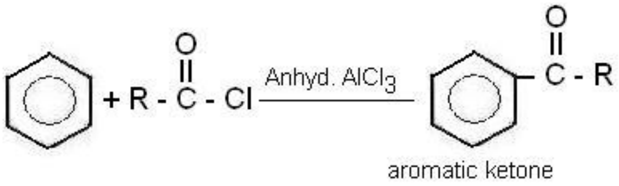
(ii) By side chain chlorination followed by hydrolysis

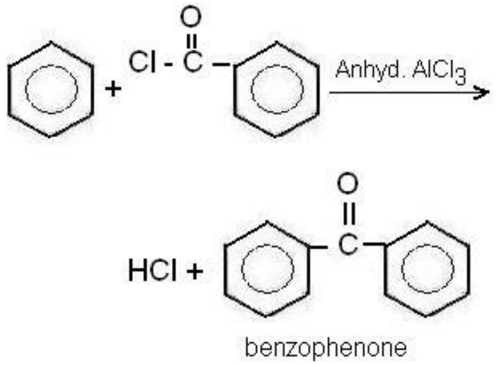


(iii) Gatterman – Koch reaction

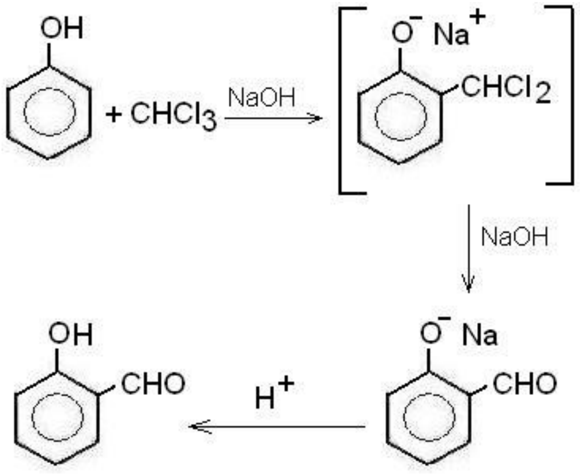


(iv) Friedel Craft Acylation





(v) Reimer – Tiemann reaction



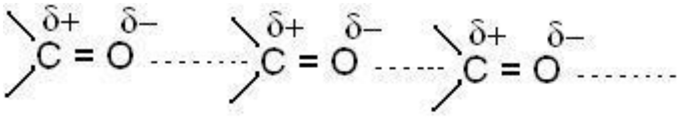
PHYSICAL PROPERTIES OF ALDEHYDES AND KETONE

1. Physical state

- Lower members of aldehydes and ketones (upto C_{10}) are colourless volatile liquids except formaldehyde which is gas at ordinary temperature
- Higher members of aldehyde and ketones are solids with fruity odour
- Lower aldehydes have unplesent odour but ketones posses pleasant smell

2. Boiling point

- Boiling point of aldehyde and ketones is slightly lower than corresponding alcohol due to lack of hydrogen bonding. However their boiling point is slightly higher than that of corresponding non-polar hydrocarbon or weakly polar ether. This may attributed to reason that aldehydes and ketones are polar compounds and thus possess intermolecular dipole-dipole interaction



- Among isomeric aldehydes and ketones, boiling point of ketones is slightly higher than that of aldehydes due to the presence of two electron donating alkyl groups making them more polar.

3. Solubility

- Lower members of aldehydes and ketones (upto C_4) are soluble in water due to H-bonding between polar carbonyl group and water.
- However, solubility decreases with increase in molecular weight
- Aromatic aldehydes and ketones are much less soluble than corresponding aliphatic aldehydes and ketones due to large benzene ring. However all carbonyl compounds are fairly soluble in organic solvents.

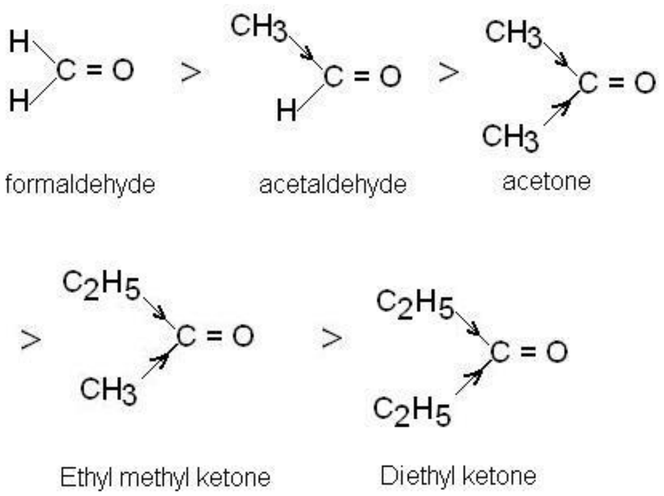
RELATIVE REACTIVITY OF ALDEHYDES AND KETONES

Aldehydes are more reactive than ketones on account of the following facts:

(a) Aliphatic aldehydes and ketones

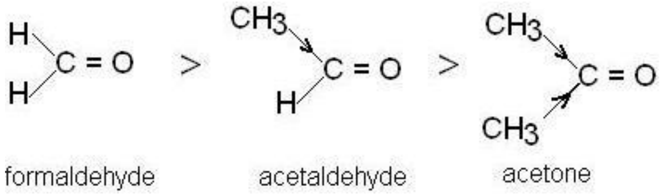
(i) Inductive effect:

The reactivity of the carbonyl group towards the addition reaction depends upon the magnitude of the positive charge on the carbonyl carbon atom. Hence, any substituent that increases the positive charge on the carbonyl carbon must increase its reactivity towards addition reactions. The introduction of negative group (-I effect) increases the reactivity, while introduction of alkyl group (+I effect) decreases the reactivity, therefore, greater the number of alkyl groups attached to the carbonyl group and hence, lower is its reactivity towards nucleophilic addition reactions. Thus, the following decreasing order of reactivity is observed



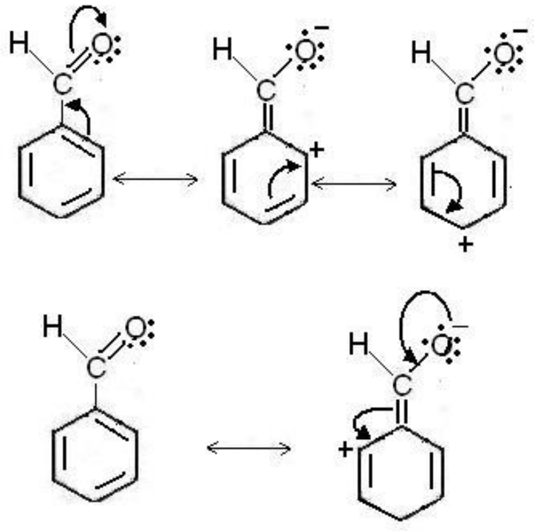
(ii) Steric effect

- In formaldehyde there is no alkyl group while in all other aldehyde there is one alkyl group so here the nucleophile attack is relatively more easy but in ketones there are two alkyl groups attached to carbonyl group and these causes hinderance, to the attacking group. This factor is called steric hinderance (crowding). In other words the hindrance increases, the reactivity decreases accordingly. Thus order of reactivity is



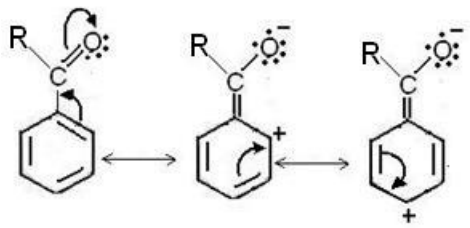
(b) Aromatic aldehydes and ketones

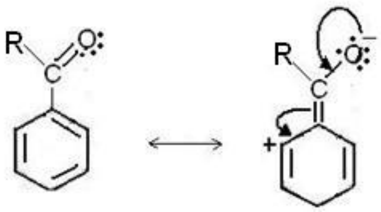
- In general, aromatic aldehydes and ketones are less reactive than the corresponding aliphatic aldehydes and ketones. It is due electron releasing resonance effect of bezene ring



ALDEHYDES AND KETONE

- Due to electron withdrawing resonance effect (-R effect) of benzene ring, the magnitude of positive charge on carbonyl group decreases and consequently it becomes less susceptible to nucleophilic attack.



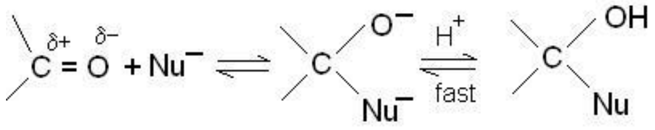


The order of reactivity of aromatic aldehydes and ketones is

$C_6H_5CH_2CHO$	>	C_6H_5CHO	>	$C_6H_5COCH_3$	>	$C_6H_5COC_6H_5$
phenyl acetaldehyde		benzaldehyde		acetophenone		benzophenone

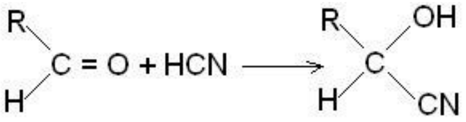
CHEMICAL PROPERTIES OF ALDEHYDES AND KETONES

Nucleophilic addition reaction

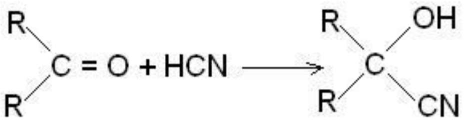


In this reaction carbon atom of carbonyl group changes from sp^2 to sp^3 hybridised

(i) Addition of hydrogen cyanide (HCN)



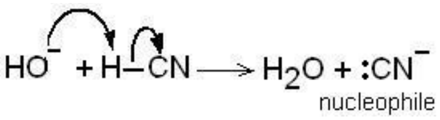
cyanohydrien



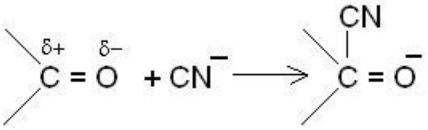
cyanohyrin

Mechanism

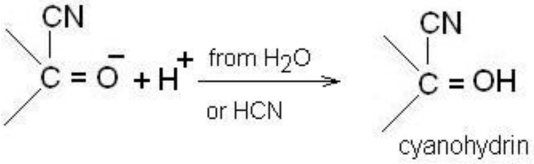
Step I : The hydrogen cyanide interacts with the base to form nucleophile



Step II : The nucleophile attacks the carbonyl carbon to form an anion

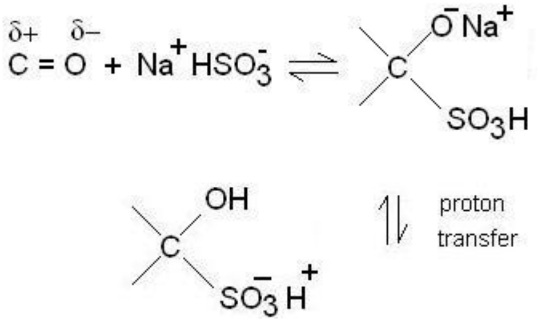


StepIII: The proton from the solvent (usually water) combines with the anion to form cyanohydrin.

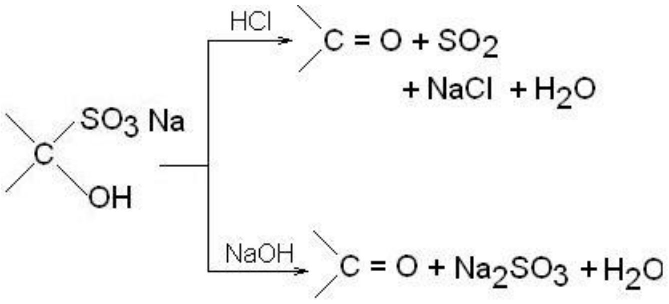


Cyanohydrins are formed by all aldehydes but in ketones, only acetone, butanone, 3-pethenone and pinacolone form cyanohydrins.

(ii) Addition of sodium bisulphate ($NaHSO_4$)

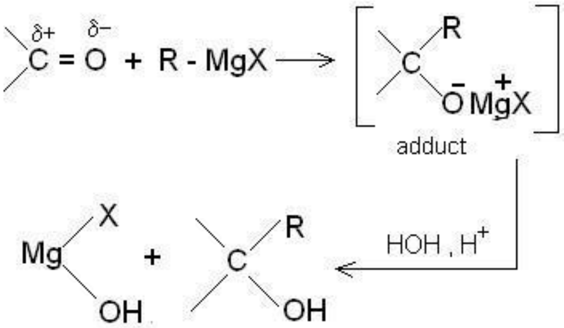


- All ketones do not undergo this reaction only methyl ketone form addition product with sodium bisulphate
- On reacting the crystalline solid bisulphate derivative with dilute HCl or alkali, these adducts decompose to regenerate the original aldehyde or ketones. Hence, this reaction is used in the separation and purification of aldehydes and ketones from non-carbonyl compounds.

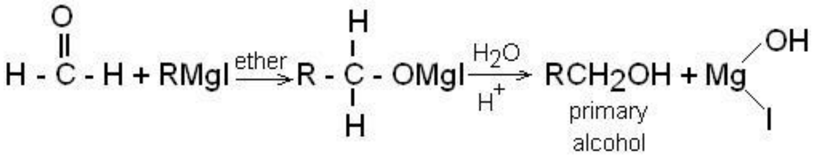


(iii) Addition of Grignard reagent

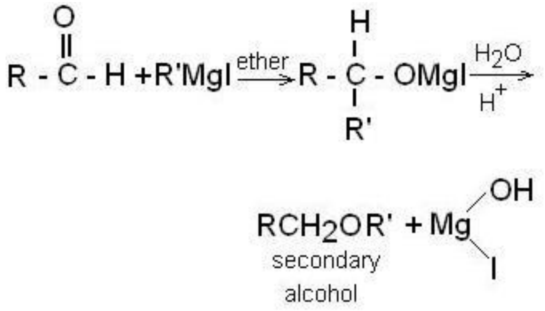
ALDEHYDES AND KETONE



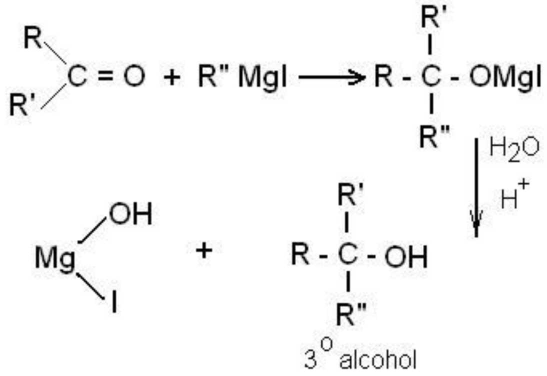
Formaldehyde form a primary alcohol



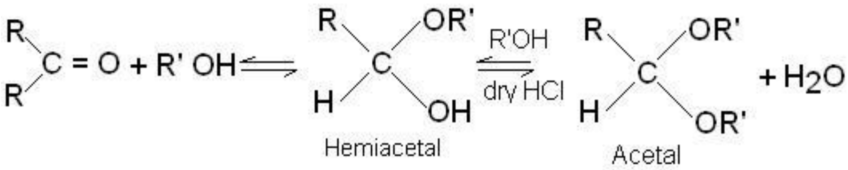
- Higher aldehydes give secondary alcohol



- Ketone give tertiary alcohols

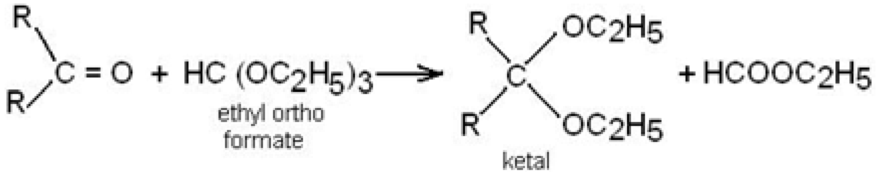


(iv) Addition of alcohols

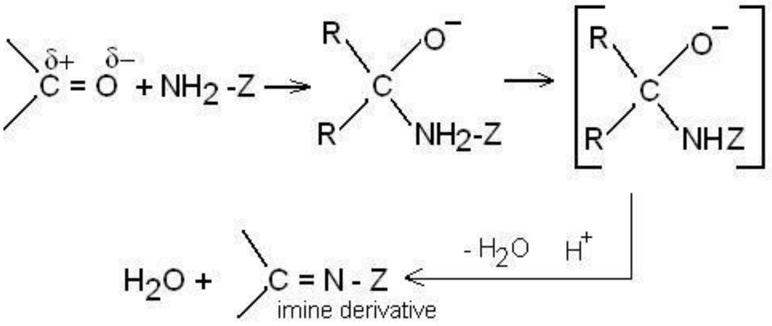


Dry HCl protonates the oxygen atom of the carbonyl compounds and therefore, increases the electrophilicity of the carbonyl carbon and hence facilitating the nucleophilic attack by the alcohol molecule. Dry HCl gas also absorbs the water produced in these reactions and thereby shifting equilibrium in forward direction.

Ketals can be prepared by treating the ketone with ethyl ortho formate



(v) Addition of ammonia derivative

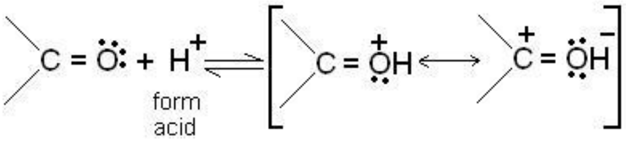


Z = OH, NH_2 , NHC_6H_5 , $NHCOCH_2$ etc.

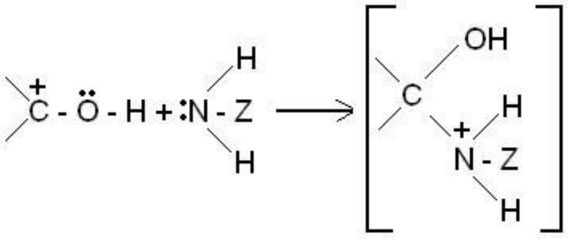
The reaction of ammonia derivatives to aldehydes and ketones is called by acids

Mechanism

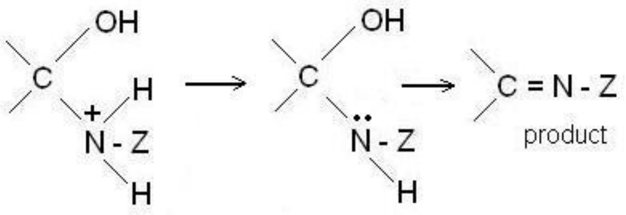
Step I: In acidic medium, the carbonyl oxygen gets protonated.



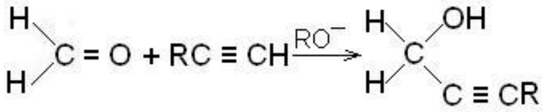
Step II : In ammonia derivatives, the nitrogen atom has a lone pair of electrons, which attack the positively charged carbonyl carbon and results in positive charge on nitrogen atom



Step III : The unstable intermediate loses a proton, H^+ and water molecule to form stable product (imines)



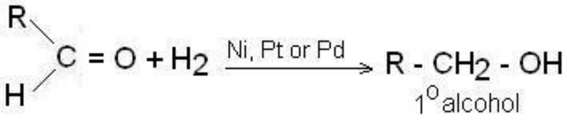
(vi) Addition of alkynes

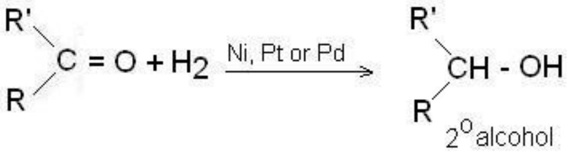


This reaction is also known as ethinylation

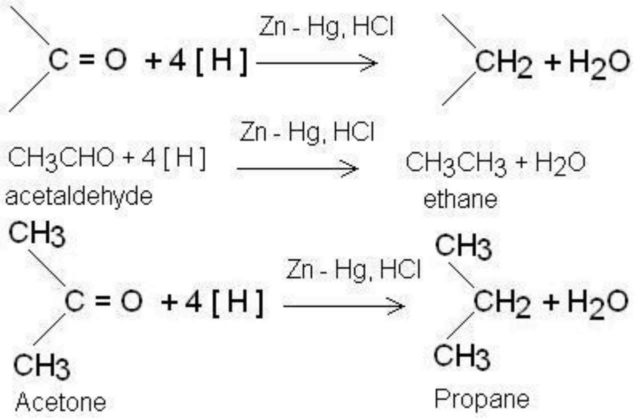
2. Reduction reactions

I. Catalytic reduction to alcohol

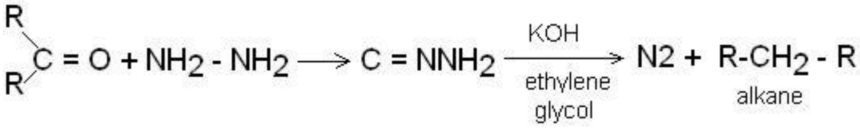


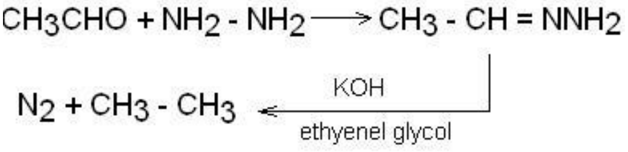


II. Clemmensen reduction



III. Wolf-Kishner reduction





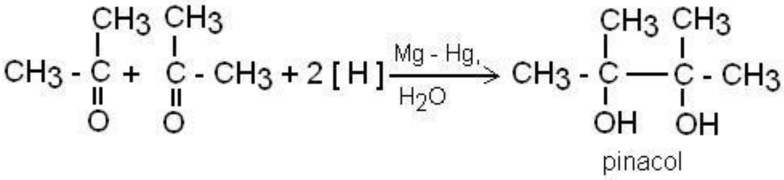
$$CH_3COCH_3 \xrightarrow[\text{ethylene glycol}]{NH_2\text{-}NH_2 + KOH} CH_3 - CH_2 - CH_3 + H_2O$$

IV. Reduction with HI + P (red)

$$CH_3 - CHO + 4HI \xrightarrow[150^0C]{\text{red P}} CH_3\text{-}CH_3 + H_2O + 2I_2$$

$$CH_3COCH_3 + 4HI \xrightarrow[150^0C]{\text{red P}} CH_3 - CH_2 - CH_3 + H_2O + 2I_2$$

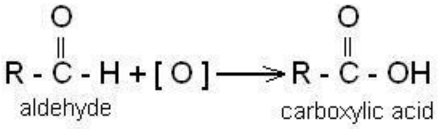
V. Reduction to pinacols



$$CH_3 - \underset{\underset{O}{\|}}{\overset{\overset{CH_3}{|}}{C}} + \underset{\underset{O}{\|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3 + 2[H] \xrightarrow[H_2O]{Mg - Hg,} \underset{\text{pinacol}}{CH_3 - \underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}} - \underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3}$$

3. Oxidation reactions

i. Oxidation with mild oxidizing agents



$$\underset{\text{aldehyde}}{R - \overset{\overset{O}{\|}}{C} - H} + [O] \longrightarrow \underset{\text{carboxylic acid}}{R - \overset{\overset{O}{\|}}{C} - OH}$$

Ketones are not oxidized by mild oxidizing agents

(a) Aldehydes reduces Tollen's reagent to metallic silver which appears as a silver mirror on wall of test tube. Thus the reaction is also known as silver mirror test.

$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow$$

$$RCOO^- + \underset{\text{silver mirror}}{2Ag\downarrow} + 4NH_3 + 2H_2O$$

(b) Reduction of Fehling's solution

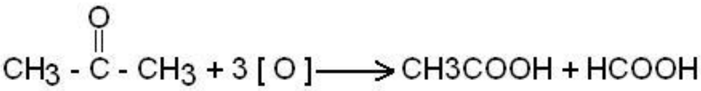
Fehling's solution is an alkaline solution of $CuSO_4$ mixed with Rochelle slat i.e. sodium potassium tartarate. Aldehydes reduces cupric ion (Cu^{2+}) of Fehling's solution to cuprous ions (Cu^+) to form red precipitate of cuprous oxide

$$RCHO + 2Cu_2^+ + 5\,OH^- \longrightarrow RCOO^- + Cu_2O + 3H_2O$$

Fehling's solution is reduced by aliphatic aldehydes only. Aromatic aldehydes and ketones so not give this reaction.

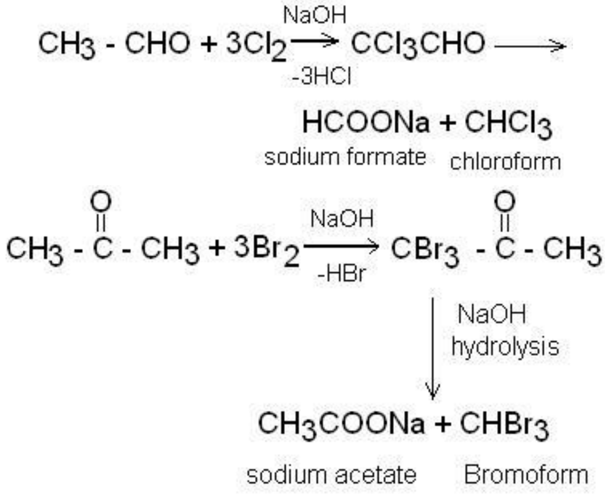
ii. Oxidation with strong oxidizing agent

$$\underset{\text{aldehyde}}{RCHO} + [O] \xrightarrow{NHO_3\text{ (conc.)}} \underset{\text{carboxylic acid}}{RCOOH}$$



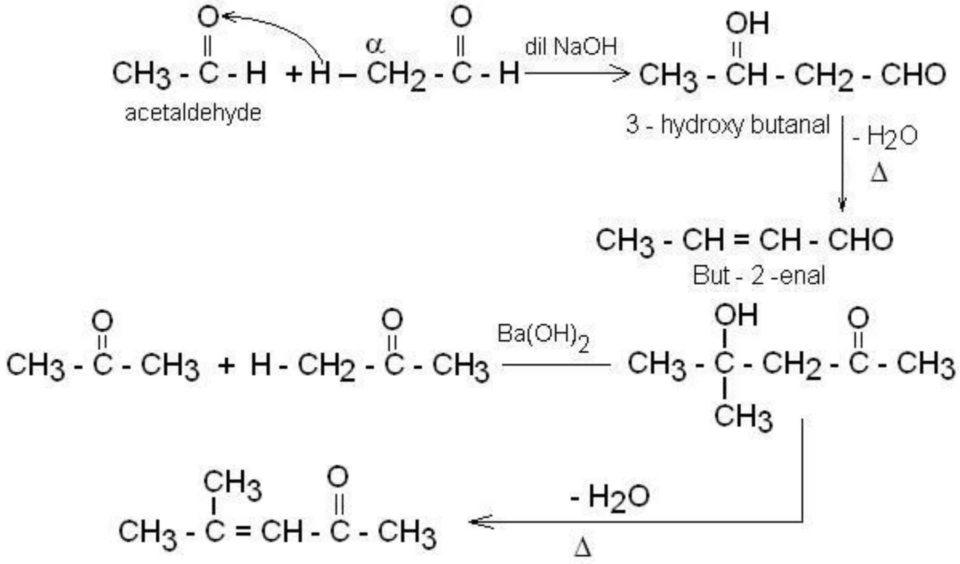
$$CH_3 - \overset{\overset{O}{\|}}{C} - CH_3 + 3[O] \longrightarrow CH3COOH + HCOOH$$

iii. Haloform reaction

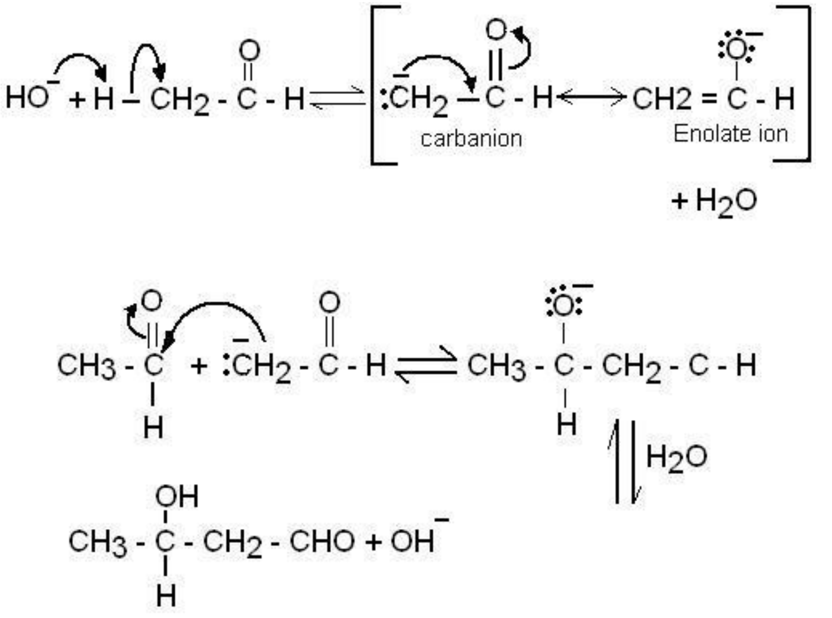


4. Condensation reactions

(1) Aldol condensation

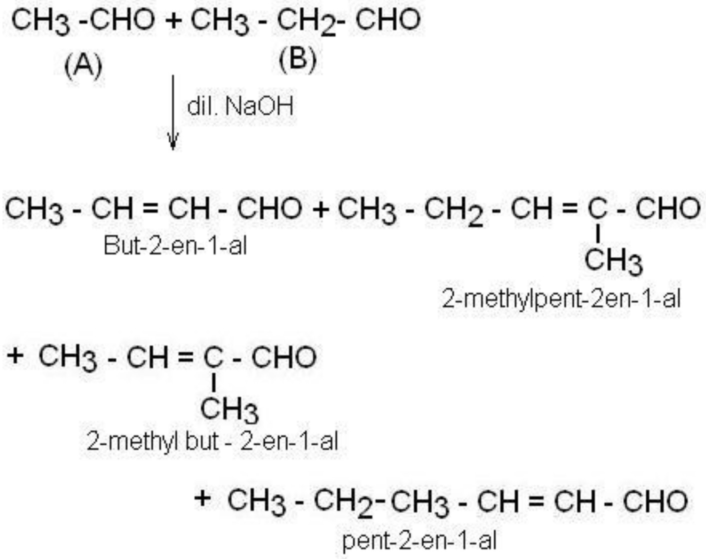


Mechanism



Aldehyde or ketones which do not contain α-hydrogen atom like formaldehyde (HCHO), benzaldehyde (C_6H_5CHO) and benzophenone ($C_6H_5COC_6H_5$) do not undergo aldol condensation.

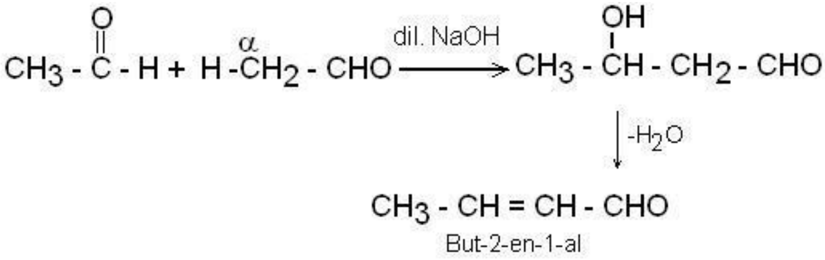
(2) Cross aldol condensation



$$\underset{(A)}{CH_3-CHO} + \underset{(B)}{CH_3-CH_2-CHO} \xrightarrow{\text{dil. NaOH}} \underset{\text{But-2-en-1-al}}{CH_3-CH=CH-CHO} + \underset{\text{2-methylpent-2en-1-al}}{CH_3-CH_2-CH=\underset{CH_3}{\underset{|}{C}}-CHO}$$

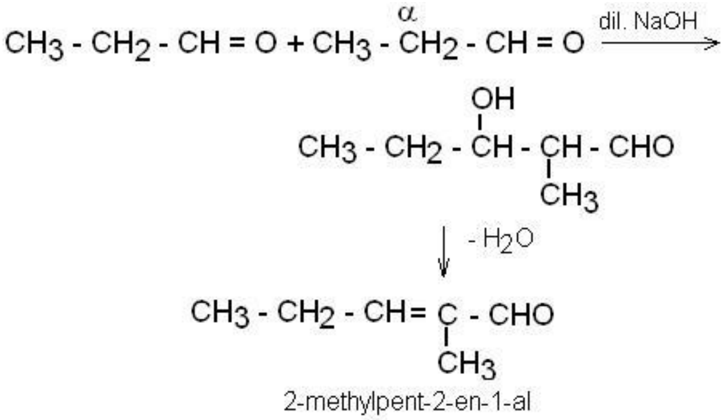
$$+ \underset{\text{2-methyl but - 2-en-1-al}}{CH_3-CH=\underset{CH_3}{\underset{|}{C}}-CHO} + \underset{\text{pent-2-en-1-al}}{CH_3-CH_2-CH_3-CH=CH-CHO}$$

 # A- A Condensation



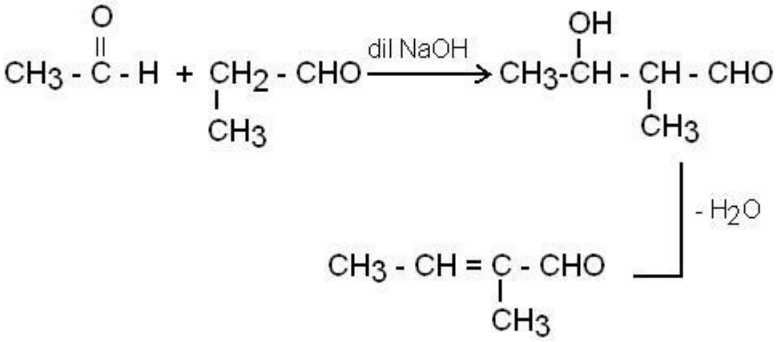
$$CH_3-\overset{O}{\overset{\|}{C}}-H + H-\overset{\alpha}{C}H_2-CHO \xrightarrow{\text{dil. NaOH}} CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-CHO \xrightarrow{-H_2O} \underset{\text{But-2-en-1-al}}{CH_3-CH=CH-CHO}$$

B-B Condensation



$$CH_3-CH_2-CH=O + CH_3-\overset{\alpha}{C}H_2-CH=O \xrightarrow{\text{dil. NaOH}} CH_3-CH_2-\overset{OH}{\overset{|}{C}H}-\underset{CH_3}{\underset{|}{C}H}-CHO \xrightarrow{-H_2O} \underset{\text{2-methylpent-2-en-1-al}}{CH_3-CH_2-CH=\underset{CH_3}{\underset{|}{C}}-CHO}$$

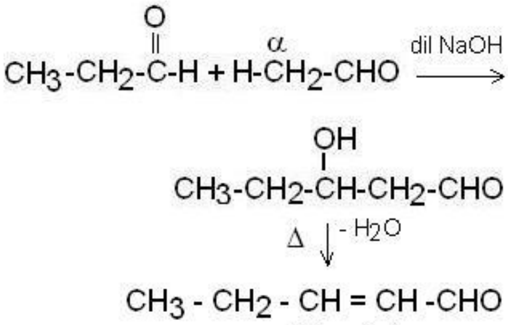
A-B Condensation



$$CH_3-\overset{O}{\overset{\|}{C}}-H + \underset{CH_3}{\underset{|}{CH_2}}-CHO \xrightarrow{\text{dil NaOH}} CH_3-\overset{OH}{\overset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CHO \xrightarrow{-H_2O} CH_3-CH=\underset{CH_3}{\underset{|}{C}}-CHO$$

2-methyl but - 2-en-1-al

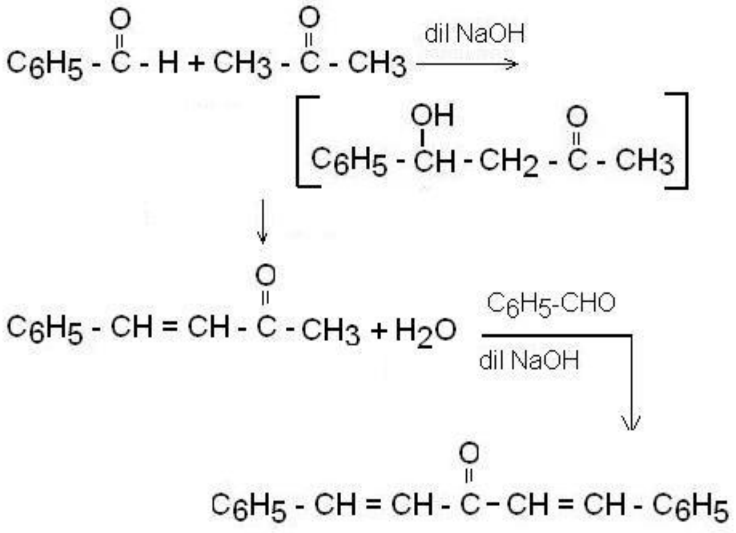
B-A Condensation



$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H + H-\overset{\alpha}{CH_2}-CHO \xrightarrow{\text{dil NaOH}} CH_3-CH_2-\overset{OH}{\overset{|}{CH}}-CH_2-CHO \xrightarrow[\Delta]{-H_2O} CH_3-CH_2-CH=CH-CHO$$

pent-2-en-1-al

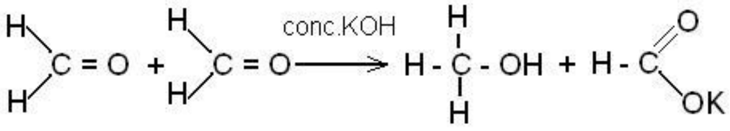
(3) Claisen – Schmidt condensation



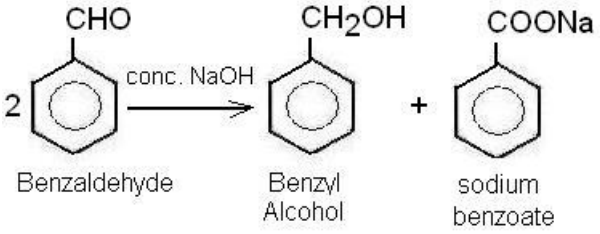
$$C_6H_5-\overset{O}{\overset{\|}{C}}-H + CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{\text{dil NaOH}} \left[C_6H_5-\overset{OH}{\overset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3\right] \rightarrow C_6H_5-CH=CH-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O \xrightarrow[\text{dil NaOH}]{C_6H_5\text{-}CHO} C_6H_5-CH=CH-\overset{O}{\overset{\|}{C}}-CH=CH-C_6H_5$$

Dibenzal acetone

5. Cannizzaro reaction

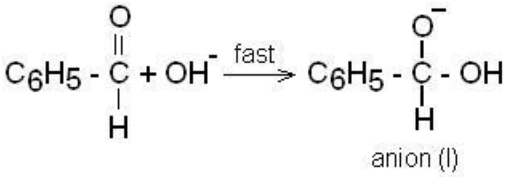


$$H_2C=O + H_2C=O \xrightarrow{\text{conc.KOH}} H-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-OH + H-C\overset{\nearrow O}{\searrow OK}$$



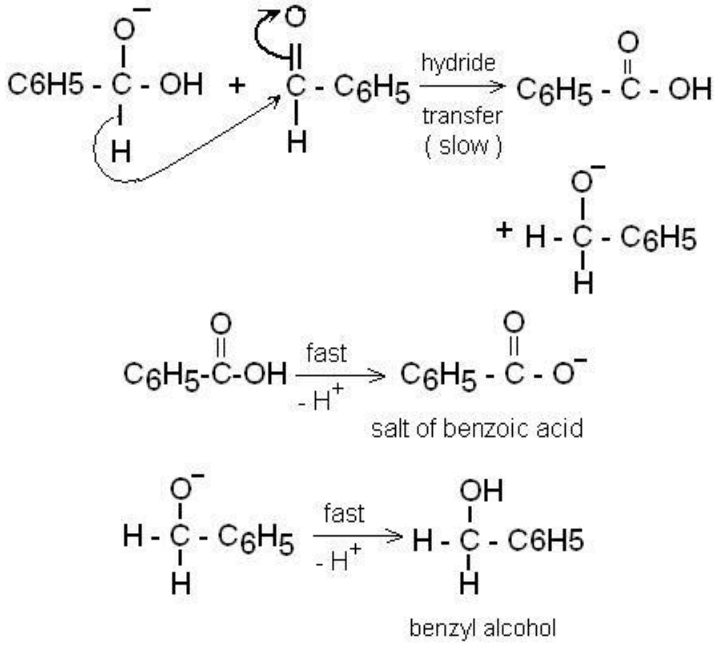
Mechanism

Step I : The OH^- ion attacks the carbonyl carbon to form hydroxyl alkoxide



$$C_6H_5-\underset{H}{\overset{O}{\overset{\|}{C}}} + OH^- \xrightarrow{\text{fast}} C_6H_5-\underset{H}{\overset{O^-}{C}}-OH$$

Step II : Anion (I) acts as hybride ion donor to the second molecule of aldehyde. In the final step of the reaction, the acid and the alkoxide ion transfer H^+ to acquire stability.

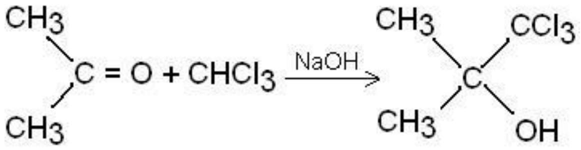


$$C6H5-\underset{H}{\overset{O^-}{C}}-OH + \underset{H}{\overset{O}{\overset{\|}{C}}}-C_6H_5 \xrightarrow[\text{transfer (slow)}]{\text{hydride}} C_6H_5-\overset{O}{\overset{\|}{C}}-OH + H-\underset{H}{\overset{O^-}{C}}-C6H5$$

$$C_6H_5-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[-H^+]{\text{fast}} C_6H_5-\overset{O}{\overset{\|}{C}}-O^-$$

$$H-\underset{H}{\overset{O^-}{C}}-C_6H_5 \xrightarrow[-H^+]{\text{fast}} H-\underset{H}{\overset{OH}{C}}-C6H5$$

6. Reaction with chloroform

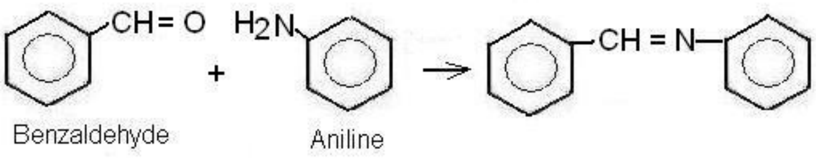


chloretone

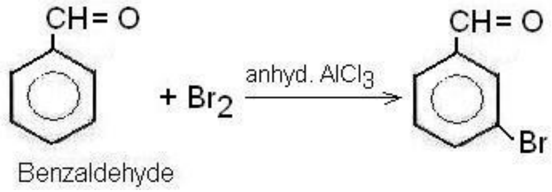
Chloretone is used as hypnotic.

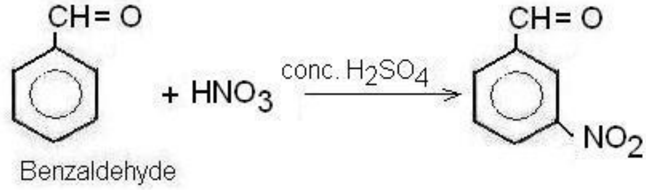
7. Reaction with primary amine

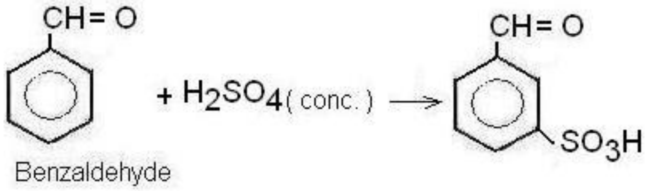
$$RCH\boxed{O + H_2}NR' \xrightarrow[\Delta]{H^+} \underset{\text{schiff's base}}{R\,CH = NR'} + H_2O$$



8. Electrophilic substitution reaction of aromatic carbonyl compounds







USES OF ALDEHYDES AND KETONES

(a) Uses of formaldehyde
  i. The 40% solution of formaldehyde in water (formaline) is used as disinfectant, germicide and antiseptic. It is used for the preservation of biological specimens
  ii. It is used for silvering of mirrors
  iii. It is used for making synthetic plastics, like Bakelite, urea- formaldehyde resin etc

(b) Uses of acetaldehyde
  i. It is used in preparation of acetic acid, dyes, drugs, etc
  ii. As an antiseptic inhalant in nose troubles

(c) Uses of benzaldehyde
  i. As flavouring agent in perfume industry
  ii. In manufacture of dyes.

