

Chapter one

Aromatic Hydrocarbons

1- Benzene

1.1- Aliphatic and aromatic compounds

Chemists have found it useful to divide all organic compounds into two broad classes: **aliphatic** compounds and **aromatic** compounds.

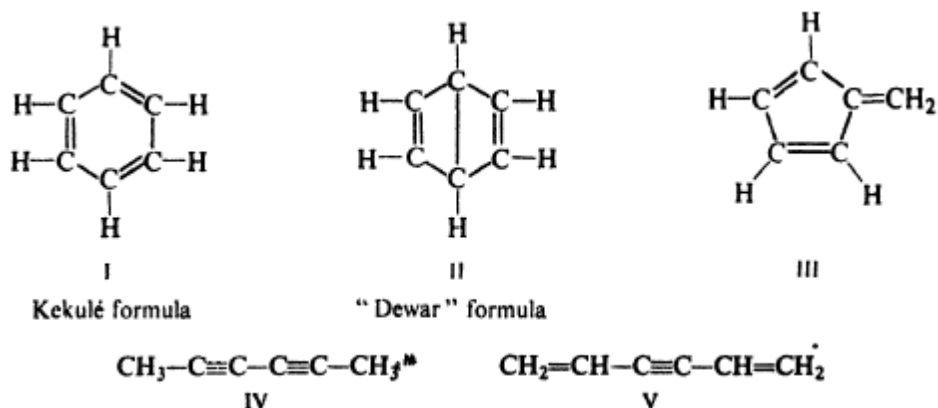
Aromatic compounds are **benzene** and compounds that resemble benzene in chemical behavior. Aromatic properties are those properties of benzene that distinguish it from aliphatic hydrocarbons. Some compounds that possess aromatic properties have structures that seem to differ considerably from the structure of benzene: actually, however, there is a basic similarity in electronic configuration.

Aliphatic hydrocarbons, as we have seen, undergo chiefly addition and free radical substitution; addition occurs at multiple bonds, and free-radical substitution occurs at other points along the aliphatic chain. In contrast, we shall find that *aromatic hydrocarbons are characterized by a tendency to undergo ionic substitution.*

1.2-Molecular formula. Isomer number. Kekule structure

Benzene has the molecular formula **C₆H₆**. From its elemental composition and molecular weight, benzene was known to contain six carbon atoms and six hydrogen atoms.

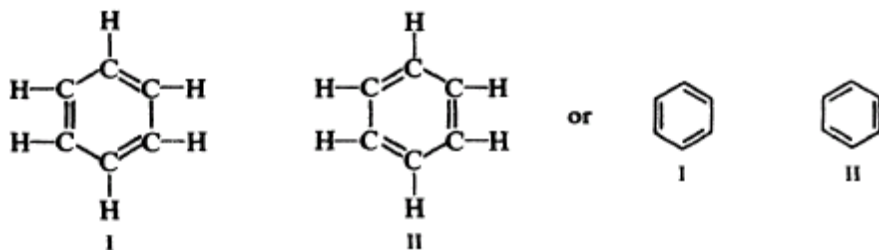
Kekule's structure of benzene was one that we would represent today as I.



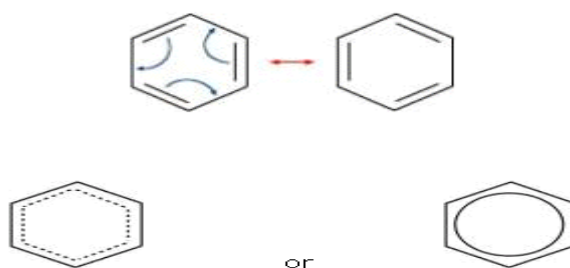
Other structures are, of course, consistent with the formula C₆H₆ : for example, II- V. Of all these, Kekule's structure was accepted as the most nearly satisfactory; the evidence was of a kind with which we are already familiar: *isomer number.*

1.3-Resonance structure of benzene

Benzenes have six carbon atoms are linked to each other in a six-membered ring. Its Lewis structure is often represented with three double bonds as shown below, but chemists often simplify it by leaving off the elements symbols and the carbon-hydrogen bonds.

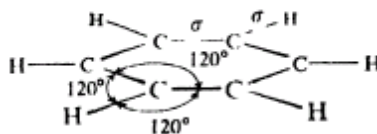


The Lewis structures above depict the benzene molecule as if it contained two types of C-C bonds, double and single. In actuality, all of benzenes C-C bonds appear to be the same, and we can explain why in terms of resonance. It is as if the benzene ring were resonating between the two structures below.