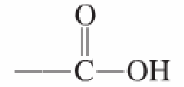
(d) Uses of acetone
  i. As a solvent for cellulose acetate, resin etc.
  ii. As a nailpolish remover
  iii. In the preparation of an artificial scent and synthetic rubber

Chapter 16: Carboxylic Acids, Esters, and Other Acid Derivatives

In Chapter 15, we discussed the carbonyl group and two families of compounds -aldehydes and ketones—that contain C=O group. In this chapter, we discuss four more families of compounds in which the carbonyl group is present: a) carboxylic acid, b) esters, c) amides, d) acid chlorides, and e) acid anhydrides and f) carboxylic acid salts.

16.1 Structure of Carboxylic Acids and Their Derivatives

A carboxylic acid is an organic compound whose functional group is the carboxyl group. What is a carboxyl group? A carboxyl group is a carbonyl group (C=O) with a hydroxyl group (—OH) bonded to the carboxyl carbon atom. A general structural representation fit a carboxyl group is

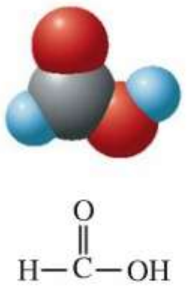


$$-\overset{\overset{\Large O}{\|}}{C}-OH$$

Abbreviated linear designations for the carboxyl group are

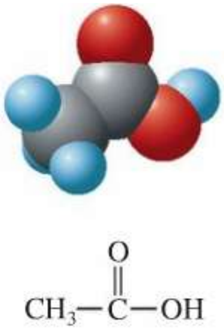
$$-COOH \quad \text{and} \quad -CO_2H$$

Although we see within a carboxyl group both a carbonyl group (C=O) and hydroxyl group (—OH).



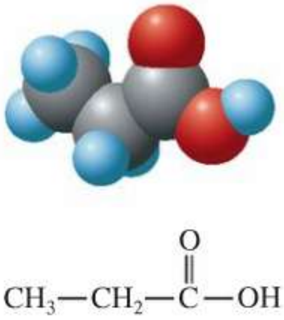
$$H-\overset{\overset{\Large O}{\|}}{C}-OH$$

Methanoic acid



$$CH_3-\overset{\overset{\Large O}{\|}}{C}-OH$$

Ethanoic acid



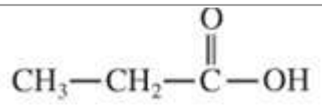
$$CH_3-CH_2-\overset{\overset{\Large O}{\|}}{C}-OH$$

Propanoic acid

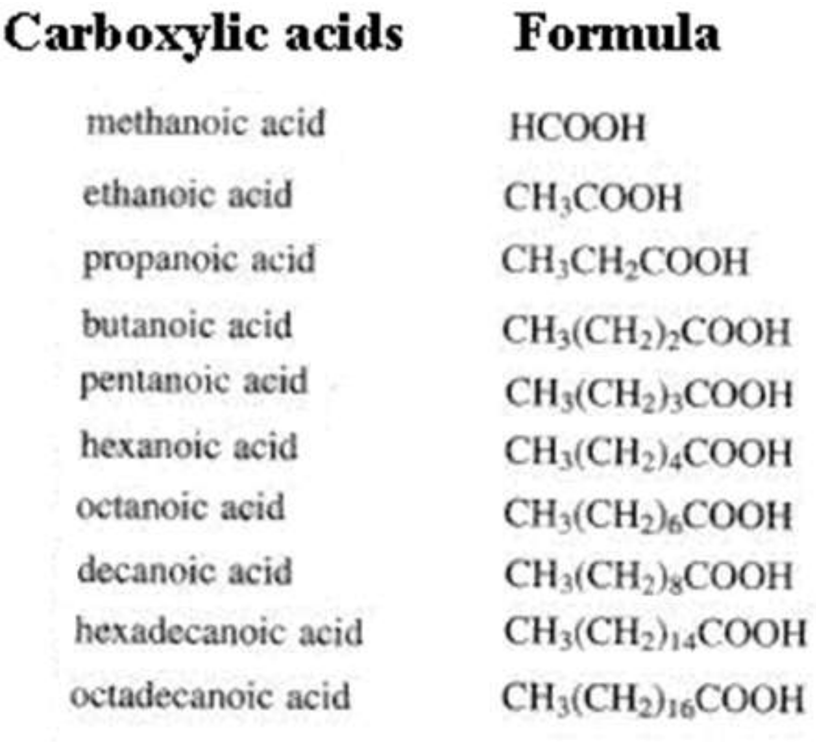
16.2 IUPAC Nomenclature for Carboxylic Acids

The naming of carboxylic acids is fairly simple. You simply find the longest carbon chain which includes the carboxylic group. Use that as the stem for the name, cross off the **-e** on the ending of the alkane name and replace it with **-oic acid**.

I think you can see how that works, if you look at this example (which is also shown in Example 1-a in your workbook). It gives you, in this case (with a three-carbon-atom chain), the name **propanoic acid**.

 $CH_3-CH_2-\overset{\overset{\Large O}{\|}}{C}-OH$
propanoic acid (from **propan** + **oic acid**)

As with aldehydes, it is **not necessary to indicate where** the acid functional group is because it has to be at the end of the molecule, on the #1 carbon. There is no way that this functional group can be anywhere else. Therefore, if there is any numbering to be done, it will be to show where additional alkyl groups or other groups are attached to the carbon chain. The numbering starts from the carboxylic group.

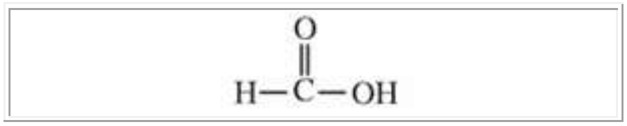


Carboxylic acids	Formula
methanoic acid	$HCOOH$
ethanoic acid	CH_3COOH
propanoic acid	CH_3CH_2COOH
butanoic acid	$CH_3(CH_2)_2COOH$
pentanoic acid	$CH_3(CH_2)_3COOH$
hexanoic acid	$CH_3(CH_2)_4COOH$
octanoic acid	$CH_3(CH_2)_6COOH$
decanoic acid	$CH_3(CH_2)_8COOH$
hexadecanoic acid	$CH_3(CH_2)_{14}COOH$
octadecanoic acid	$CH_3(CH_2)_{16}COOH$

16.3 Common Names for Carboxylic Acids

Carboxylic acids are another example of a situation where the compounds were known and named long before anyone thought of the IUPAC method of naming compounds. Consequently, many carboxylic acids have their own common name which is distinct from the IUPAC name. The two most important of these (and the only two you will be held responsible for in this course) are shown below. They are **formic acid** and **acetic acid**. (These are also shown in Examples 1b and c in your workbook.)

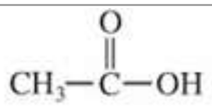
Here is the structural formula for **formic acid**. Its IUPAC name is methanoic acid, using the **meth-** stem because it has **one** carbon atom.



$$H-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

formic acid
methanoic acid

Acetic acid has two carbon atoms. Therefore it can also be called ethanoic acid.

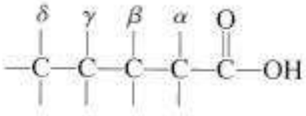

$CH_3-C(=O)-OH$

acetic acid
ethanoic acid

Structural Formula	Latin or Greek Root	Common Name*
$H-COOH$	form-	formic acid
CH_3-COOH	acet-	acetic acid
CH_3-CH_2-COOH	propion-	propionic acid
$CH_3-(CH_2)_2-COOH$	butyr-	butyric acid
$CH_3-(CH_2)_3-COOH$	valer-	valeric acid
$CH_3-(CH_2)_4-COOH$	capro-	caproic acid

Naming using Greek letters ε δ γ β α

There are two ways to identify substituent carbons in carboxylic acid: numbers or Greek letters.
Using numbers, the carboxyl group carbon is given the number one.

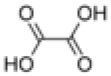
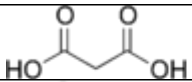
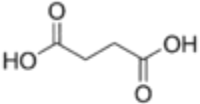
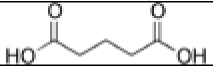
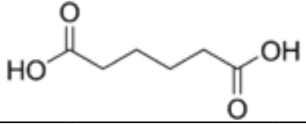
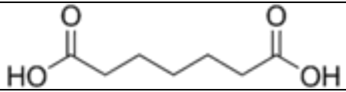


6 5 4 3 2 1
C-C-C-C-C-COOH
ε δ γ β α

When Greek letters are used, Greek letters are used to designate the position of substituent relative to the carbon of the carboxyl group. The carbon of the carboxyl group is **NOT** given a Greek letter.
6) A special group of carboxylic acids are those that also have a keto group. They are called alpha-keto carboxylic acids

16.4 Polyfunctional Carboxylic Acids

Dicarboxylic acids are organic compounds that are substituted with two carboxylic acid functional groups.They are important metabolic products of fatty acids when they undergo oxidation.

Common Name	**IUPAC Name**	**Condensed Formula**	**Structural Fromula**
Oxalic acid	**ethanedioic acid**	$HOOC-COOH$	
Malonic acid	**propanedioic acid**	$HOOC-(CH_2)-COOH$	
Succinic acid	**butanedioic acid**	$HOOC-(CH_2)_2-COOH$	
Glutaric acid	**pentanedioic acid**	$HOOC-(CH_2)_3-COOH$	
Adipic acid	**hexanedioic acid**	$HOOC-(CH_2)_4-COOH$	
Pimelic acid	**heptanedioic acid**	$HOOC-(CH_2)_5-COOH$	

16.5 "Metabolic" Acids

Metabolism is the set of chemical reactions that occur in a cell, which enable it to keep living, growing and dividing. There many acids involved in metabolic processes and a basic understanding of their structures and properties are necessary to understand the biochemistry.

Metabolic acids are polyfunctional acids formed as intermediates of metabolic reactions in the human body. There are eight such acids that will appear repeatedly in the biochemical pathways.

Metabolic acids are derived from:

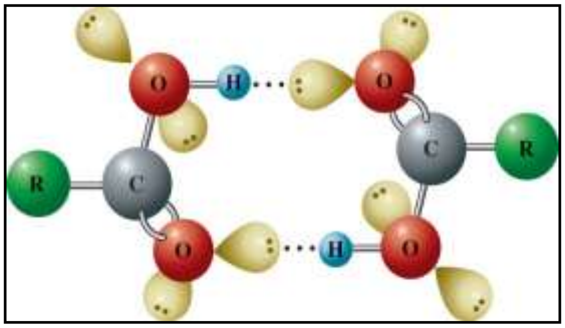
Propionic acid, (C3 mono acids):
lactic, glyceric, and
pyruvic acids

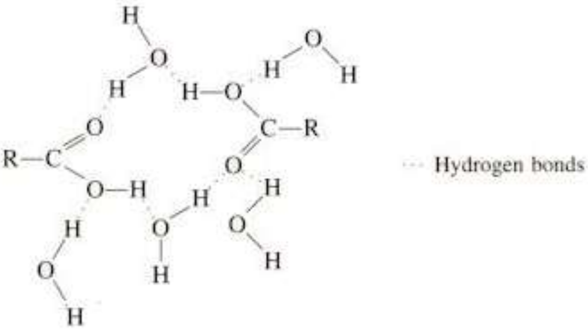
Succinic acid (C4 diacid): fumaric, oxaloacetic, and malic acids
Glutaric acid (C5 diacid): α-ketoglutaric and citric acids

16.6 Physical Properties of Carboxylic Acids

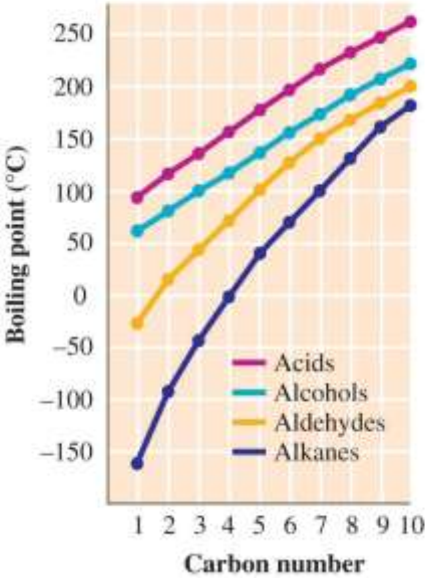
Carboxyl groups exhibit very strong hydrogen bonding. A given carboxylic acid molecule form two hydrogen bonds to another carboxylic acid molecule, producing a “dimer”, a complex with a mass twice that of a single molecule.

Compounds with carboxyl groups have higher boiling points than alcohols. This is because the carboxyl groups hydrogen bond more strongly than alcohols.





Carboxyl groups make molecules very soluble in water because the group can strongly hydrogen bond with water.



Physical Properties of carboxylic acids derivatives

Depending upon the substituent replacing -OH of the caboxylic functional group the physical properties could change.
However, they have lower boiling and melting points than parent acid.

16.7 Preparation of Carboxylic Acids

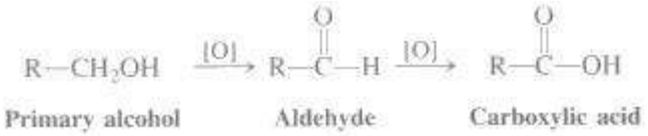
Carboxylic acids are easily by oxidation of primary alcohols and aldehydes. When the oxidation process begins with an alcohol it is difficult to stop at the aldehyde stage of oxidation.

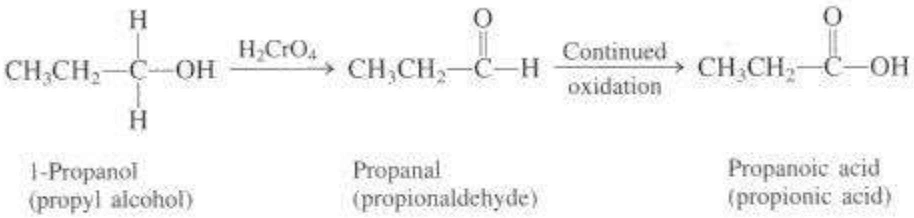
Oxidation of primary alcohol to carboxylic acid.

Chemical equations

$CH_3CH_2CH_2OH$ ---> CH_3CH_2CHO ---> CH_3CH_2COOH
primary alcohol aldehyde acid

Ar-CH_2-OH ---> ArCHO ---> Ar-COOH





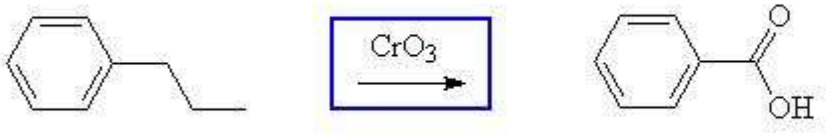
Oxidation using basic $Ag(NH_3)_2^+$

A basic $Ag(NH_3)_2^+$ in aqueous ammonia reduces to metallic silver (mirror) with aldehyde oxidized to carboxylic acid.

The commercial manufacture of silver mirrors uses a similar process.

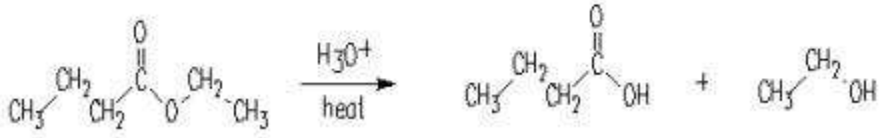
Oxidation of alkyl side chain substituted on a benzene ring to an acid functional group.

Ar- CH_2 -CH_3 ---> Ar- COOH



hydrolysis of esters.

acid-catalyzed hydrolysis is the exact reverse of Fisher esterification (same mechanism)



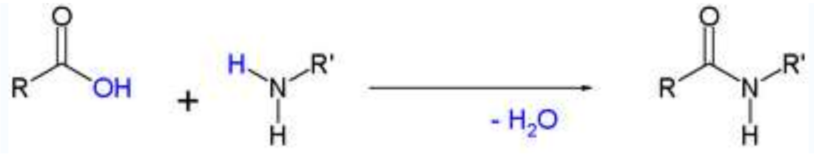
Reactions of Carboxylic Acid

Reaction with strong bases to form acid salts (described below in preparation of acid salts)

Reaction with strong alcohols to form esters (described below in preparation of esters-esterification)

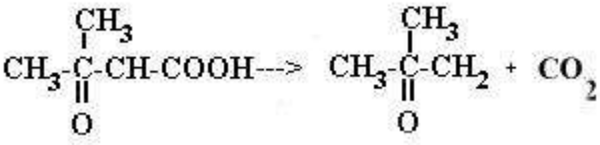
Reaction with halogen compounds to form acid chlorides(described below in preparation of acid chloride preparations)

Reaction with ammonia and amine compounds to form amides (described below in preparation of amides chapter 18)



Reactions of β-keto acids.

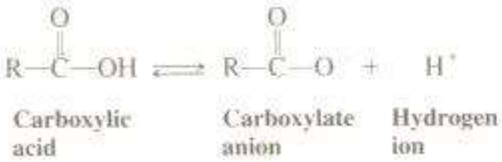
β-keto acids are readily decarboxylated.



$$CH_3-\underset{\overset{\|}{O}}{\overset{\overset{CH_3}{|}}{C}}-CH-COOH \dashrightarrow CH_3-\underset{\overset{\|}{O}}{\overset{\overset{CH_3}{|}}{C}}-CH_2 + CO_2$$

16.8 Acidity of Carboxylic Acids

Carboxylic acids are weak acids.

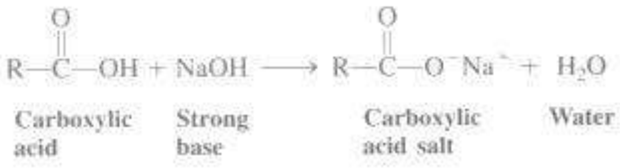


$$R-\overset{\overset{O}{\|}}{C}-OH \rightleftharpoons R-\overset{\overset{O}{\|}}{C}-O^- + H^+$$

$HCl + H_2O \dashrightarrow H^+ + Cl^-$ (100%)

CH_3-COOH (95%) $\rightleftharpoons$ CH_3-COO^- (5%) + H^+

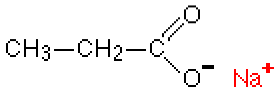
Acid base reactions:



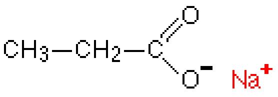
$$R{-}\overset{\overset{O}{\|}}{C}{-}OH + NaOH \longrightarrow R{-}\overset{\overset{O}{\|}}{C}{-}O^-Na^+ + H_2O$$

16.9 Carboxylic Acid Salts

Naming carboxylic acid follows certain pattern for example the structural formula for the compound. Since this sodium salt of propanoic acid - so start from propanoic acid is a three carbon acid with no carbon-carbon double bonds and this negative ion without the H^+ atom is called propanoate. There this salt is named: **sodium propanoate**



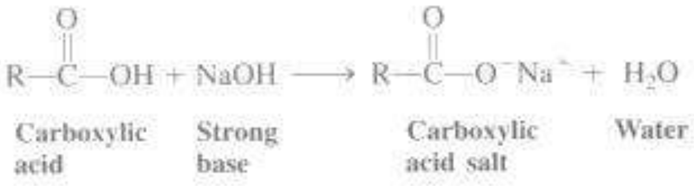
When the carboxylic acids form salts, the hydrogen in the -COOH group is replaced by a metal. Sodium alkan**oate** **(propan-oate)** is therefore:



sodium propanoate

Preparation of acid salts

Acid salts are prepared by the reaction of acid with a base such as sodium hydroxide.



$$R{-}\overset{\overset{O}{\|}}{C}{-}OH + NaOH \longrightarrow R{-}\overset{\overset{O}{\|}}{C}{-}O^-Na^+ + H_2O$$

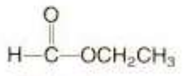
16.11 Preparation of Esters

Naming Esters:

1. Identify the alkyl group that is attached to the oxygen atom
2. Number according to the end closest to the -CO- group regardless of where alkyl substituents are.
3. Determine the alkane that links the carbon atoms together. If there is a separation of a continuous link of carbon atoms due to the oxygen atom, individually name the two alkanes before and after the oxygen atom. The longer structural alkane is the one that should contain the carbonyl atom.

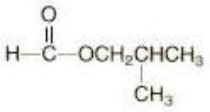
4. The format is as follows: (alkane further from carbonyl) (alkane closest to carbony)(parent chain)
5. Change the parent chain -e ending and replace it with an -oate.
   Example:
      $CH_3COOC_7H_{14}CH_3$
      octyl ethanoate

Common Esters


$H-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$

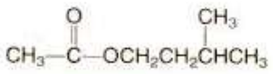
Rum

Ethyl methanoate
(ethyl formate)


$H-\overset{O}{\overset{\|}{C}}-OCH_2\underset{\underset{CH_3}{|}}{C}HCH_3$

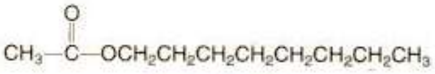
Raspberries

Isobutyl methanoate
(isobutyl formate)


$CH_3-\overset{O}{\overset{\|}{C}}-OCH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_3$

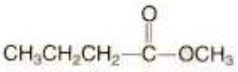
Bananas

3-Methylbutyl ethanoate
(isoamyl acetate)


$CH_3-\overset{O}{\overset{\|}{C}}-OCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

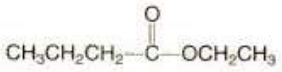
Oranges

Octyl ethanoate
(octyl acetate)


$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-OCH_3$

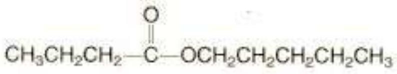
Apples

Methyl butanoate
(methyl butyrate)


$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$

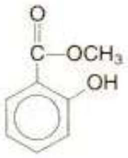
Pineapples

Ethyl butanoate
(ethyl butyrate)

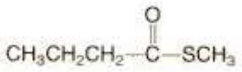

$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-OCH_2CH_2CH_2CH_2CH_3$

Apricots

Pentyl butanoate
(pentyl butyrate)


Oil of wintergreen

Methyl salicylate

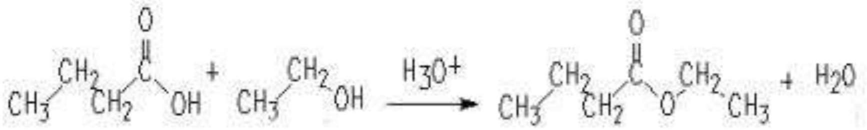

$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-SCH_3$

Strawberries

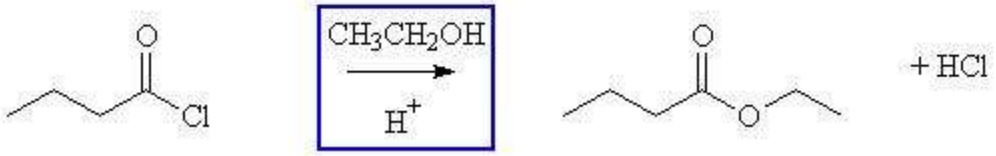
Methyl thiobutanoate
(methyl thiobutyrate)

Esterification form acid and alcohol

acid + alcohol ----> ester + H_2O



Esterification from acid chlorides and alcohol



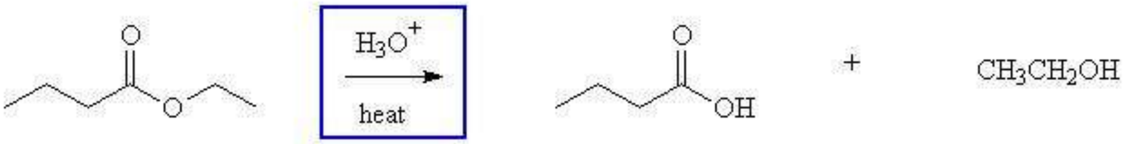
Note: the acid loses an -OH units and the alcohol loses a -H in this reaction.

16.14 Isomerism for Carboxylic Acids and Esters

16.16 Chemical Reactions of Esters

Hydrolysis

1) **acid-catalyzed hydrolysis** is the exact reverse of Fisher esterification (same mechanism)

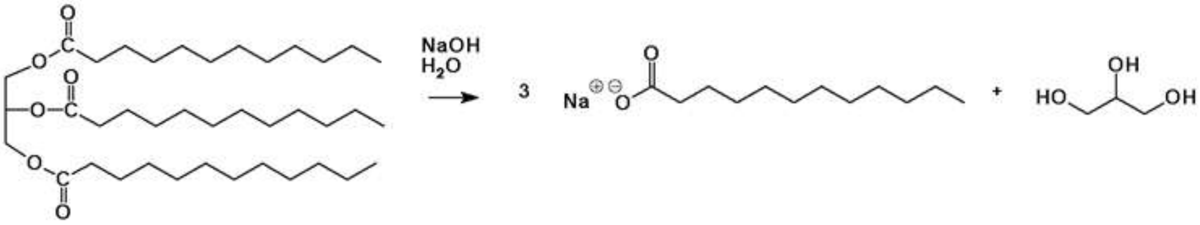


2) **base-catalyzed hydrolysis** is often called **saponification** (soap-making) saponification is irreversible because a carboxylate salt is formed.

Saponification of triglycerides and action of soap in the emulsification of grease and oils.

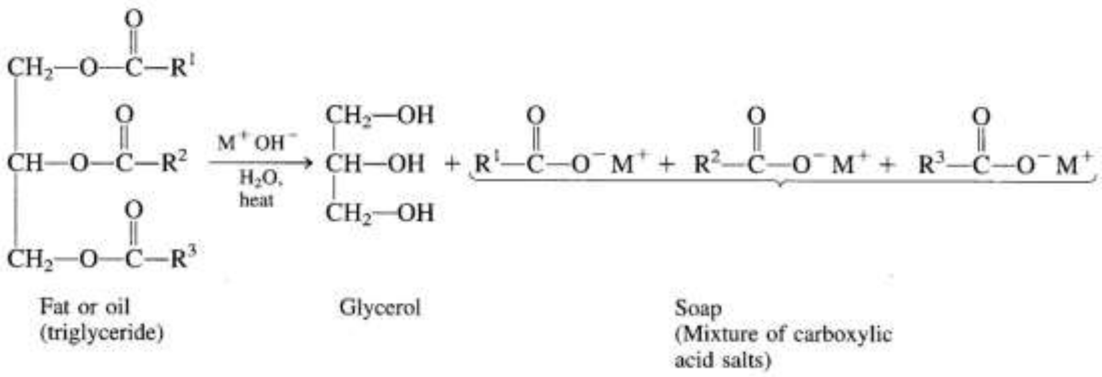
Soap has been around for hundreds of years. In it's simplest form, soap is made by heating fat in boiling water that also has sodium hydroxide (NaOH)or potsssium hydroxide (KOH) ions in it. Each fat molecue breaks down into three molecules of fatty acids. The molecules of fatty acids then react with the sodium or potassium ions to form soap molecules and glycerin.

triglyceride



glycerol

If the triglyceride had three different fatty acids following products with three fatty acids are formed.



where $M^+ = Na^+$ or K^+

Soaps are water-soluble sodium or potassium salts of long-chain (fatty) acids (C8-C20). Fats are the esters of fatty acids and glycerol (1,2,3-propanetriol). Base-catalyzed hydrolysis is often called saponification (soap-making) saponification is irreversible because a carboxylate salt is formed.

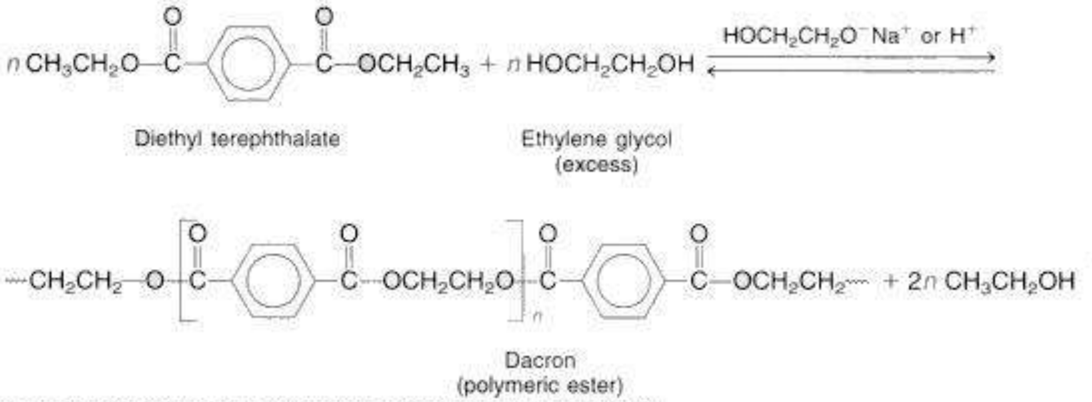
How does soap work?

In the cleaning process, surface tension must be reduced so water can spread and wet surfaces. Chemicals that are able to do this effectively are called surface active agents, or surfactants. They are said to make water "wetter." Soap perform other important functions in cleaning, such as loosening, emulsifying (dispersing in water) and holding soil in suspension until it can be rinsed away. Soap can also provide alkalinity, which is useful in removing acidic soils.

16.18 Polyesters

Polyesters are formed by condensation polymers are any kind of polymers formed through a condensation reaction, releasing small molecules as by-products such as water or methanol, as opposed to addition polymers which involve the reaction of unsaturated monomers. Types of condensation polymers also include polyamides, polyacetals.

Condensation polymerization

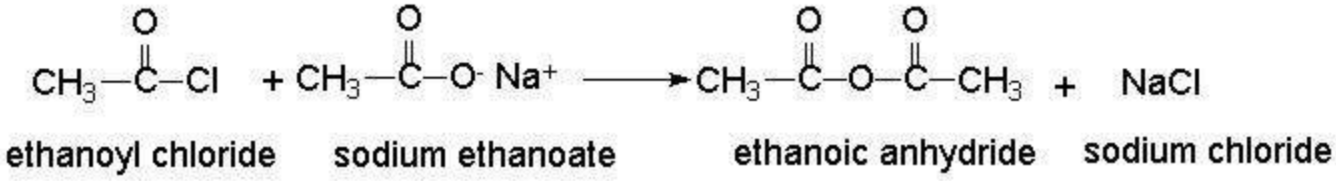


The polymerization process for difunctional compounds (shown for Dacron).

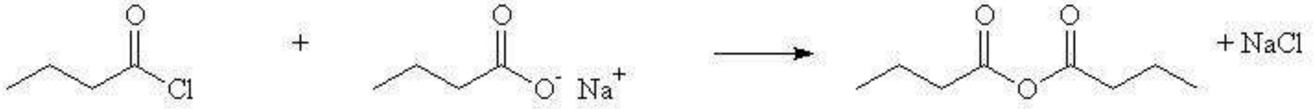
16.19 Acid Chlorides and Acid Anhydrides

Preparation of acid anhydrides

Acid chlorides are prepared by the rection of acid with PCl_3, PCl_5 or $SOCl_2$..
Acid anhydrides are prepared by the rection of acid chlorides with its sodium salt.



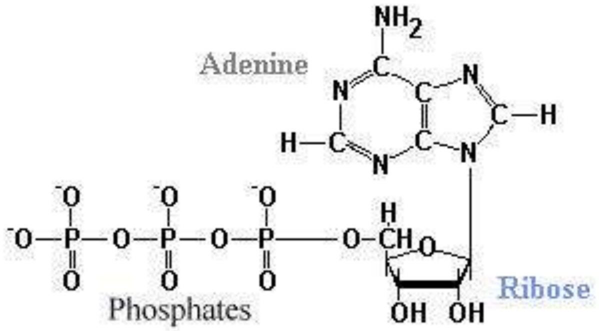
$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + CH_3-\overset{O}{\overset{\|}{C}}-O^- Na^+ \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + NaCl$$



Butanoyl chloride **sodium butanoate** **butanoic anhydride**

16.20 Esters and Anhydrides of Inorganic Acids

Adenosine triphosphate (ATP) consists of the nitrogenous base adenine bonded to the sugar ribose, which is connected to a chain of 3 phosphate groups.

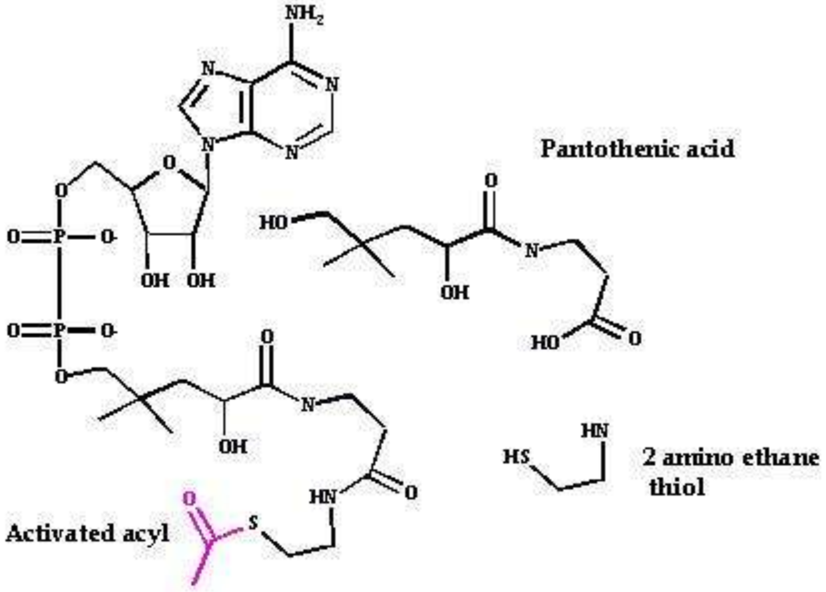


ATP hydrolysis releases energy

Phosphate groups are negatively charged, and repel in ATP.   Release of phosphate gives a large positive entropy change. We synthesize an amount of ATP equal to our body weight every day.
The first step in glycolysis is the formation of glucose-6 phosphate from glucose. The direct reaction of inorganic phosphate (Pi) with glucose is unfavorable. However, the hydrolysis of ATP is extremely favorable. In a cell the enzyme hexokinase catalyzes the coupled reaction of ATP with glucose favoring the formation of glucose-6-phosphate.

Thioesters : Acetyl CoA

Thioesters are more susceptible toward nucleophilic attack than are esters and acids. Thioesters are intermediate in reactivity between acid chlorides and esters making them perfect functional groups for biological systems.



References

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2- **Organic chemistry, Robert J. Ouellette, J. David Rawn, 2018.**

3- **Organic chemistry, Jonathan Clayden, Nick Greeves, and Stuart Warren, 2012.**

4- **Advanced organic chemistry, Francias A. Carey, Richard J. Sundberg, 2010.**

5- **Fundamentals of organic chemistry, John McMurry, 2013.**

6- **The organic chemistry lab. Survival manual, James W. Zubrick, 2016.**

7- **Fundamentals of reaction mechanism in organic chemistry, R. P. Narain, 2011.**

AROMATIC CHEMISTRY

لطلاب الفرقة الاولي تربية بيولوجي

تجميع واعداد

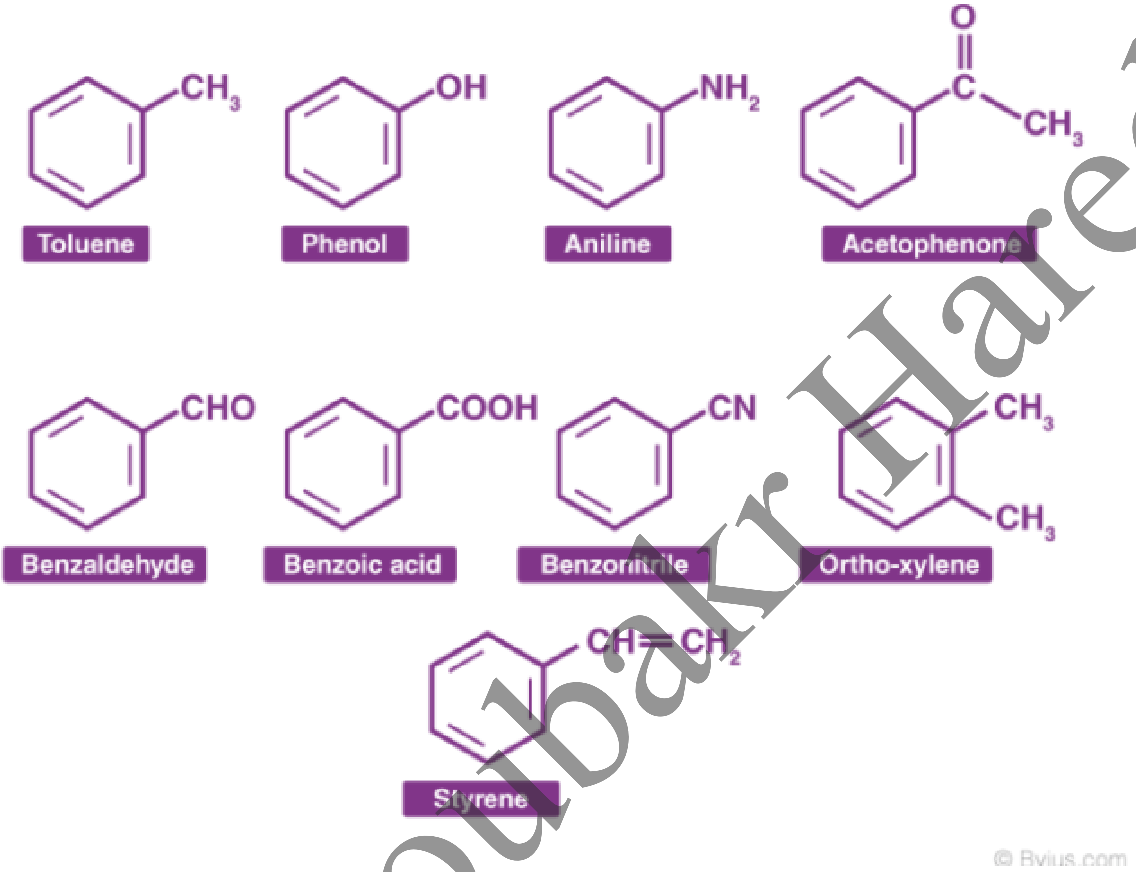
د. ابوبكر هريدي حجاب

Contents

What are Aromatic Compounds?

Aromatic compounds are chemical compounds that consist of conjugated planar ring systems accompanied by delocalized pi-electron clouds in place of individual alternating double and single bonds. They are also called *aromatics or arenes*. The best examples are toluene and benzene. *Aromatics require satisfying Huckel's rule.* Plants and micro-organisms have an exclusive route to benzene-ring compounds. The great majority of aromatic compounds in nature, therefore, are produced by plants and micro-organisms, and animals are dependent upon plants for many aromatic compounds either directly or indirectly.

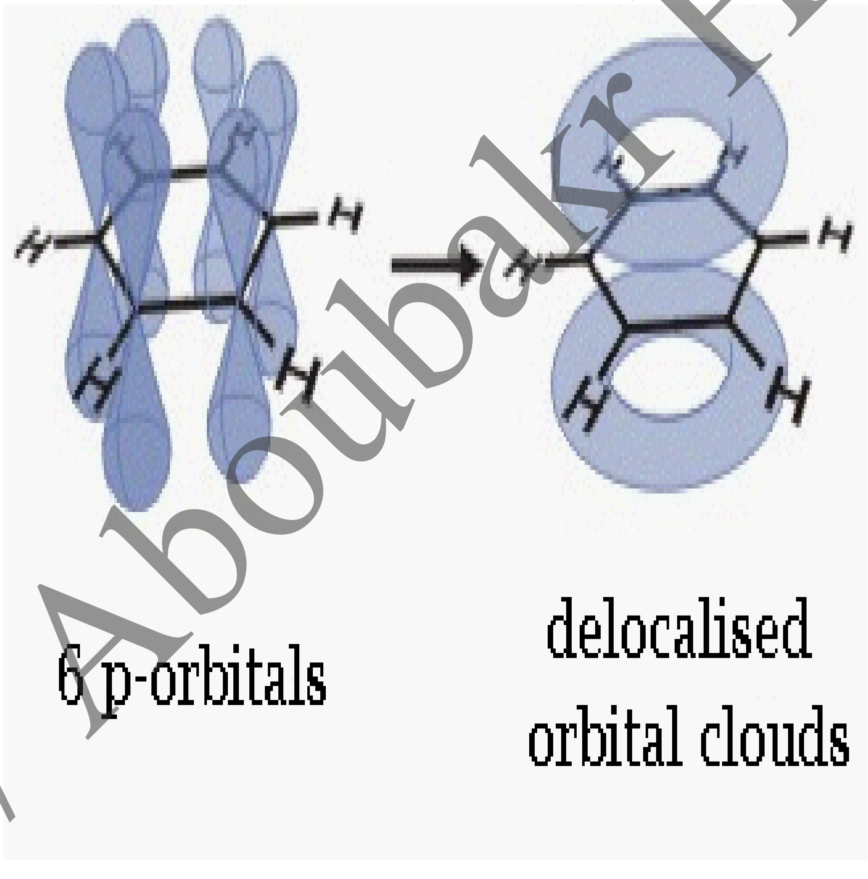
Aromatic Compounds Examples



CHEMISTRY OF BENZENE

Benzene-orbitals

It was also found that benzene was a flat (planar) molecule.



CHARACTERISTICS OF AROMATIC COMPOUNDS

1. **A delocalized conjugated π system, most commonly an arrangement of alternating single and double bonds: Conjugated**

2. **Coplanar structure, with all the contributing atoms in the same plane**

3. **Contributing atoms arranged in one or more rings**

4. **A number of π delocalized electrons that is, 4n + 2 number of π electrons, where n=0, 1, 2, 3, and so on. This is known as Huckel's Rule.**

Benzene

n = 1
$(4 \times 1 + 2) = 6\pi$
Electrons

Naphthalene

n = 2
$(4 \times 2 + 2) = 10\pi$
Electrons

Anthracene

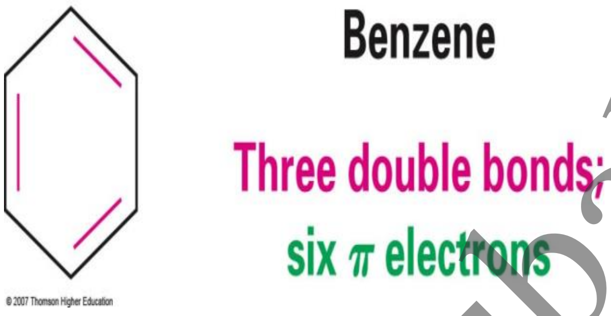
n =3
$(4 \times 3 + 2) = 14\pi$
Electrons

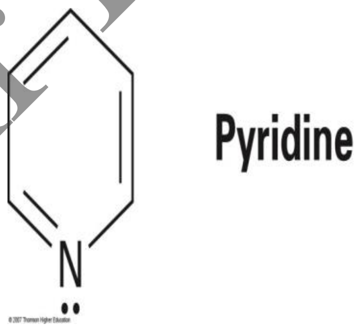
Huckel's Rule: The 4n+2 Rule

- **Planar monocyclic rings with a continuous system of *p***
- **orbitalsand 4n + 2p electrons are aromatic(n = 0, 1, 2, 3 etc)**
- **Aromatic means substantial resonance stabilization**
- **Benzene is aromatic:**
- **planar**
- **Cyclic**
- **orbital at every carbon 6 p electrons (n=1)**
- **Benzene has 3 bonding and 3 antibonding orbitals**
- **All the bonding orbitals are full and there are no electrons in antibonding orbitals; benzene has a closed shell of delocalized electrons and is very stable.**

Aromaticity and the Hückel 4n+2 Rule

- Unusually stable - heat of hydrogenation 150 kJ/mol less negative than a cyclic triene
- Planar hexagon: bond angles are 120°, carbon–carbon bond lengths 139 pm
- Undergoes substitution rather than electrophilic addition
- Resonance hybrid with structure between two line-bond structures

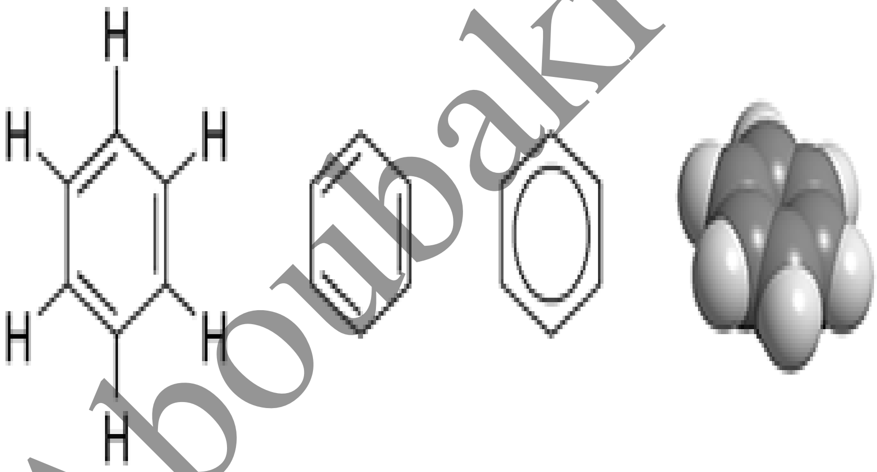


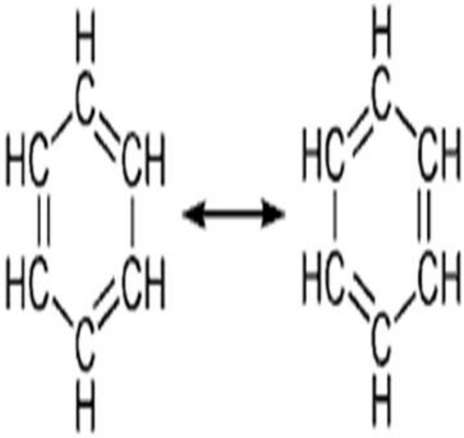


- Huckel's rule, based on calculations – a planar cyclic molecule with alternating double and single bonds has aromatic stability if it has ***4n+ 2*** *π electrons (n is 0,1,2,3,4*)
- For n=1: 4n+2 = 6; **benzene** is stable and the electrons are delocalized.

BENZENE : Resonance description

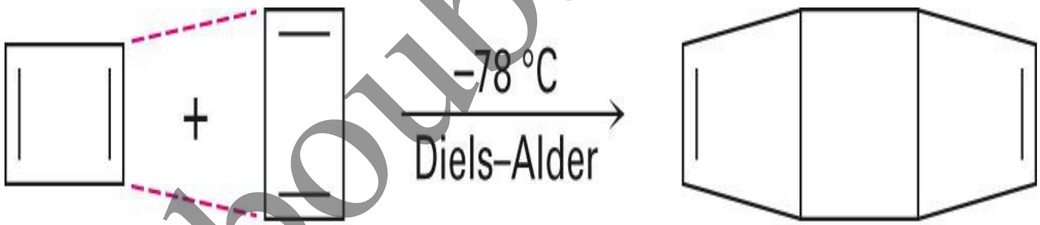
- Later spectroscopic evidence showed all bond lengths in benzene to be **equal** and intermediate between single and double bond lengths (1.39 Å).
- Resonance instead considers such molecules to be an intermediate or average (called a **resonance hybrid**) between several structures that differ only in the placement of the valence electrons





Compounds With 4n π Electrons Are Not Aromatic (May be Antiaromatic)

- **Planar, cyclic molecules with *4 n π* electrons are much *less* stable than expected (antiaromatic)**
- **They will distort out of plane and behave like ordinary alkenes**
- **4- and 8-electron compounds are not delocalized (single and double bonds)**
- **Cyclobutadiene is so unstable that it dimerizes by a self-Diels-Alder reaction at low temperature**
- **Cyclooctatetraene has four double bonds, reacting with Br_2, $KMnO_4$, and HCl as if it were four alkenes**



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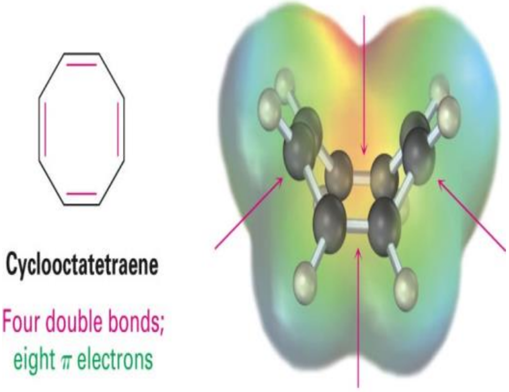

Cyclooctatetraene

Four double bonds; eight π electrons

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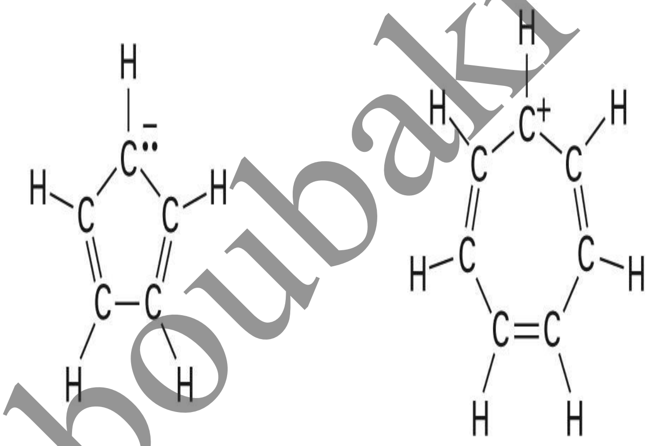
- **The 4*n* + 2 rule applies to ions as well as neutral species**
- **Both the cyclopentadienyl *anion* and the cycloheptatrienyl *cation* are aromatic**
- **The key feature of both is that they contain 6 π electrons in a ring of continuous p orbitals**



Cyclopentadienyl anion Cycloheptatrienyl cation

Six π electrons; aromatic ions

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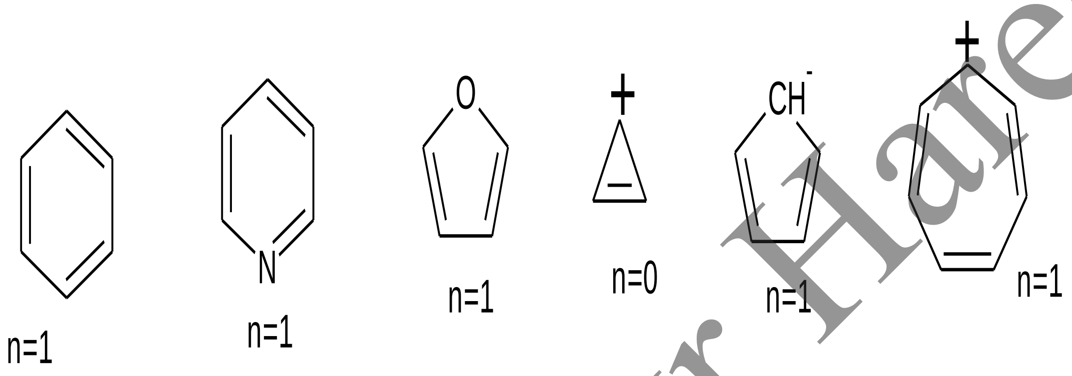
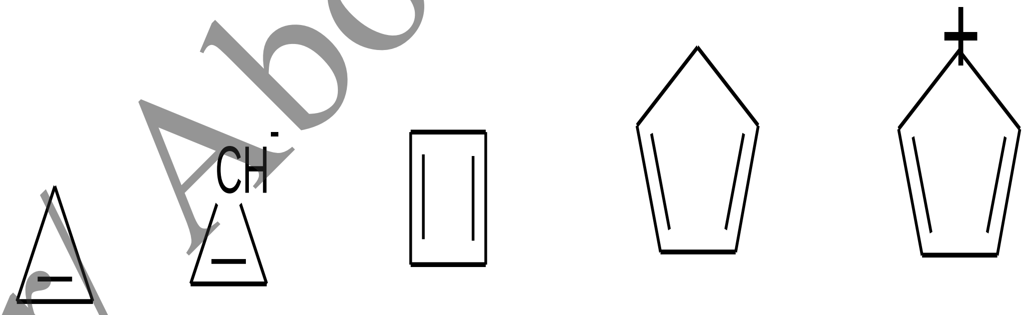
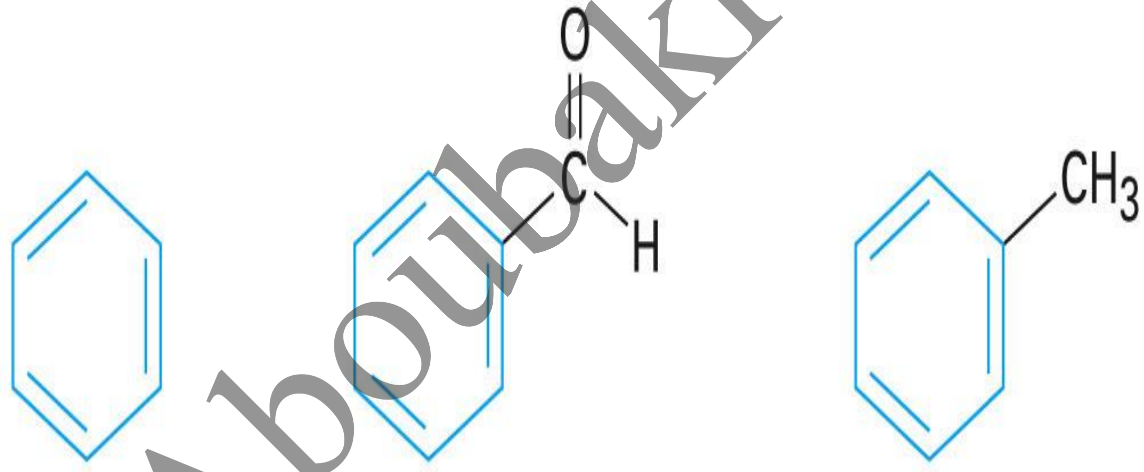
Aromatic compounds



Non Aromatic compounds



- ***Aromatic*** **was used to described some fragrant compounds in early 19th century**
  - **Not correct: later they are grouped by chemical behavior (unsaturated compounds that undergo substitution rather than addition)**
- **Current: distinguished from *aliphatic* compounds by electronic configuration**



Benzene Benzaldehyde Toluene

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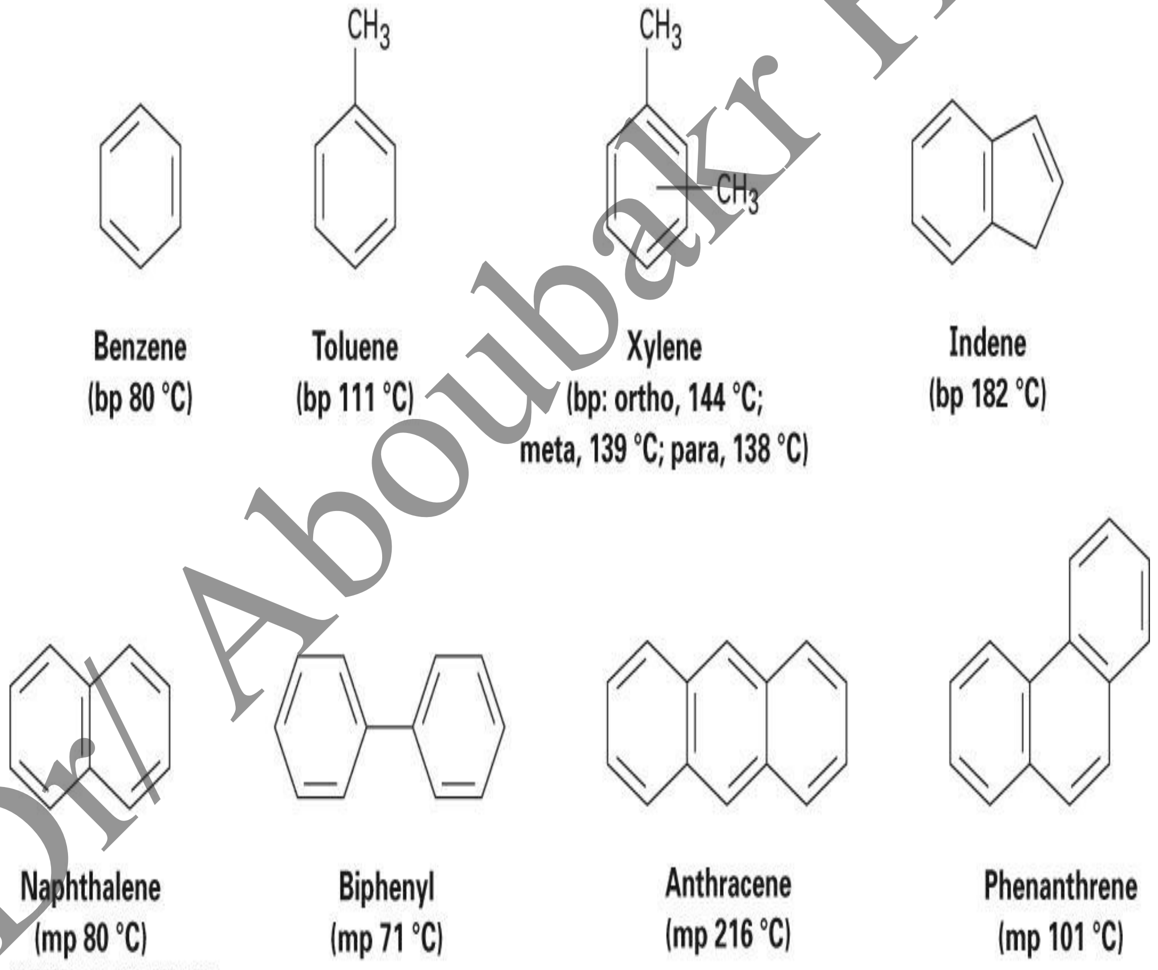
Sources and Names of Aromatic Hydrocarbons

- From high temperature distillation of coal tar
- Heating petroleum at high temperature and pressure over a catalyst



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Naming Aromatic Compounds

- Many common names (toluene = methylbenzene; aniline = aminobenzene)
- Monosubstituted benzenes systematic names as hydrocarbons with –*benzene*
  - C_6H_5Br = bromobenzene
  - $C_6H_5NO_2$ = nitrobenzene, and $C_6H_5CH_2CH_2CH_3$ is propylbenzene

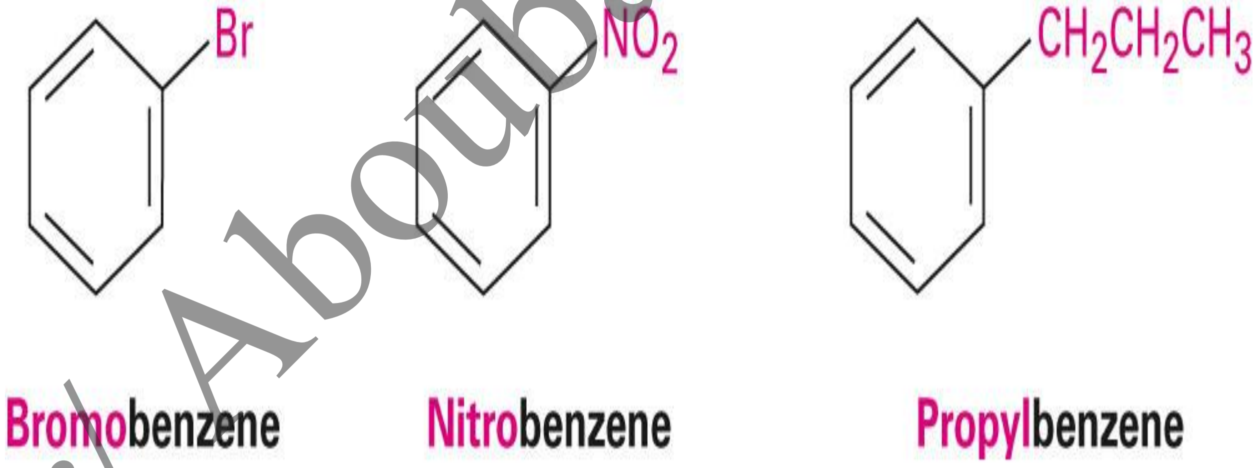

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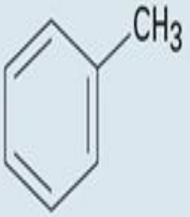
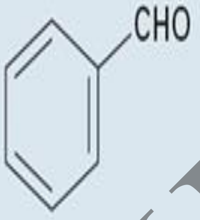
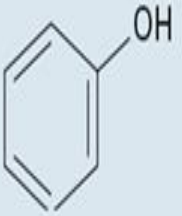
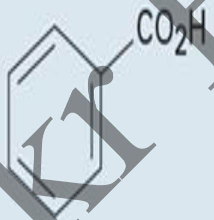
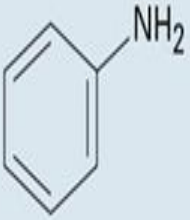
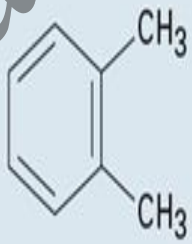
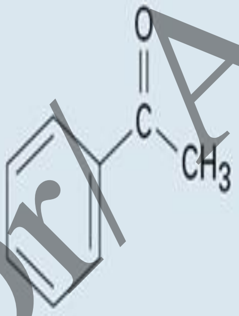
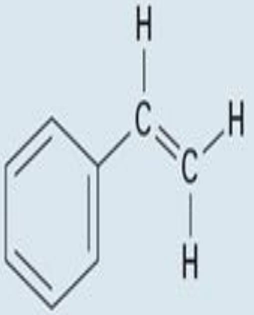
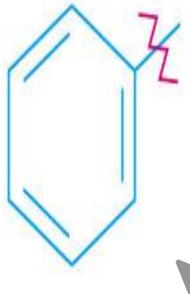
Table 1 Common Names of Some Aromatic Compounds

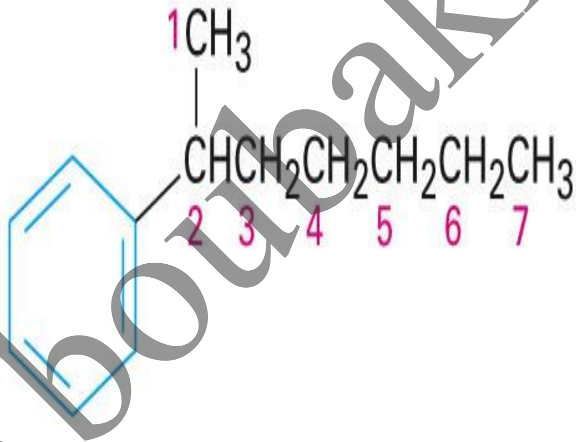
Structure	Name	Structure	Name
	Toluene (bp 111 °C)		Benzaldehyde (bp 178 °C)
	Phenol (mp 43 °C)		Benzoic acid (mp 122 °C)
	Aniline (bp 184 °C)		*ortho*-Xylene (bp 144 °C)
	Acetophenone (mp 21 °C)		Styrene (bp 145 °C)

The Phenyl Group

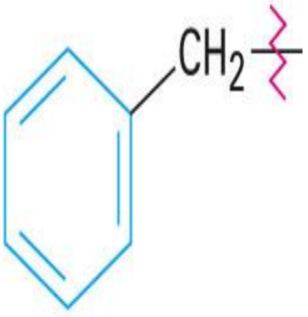
- When a benzene ring is a substituent, the term **phenyl** is used (for C_6H_5□)
  - – You may also see “Ph” or “ϕ” in place of “C_6H_5”
- “**Benzyl**” refers to “$C_6H_5CH_2$□”



A phenyl group



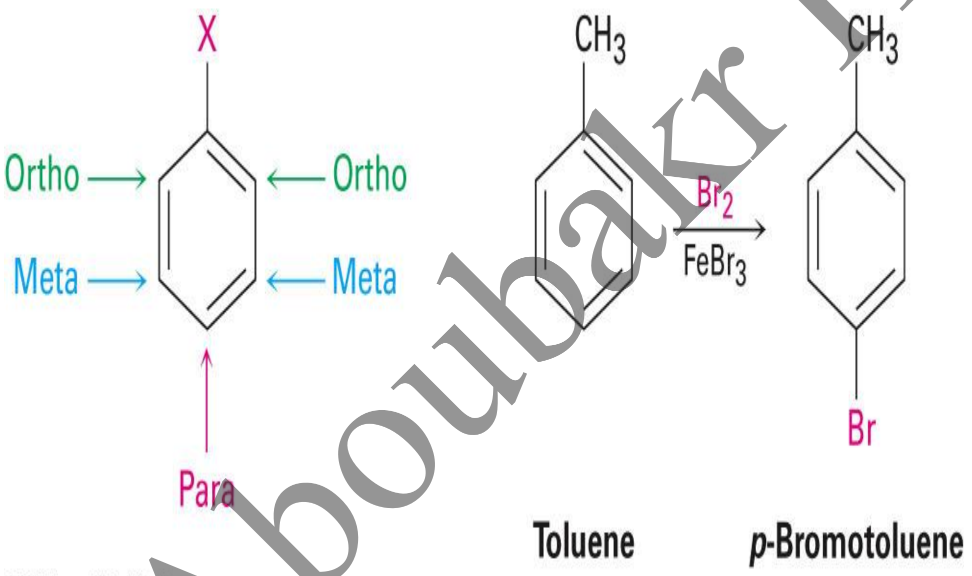
2-Phenylheptane



A benzyl group

Disubstituted Benzenes

- Relative positions on a benzene ring
  - ***ortho- (o)*** on adjacent carbons (1,2)
  - ***meta- (m)*** separated by one carbon (1,3)
  - ***para- (p)*** separated by two carbons (1,4)
- Describes reaction patterns (“occurs at the para position”)



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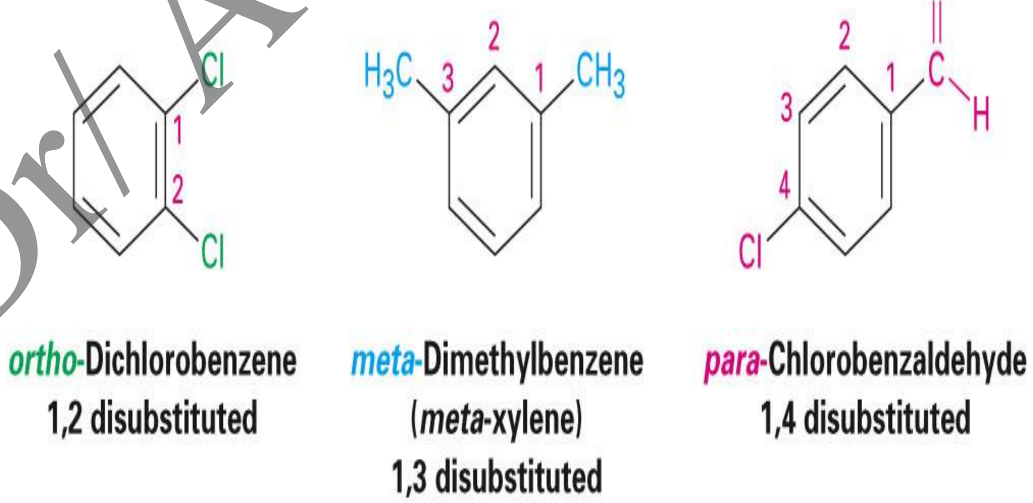

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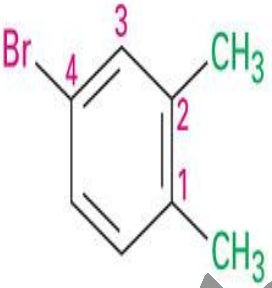
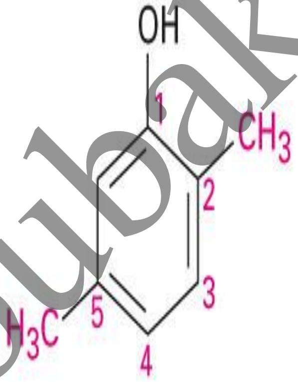
Naming Benzenes With More Than Two Substituents

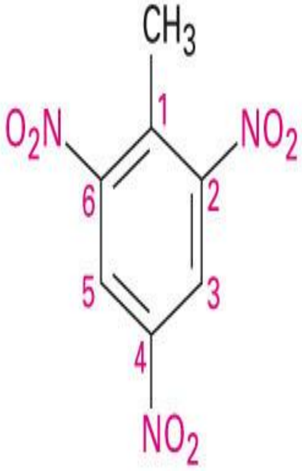
- Choose numbers to get lowest possible values
- List substituents alphabetically with hyphenated numbers
- Common names, such as “toluene” can serve as root name (as in TNT)



4-Bromo-1,2-dimethylbenzene



2,5-Dimethylphenol



2,4,6-Trinitrotoluene (TNT)

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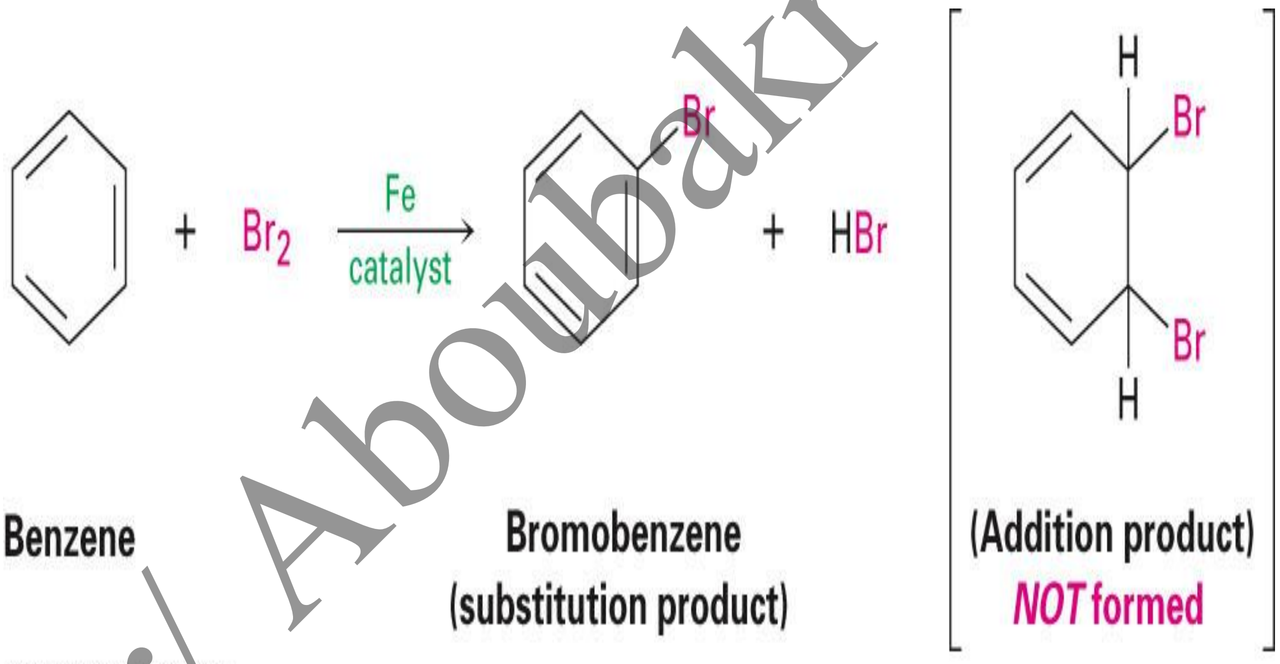
Structure and Stability of Benzene: Molecular Orbital Theory

- Benzene reacts slowly with Br_2 to give bromobenzene (where Br replaces H)
- This is substitution rather than the rapid addition reaction common to compounds with C=C, suggesting that in benzene there is a higher barrier



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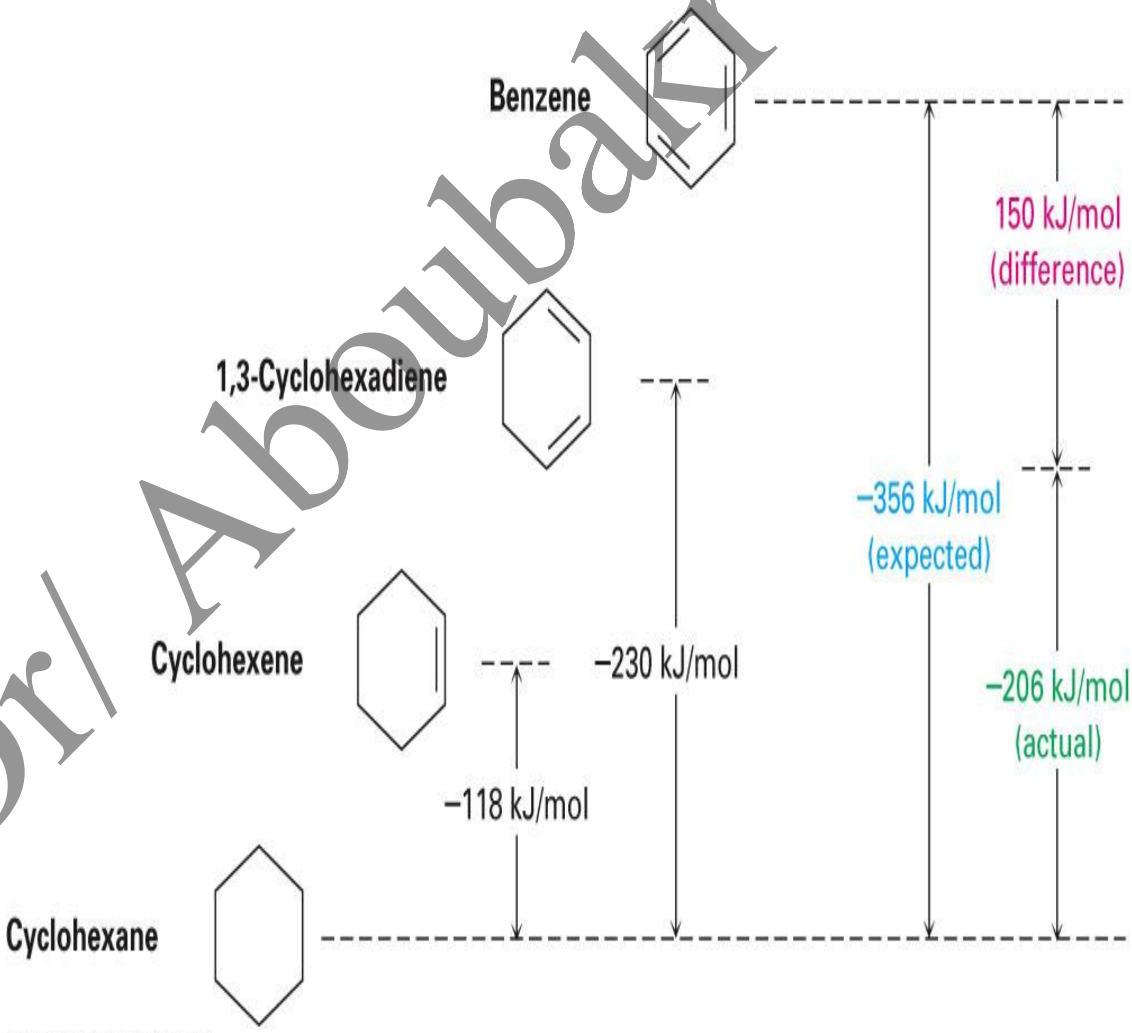
Heats of Hydrogenation as Indicators of Stability

- The addition of H_2 to C=C normally gives off about 118 kJ/mol – 3 double bonds would give off 356kJ/mol
  - Two conjugated double bonds in cyclohexadiene add 2 H_2 to give off 230 kJ/mol
- Benzene has 3 unsaturation sites but gives off only 206 kJ/mol on reacting with 3 H_2 molecules
- Therefore it has about 150 kJ more “stability” than an isolated set of three double bonds



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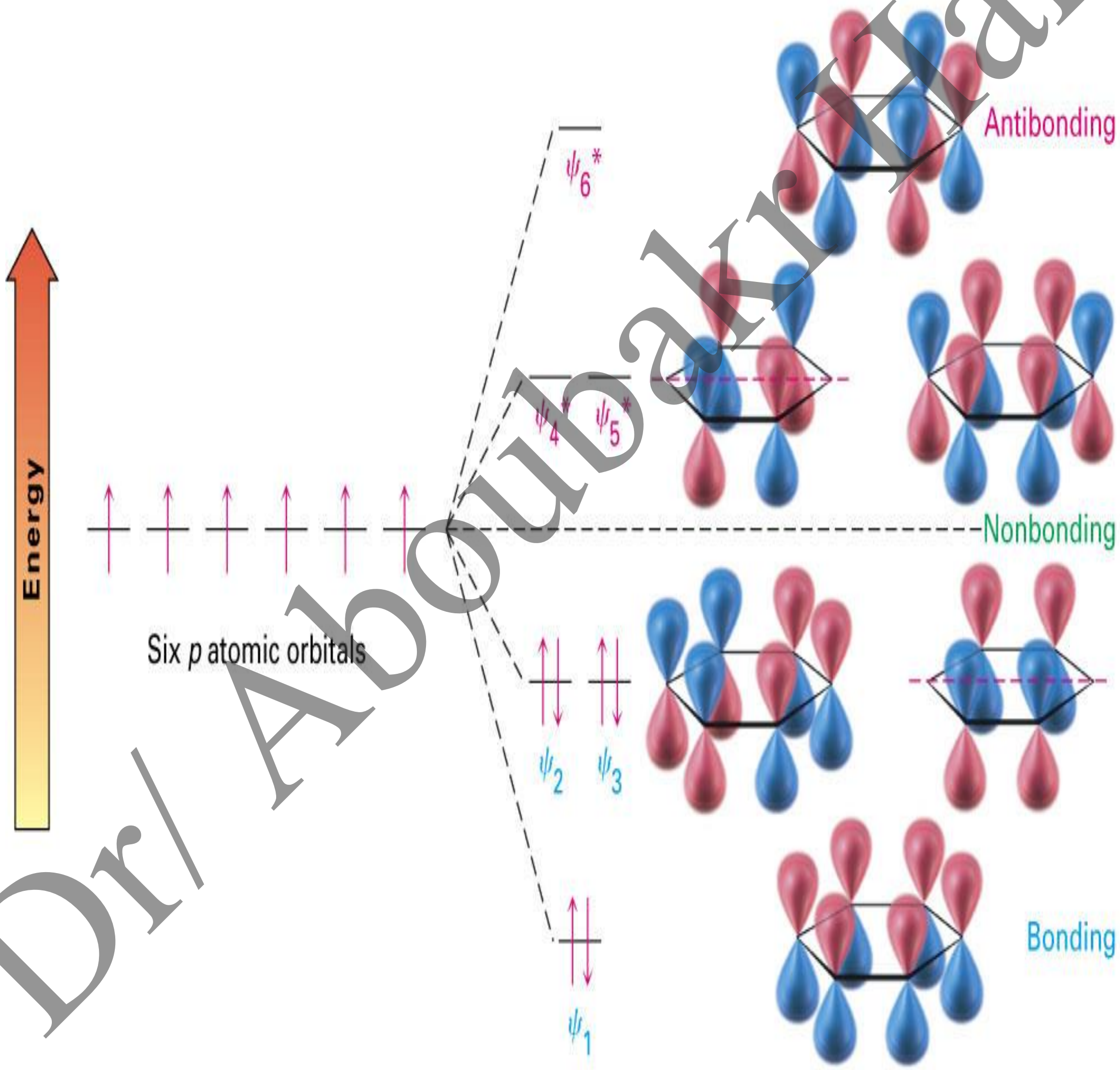
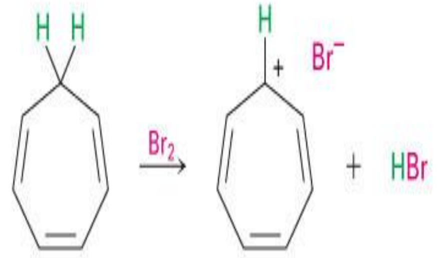
Molecular Orbital Description of Benzene

- The 6 p-orbitals combine to give
  - Three bonding orbitals with 6 π electrons,
  - Three antibonding with no electrons
- Orbitals with the same energy are degenerate



Six benzene molecular orbitals

- Cycloheptatriene has 3 conjugated double bonds joined by a CH_2
- Removal of “H^-” leaves the cation
- The cation has 6 electrons and is aromatic



Cyclohepta-triene

Cyclohepta-trienylium bromide

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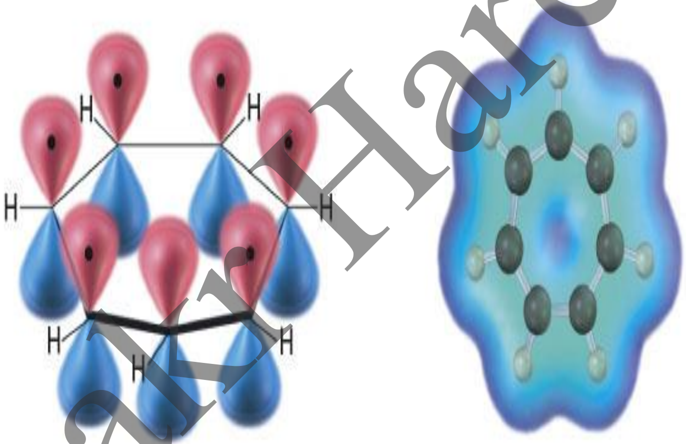


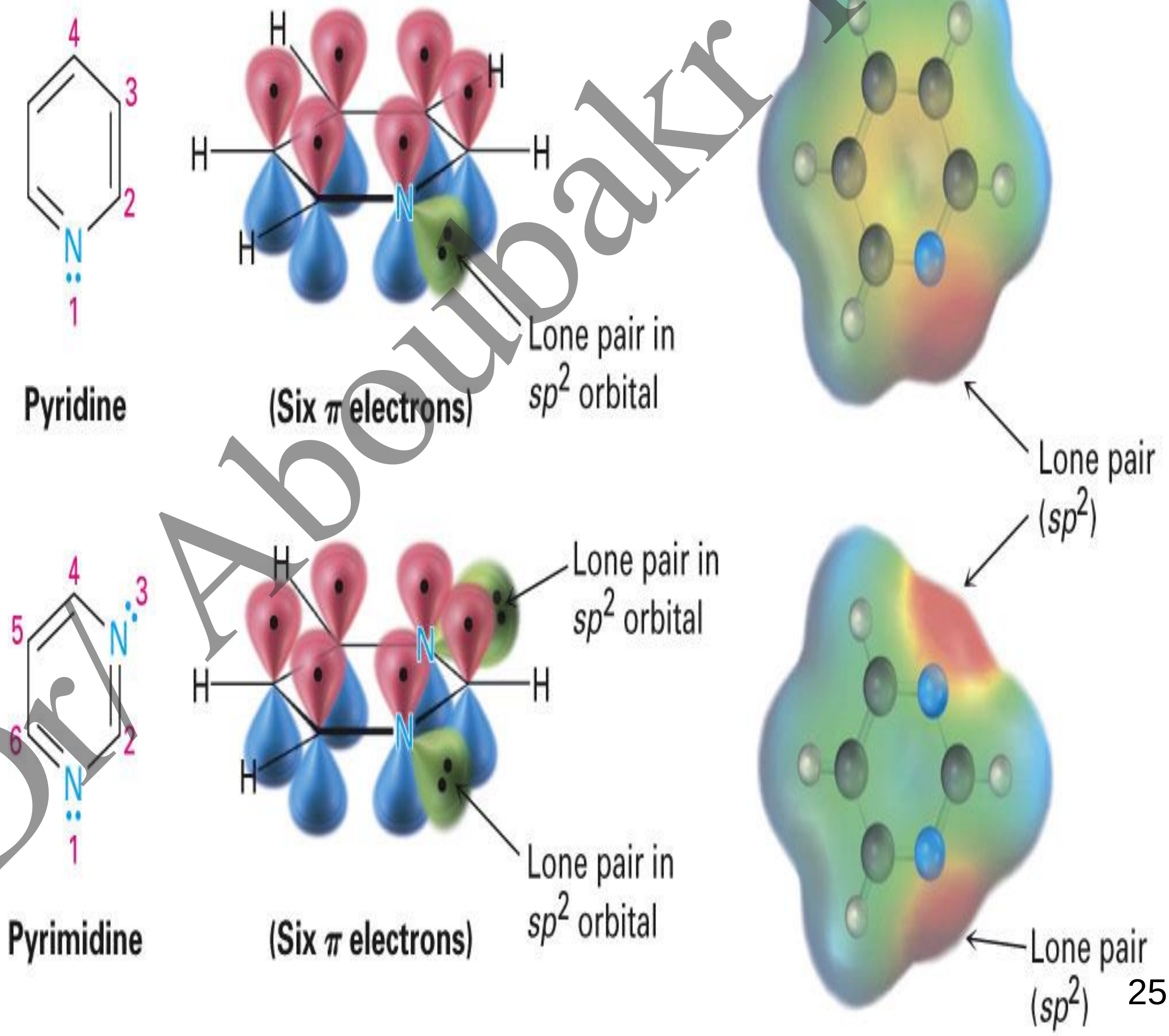
Cycloheptatrienyl cation
six π electrons

Aromatic Heterocycles: Pyridine and Pyrrole

- Heterocyclic compounds contain elements other than carbon in a ring, such as N,S,O,P
- Aromatic compounds can have elements other than carbon in the ring
- There are many heterocyclic aromatic compounds and many are very common
- Cyclic compounds that contain only carbon are called carbocycles (not homocycles)
- Nomenclature is specialized