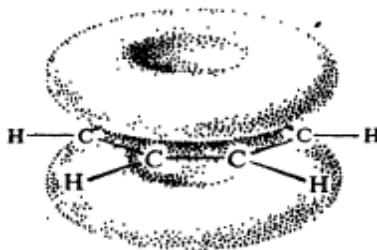


1.4- Orbital picture of benzene

Since each carbon is bonded to three other atoms, it uses sp^2 orbitals. These lie in the same plane, that of the carbon nucleus, and are directed toward the corners of an equilateral triangle. If we arrange the six carbons and six hydrogens of benzene to permit maximum overlap of these orbitals.



The result two continuous doughnut-shaped electron clouds, one lying above and the other below the plane of the atoms.



As with the allyl radical, it is the overlap of the p orbitals in both directions, and the resulting participation of each electron in several bonds that corresponds to our description of the molecule as a resonance hybrid of two structures. Again it is the delocalization of the n electrons their participation in several bonds that makes the molecule more stable.

1.5- Aromatic character. The Hückel's Rule

Besides the compounds that contain benzene rings, there are many other substances that are called aromatic; yet some of these superficially bear little resemblance to benzene.

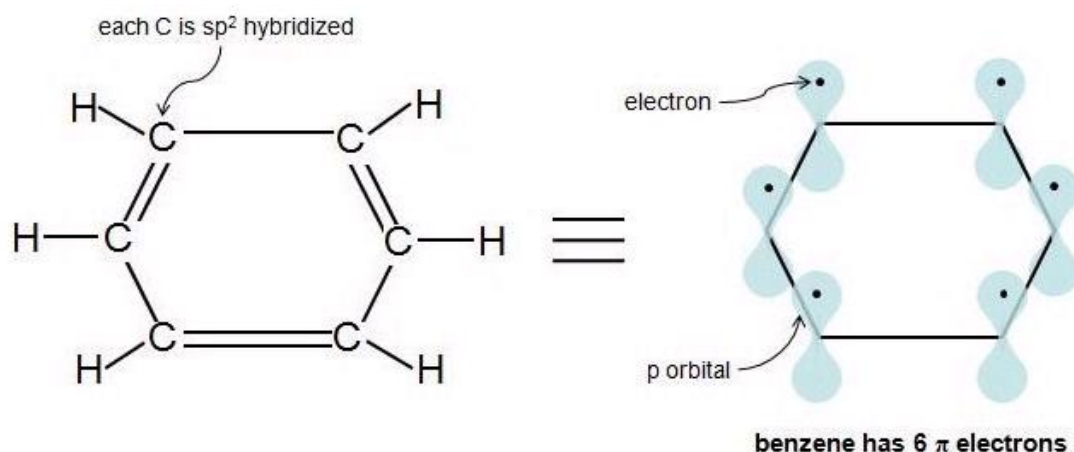
There are four main criteria to decide the Aromaticity of an organic compound:

- 1- A compound must have a molecule that contains cyclic clouds of delocalized π electrons
- 2- The compound should have a planar structure to ensure a good overlap of p-orbitals
- 3- The compound should be conjugated i.e. each atom of the ring should have a p-orbital for continuous delocalisation of the electrons within the pi-cloud of the ring
- 4- The compound should have $(4n+2)\pi$ electrons [Huckel Rule]
{ where $n = 0$ or any positive integer, 1,2,3... }

Systems containing $4n \pi$ -electrons

Hückel's Rule							
$4n+2:$	2	6	10	14	18	22	26
$4n:$	4	8	12	16	20	24	28

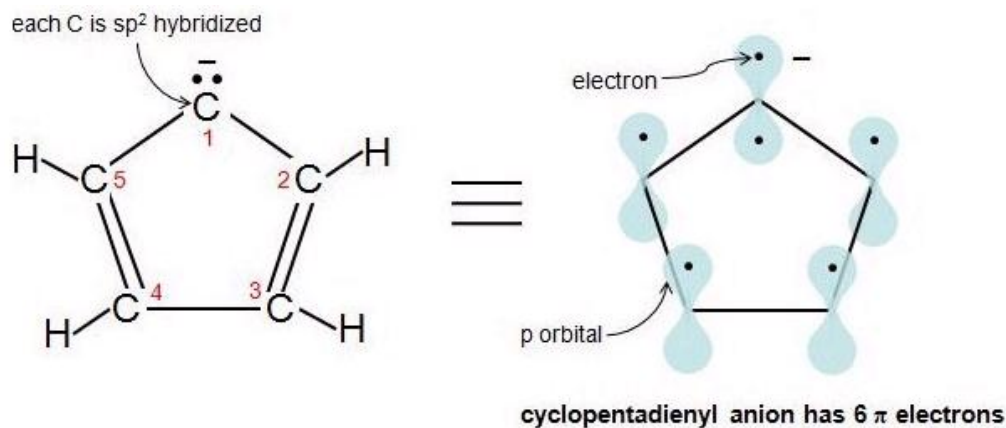
In **benzene** each double bond (π bond) always contributes 2 π electrons. Benzene has 3 double bonds, so it has 6 π electrons.