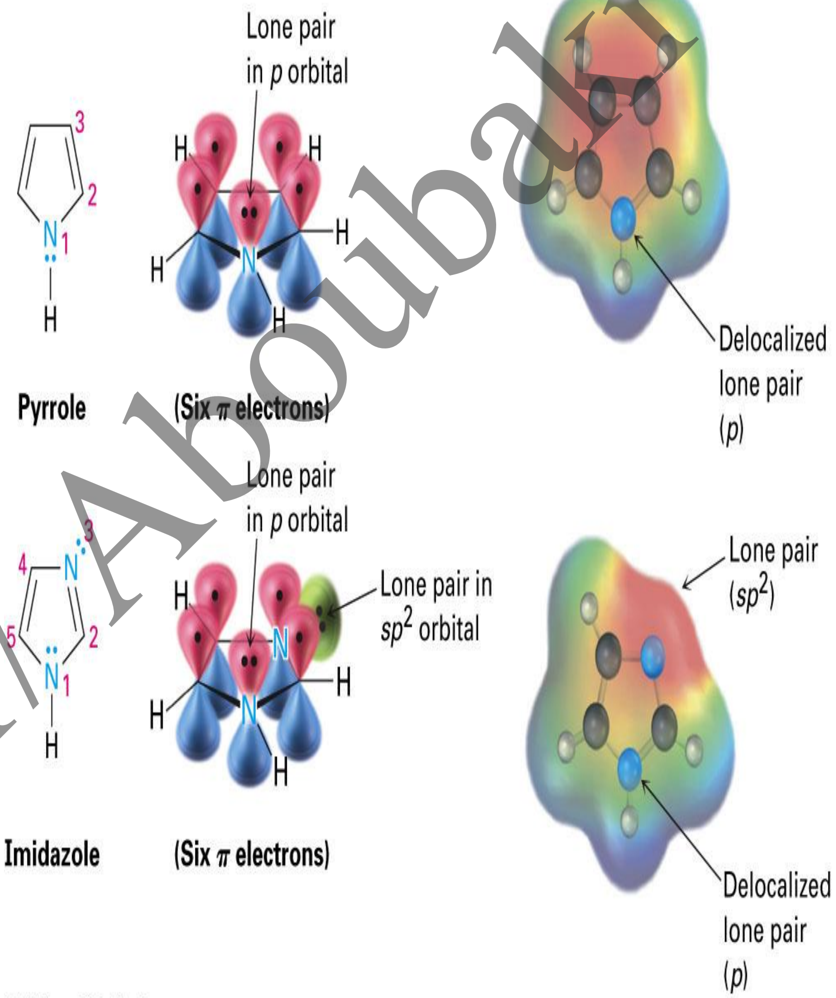
Pyridine

- A six-membered heterocycle with a nitrogen atom in its ring
- π electron structure resembles benzene (6 electrons).
- The nitrogen lone pair electrons are not part of the aromatic system (perpendicular orbital)
- Pyridine is a relatively weak base compared to normal amines but protonation does not affect aromaticity



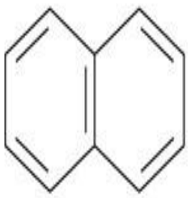
Pyrrole

- A five-membered heterocycle with one nitrogen
- π electron system similar to that of cyclopentadienyl anion
- Four *sp*²-hybridized carbons with 4 *p* orbitals perpendicular to the ring and 4 p electrons
- Nitrogen atom is *sp*²-hybridized, and lone pair of electrons occupies a *p* orbital (6 π electrons)
- Since lone pair electrons are in the aromatic ring, protonation destroys aromaticity, making pyrrole a very weak base

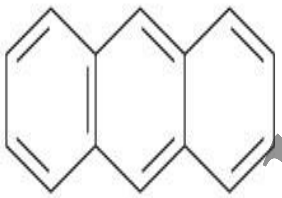


Polycyclic Aromatic Compounds

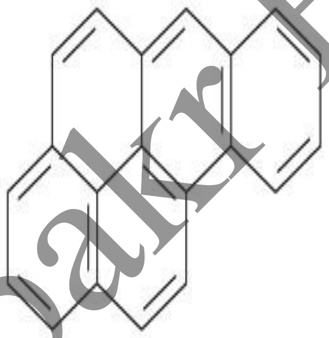
- Aromatic compounds can have rings that share a set of carbon atoms (fused rings)
- Compounds from fused benzene or aromatic heterocycle rings are themselves aromatic



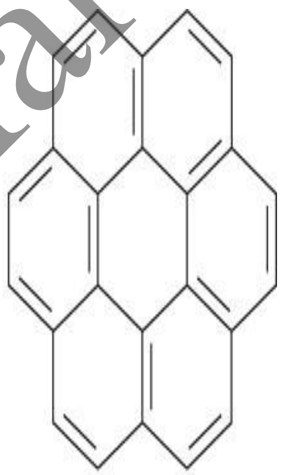
Naphthalene



Anthracene



Benzo[a]pyrene



Coronene

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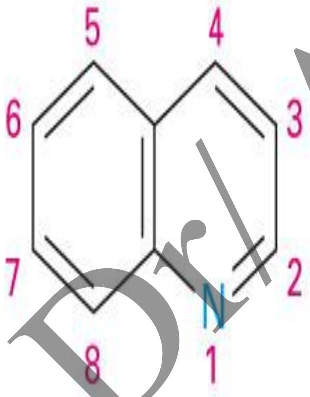
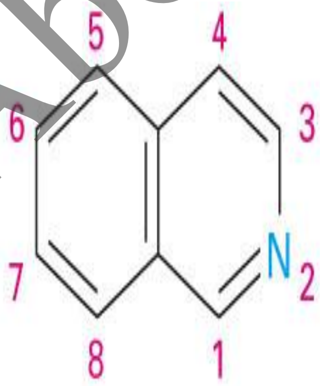
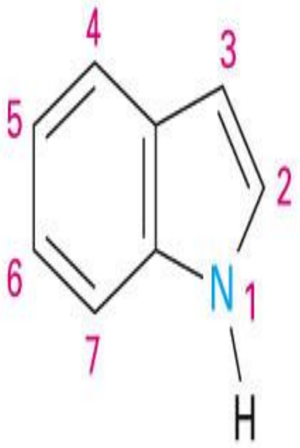


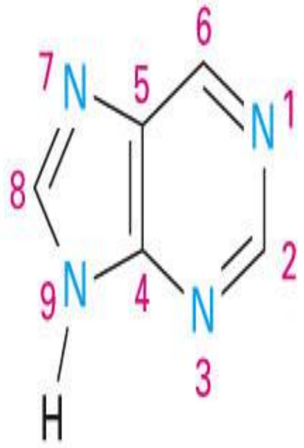
Quinoline



Isoquinoline



Indole



Purine

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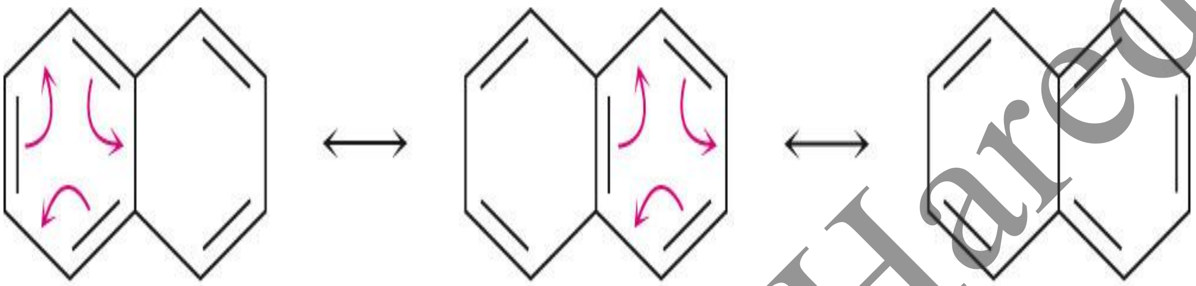
Naphthalene Orbitals

- Three resonance forms and delocalized electrons



Naphthalene

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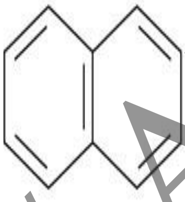

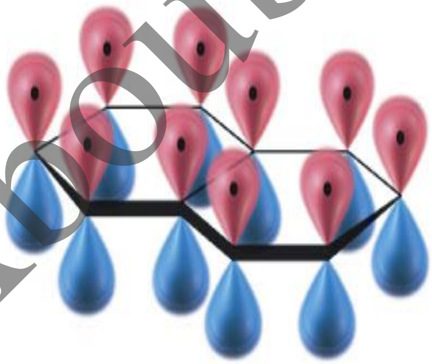

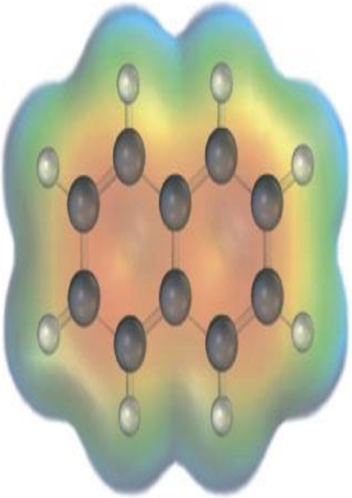

Naphthalene

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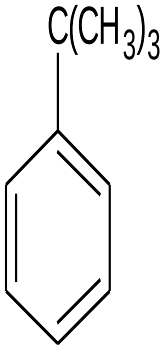
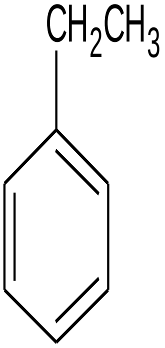
Nomenclature of Aromatic Compounds

1. Monosubstituted Benzenes

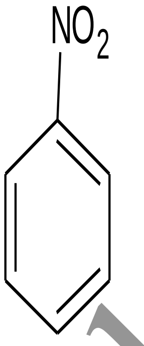
a. IUPAC name



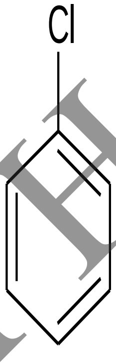
t-Butylbenzene



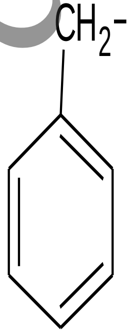
Ethylbenzene



Nitrobenzene

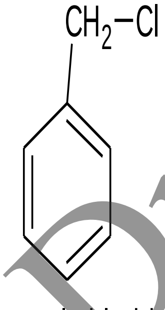


Chlorobenzene

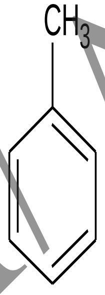


Benzyl group

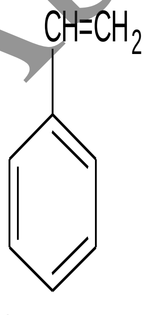
b. Common name



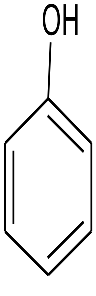
Benzyl chloride



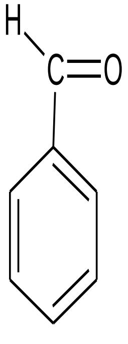
Toluene



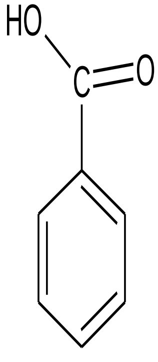
Styrene



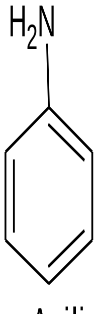
Phenol



Benzaldehyde



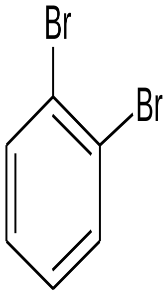
Benzoic acid



Aniline

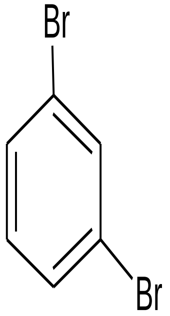
2. Disubstituted Benzenes

All disubstituted benzenes, can give rise to three possible isomers. The differentiate between the isomers, the relative positions of the substituents are designated by number or, more commonly, by the prefixes ortho (o: 1,2), meta (m:1,3) or para (p:1,4).



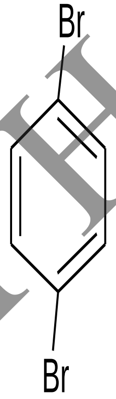
1,2-Dibromobenzene

o-Dibromobenzene



1,3-Dibromobenzene

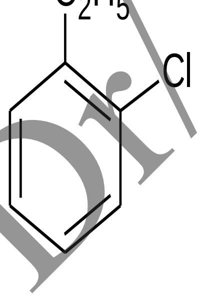
m-Dibromobenzene



1,4-Dibromobenzen

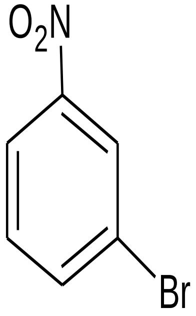
p-Dibromobenzene

When the substituents are different, they are listed in alphabetical order



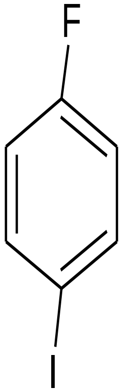
1-Chloro-2-ethylbenzene

o-Chloroethylbenzene



1-Bromo-3-nitrobenzene

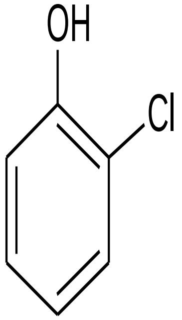
m-Bromonitrobenzene



1-Fluoro-4-iodobenzen

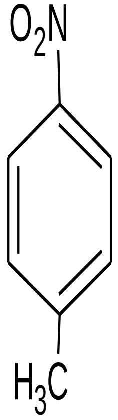
p-Fluoroiodobenzene

If one of the substituents is part of a parent compound, then the disubstituted benzene is named as a derivative of the parent compound.



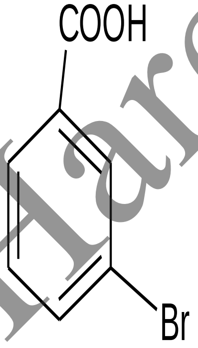
2-Chlorophenol

o-Chlorophenol



4-Nitrotoluene

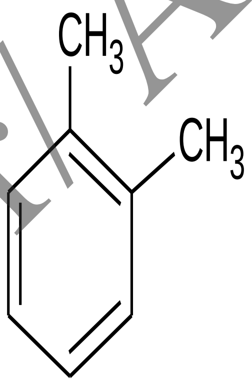
p-Nitrotoluene



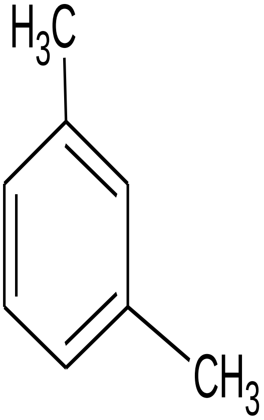
3-Bromobenzoic acid

m-Bromobenzoic aci

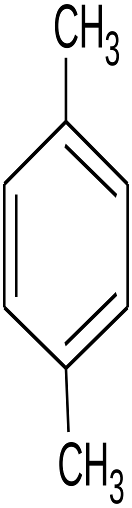
Certain disubstituted benzenes are referred to by their common names.



o-Xylene



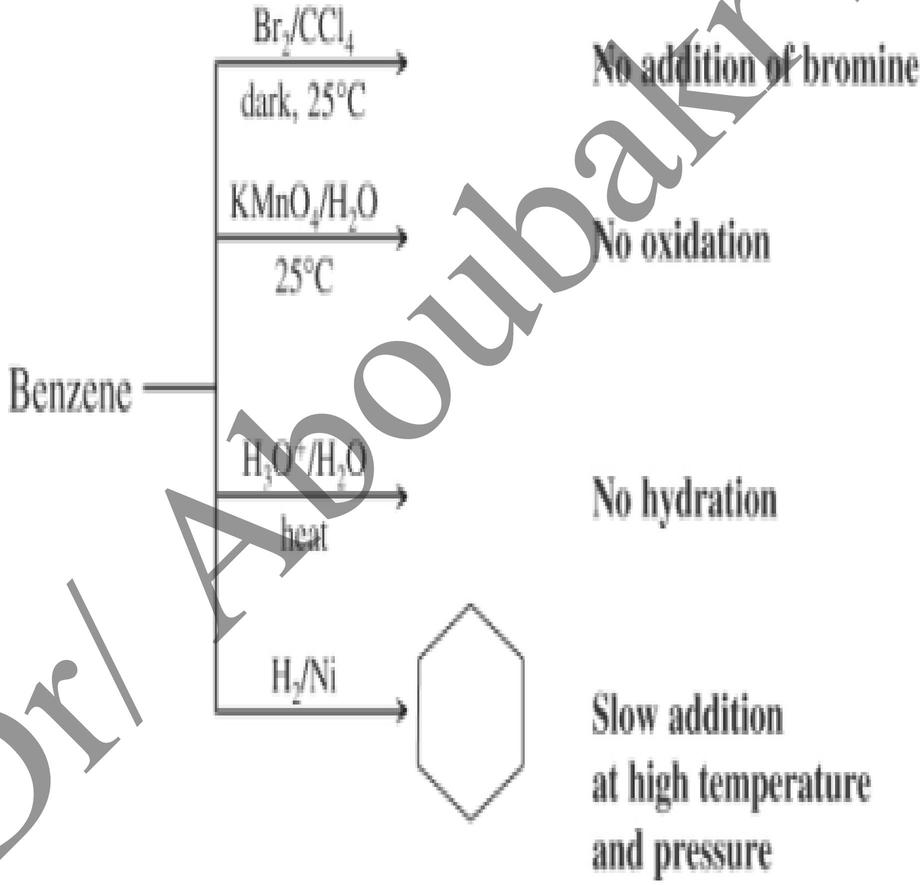
m-Xylene



p-Xylen

Reactions of Benzene

- **Even though benzene is highly unsaturated, it does not**
- **undergo any of the regular reactions of alkenes**



Reactions of Benzene

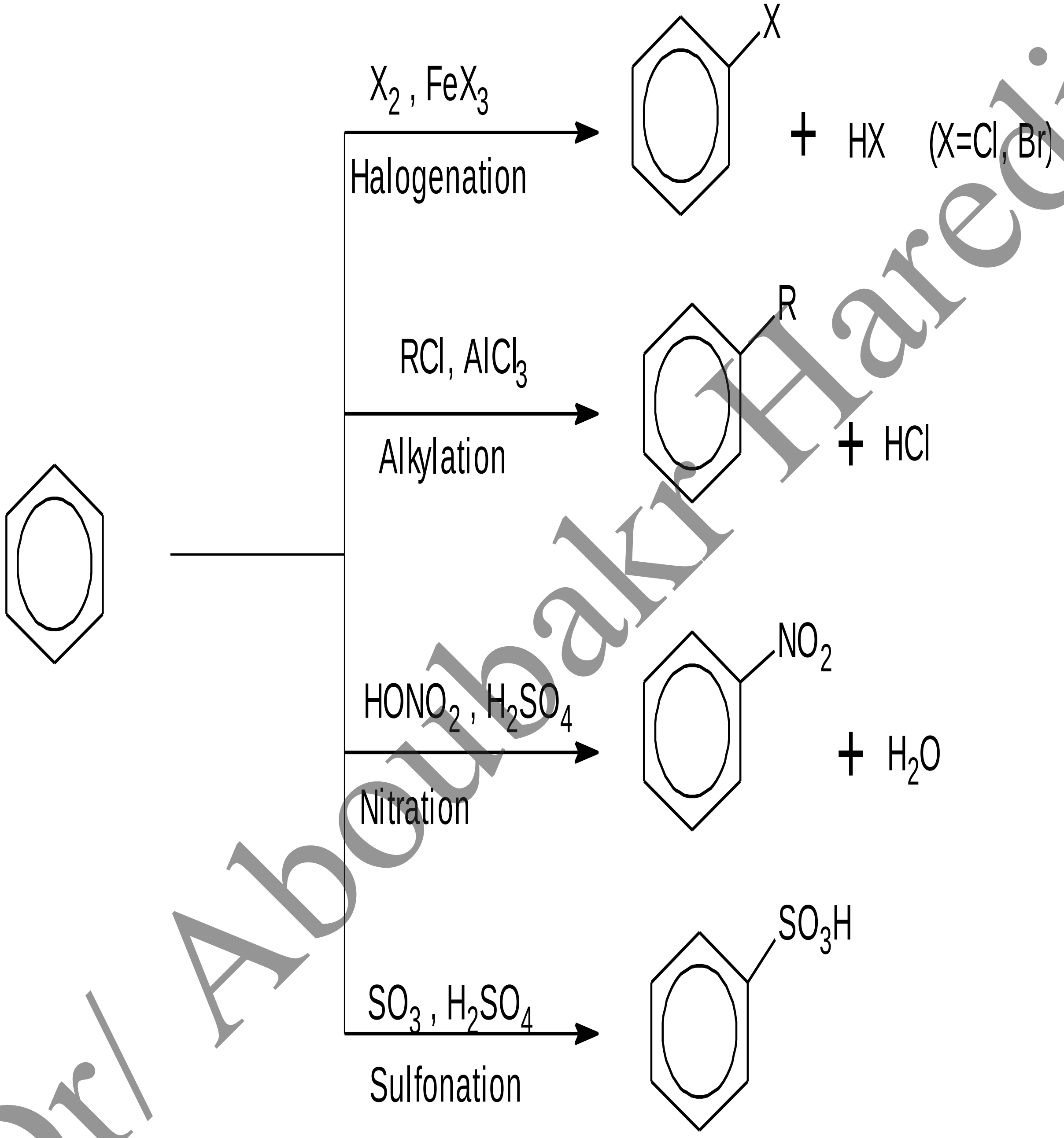
- Benzene can be induced to react with bromine if a Lewis acid catalyst is present
- The reaction is a *substitution* and not an addition!

$$C_6H_6 + Br_2 \xrightarrow{FeBr_3} C_6H_5Br + HBr \qquad \text{Observed}$$

$$C_6H_6 + Br_2 \nrightarrow C_6H_6Br_2 + C_6H_6Br_4 + C_6H_6Br_6 \qquad \text{Not observed}$$

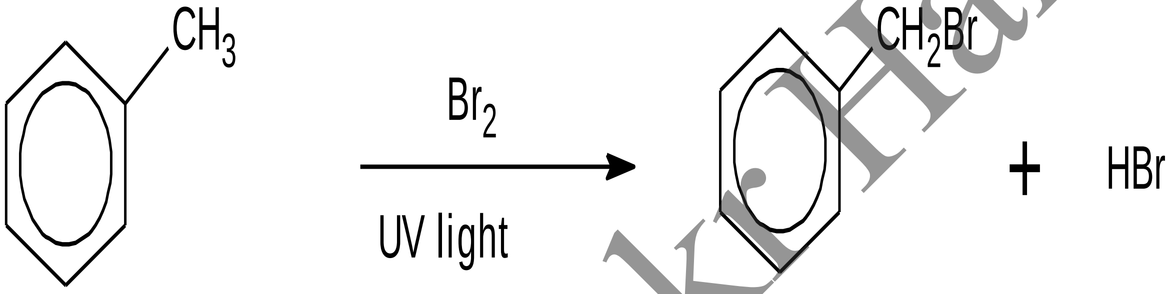
Benzene produces only one monobrominatedcompound
All 6 carbon-hydrogen bonds are equivalent in benzene

Specific Electrophilic Aromatic : Substitution Reactions



Side-Chain Reactions of Aromatic Compounds

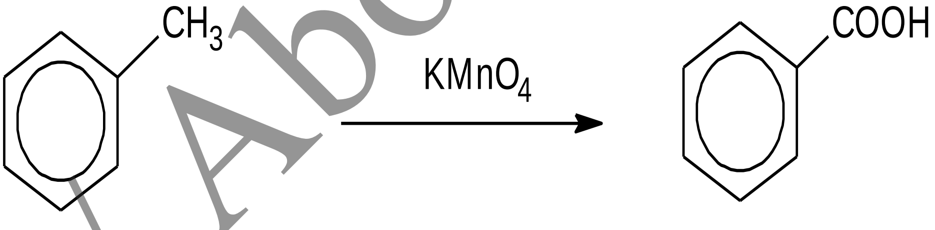
a. Halogenation of an Alkyl Side Chain



Toluene

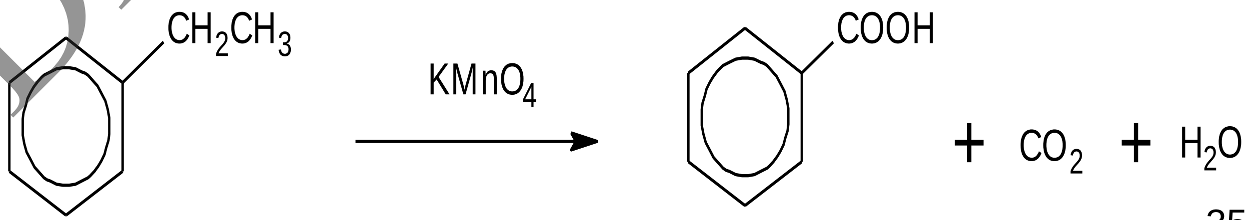
Benzyl Bromide

b. Oxidation of an Alkyl Side Chain



Toluene

Benzoic acid

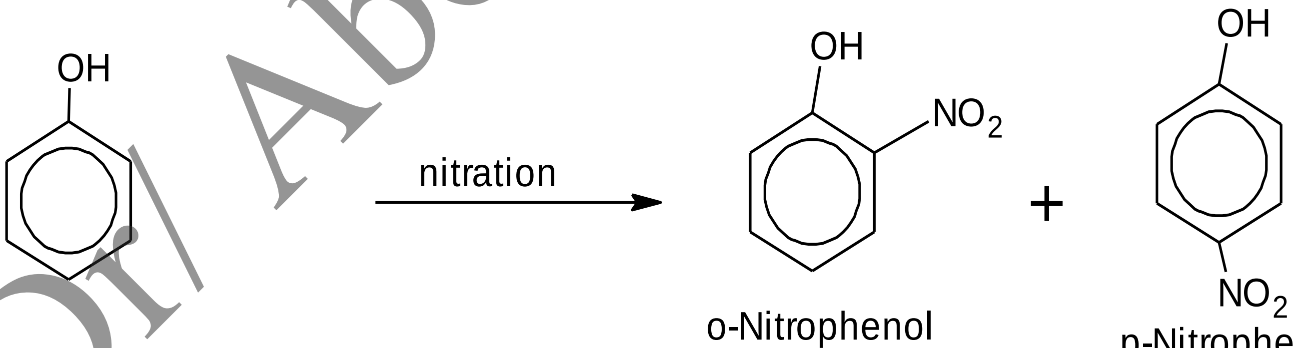


Benzoic acid

Disubstituted Benzenes : Orientation

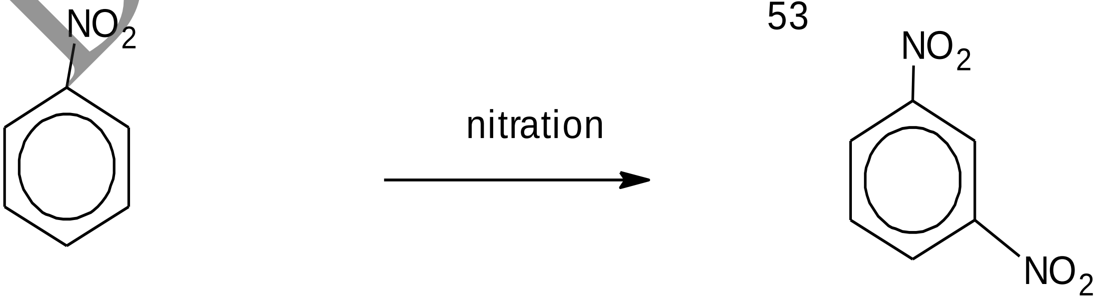
Orientation Effects of Substituents in Electrophilic Aromatic Substitution :

Ortho , para directors	Meta directors
-OH, -OR -NH2, -NHR, -NR2 -C6H5 -CH3, -R (alkyl) -F, -Cl, -Br, -I	-NO2 -SO3H -COOH, -COOR -CHO, -COR -CN



o-Nitrophenol
53

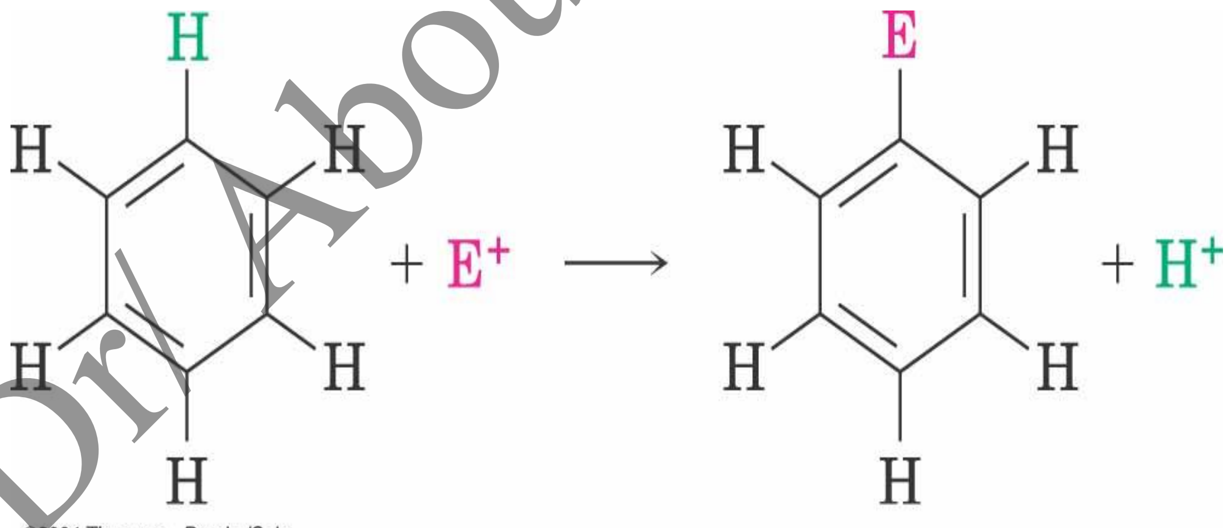
p-Nitropheno
47



Substitution Reactions of Benzene and Its Derivatives

- Benzene **does not** undergo electrophilic addition
- It undergoes electrophilic aromatic substitution maintaining the aromatic core
- Electrophilic aromatic substitution replaces a proton on benzene with another electrophile

electrophilic aromatic substitution



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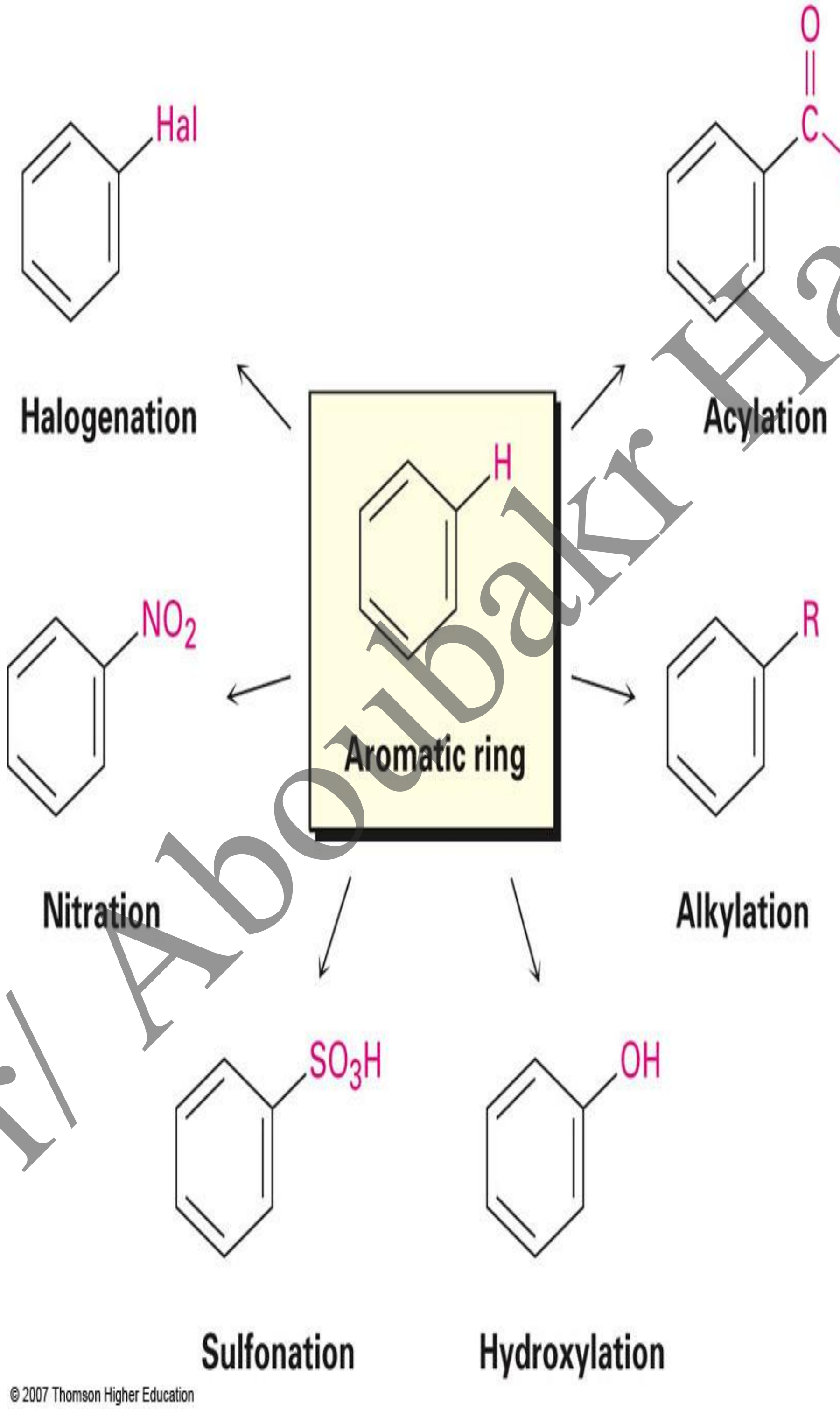
Electrophilic Aromatic Substitution

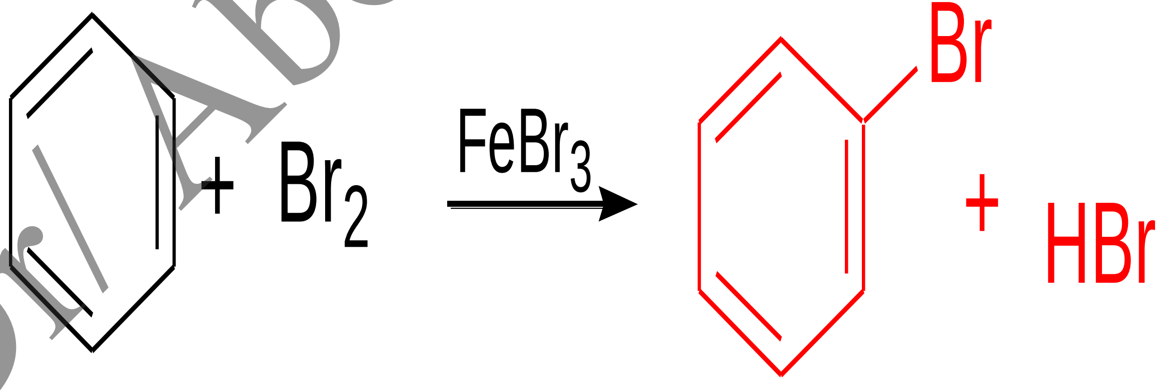


Halogenation of Benzene

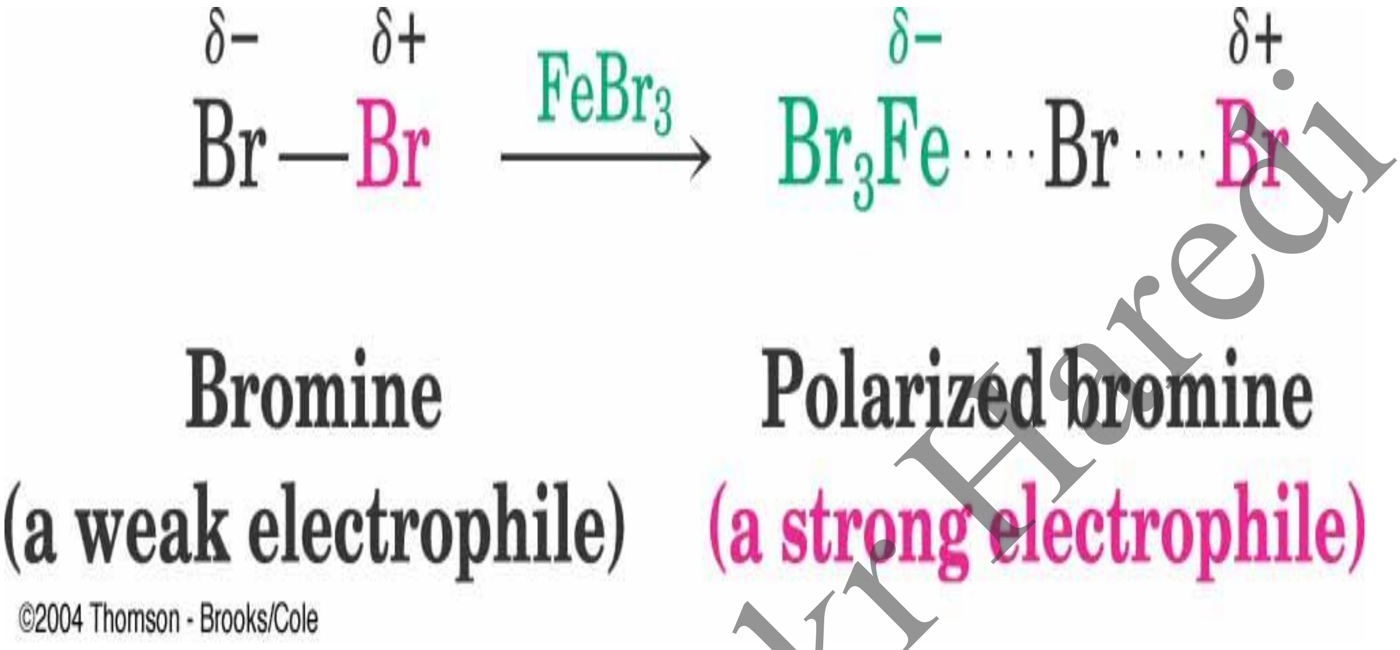
- Benzene’s π electrons participate as a Lewis base in reactions with Lewis acids
  - Lewis acid: electron pair acceptor
  - Lewis base: electron pair donor
- The product is formed by loss of a proton, which is replaced by a halogen

Bromination of Aromatic Rings

- Benzene's π electrons participate as a Lewis base in reactions with Lewis acids
- The product is formed by loss of a proton, which is replaced by bromine
- $FeBr_3$ is added as a catalyst to polarize the bromine reagent



Bromine Polarization



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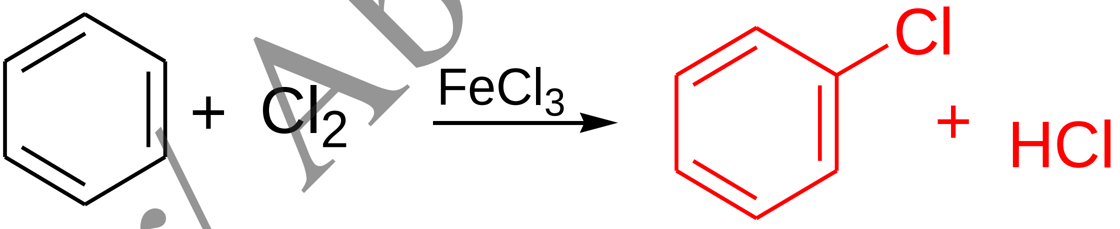
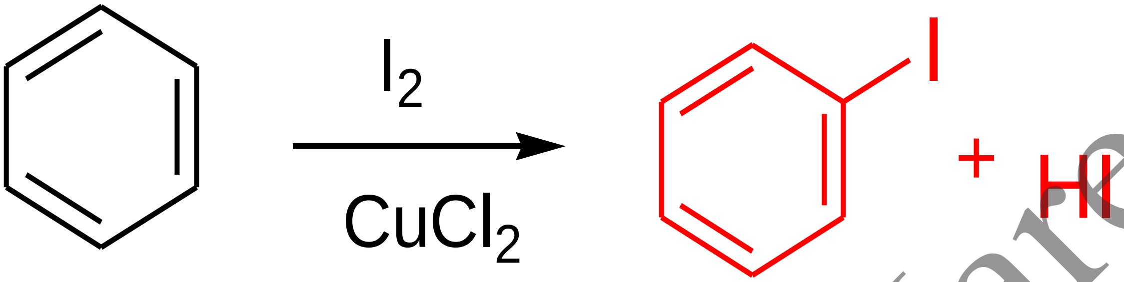
Chlorination of Aromatic Rings



Same mechanism as Br_2 with $FeBr_3$

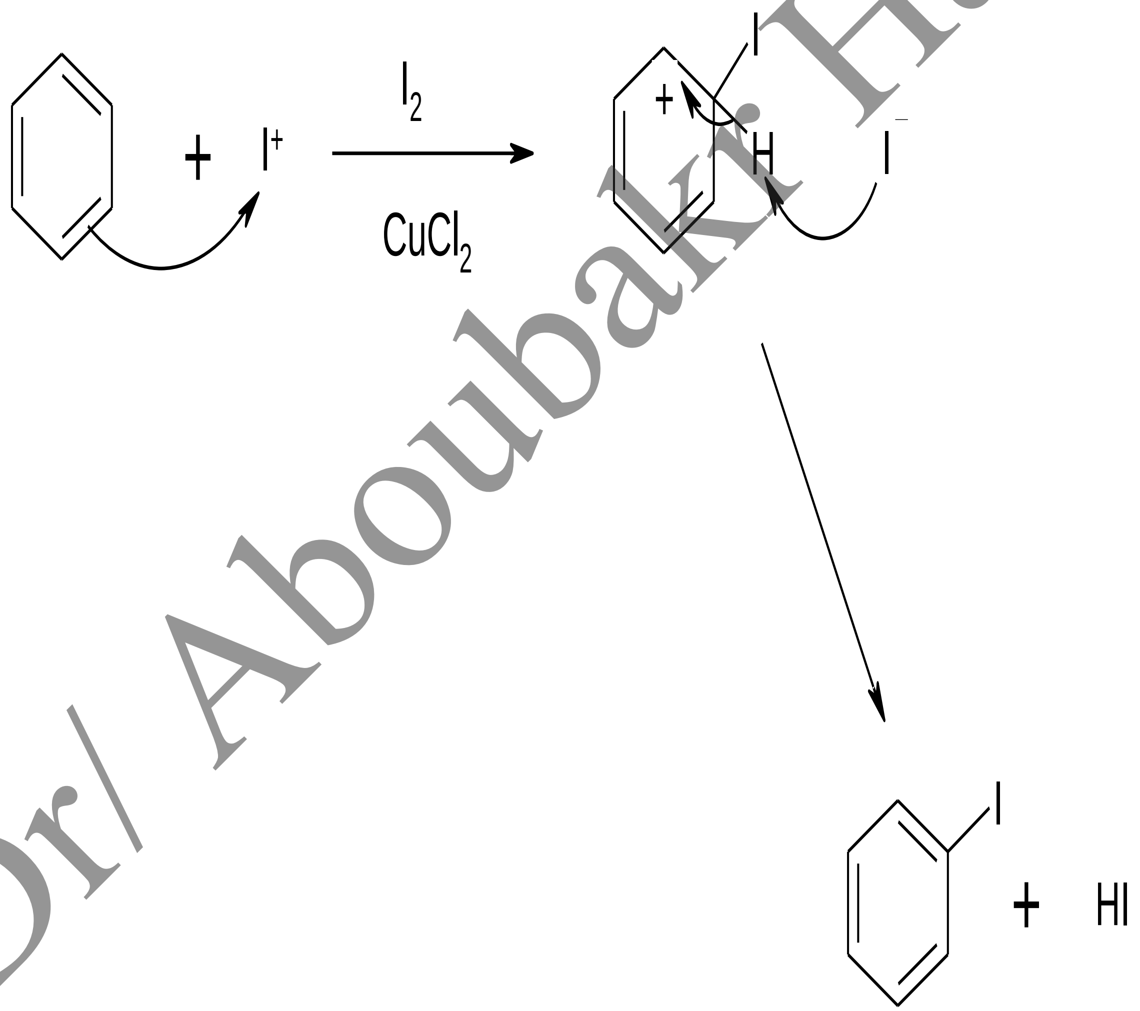
Iodination of Aromatic Rings



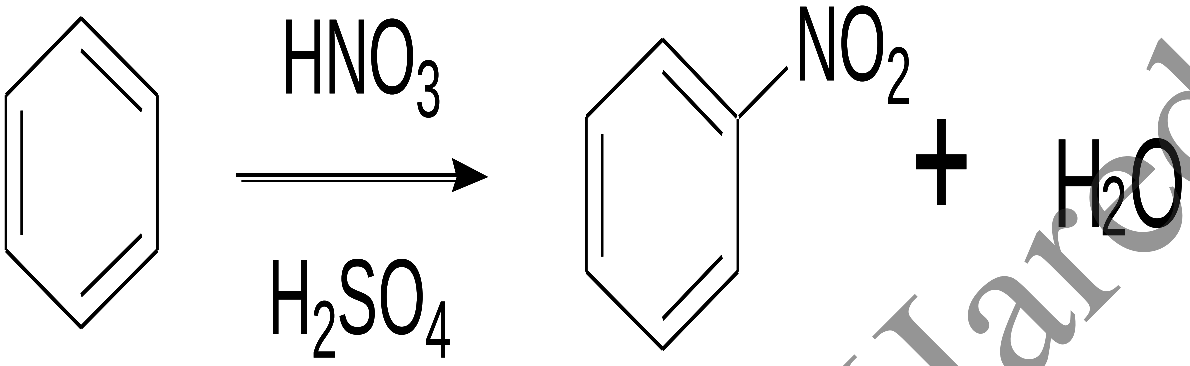
- Iodine is unreactive towards aromatic rings
- Oxidizing agents must be added to make reaction go (H_2O_2 or $CuCl_2$)
- Oxidizing agents oxidize I_2 to a usable form (electrohphillic) that reacts as if it were I^+

Mechanism : Iodination of Aromatic Rings

$$I_2 + 2\,Cu^{2+} \longrightarrow 2\,I^{+} + 2\,Cu^{+}$$



Nitration of Aromatic Rings

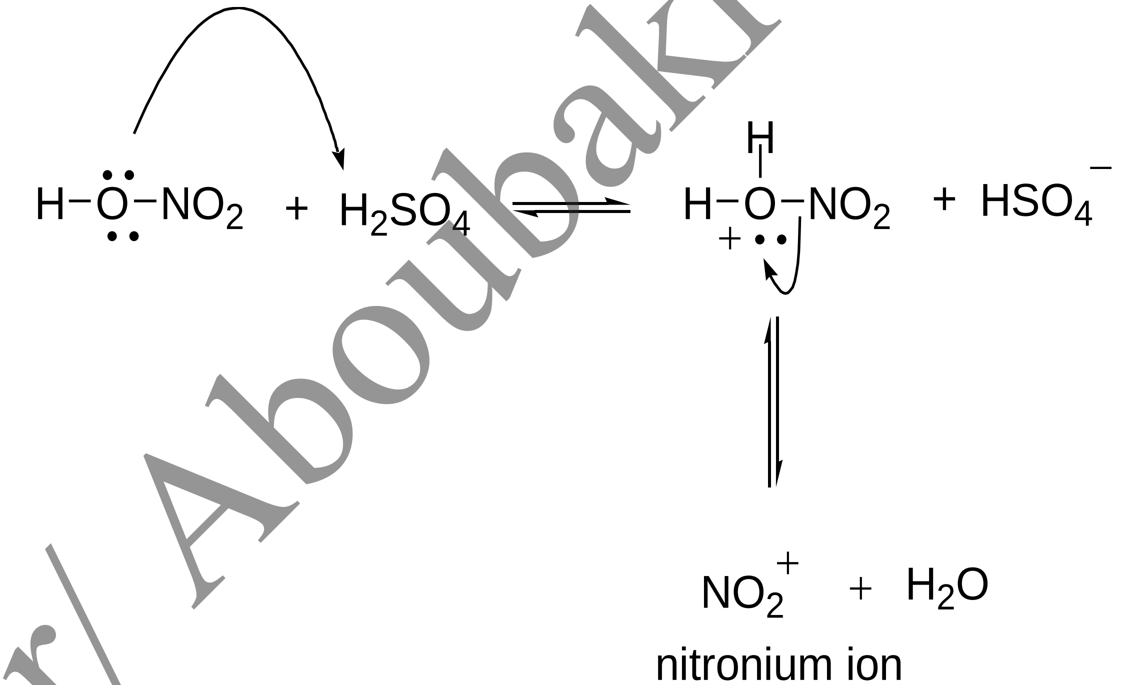


Electrophile is the nitronium ion (NO_2^+)

Generated from HNO_3 by protonation and loss of water

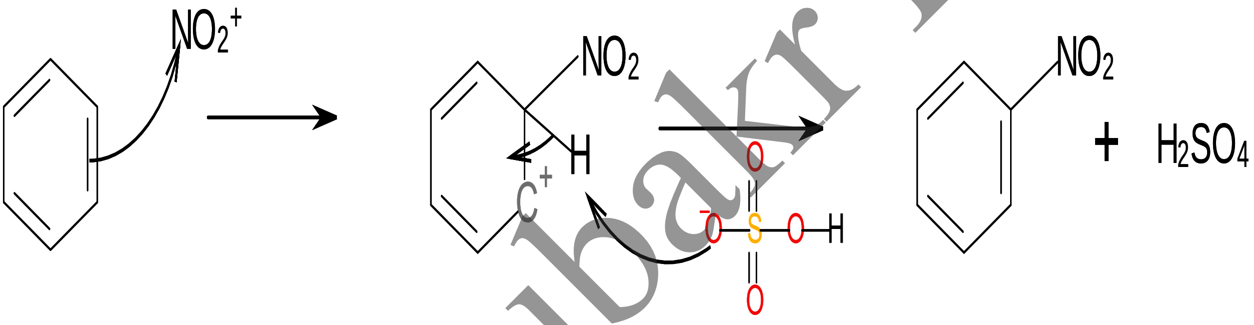
Mechanism : Nitration of Aromatic Rings

- An electrophile must first be generated by treating concentrated nitric acid with concentrated sulfuric acid

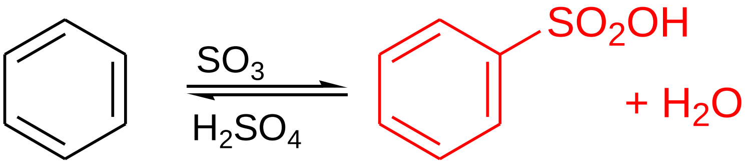


Mechanism : Nitration of Aromatic Rings

- The nitronium electrophile is attacked by the benzene ring (nucleophile)



Sulfonation of Aromatic Rings



Fuming sulfuric acid – combination of SO_3 and H_2SO_4

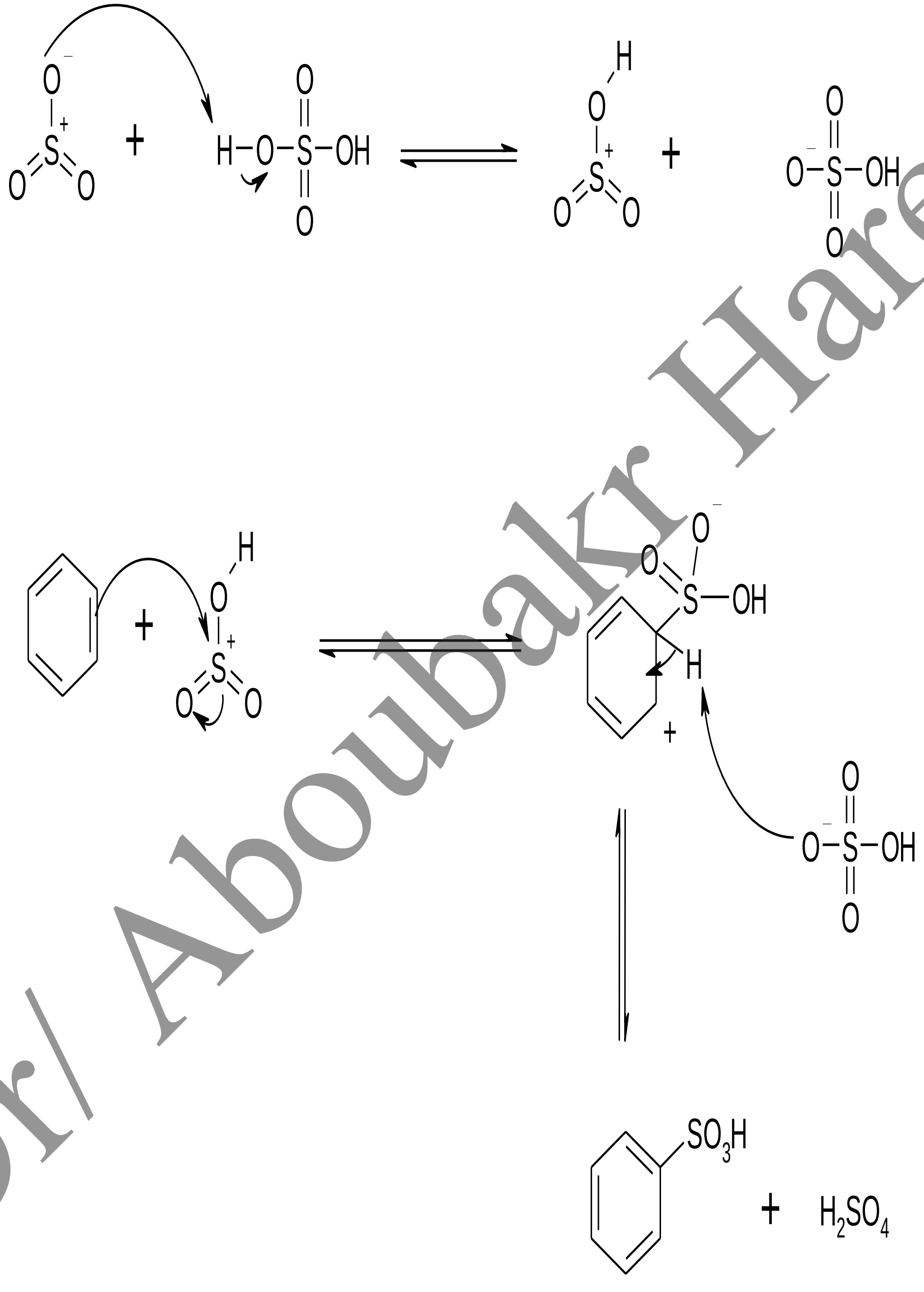
Electrophile is HSO_3^+ or SO_3

Reaction is reversible

Favored in forward direction with strong acid

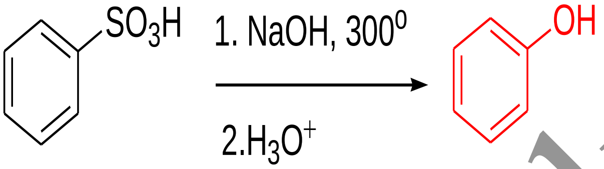
Favored in reverse direction with hot dilute aqueous acid

Mechanism : Sulfonation of Aromatic Rings



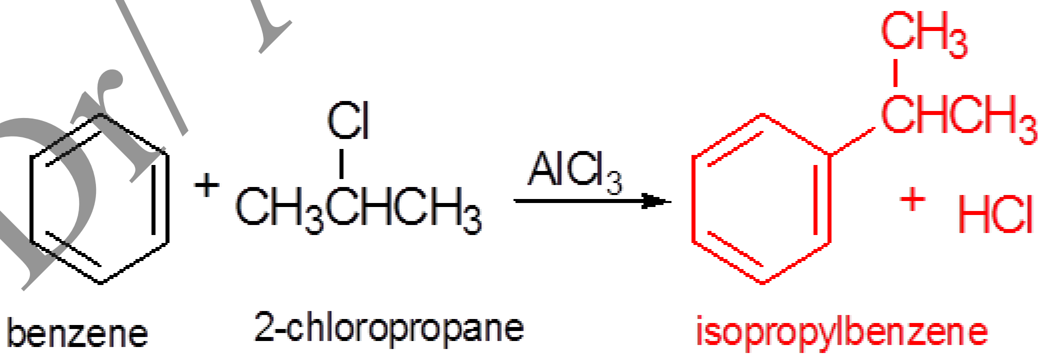
Conversion of sulfonic acids

- Heating with NaOH at 300 ºC followed by neutralization with acid replaces the SO_3H group with an OH

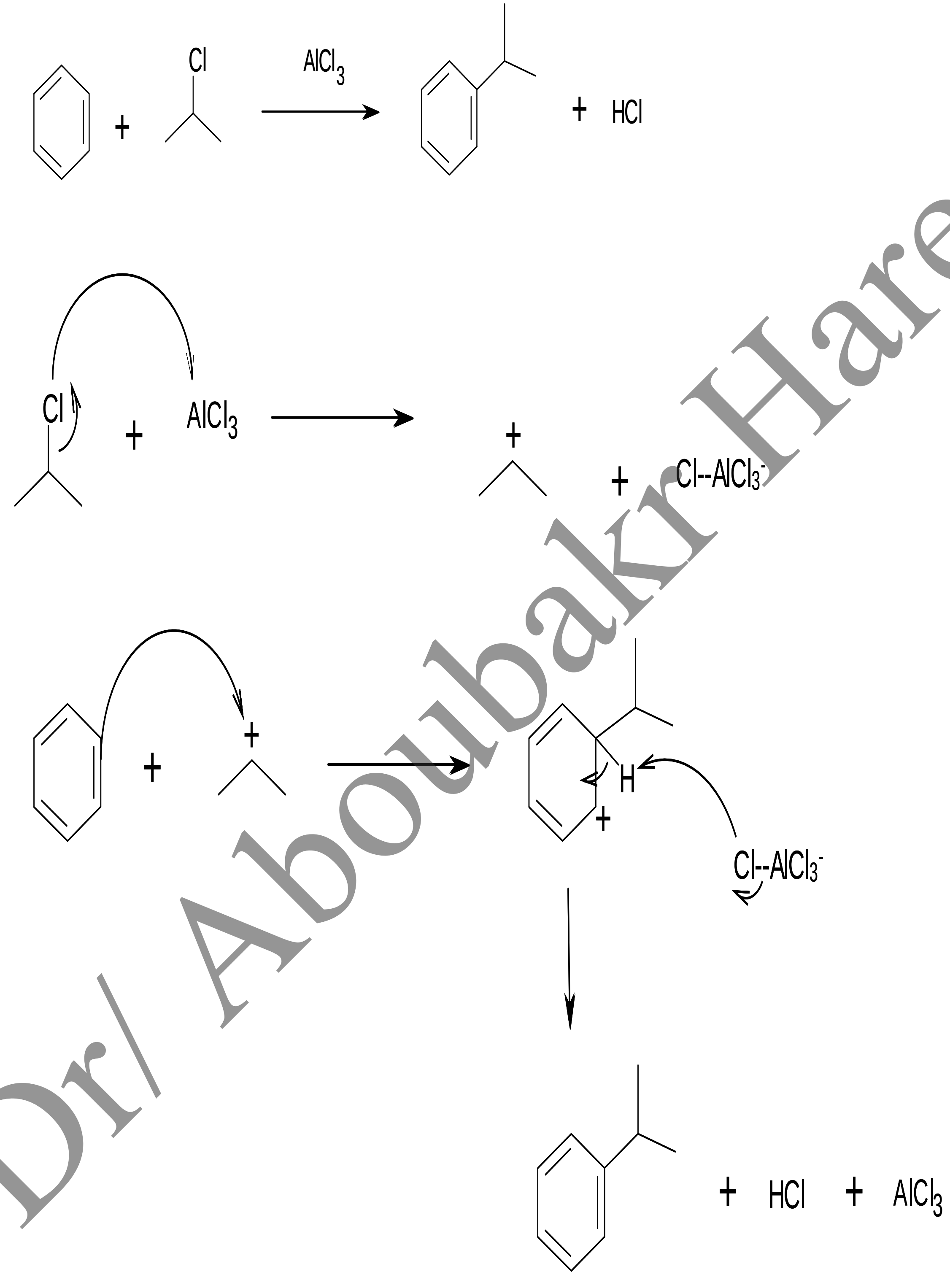


No mechanism

Friedel-Crafts Reaction



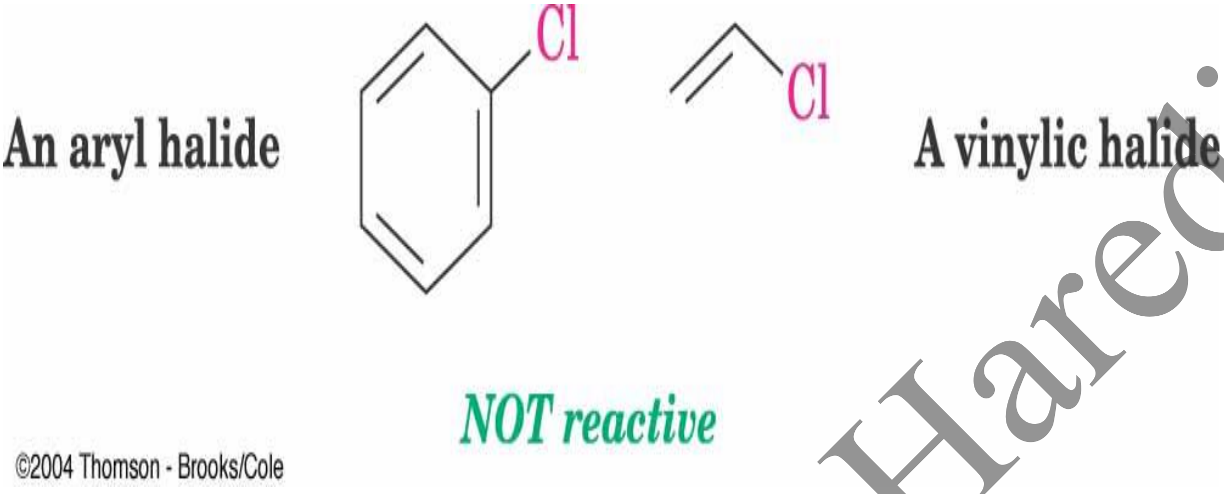
Mechanism : Friedel-Crafts Reaction



Friedel-Crafts Reaction (Alkylation of Aromatic Rings)

- the electrophile is a carbocation, R^+
- only alkyl halides can be used
  - **aryl halides and vinylic halides do not react.**
- will not occur on aromatic rings substituted by electron withdrawing substituents
- can’t eat just one! It’s hard to stop after one substitution
- skeletal rearrangements of the alkyl group often occur when using primary alkyl halides

Non-reactive



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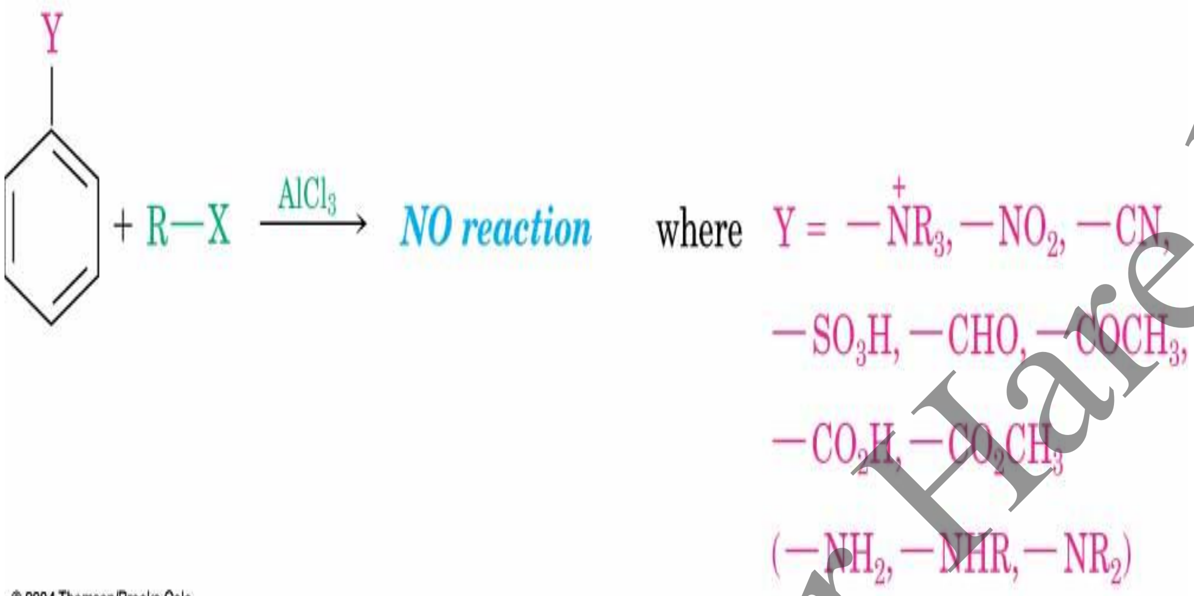
Ring Deactivators



where $Y = -\overset{+}{N}R_3, -NO_2, -CN,$
$-SO_3H, -CHO, -COCH_3,$
$-CO_2H, -CO_2CH_3$
$(-NH_2, -NHR, -NR_2)$

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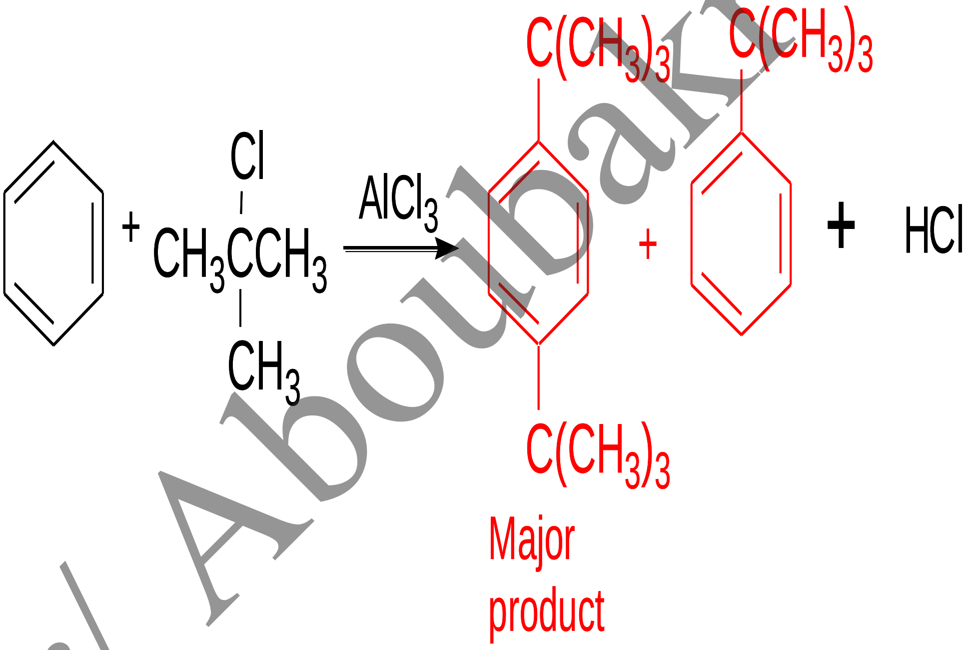
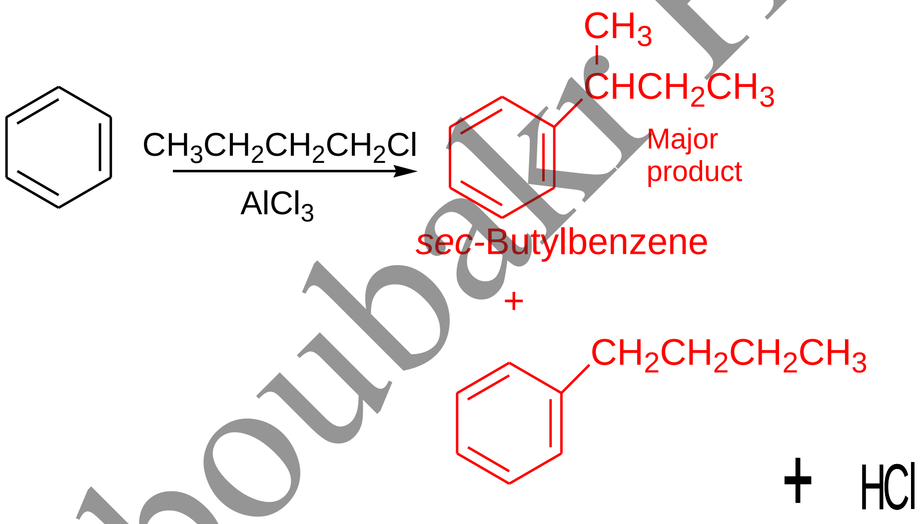
Friedel-Crafts Reaction

- Multiple substitutions:
  - Reaction of benzene with 2-chloro-2methylpropane.
  - Polyalkylation



Friedel-Crafts Reaction

- Skeletal rearrangements in Friedel-Crafts reactions (hydride shift):
  - Will rearrange to form more stable carbocation intermediates

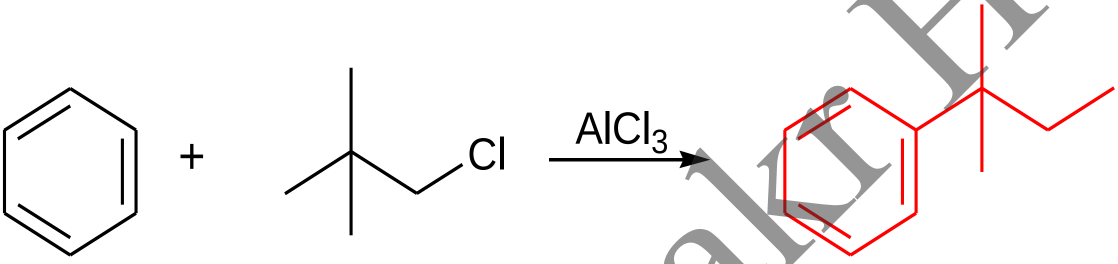


sec-Butylbenzene

Butylbenzene

Friedel-Crafts Reaction

- Skeletal rearrangements in Friedel-Crafts reactions (alkyl shift):
  - Will rearrange to form more stable carbocation intermediates



1-Chloro-2,2-dimethylpropane

(1,1-Dimethylpropyl)-benzene

$+ \ HCl$

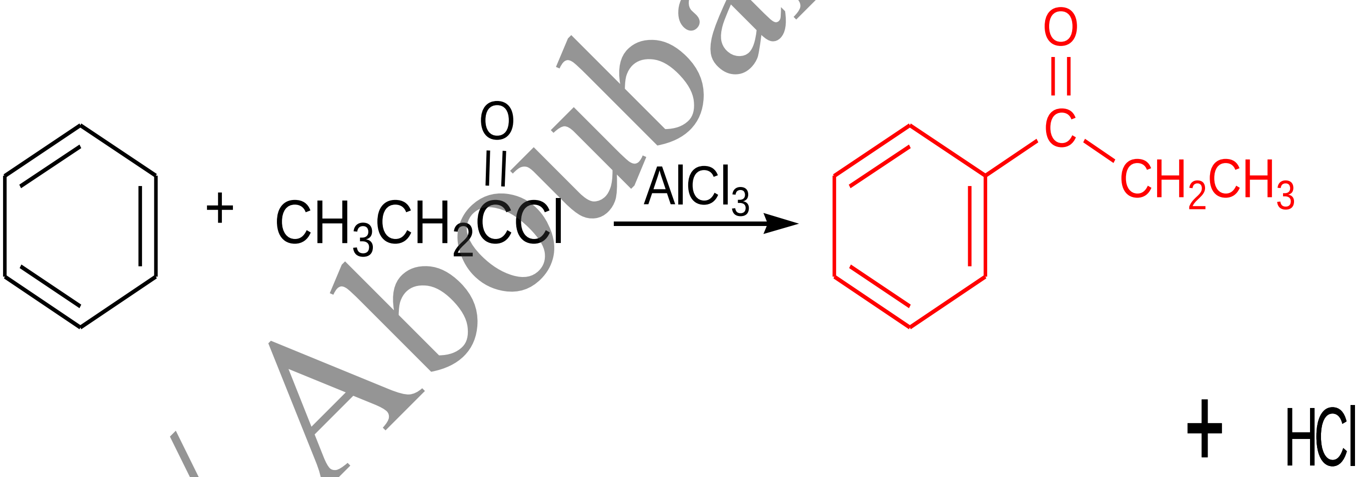
Friedel-Crafts Alkylation Summary

- Only alkyl halides can be used!!
- Will not occur on aromatic rings substituted by electron withdrawing substituents
  - Carbonyl and amino groups
- Will have polyalkylation
- Will have rearrangement to form more stable carbocation intermediate
  - Hydride shift or methyl shift
- You need to know the mechanism!!!

Friedel-Crafts Acylation

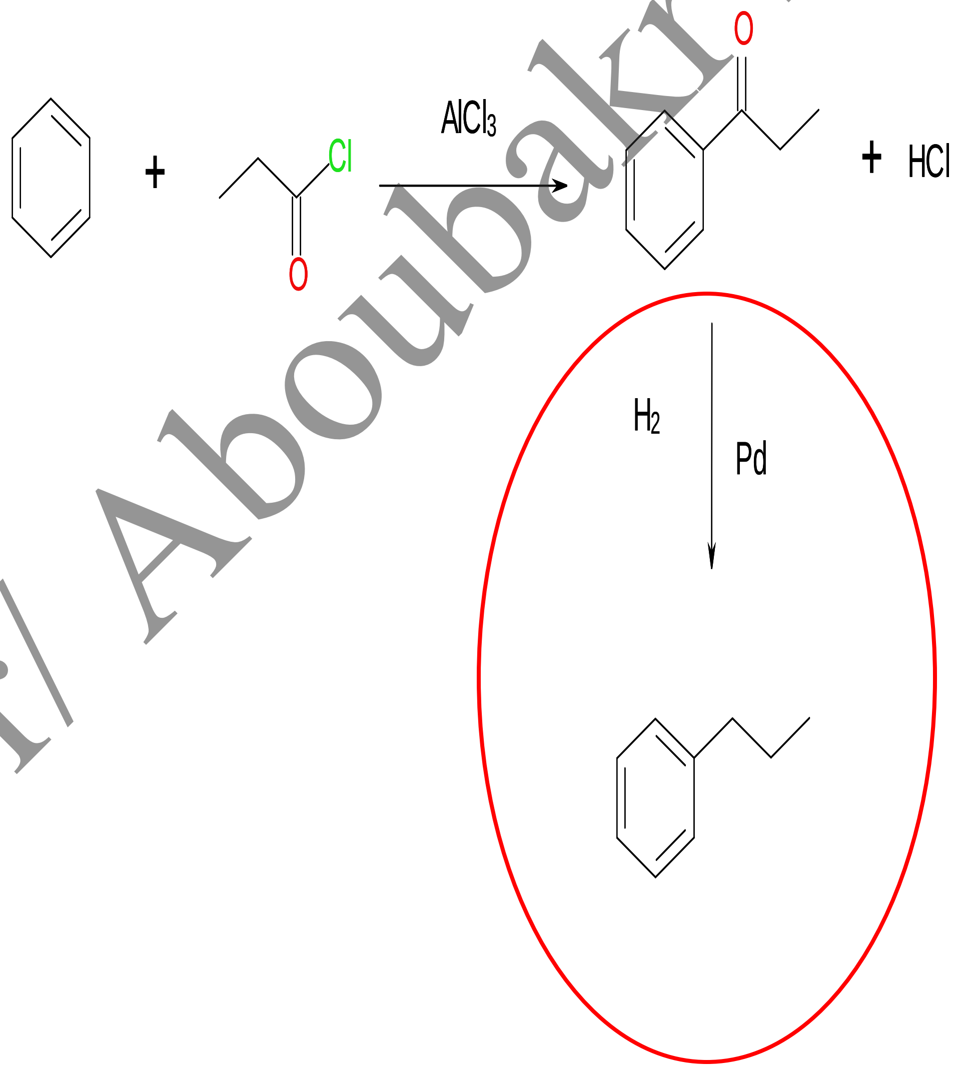
- Reaction of benzene with a carboxylic acid chloride, RCOCl in the presence of $AlCl_3$

- Note: the acyl cation **does not** undergo rearrangement. It also is **not** prone to multiple substitutions.

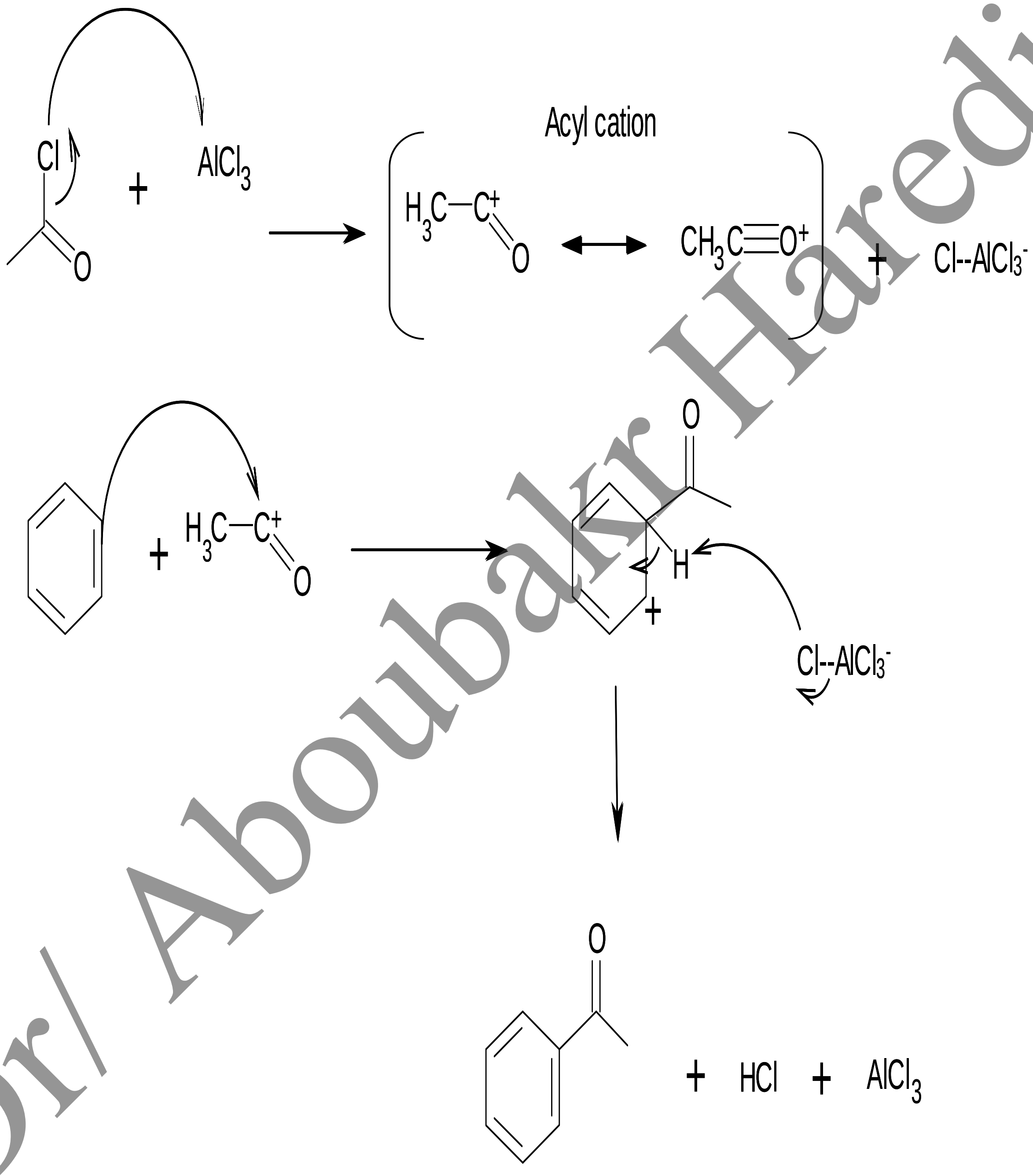


Friedel-Crafts Acylation

- After acylation we can do a hydrogenation to get desired alkylated product



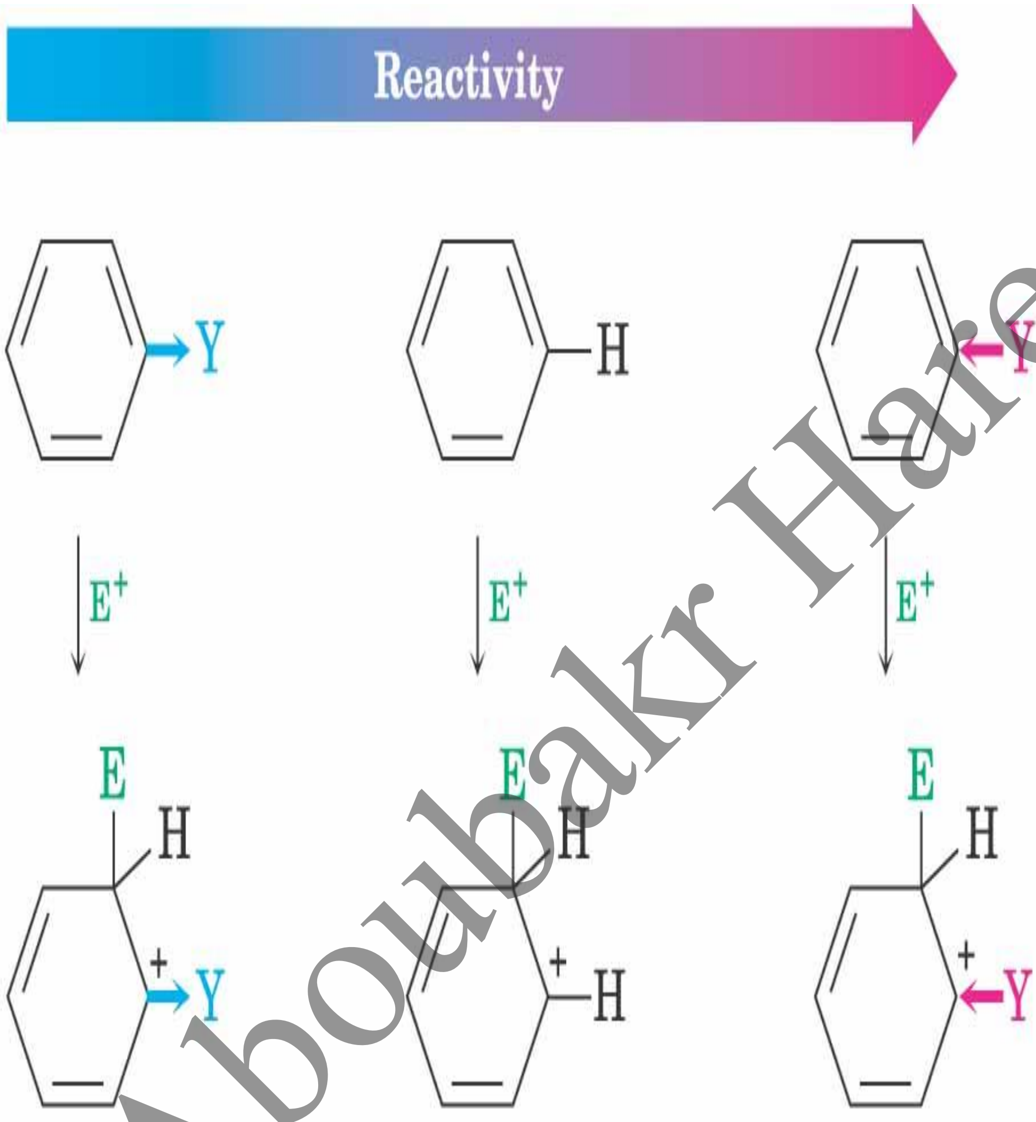
Mechanism : Friedel-Crafts Acylation



Substituent Effects in Aromatic Rings

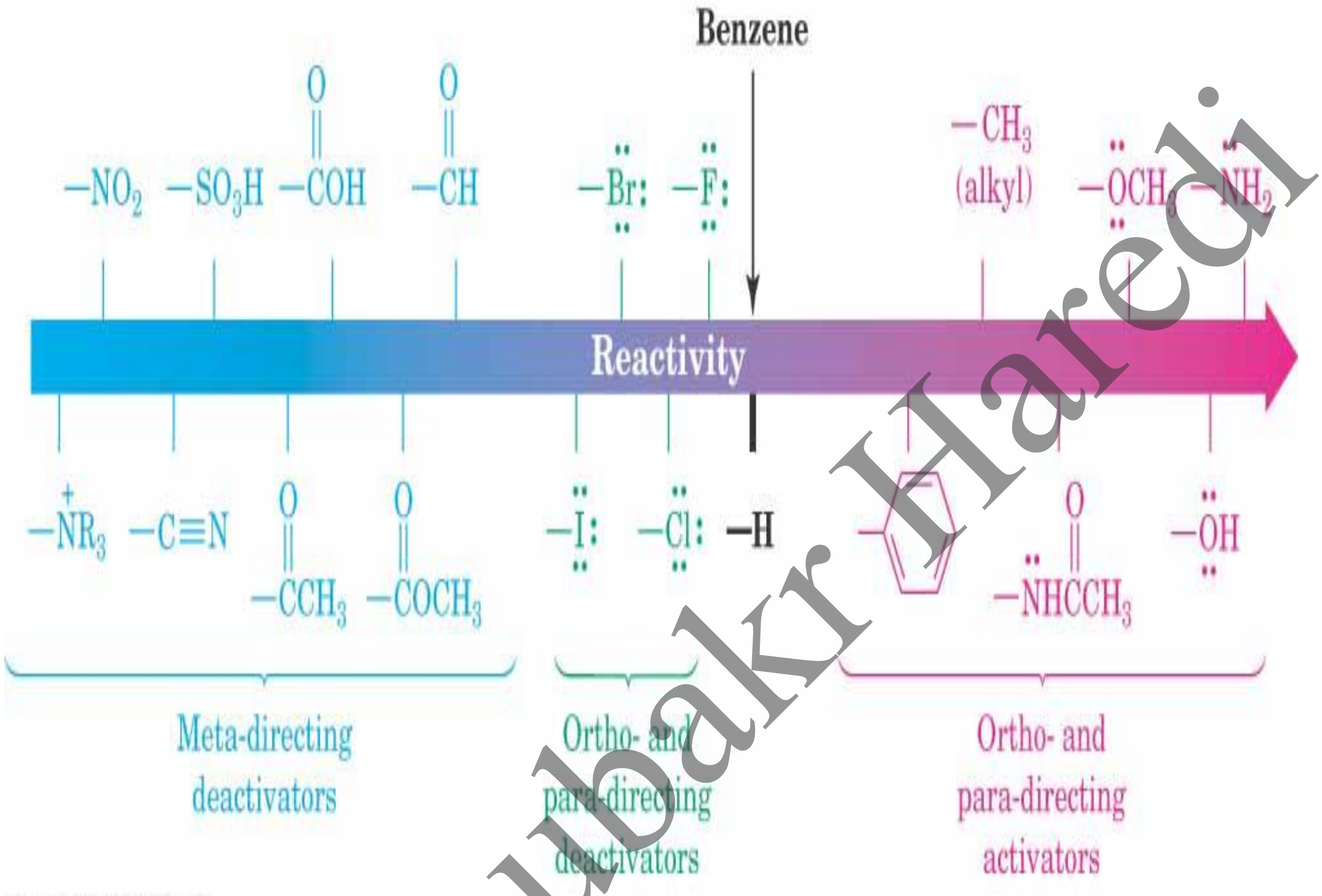
- Substituents can cause a compound to be (much) more or (much) less reactive than benzene

- Substituents affect the orientation of the reaction – the positional relationship is controlled
  - ortho- and para-directing activators, ortho- and para-directing deactivators, and meta-directing deactivators



Y withdraws electrons; carbocation intermediate is less stable, and ring is less reactive.

Y donates electrons; carbocation intermediate is more stable, and ring is more reactive.

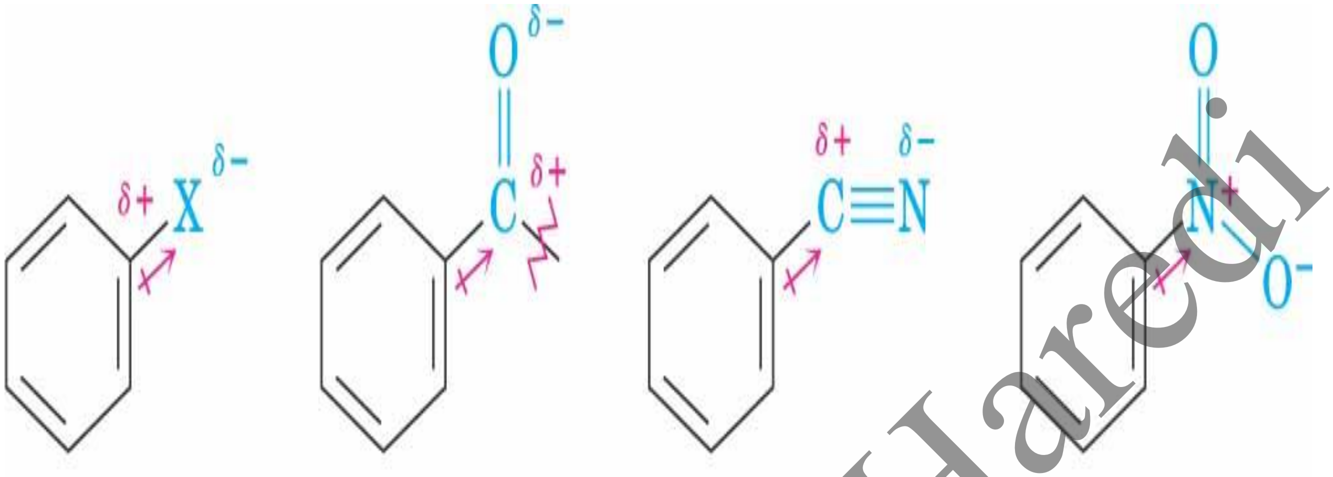

Benzene
−NO2
−SO3H
−COH
−CH
−Br:
−F:
−CH3
(alkyl)
−OCH3
−NH2
Reactivity
−NR3
−C≡N
−CCH3
−COCH3
−I:
−Cl:
−H
−NHCCH3
−OH
Meta-directing
deactivators
Ortho- and
para-directing
deactivators
Ortho- and
para-directing
activators

Origins of Substituent Effects

- An interplay of *inductive effects* and *resonance effects*
- Inductive effect - withdrawal or donation of electrons through a σ bond (comparative electronegativity)
- Resonance effect - withdrawal or donation of electrons through a π bond due to the overlap of a *p* orbital on the substituent with a *p* orbital on the aromatic ring

Inductive Effects

- Controlled by electronegativity and the polarity of bonds in functional groups
- Halogens, C=O, CN, and NO_2 *withdraw* electrons through σ bond connected to ring
- Alkyl groups *donate* electrons



(X = F, Cl, Br, I)

The groups attached to the aromatic rings are inductively electron-withdrawing because of the polarity of their bonds.

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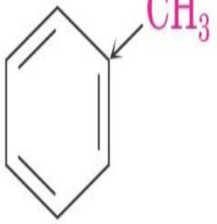

Alkyl group; inductively electron-donating

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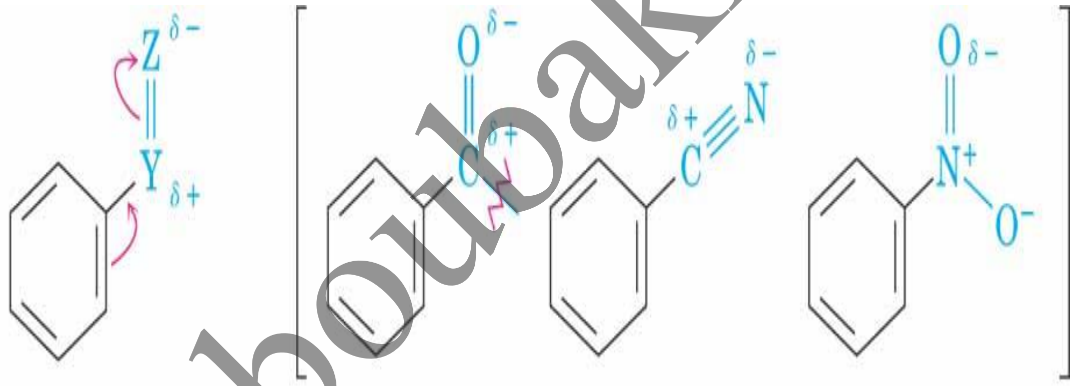
Resonance Effects – Electron Withdrawal

- $C=O$, CN, NO_2 substituents *withdraw* electrons from the aromatic ring by resonance

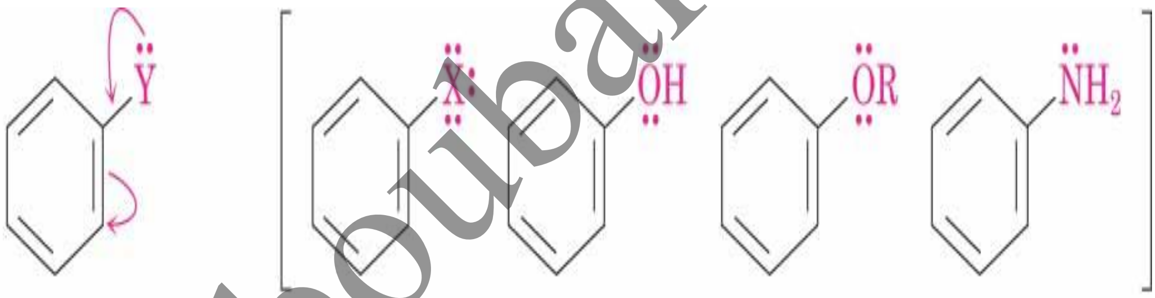
- π electrons flow from the rings to the substituents



Rings substituted by a group with an electron-withdrawing resonance effect have this general structure.

Resonance Effects – Electron Donation

- Halogen, OH, alkoxyl (OR), and amino substituents *donate* electrons
- π electrons flow from the substituents to the ring
- Effect is greatest at ortho and para



Rings substituted by a group with an electron-donating resonance effect have this general structure.

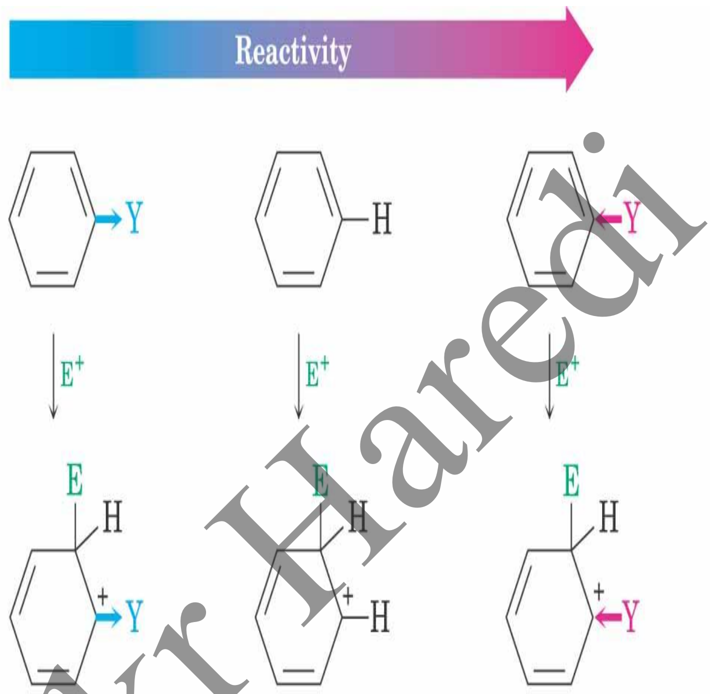
Contrasting Effects

- Halogen, OH, OR, withdraw electrons inductively so that they deactivate the ring
- Resonance interactions are generally weaker, affecting orientation
- The strongest effects dominate

An Explanation of Substituent Effects

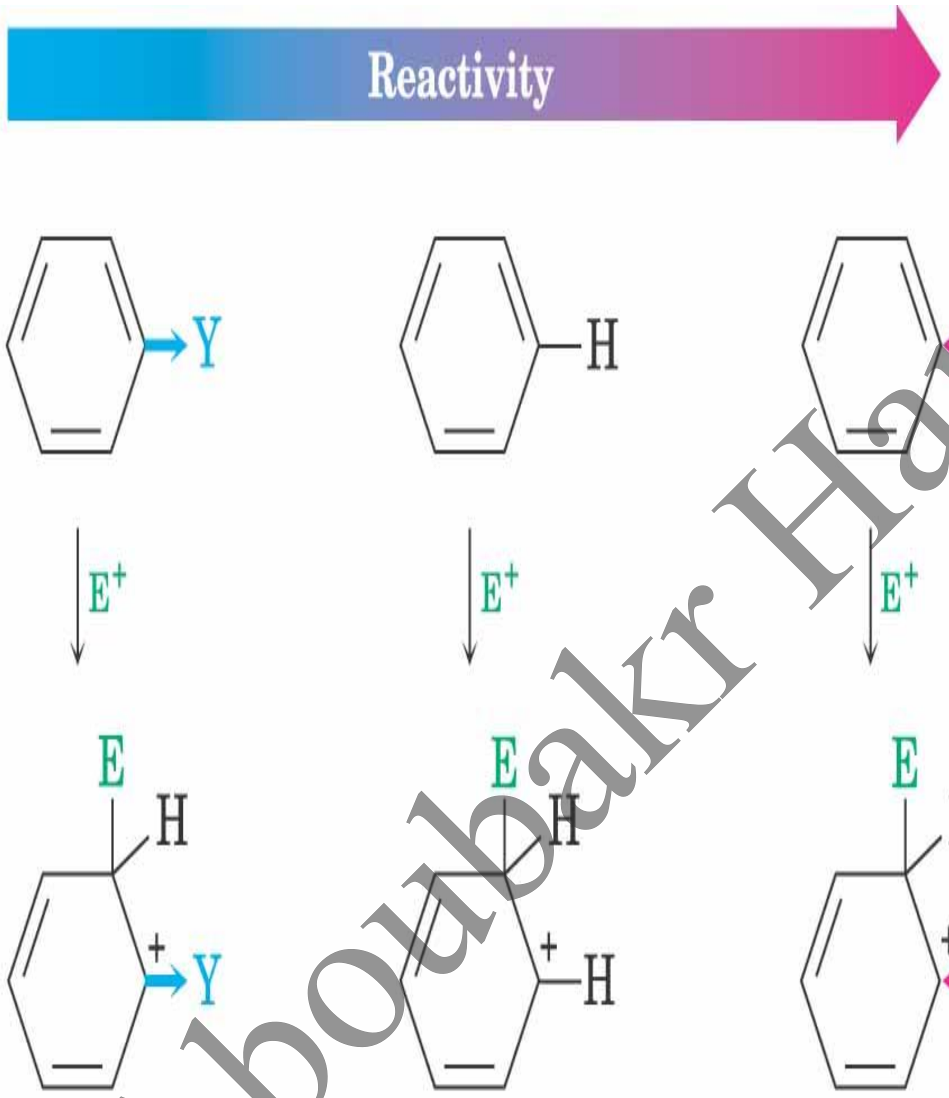
- Activating groups donate electrons to the ring, stabilizing the Wheland intermediate (carbocation)

- Deactivating groups withdraw electrons from the ring, destabilizing the Wheland intermediate



Y withdraws electrons; carbocation intermediate is less stable, and ring is less reactive.

Y donates electrons; carbocation intermediate is more stable, and ring is more reactive.



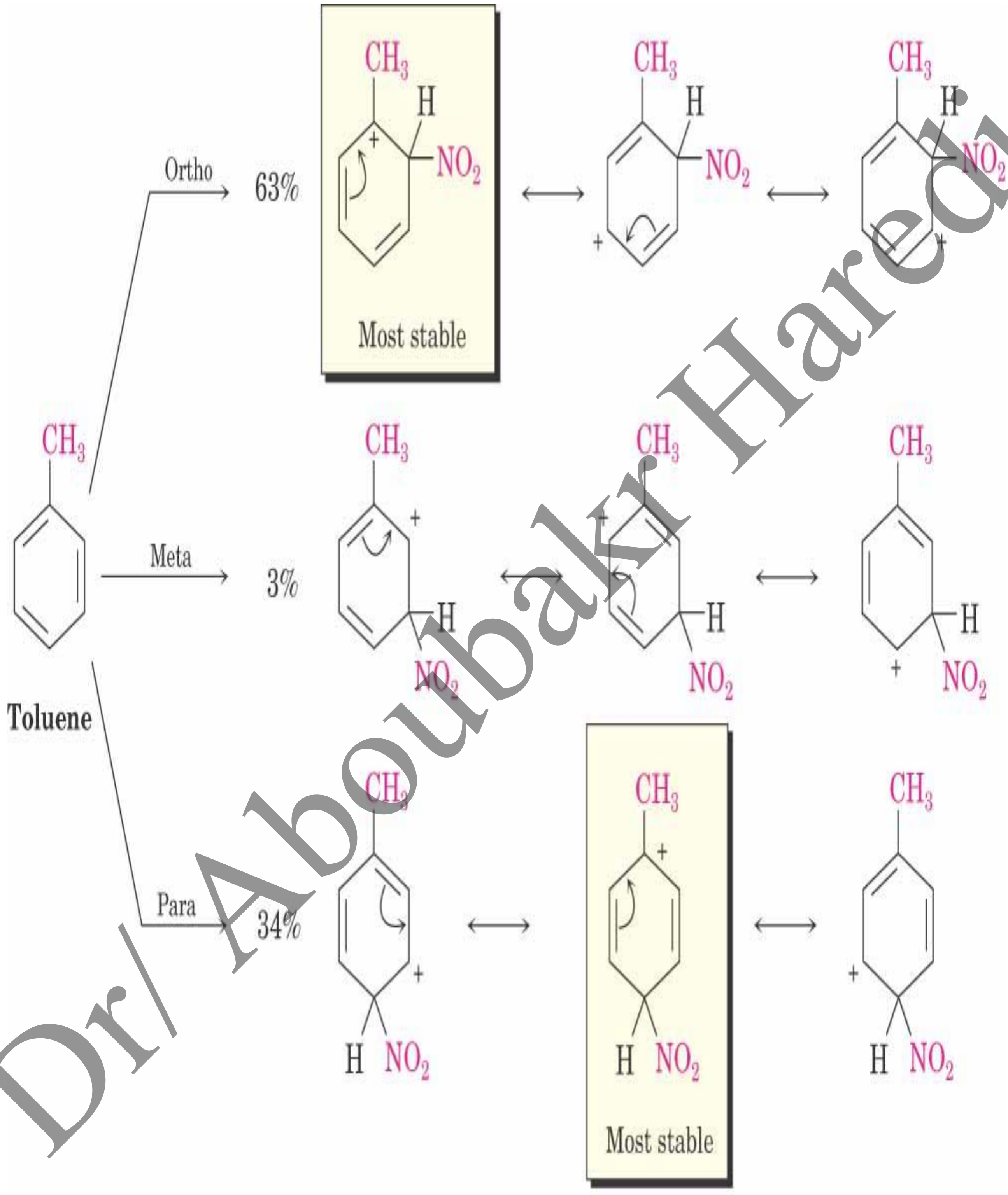
Y withdraws electrons; carbocation intermediate is less stable, and ring is less reactive.

Y donates electrons; carbocation intermediate is more stable, and ring is more reactive.

Ortho- and Para-Directing Activators: Alkyl Groups

- Alkyl groups activate: direct further substitution to positions ortho and para to themselves

- Alkyl group is most effective in the ortho and para positions

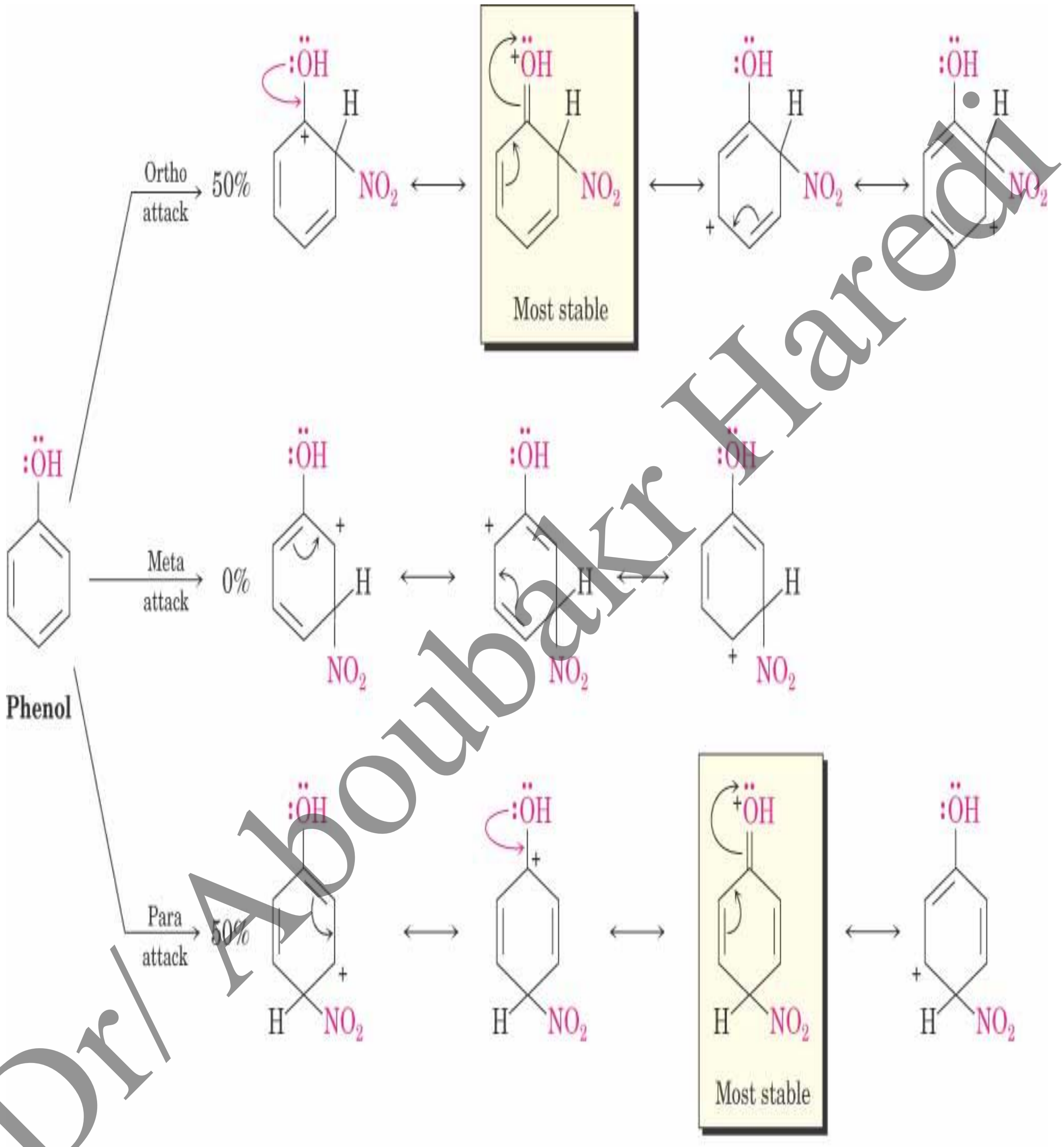


Toluene
Ortho
63%
Most stable
Meta
3%
Para
34%
Most stable
CH_3
H
NO_2

Ortho- and Para-Directing Activators: OH and NH_2

- Alkoxyl, and amino groups have a strong, electron-donating resonance effect

- Most pronounced at the ortho and para positions



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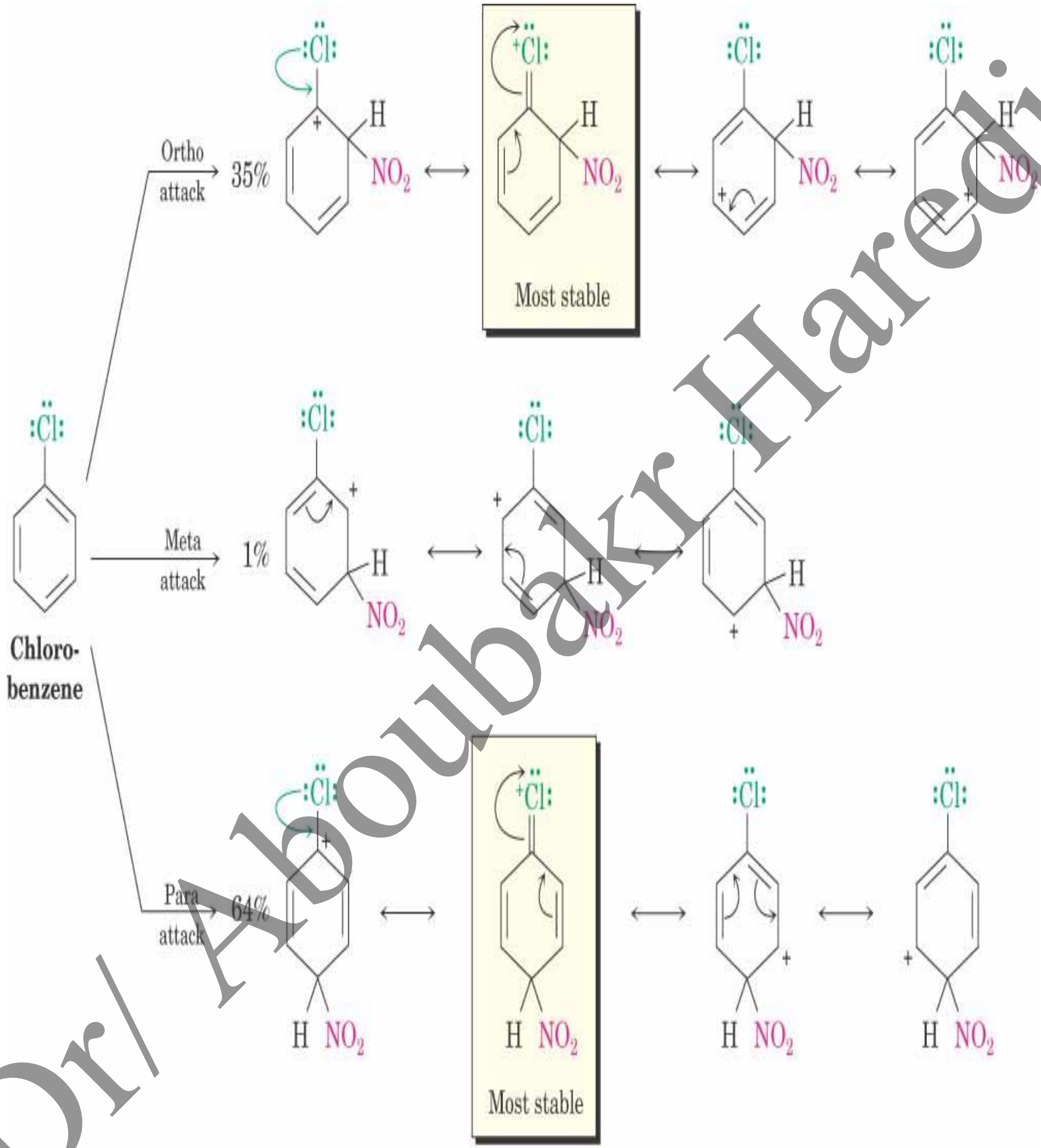
Ortho- and Para-Directing Deactivators: Halogens

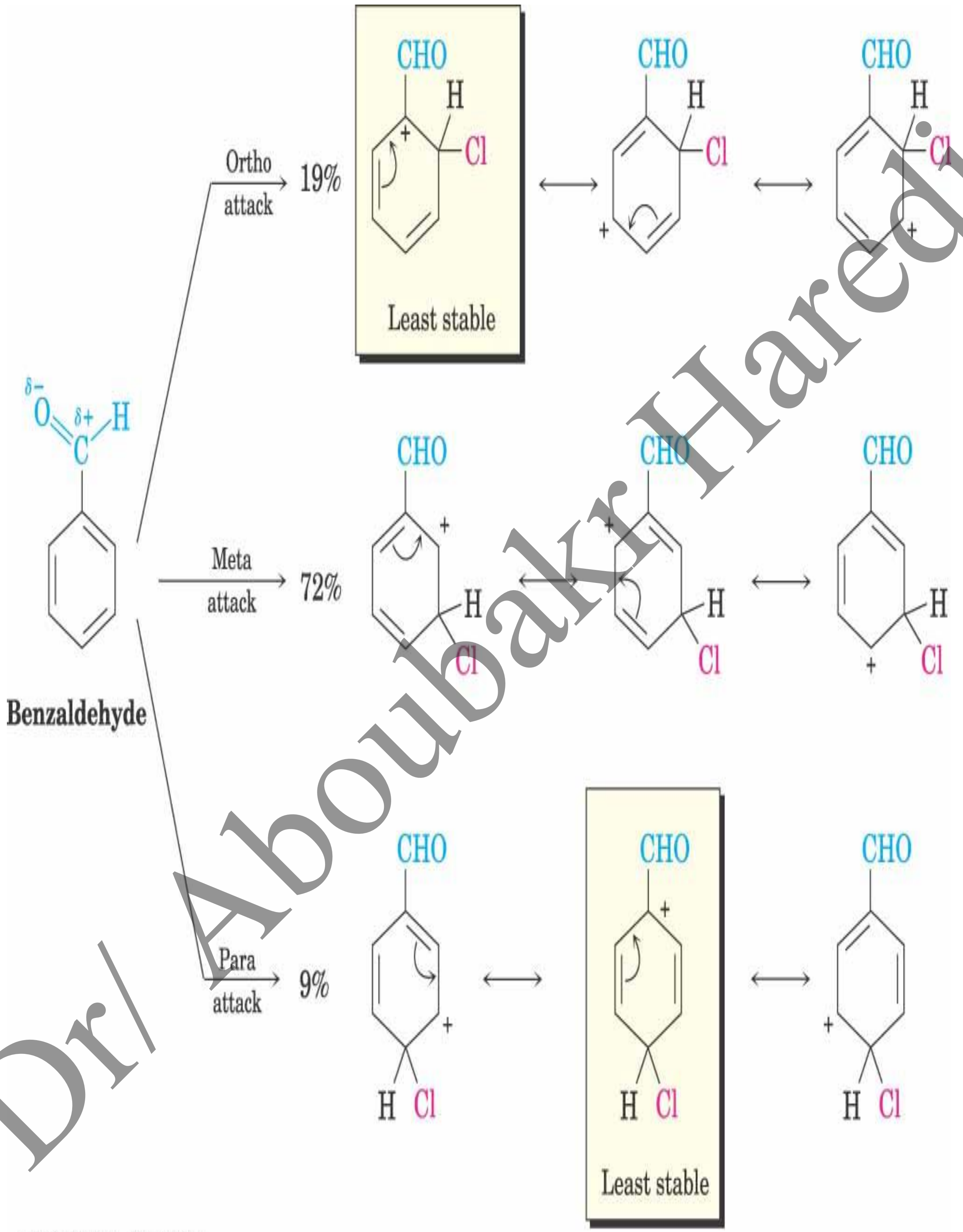
- Electron-withdrawing inductive effect outweighs weaker electron-donating resonance effect

- Resonance effect is only at the ortho and para positions, stabilizing carbocation intermediate

Ortho attack
35%
H
NO_2
:Cl:
Most stable
Meta attack
1%
Chlorobenzene
Para attack
64%
Most stable

Meta-Directing Deactivators

- Inductive and resonance effects reinforce each other
- Ortho and para intermediates destabilized by deactivation from carbocation intermediate
- Resonance cannot produce stabilization



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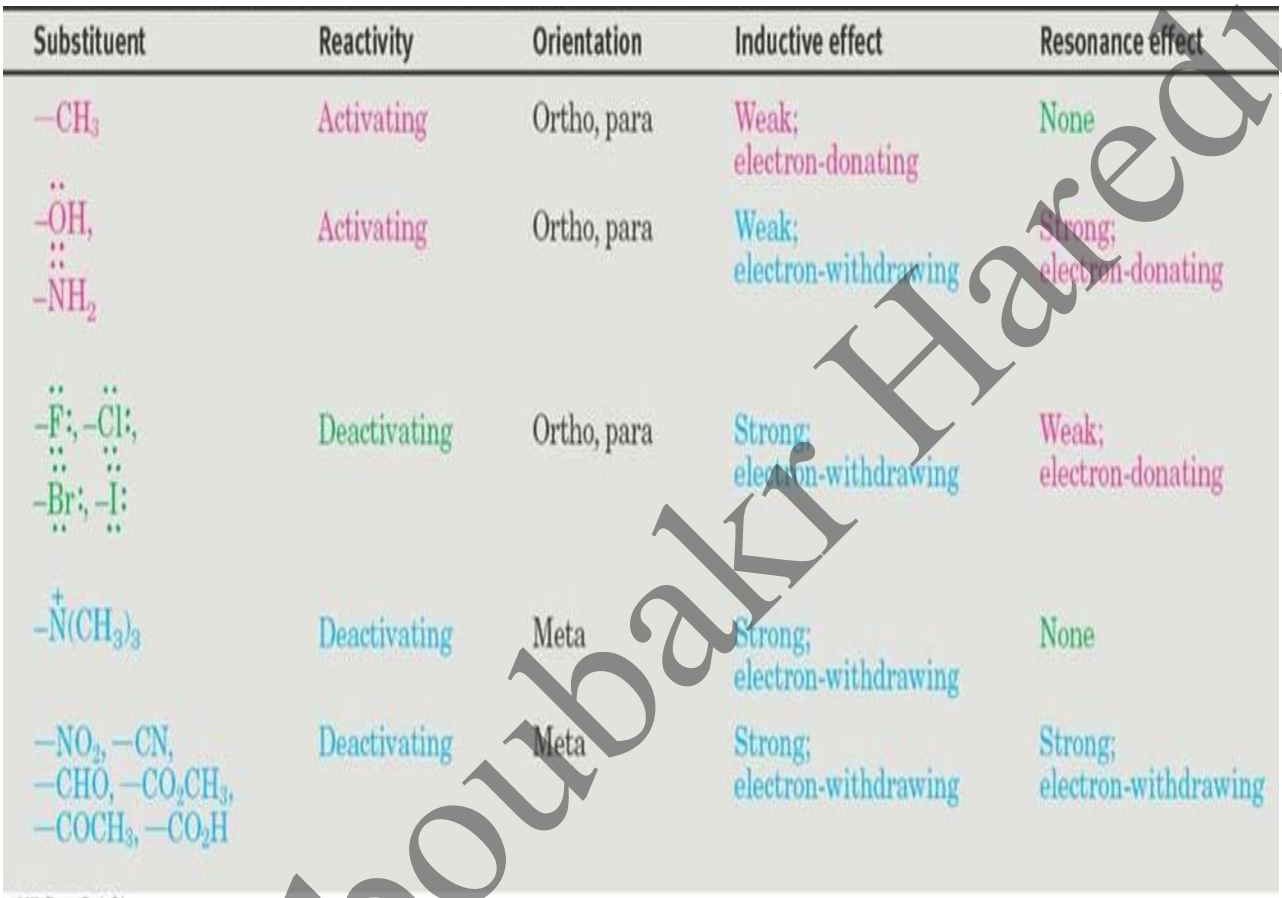
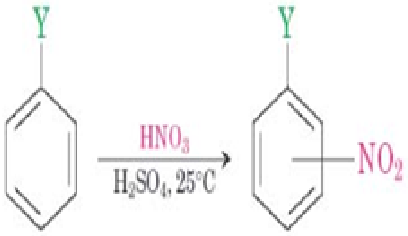
Summary Table: Effect of Substituents in Aromatic Substitution



Substituent	Reactivity	Orientation	Inductive effect	Resonance effect
$-CH_3$	Activating	Ortho, para	Weak; electron-donating	None
$-\ddot{\underset{..}{O}}H$, $-\ddot{N}H_2$	Activating	Ortho, para	Weak; electron-withdrawing	Strong; electron-donating
$-\ddot{\underset{..}{F}}:$, $-\ddot{\underset{..}{Cl}}:$, $-\ddot{\underset{..}{Br}}:$, $-\ddot{\underset{..}{I}}:$	Deactivating	Ortho, para	Strong; electron-withdrawing	Weak; electron-donating
$-\overset{+}{N}(CH_3)_3$	Deactivating	Meta	Strong; electron-withdrawing	None
$-NO_2$, $-CN$, $-CHO$, $-CO_2CH_3$, $-COCH_3$, $-CO_2H$	Deactivating	Meta	Strong; electron-withdrawing	Strong; electron-withdrawing

TABLE Orientation of Nitration in Substituted Benzenes



	Product (%)				Product (%)		
	Ortho	Meta	Para		Ortho	Meta	Para
Meta-directing deactivators				**Ortho- and para-directing deactivators**			
$-\overset{+}{N}(CH_3)_3$	2	87	11	$-F$	13	1	86
$-NO_2$	7	91	2	$-Cl$	35	1	64
$-CO_2H$	22	76	2	$-Br$	43	1	56
$-CN$	17	81	2	$-I$	45	1	54
$-CO_2CH_2CH_3$	28	66	6	**Ortho- and para-directing activators**			
$-COCH_3$	26	72	2	$-CH_3$	63	3	34
$-CHO$	19	72	9	$-\ddot{\underset{\cdot\cdot}{O}}H$	50	0	50
				$-\ddot{N}HCOCH_3$	19	2	79

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Is it ortho/para or meta directing?????

- All ortho- and para- directors have a lone pair of electrons on the atom directly attached to the ring (with the exception of alkyl, aryl, and CH=CHR groups).

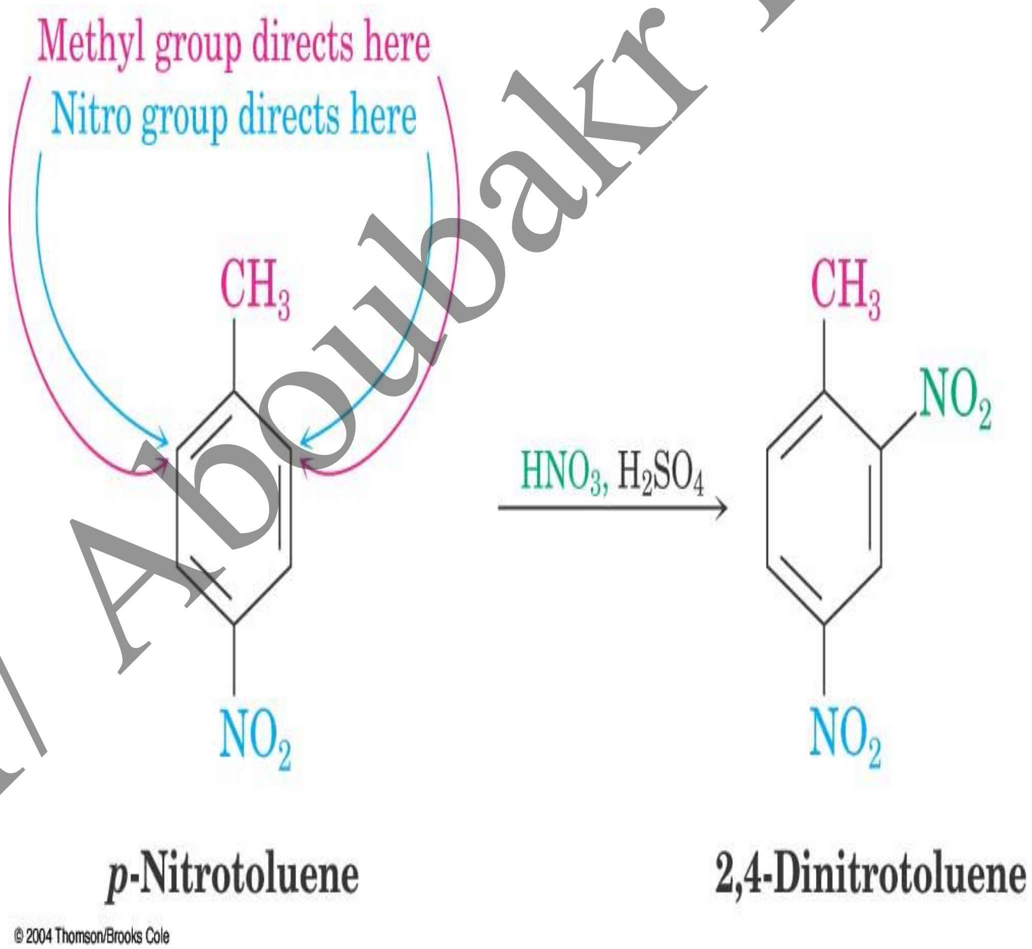
- All meta- directors have a positive charge or a partial positive charge on the atom attached to the ring.

In Summary:

- All activating substituents are ortho/para directors
- The weakly deactivating halogens are ortho/para directors
- All other deactivating substituents are meta directors

Trisubstituted Benzenes: Additivity of Effects

- If the directing effects of the two groups are the same, the result is additive



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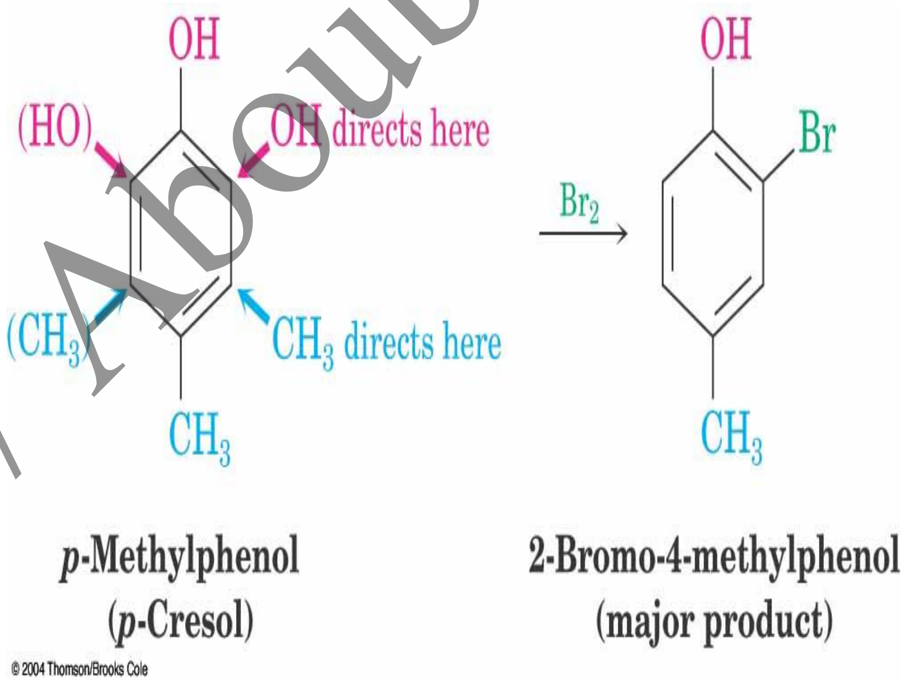
Substituents with Opposite Effects

- If the directing effects of two groups oppose each other, the more powerful activating group decides the principal outcome
- Usually gives mixtures of products



p-Methylphenol (*p*-Cresol)

2-Bromo-4-methylphenol (major product)

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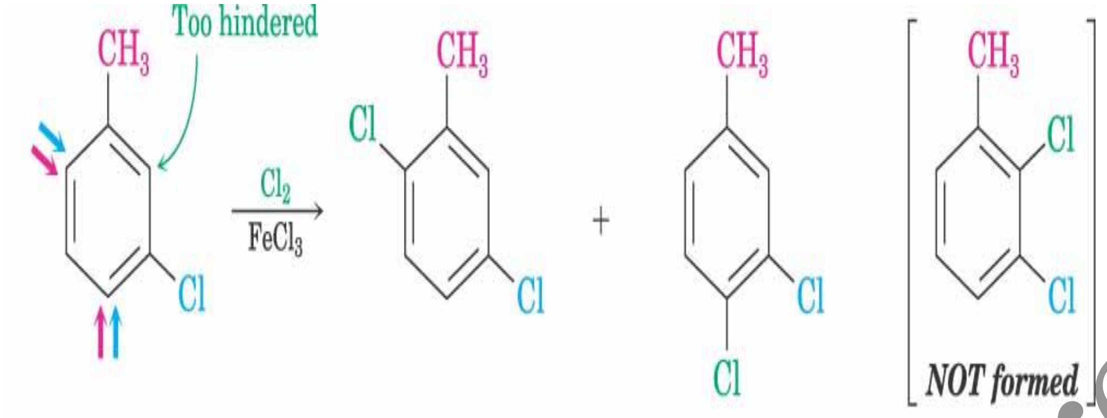
Meta-Disubstituted Compounds Are Unreactive

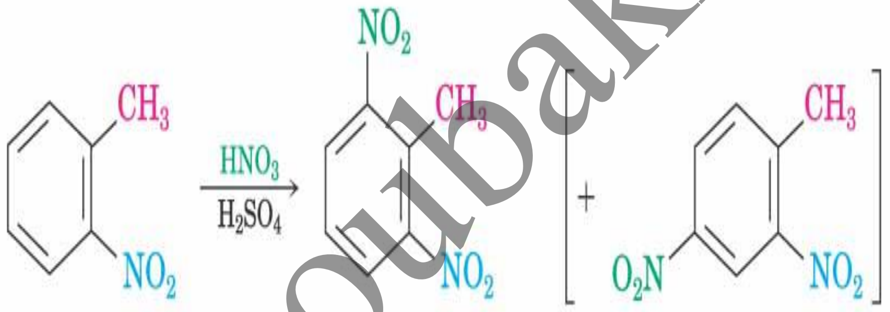
- The reaction site is too hindered

- To make aromatic rings with three adjacent substituents, it is best to start with an ortho-disubstituted compound



m-Chlorotoluene 2,5-Dichlorotoluene 3,4-Dichlorotoluene

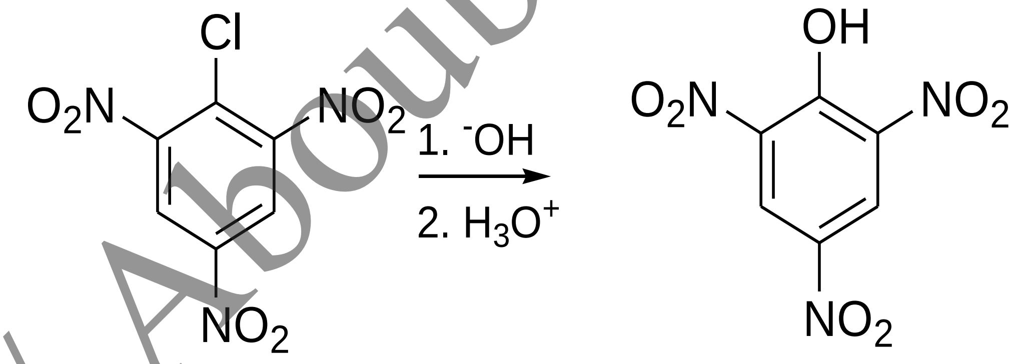
But:



o-Nitrotoluene 2,6-Dinitrotoluene 2,4-Dinitrotoluene

Nucleophilic Aromatic Substitution

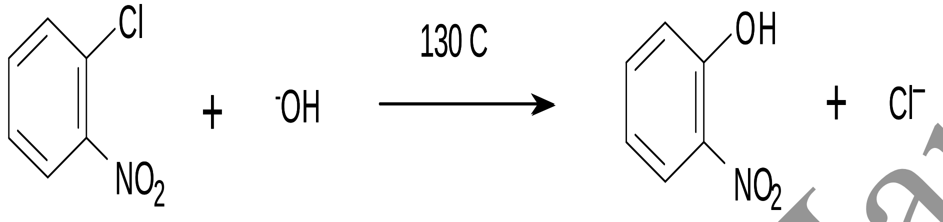
- Aryl halides with electron-withdrawing substituents ortho and para react with nucleophiles
- Form addition intermediate (Meisenheimer complex) that is stabilized by electron-withdrawal
- Halide ion is lost

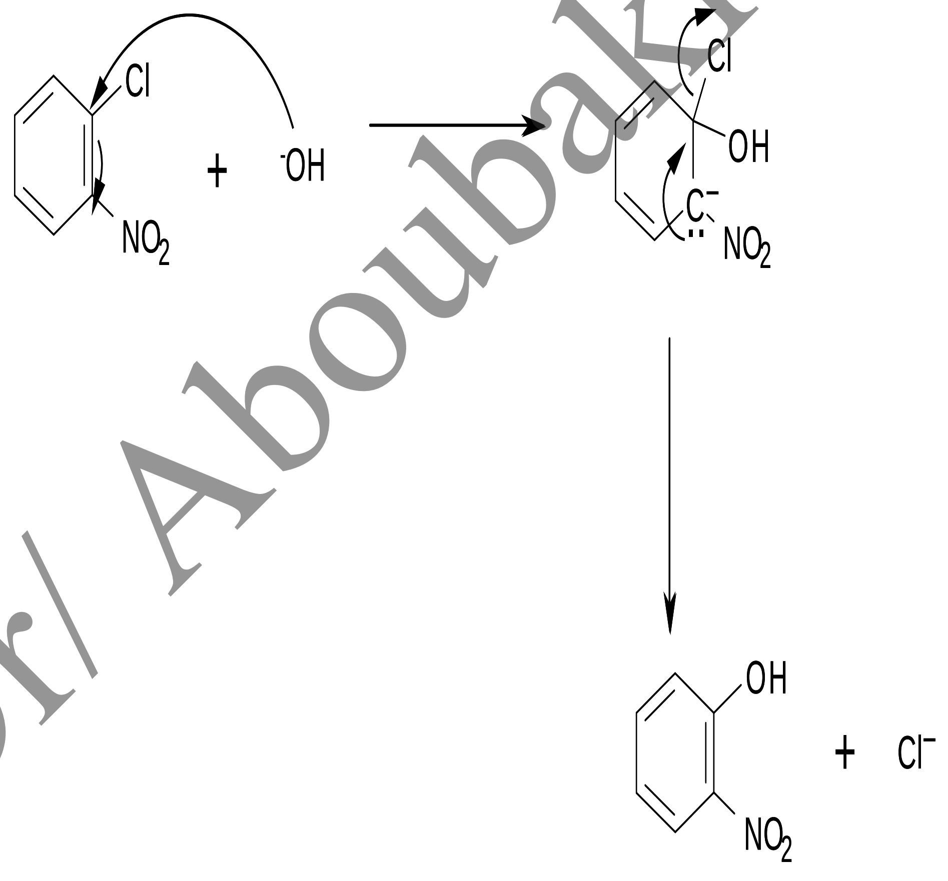


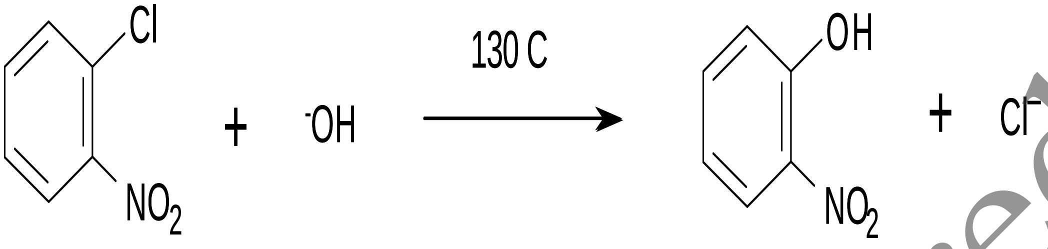
2,4,6-trinitrochlorobenzene

2,4,6-trinitrophenol

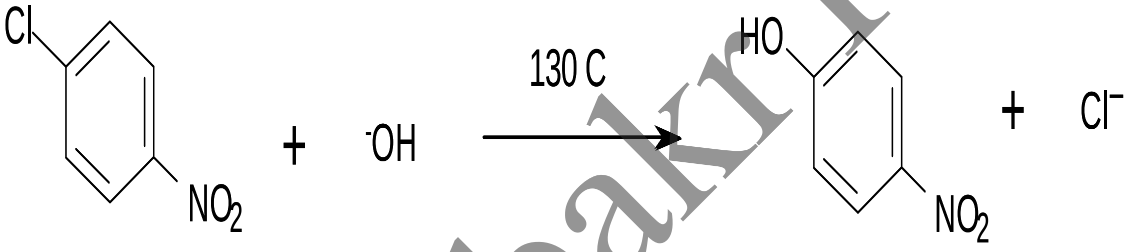
Mechanism : Nucleophilic Aromatic Substitution



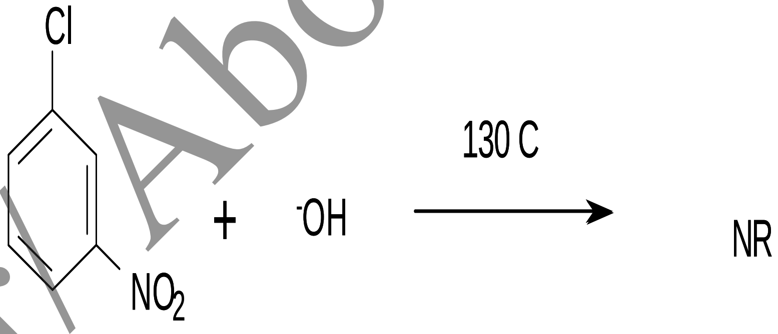




o-chloronitrobenzene

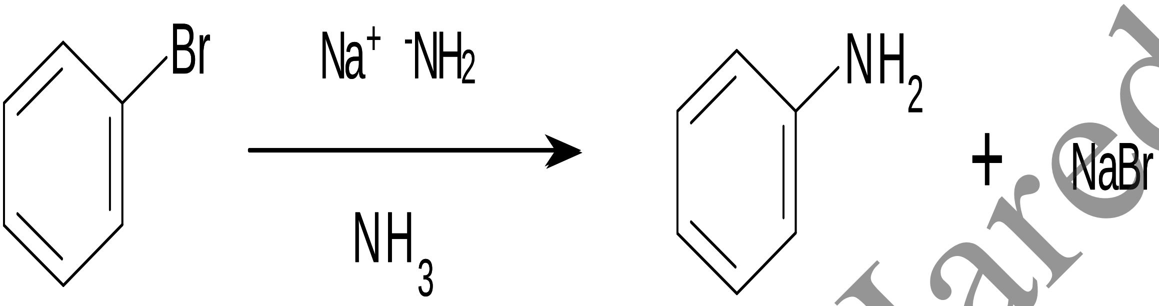


p-chloronitrobenzene



m-chloronitrobenzene

Nucleophilic Aromatic Substitution



No
Mechanism

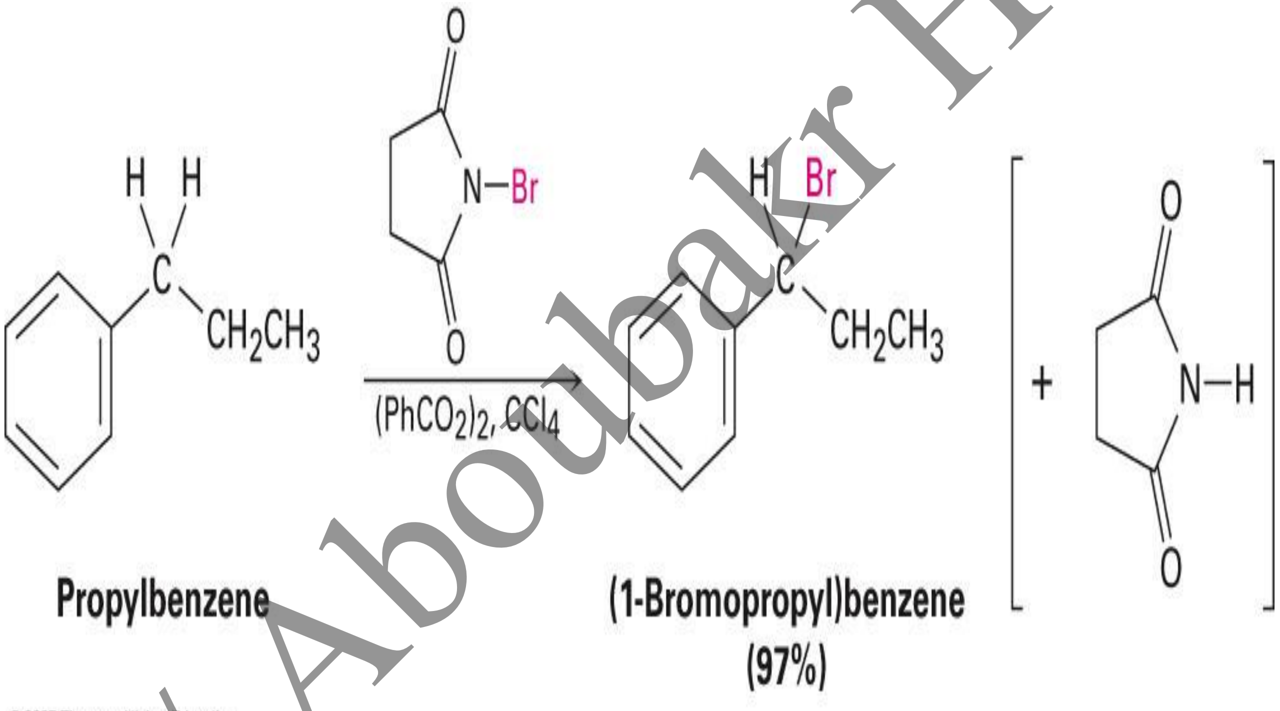
Electrophilic and Nucleophilic Substitution

- Electrophilic Sub
  - Favored by electron donating substituents
    - Stabilize carbocation intermediate

- Nucleophilic Sub
  - Favored by electron withdrawing substituents
    - Stabilize carbanion intermediate

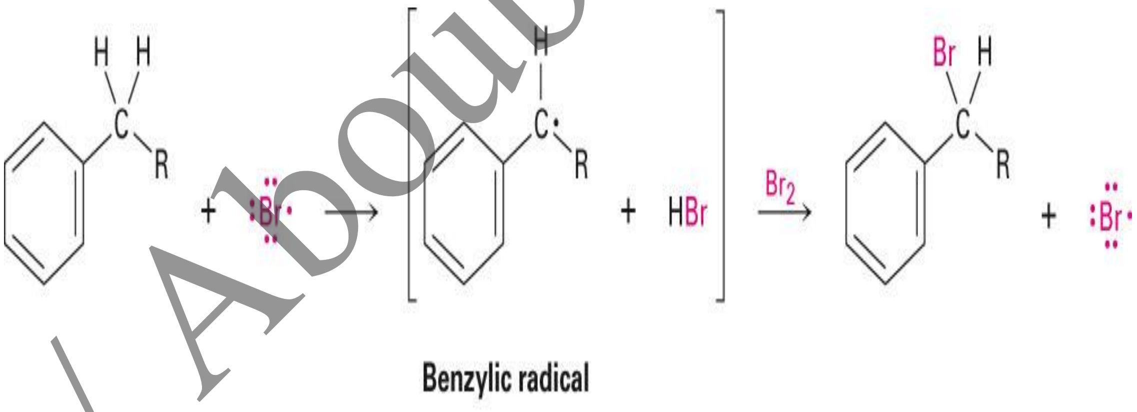
Bromination of Alkylbenzene Side Chains

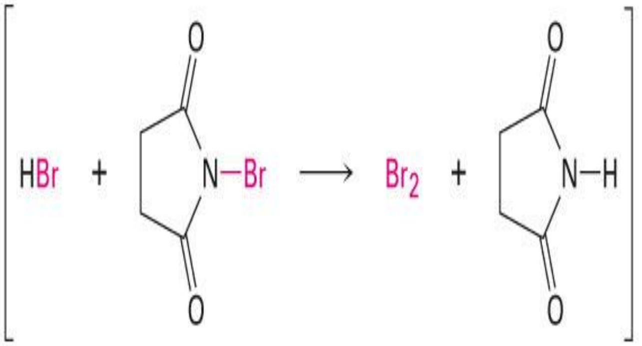
- Reaction of an alkylbenzene with *N*-bromo-succinimide (NBS) and benzoyl peroxide (radical initiator) introduces Br into the side chain



Bromination of Alkylbenzene Side Chains

- Abstraction of a benzylic hydrogen atom generates an intermediate benzylic radical
- Reacts with Br_2 to yield product
- Br· radical cycles back into reaction to carry chain

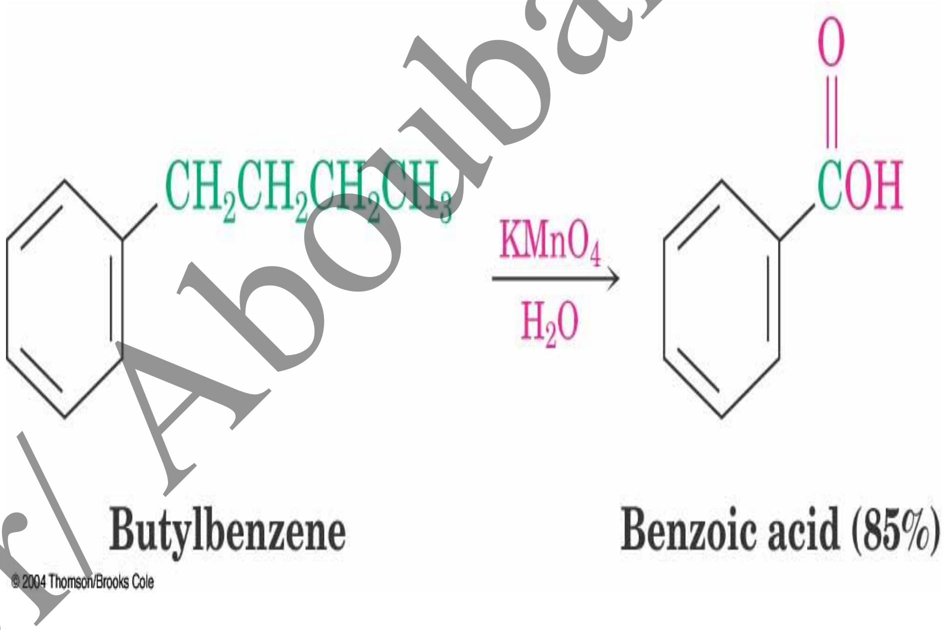




No Mechanism

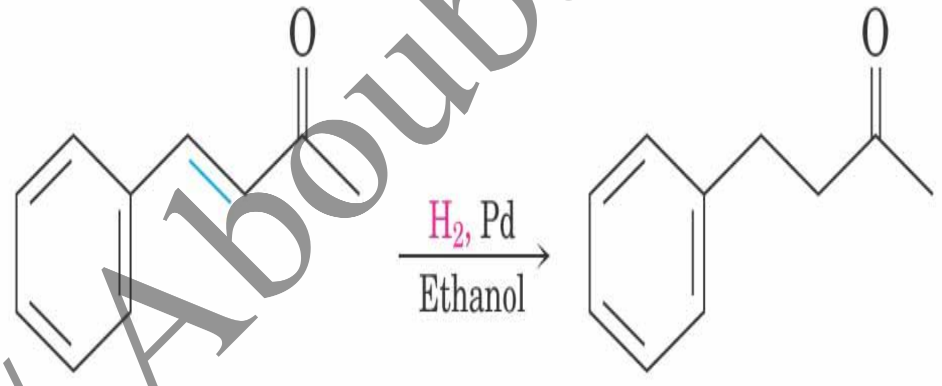
Oxidation of Aromatic Compounds

- Alkyl side chains can be oxidized to —CO_2H by strong reagents such as $KMnO_4$ and $Na_2Cr_2O_7$ if they have a C-H next to the ring
- Converts an alkylbenzene into a benzoic acid, Ar—R → Ar—CO_2H



Reduction of Aromatic Compounds

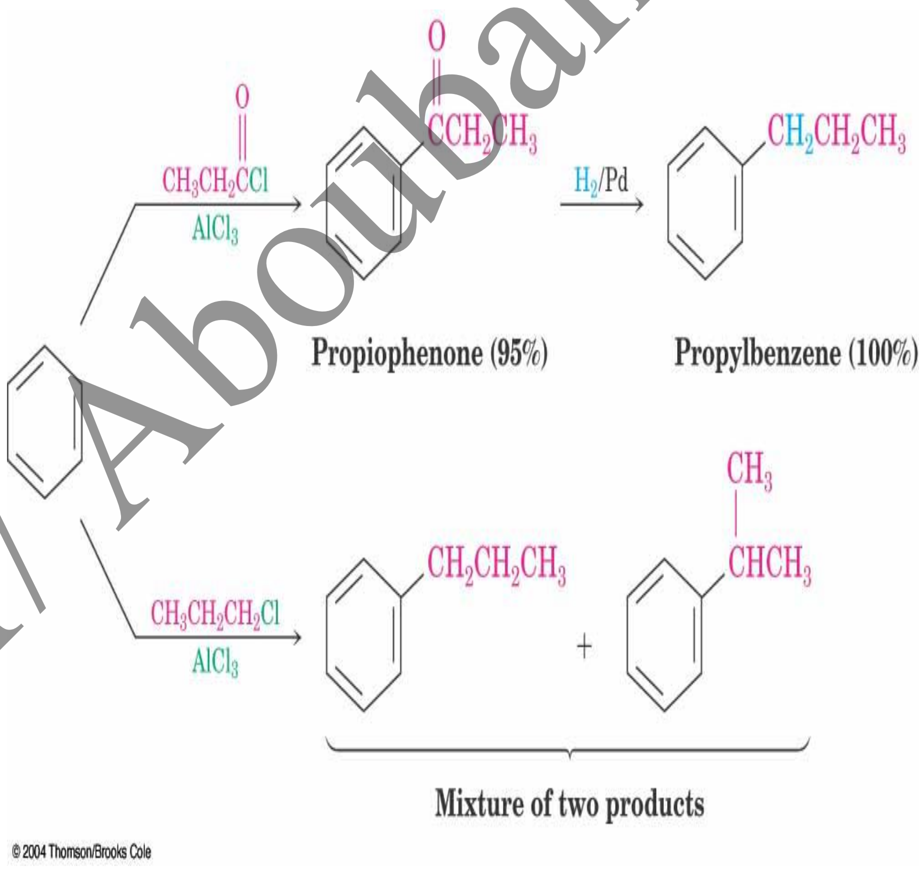
- Aromatic rings are inert to catalytic hydrogenation under conditions that reduce alkene double bonds
- Can selectively reduce an alkene double bond in the presence of an aromatic ring
- Reduction of an aromatic ring requires more powerful reducing conditions (high pressure or rhodium catalysts)



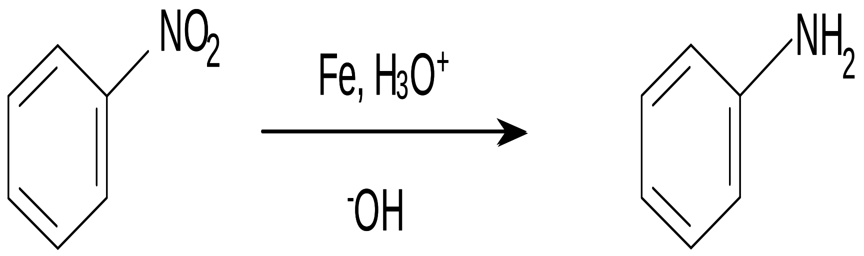
4-Phenyl-3-buten-2-one 4-Phenyl-2-butanone (100%)

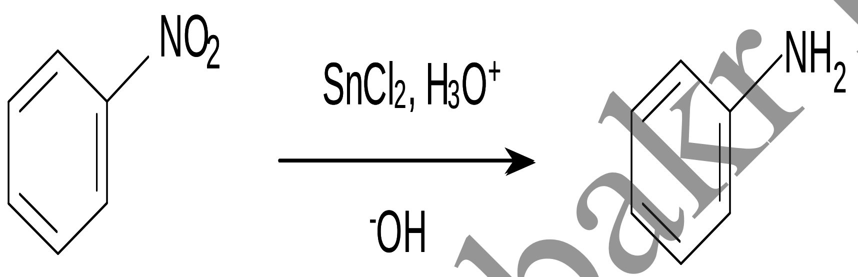
Reduction of Aryl Alkyl Ketones

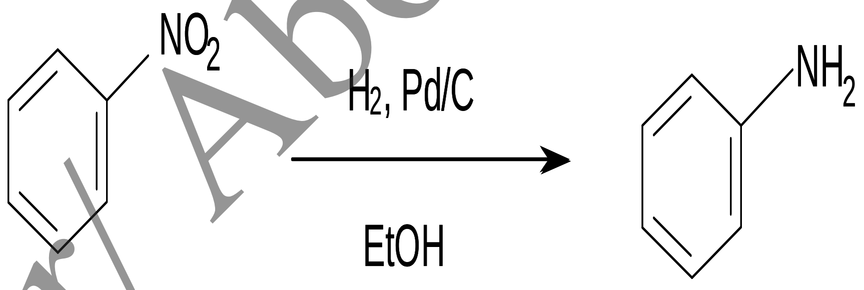
- Aromatic ring activates neighboring carbonyl group toward reduction
- Ketone is converted into an alkylbenzene by catalytic hydrogenation over Pd catalyst



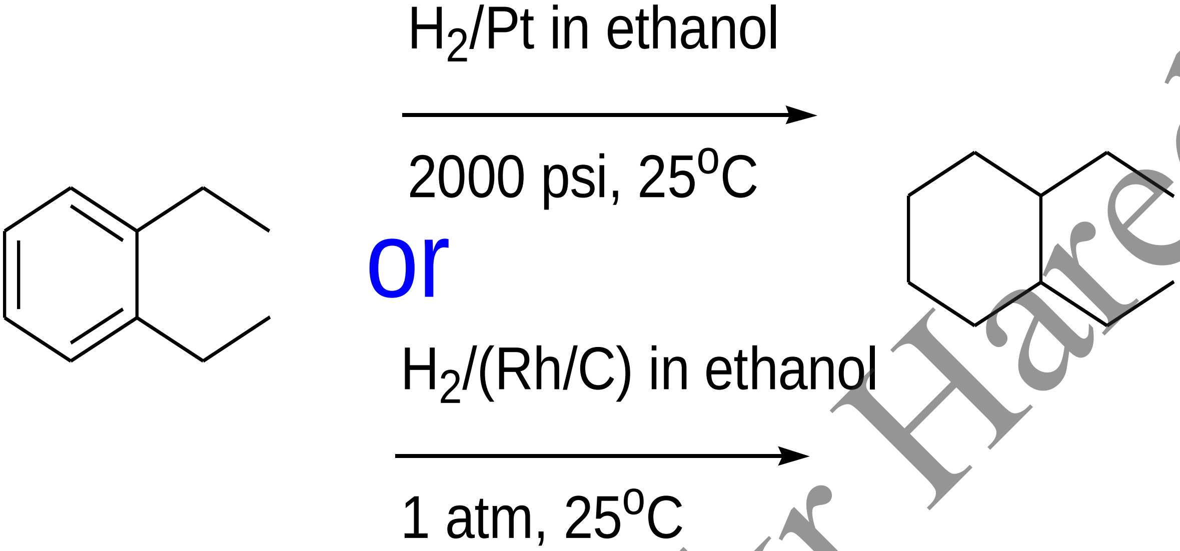
Reduction of Aryl Nitro Compounds







Reduction of Aromatic Ring



H_2/Pt in ethanol

2000 psi, 25^{o}C

or

H_2/(Rh/C) in ethanol

1 atm, 25^{o}C

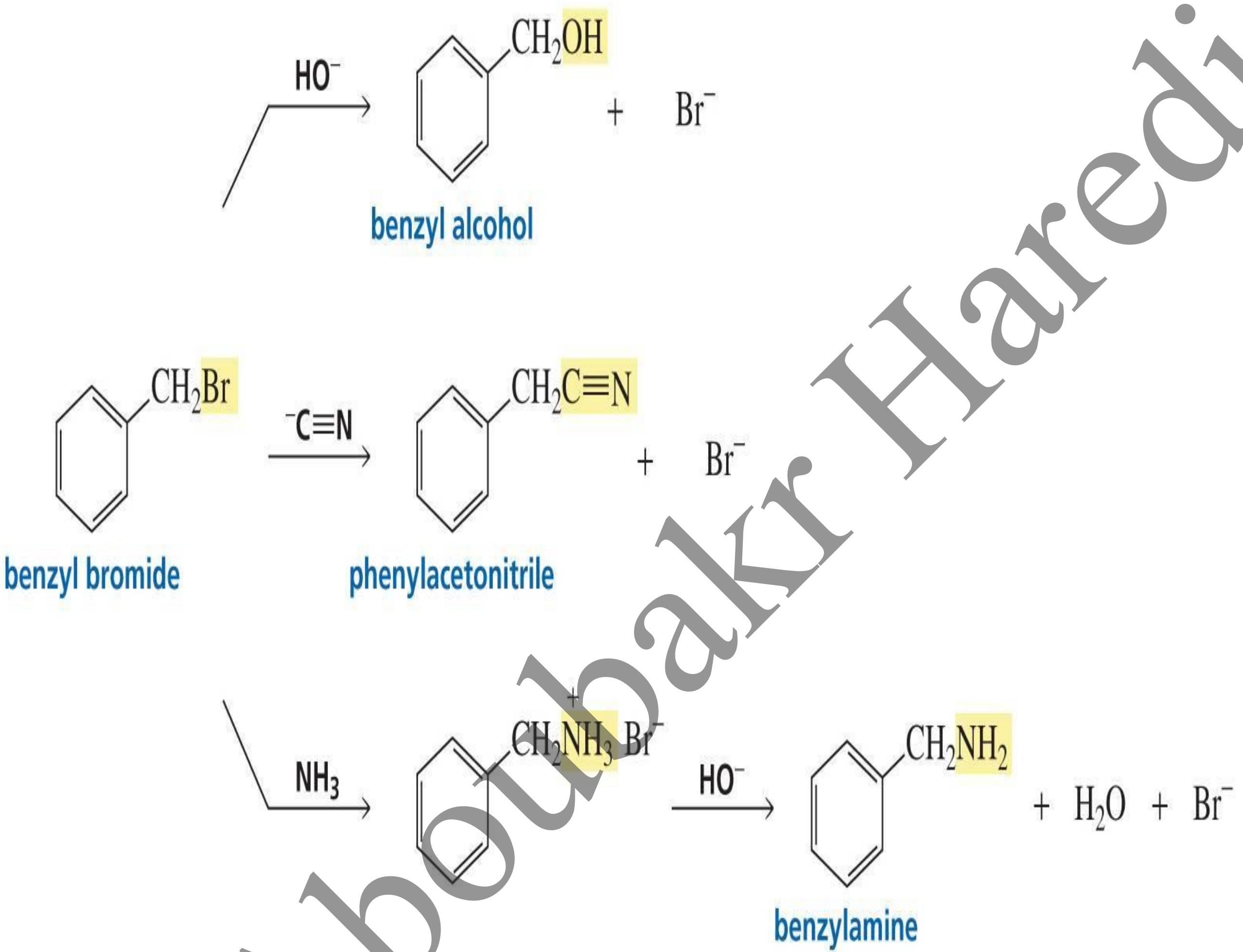
Synthesis Strategies

- These syntheses require planning and consideration of alternative routes

- It's important to pay attention to the order in which substituents are placed on the ring
  - meta or or ortho/para directing

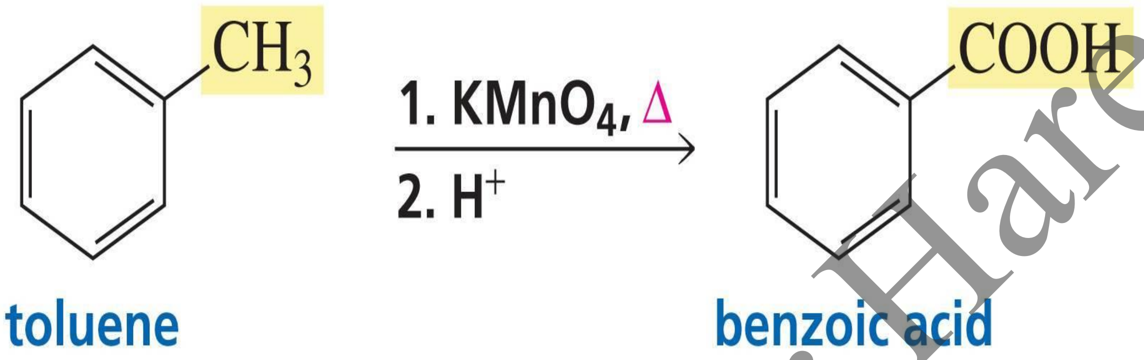
- When should an added substituent be modified?

Reactions of benzyl bromide



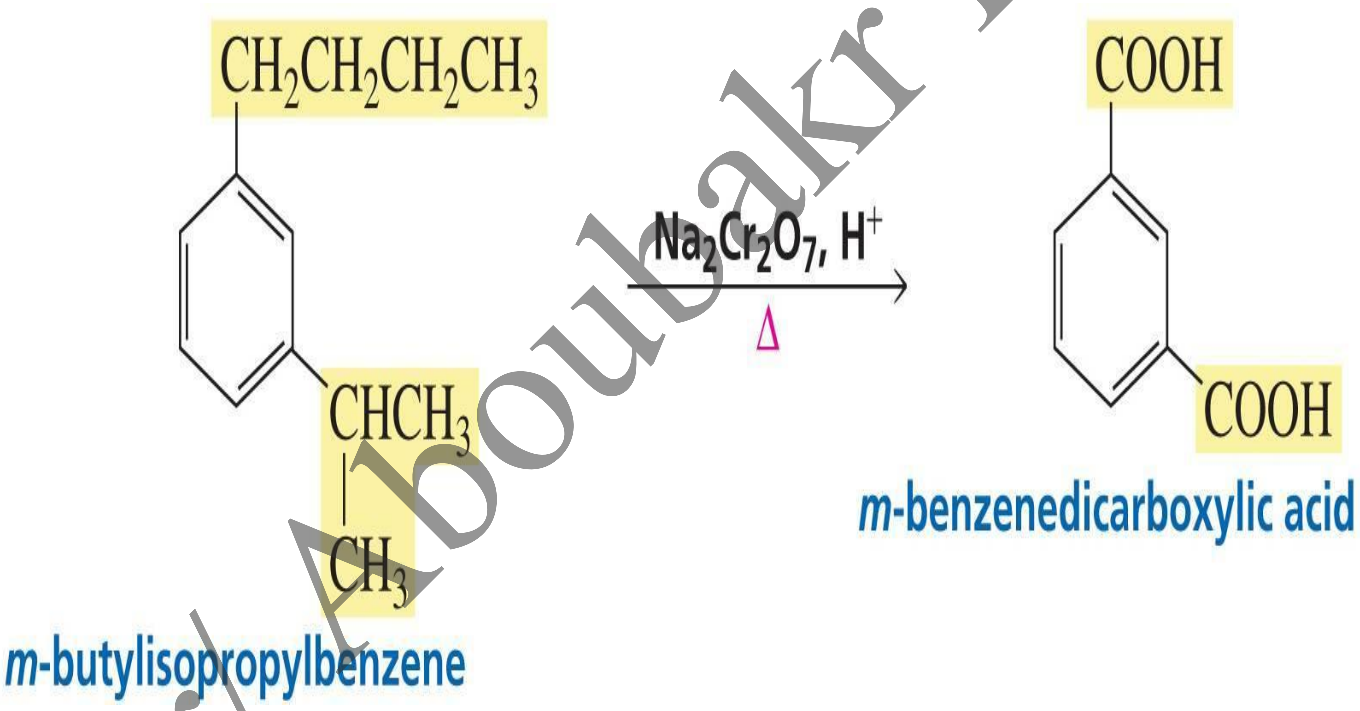
Reaction with Substituent of Benzene

- Oxidation of toluene to benzoic acid



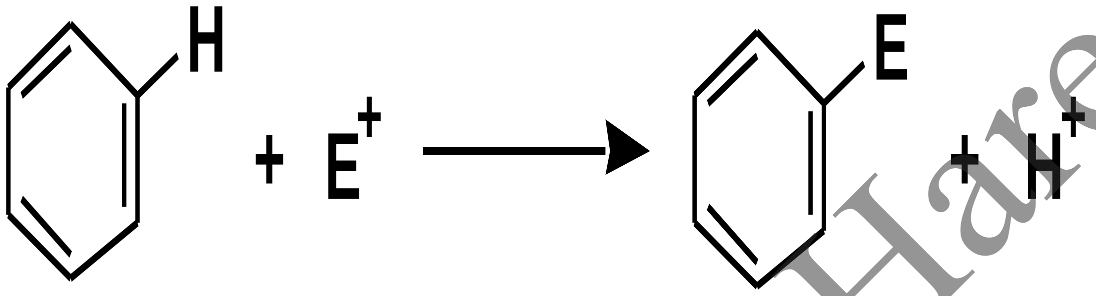
Reaction with Substituent of Benzene

- Any alkyl group, except tertiary alkyl groups, on the benzene is oxidized to a carboxylic acid
- 1-Butylisopropylbenzene is oxidized to isophthalic acid



Electrophilic Aromatic Substitution

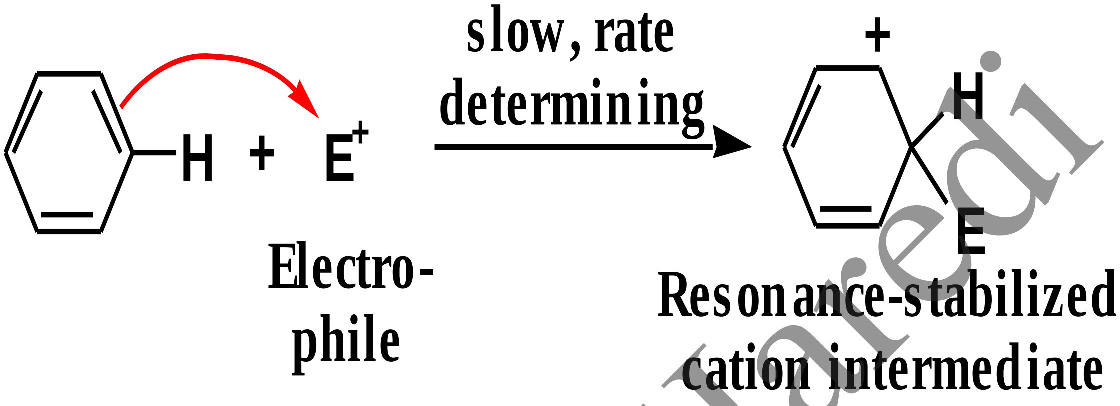
- **Electrophilic aromatic substitution:**



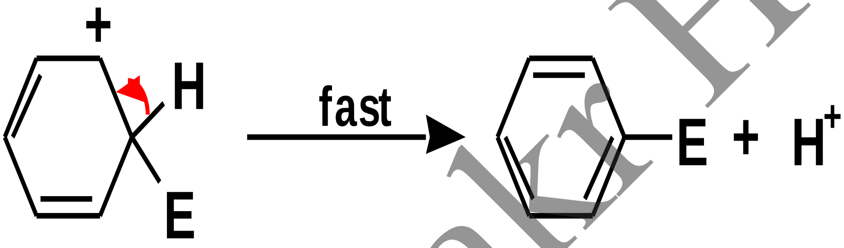
- We study several common electrophiles
  - – how each is generated.
  - – the mechanism by which each replaces hydrogen.

- A general mechanism

Step 1:



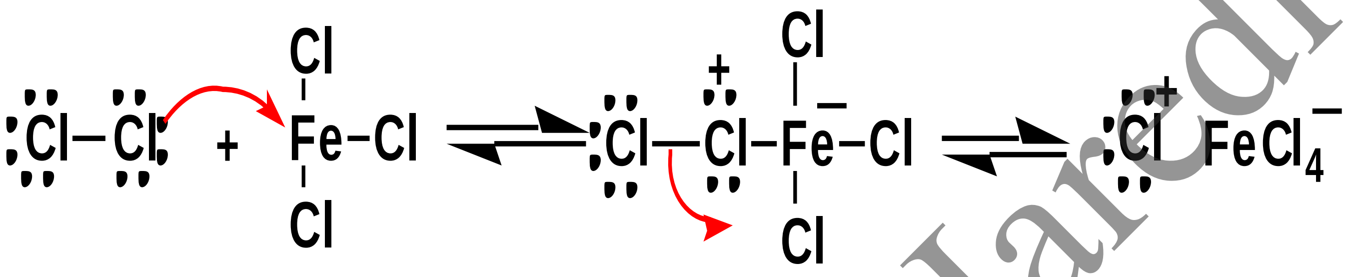
Step 2:



- General question: What are the electrophiles and how are they generated? Look at particular reactions.

Chlorination

Step 1: Generation of the electrophile: a chloronium ion.



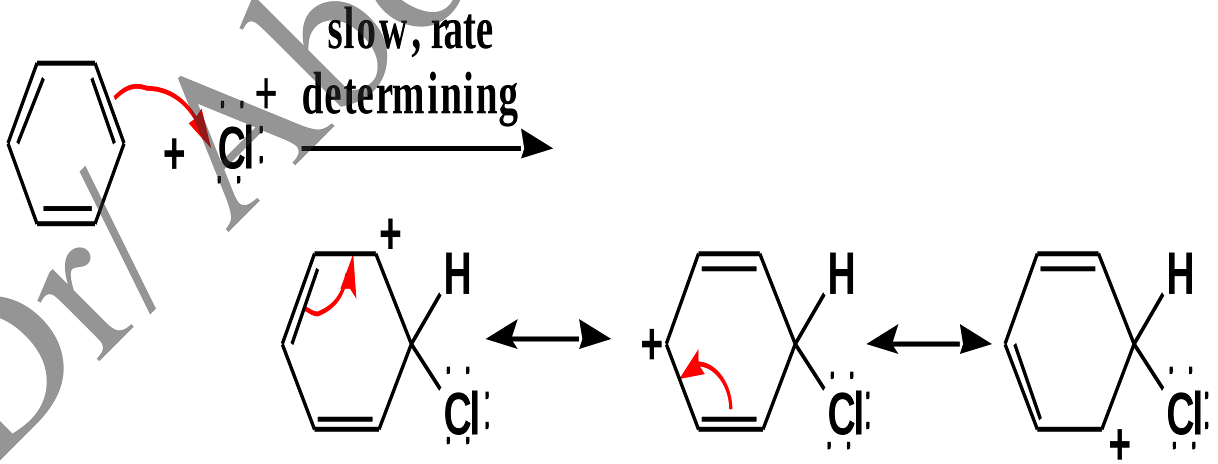
Chlorine (a Lewis base)

Ferric chloride (a Lewis acid)

A molecular complex with a positive charge on chlorine

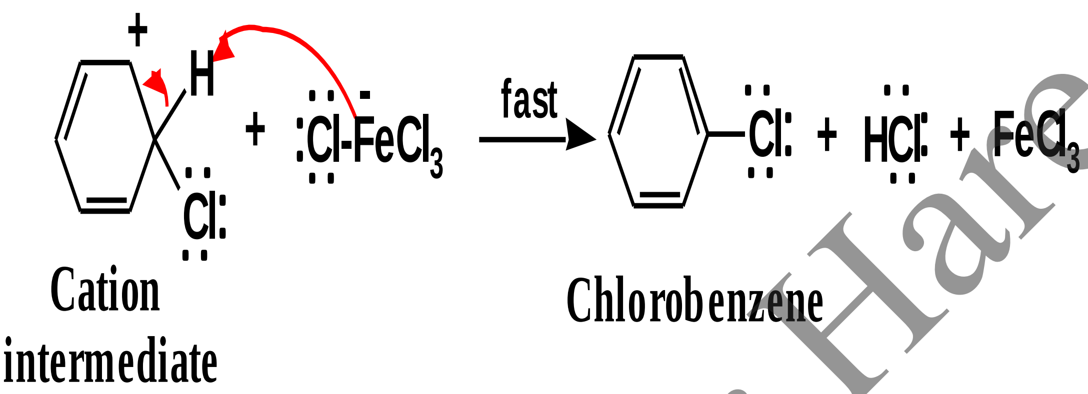
An ion pair containing a chloronium ion

Step 2: Attack of the chloronium ion on the ring.



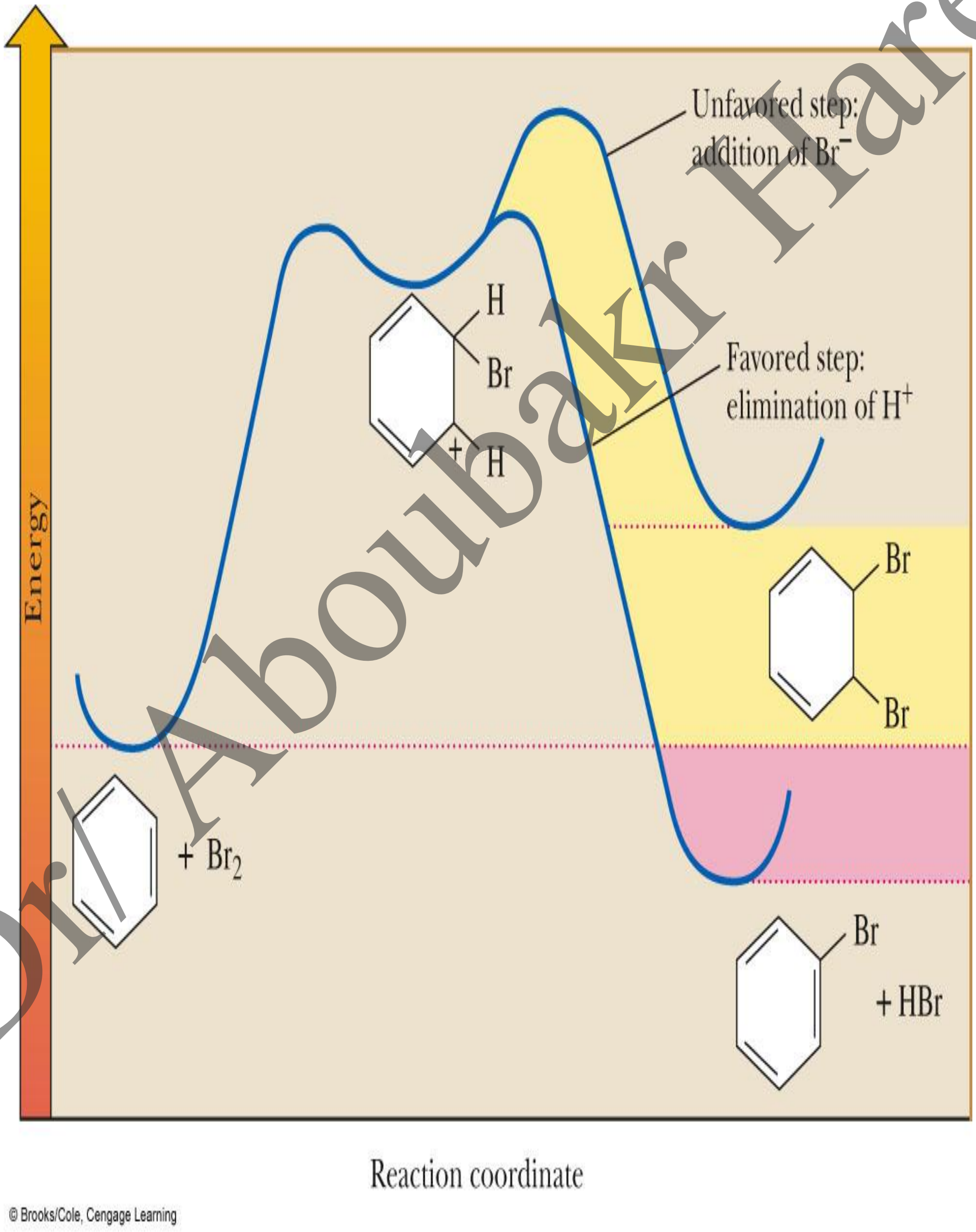
Resonance-stabilized cation intermediate; the positive charge is delocalized onto three atoms of the ring

Step 3: Proton ejection regenerates the aromatic character of the ring.



Addition vs Substitution

- Energy diagram for the bromination of benzene.



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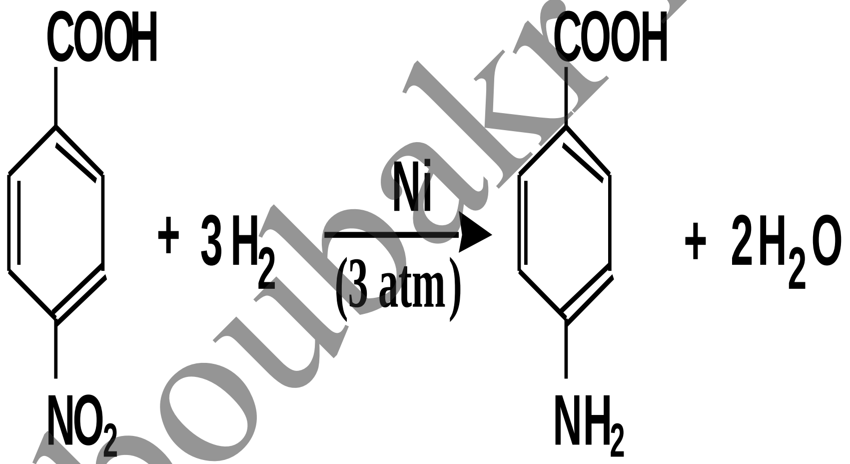
Synthesis, Nitro → Amines

- The nitro group can be reduced to a 1° amino group.

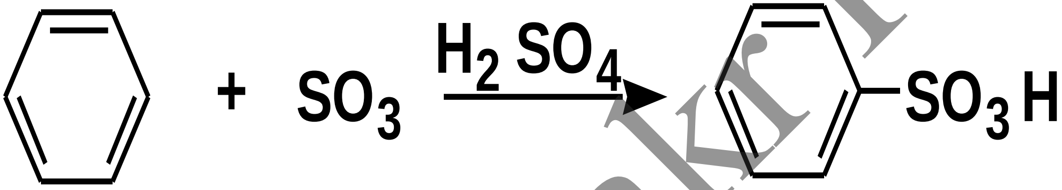


4-Nitrobenzoic acid 4-Aminobenzoic acid

Notice the carboxylic was untouched.

Sulfonation

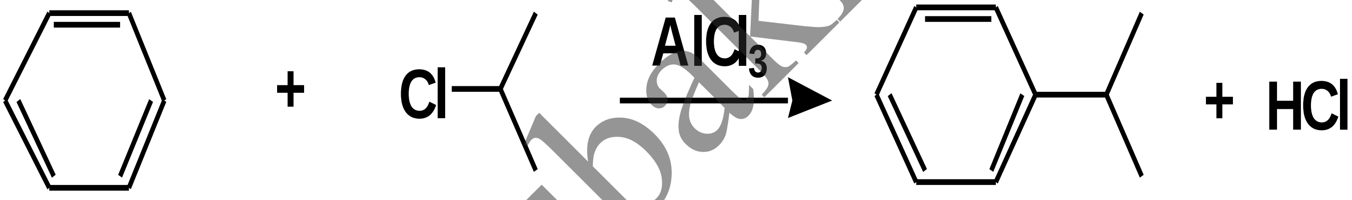
- Carried out using concentrated sulfuric acid containing dissolved sulfur trioxide.



Benzene **Benzenesulfonic acid**

Friedel-Crafts Alkylation

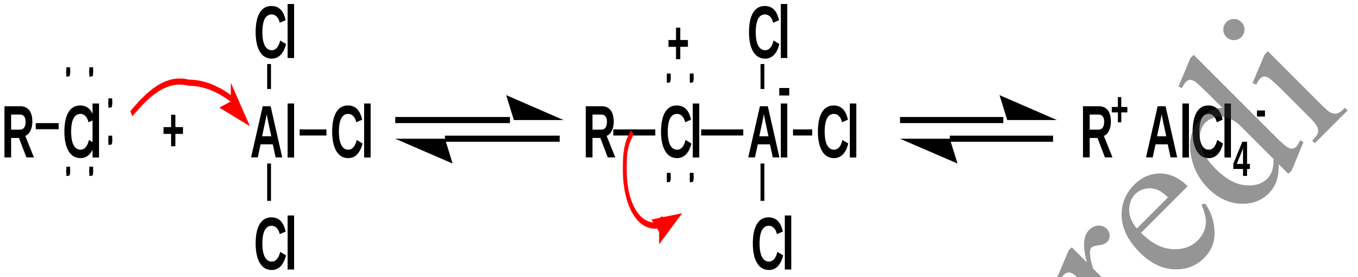
- Friedel-Crafts alkylation forms a new C-C bond between an aromatic ring and an alkyl group.



Benzene **2-Chloropropane (Isopropyl chloride)** **Cumene (Isopropylbenzene)**

Friedel-Crafts Alkylation

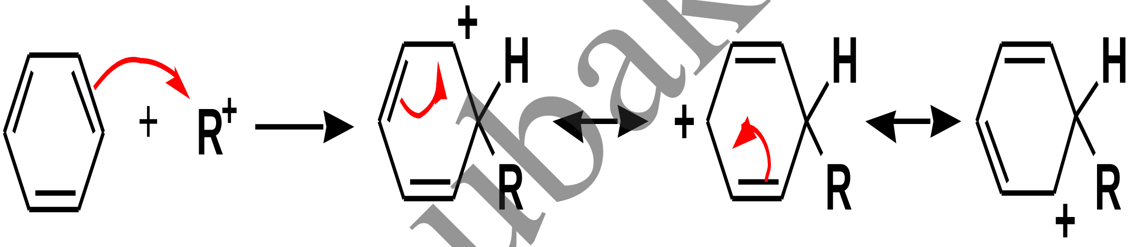
Step 1: Formation of an alkyl cation as an ion pair.



A molecular complex

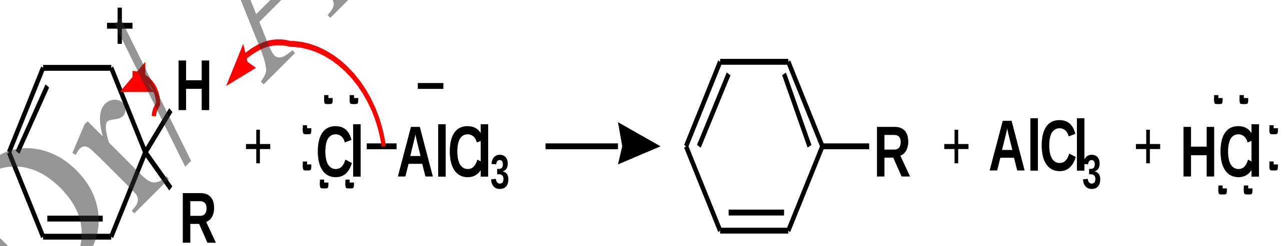
An ion pair containing a carbocation

Step 2: Attack of the alkyl cation.



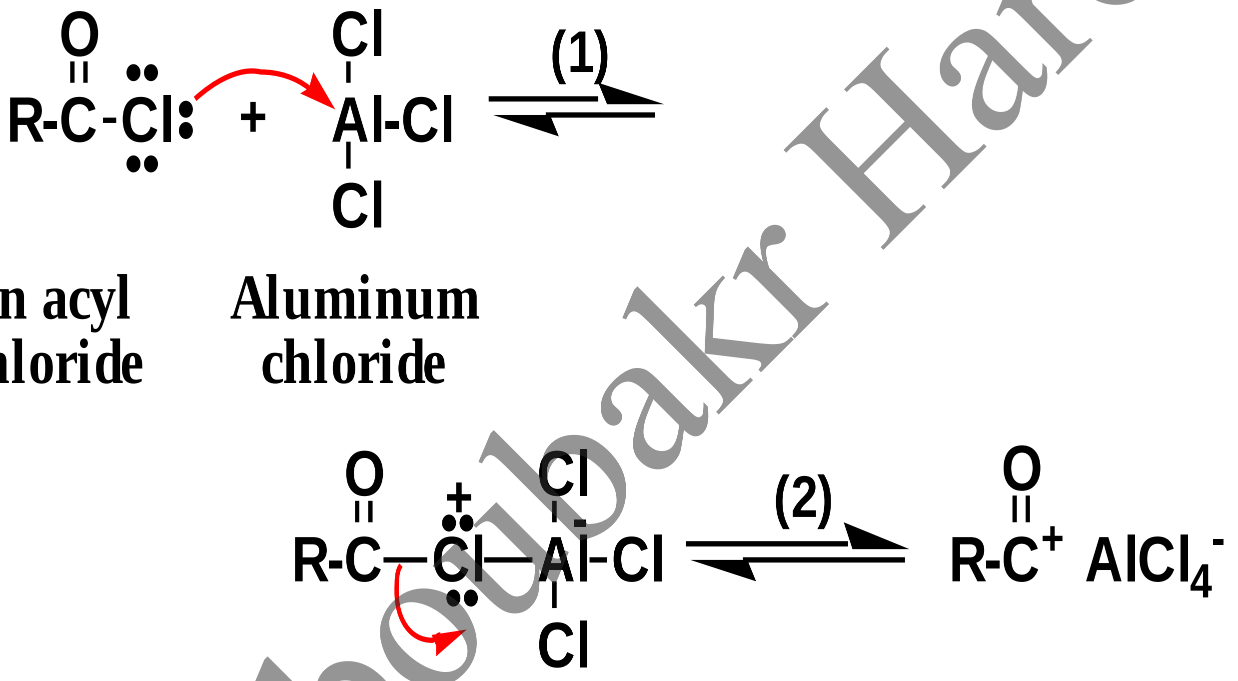
A resonance-stabilized cation

Step 3: Proton transfer regenerates the aromatic ring.



Friedel-Crafts Acylation

- The electrophile is an acylium ion.



An acyl chloride

Aluminum chloride

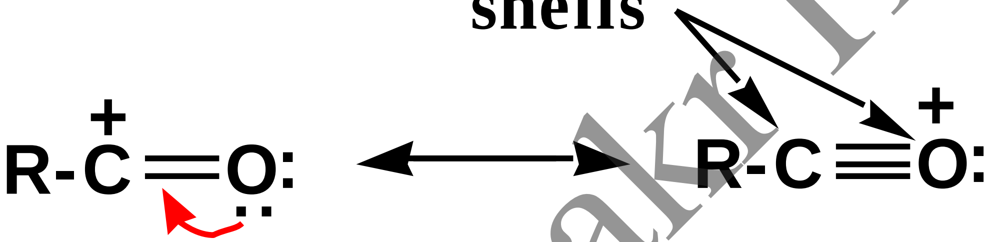
A molecular complex with a positive charge charge on chlorine

An ion pair containing an acylium ion

Friedel-Crafts Acylation

- An acylium ion is represented as a resonance hybrid of two major contributing structures.

complete valence shells

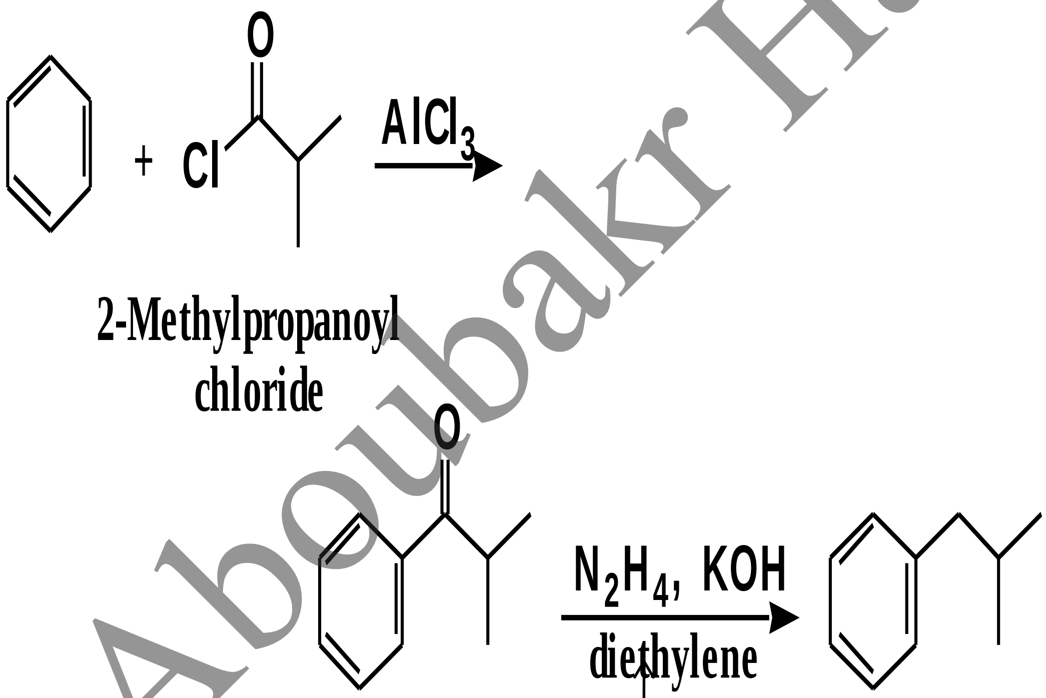


The more important contributing structure

- Friedel-Crafts acylations are free of major limitation of Friedel-Crafts alkylations; acylium ions do not rearrange, do not polyacylate (why?), do not rearrange.

Synthesis, Friedel-Crafts Acylation

- preparation of unrearranged alkylbenzenes.



2-Methylpropanoyl chloride

2-Methyl-1-phenyl-1-propanone

Isobutylbenzene

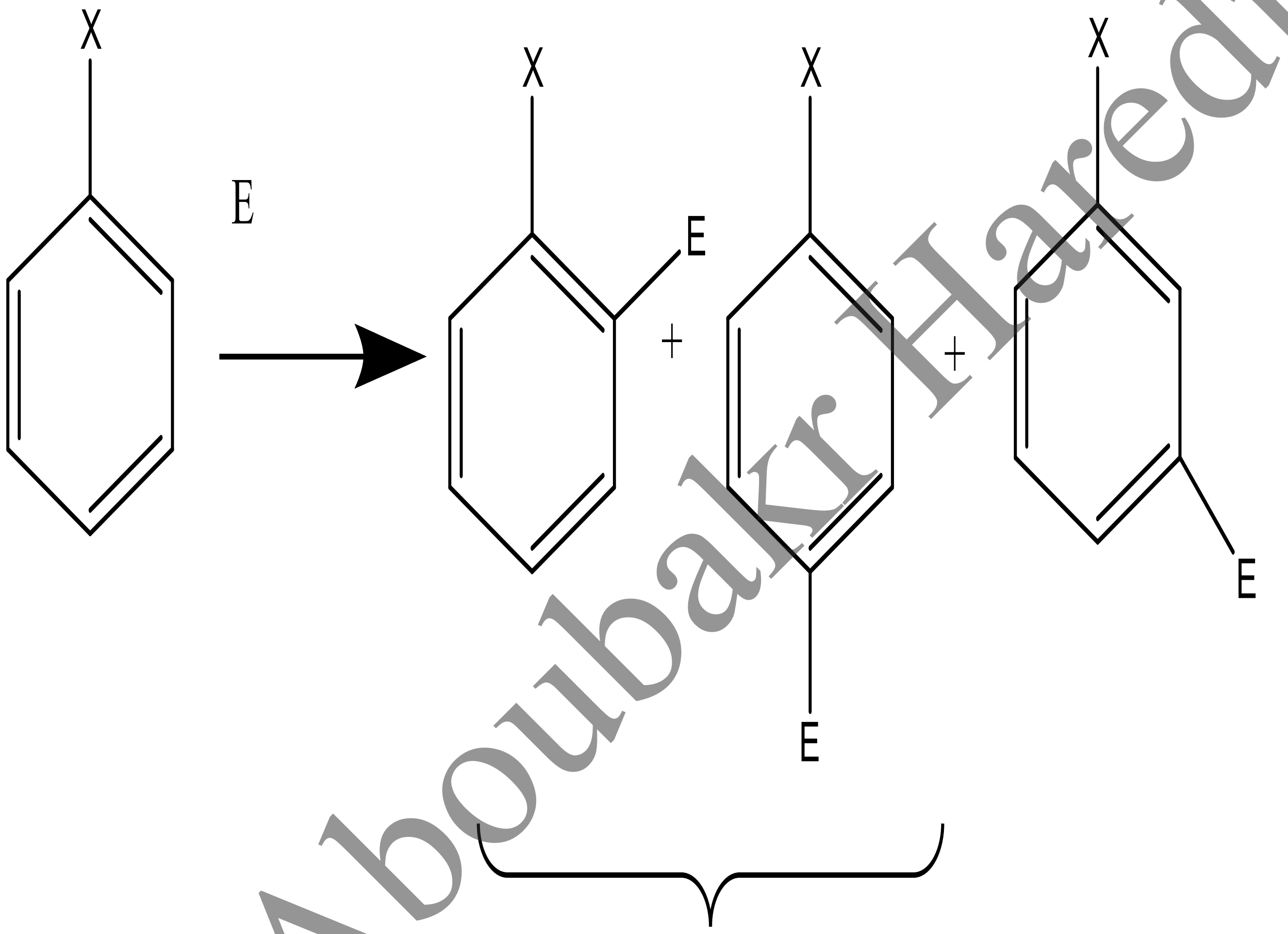
What else could be used here?

Di- and Polysubstitution

- Orientation on nitration of monosubstituted benzenes.

	Substituent	ortho	meta	para	ortho + para	meta
Favor ortho/para substitution	$-OCH_3$	44	-	55	99	trace
	$-CH_3$	58	4	38	96	4
	$-Cl$	70	-	30	100	trace
	$-Br$	37	1	62	99	1
Favor meta substitution	$-COOH$	18	80	2	20	80
	$-CN$	19	80	1	20	80
	$-NO_2$	6.4	93.2	0.3	6.7	93.2

Directivity of substituents



ortho and para, appear together
X is o,p director

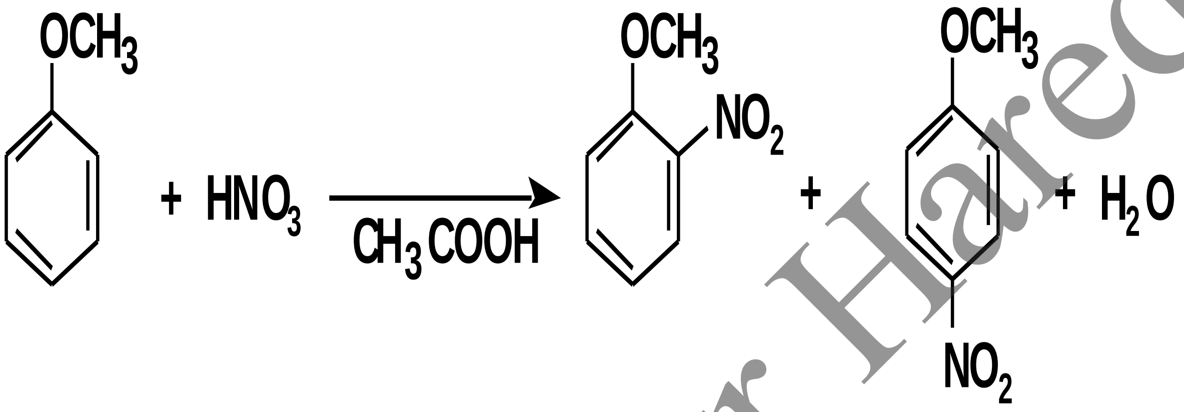
meta
X is m director

Di- and Polysubstitution

- Two ways to characterize the substituent
  - Orientation:
    - Some substituents direct preferentially to ortho & para positions; others to meta positions.
    - Substituents are classified as either ortho-para directing or meta directing toward further substitution.
  - Rate
    - Some substituents cause the rate of a second substitution to be greater than that for benzene itself; others cause the rate to be lower.
    - Substituents are classified as activating or deactivating toward further substitution.

Di- and Polysubstitution

- -OCH_3 is ortho-para directing.

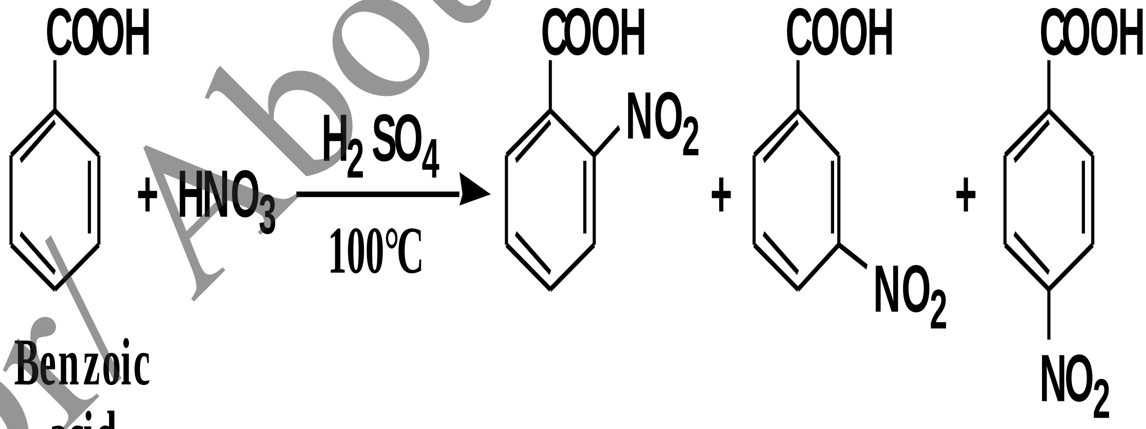


Anisole

***o*-Nitroanisole (44%)**

***p*-Nitroanisole (55%)**

- -COOH is meta directing.



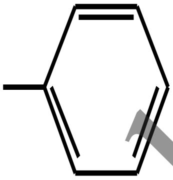
Benzoic acid

***o*-Nitro-benzoic acid (18%)**

***m*-Nitro-benzoic acid (80%)**

***p*-Nitro-benzoic acid (2%)**

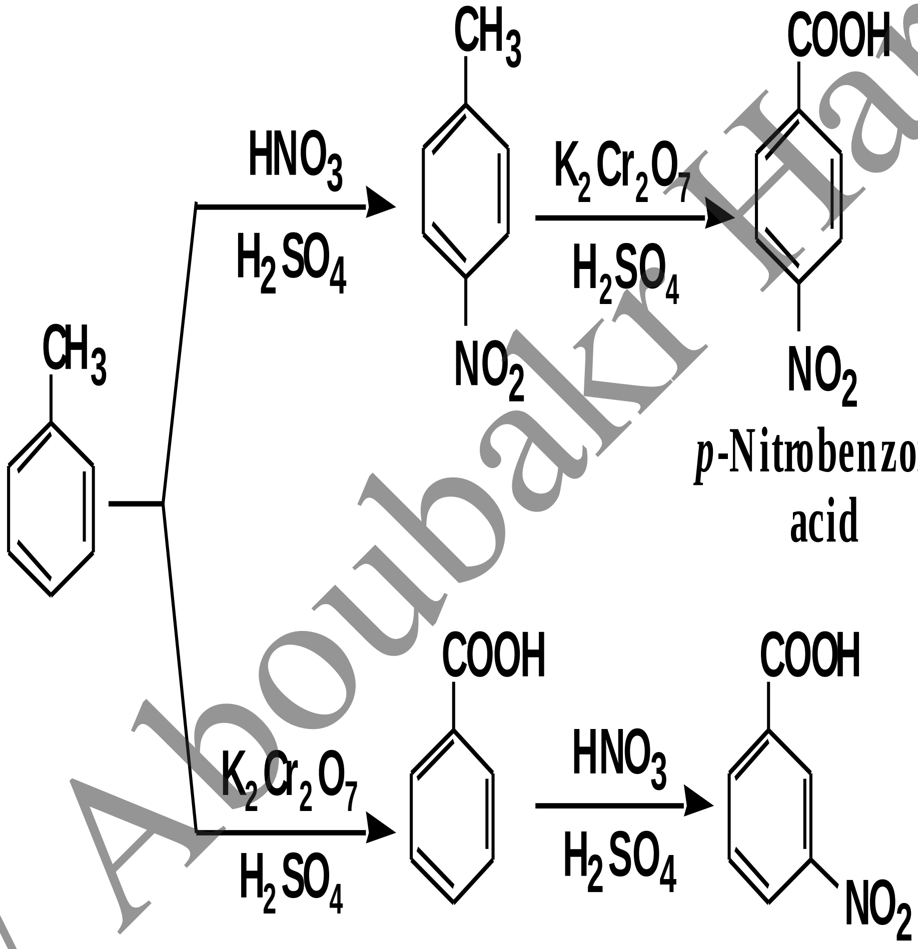
Di- and Polysubstitution

Ortho-para Directing	**Strongly activating**	$-\ddot{N}H_2$ $-\ddot{N}HR$ $-\ddot{N}R_2$ $-\underset{\cdot\cdot}{\ddot{O}}H$ $-\underset{\cdot\cdot}{\ddot{O}}R$
	Moderately activating	$-\ddot{N}H\overset{O}{\overset{\|}{C}}R$ $-\ddot{N}H\overset{O}{\overset{\|}{C}}Ar$ $-\underset{\cdot\cdot}{\ddot{O}}\overset{O}{\overset{\|}{C}}R$ $-\underset{\cdot\cdot}{\ddot{O}}\overset{O}{\overset{\|}{C}}Ar$
	Weakly activating	$-R$ 
	Weakly deactivating	$-\underset{\cdot\cdot}{\ddot{F}}:$ $-\underset{\cdot\cdot}{\ddot{Cl}}:$ $-\underset{\cdot\cdot}{\ddot{Br}}:$ $-\underset{\cdot\cdot}{\ddot{I}}:$
Meta Directing	**Moderately deactivating**	$-\overset{O}{\overset{\|}{C}}H$ $-\overset{O}{\overset{\|}{C}}R$ $-\overset{O}{\overset{\|}{C}}OH$ $-\overset{O}{\overset{\|}{C}}OR$ $-\overset{O}{\overset{\|}{C}}NH_2$ $-SO_3H$ $-C{\equiv}N$
	Strongly deactivating	$-NO_2$ $-NH_3^{+}$ $-CF_3$ $-CCl_3$

Recall the polysubstitution in FC alkylation.

Di- and Polysubstitution

- The order of steps is important.



p-Nitrobenzoic acid

m-Nitrobenzoic acid

Theory of Directing Effects

- **The rate of EAS is limited by the slowest step in the reaction.**
- **For almost every EAS, the rate-determining step is attack of E^+ on the aromatic ring to give a resonance-stabilized cation intermediate.**
- **The more stable this cation intermediate, the faster the rate-determining step and the faster the overall reaction.**

Theory of Directing Effects

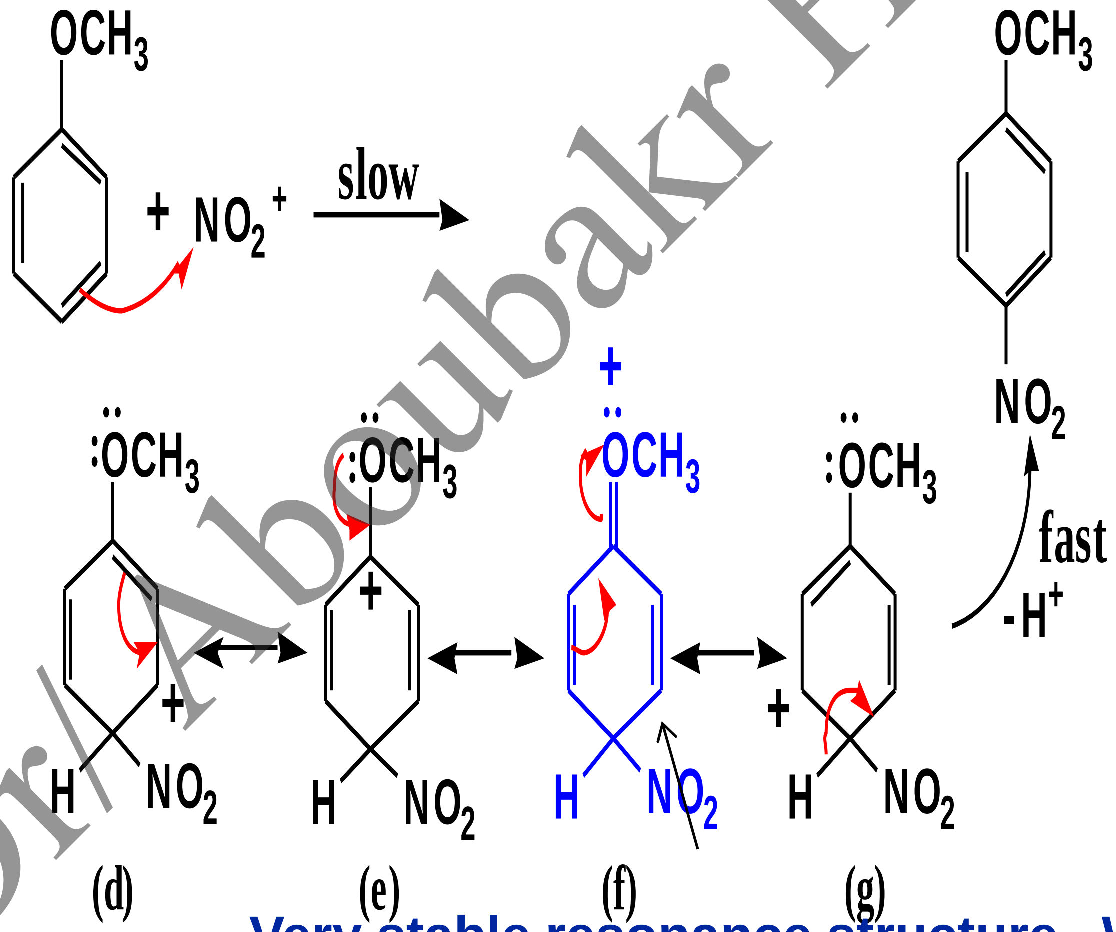
- The orientation is controlled by the stability of the carbocation being formed by attack of the electrophile.

- Products are formed under kintic control.

Theory of Directing Effects, ortho-para director.

- -OCH_3: <u>assume ortho-para attack</u>. Here only para attack is shown.

o/p director

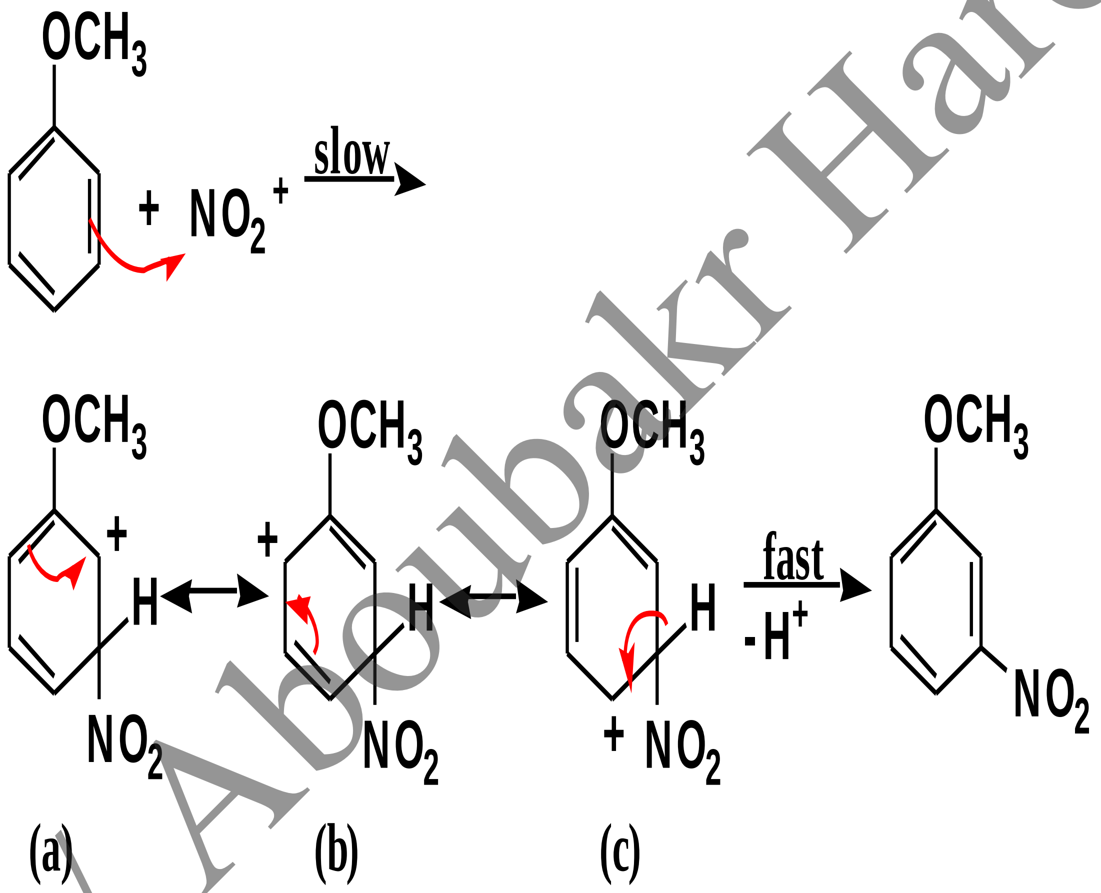


Very stable resonance structure. Why?

Theory of Directing Effects , ortho-para director.

– -OCH_3; look at meta attack.

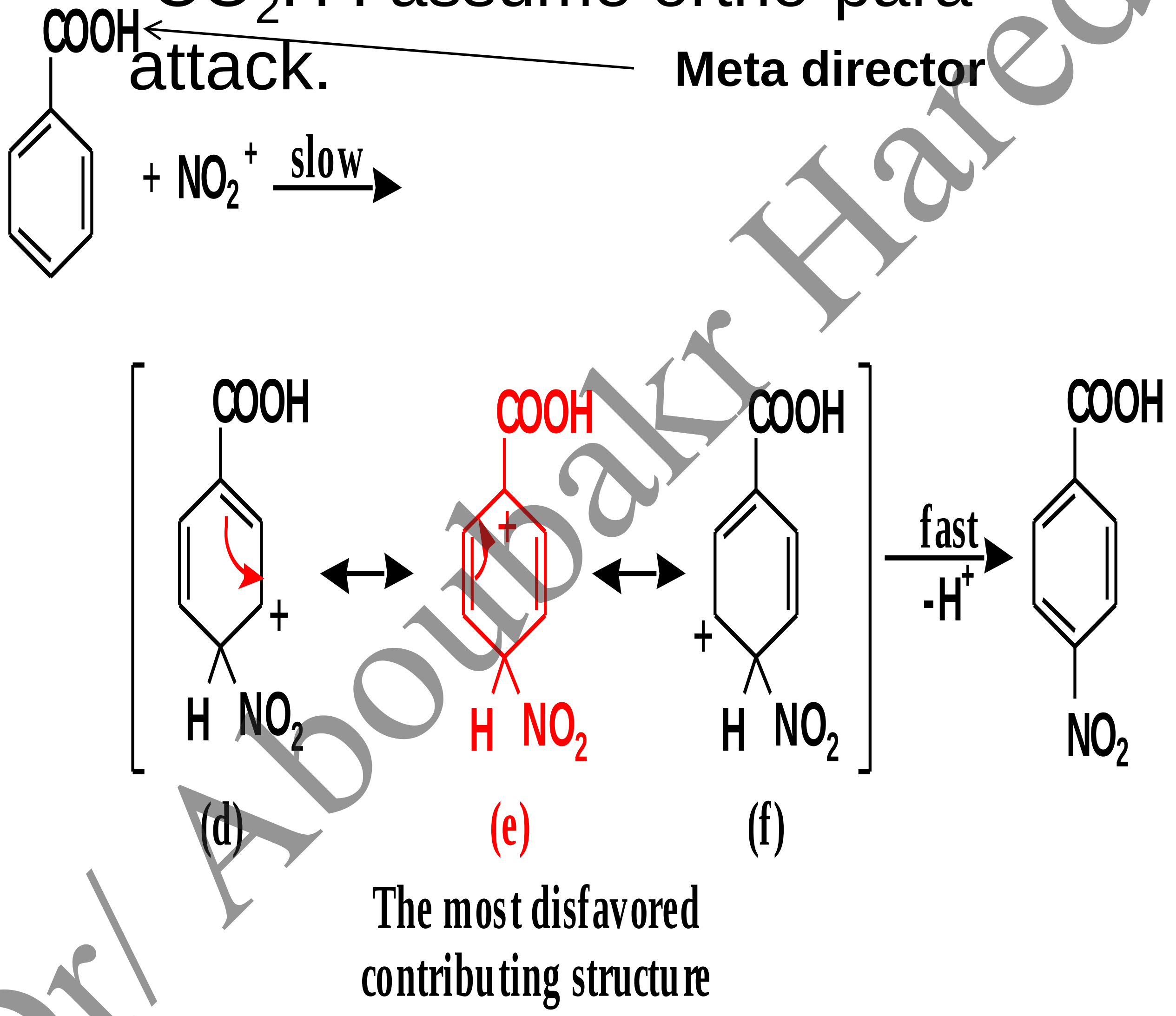
← **o,p director**



No corresponding resonance structure putting positive charge on oxygen.

Theory of Directing Effects, meta director.

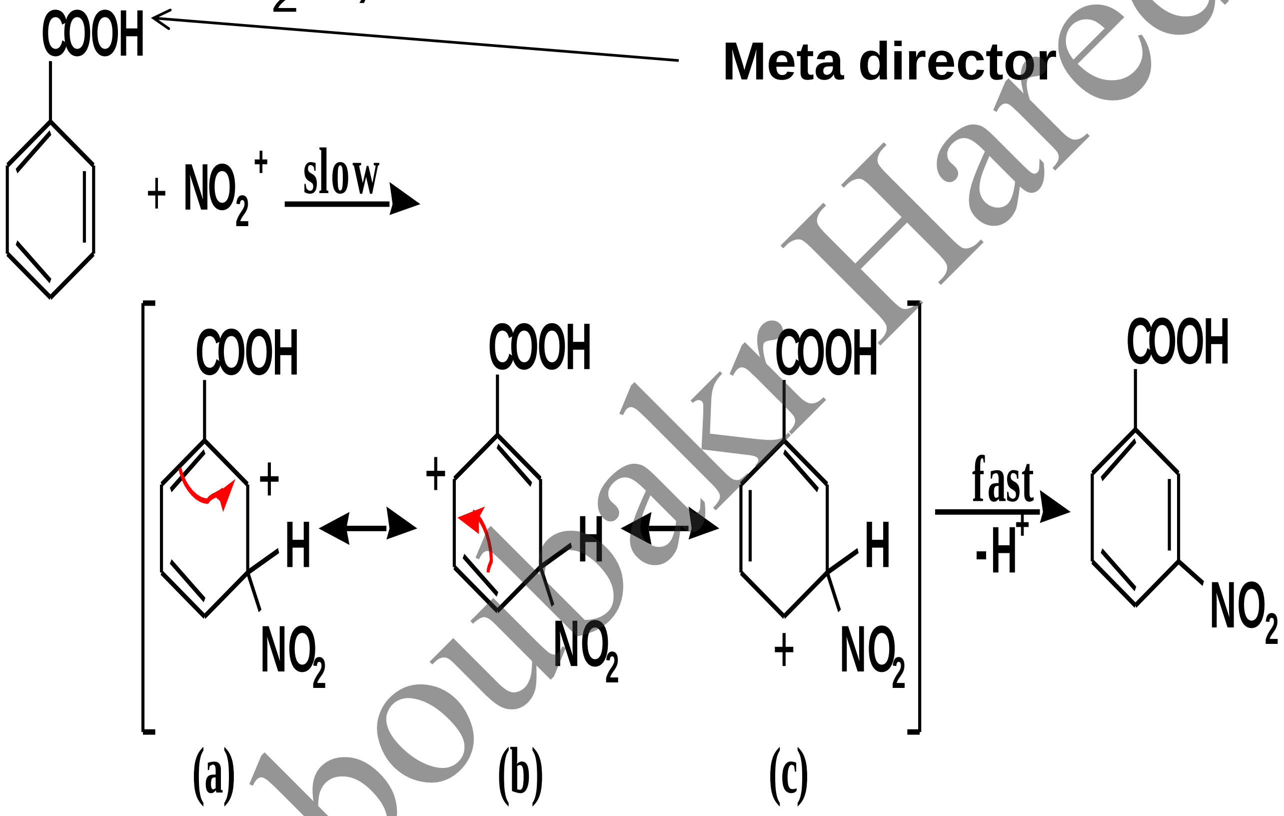
- $-CO_2H$: assume ortho-para attack.



Disfavored because CO_2H is electron withdrawing

Theory of Directing Effects, meta director.

- $-CO_2H$; assume meta attack.



Meta director

Activating-Deactivating Resonance Effects

- Any resonance effect, such as that of -NH_2, -OH, and -OR, that delocalizes the positive charge on the cation by has an activating effect toward further EAS.

- Any resonance effect, such as that of -NO_2, -CN, -C=O, and -SO_3H, that decreases electron density on the ring deactivates the ring toward further EAS.

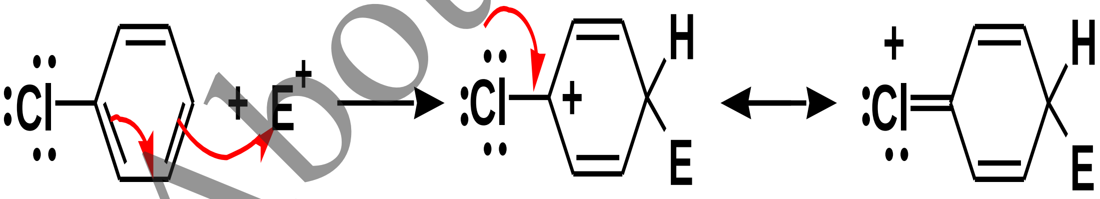
Activating-Deactivating Inductive Effects

- **Any inductive effect**, such as that of -CH_3 or other alkyl group, that releases electron density toward the ring activates the ring toward further EAS.

- **Any inductive effect**, such as that of halogen, -NR_3^+, -CCl_3, or -CF_3, that decreases electron density on the ring deactivates the ring toward further EAS.

Activating-Deactivating: Halogens

- For the halogens, the inductive and resonance effects oppose each other. Inductive is somewhat stronger.
- Result: halogens are deactivating but ortho-para directing.



Nucleophilic Aromatic Substitution

- Aryl halides do not undergo nucleophilic substitution by either S_N1 or S_N2 pathways.
- They do undergo nucleophilic substitutions, but by two mechanisms.
  - Benzyne using strong base.
  - Addition/elimination typically with nitro activating groups.

Orientation

- The methyl group is essentially just a marker to allow the observation of the mixture of products.
- Consider the methoxy group, -OCH_3, stabilizing of positive charge via resonance but also inductively withdrawing.
- The methoxy group is not in resonance with the negative charge of the anion, Inductive Effect dominates. Next slide.

Sources and References

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