Aromatic Ions

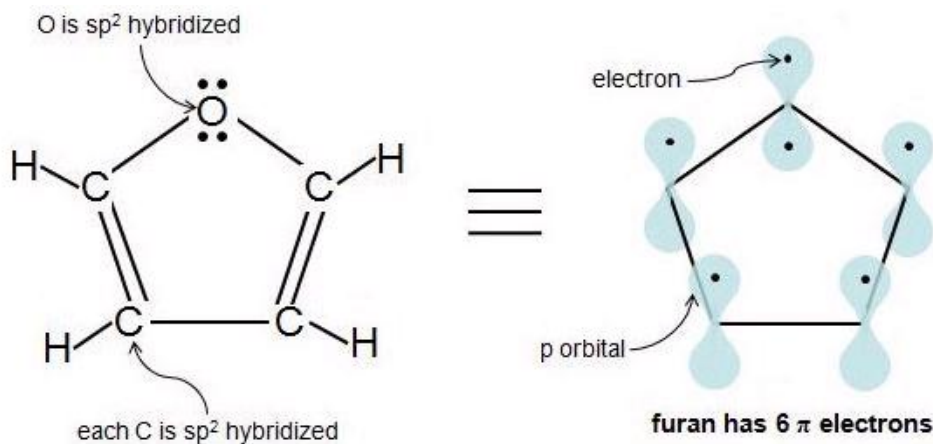
Hückel's Rule also applies to ions. As long as a compound has $4n+2 \pi$ electrons, it does not matter if the molecule is neutral or has a charge. For example, cyclopentadienyl anion is an aromatic ion. How do we know that it is fully conjugated? That is, how do we know that each atom in this molecule has 1 p orbital? Let's look at the following figure. Carbons 2-5 are sp^2 hybridized because they have 3 attached atoms and have no lone electron pairs. Another simple rule to determine if an atom is sp^2 hybridized is if an atom has 1 or more lone pairs and is

attached to an sp^2 hybridized atom, then that atom is sp^2 hybridized also. Therefore, carbon 1 has a p orbital. Cyclopentadienyl anion has 6 π electrons and fulfills the $4n+2$ rule.

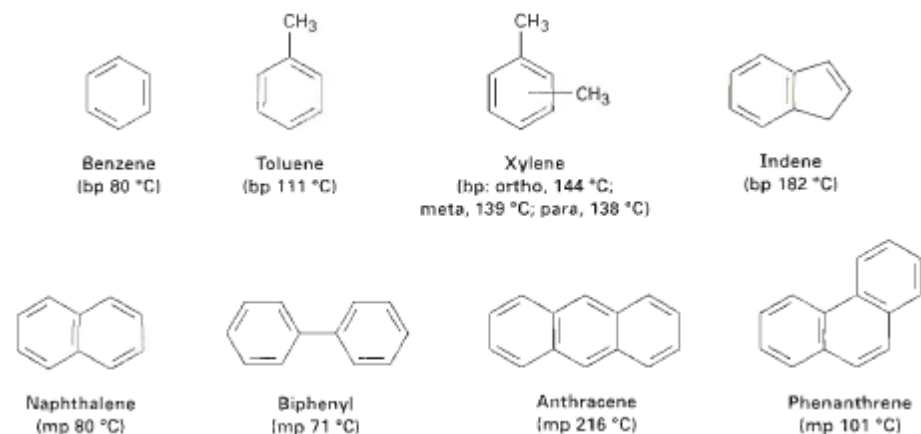


Heterocyclic Aromatic Compounds

So far, you have encountered many carbon homocyclic rings, but compounds with elements other than carbon in the ring can also be aromatic, as long as they fulfill the criteria for aromaticity. These molecules are called heterocyclic compounds because they contain 1 or more different atoms other than carbon in the ring. A common example is furan, which contains an oxygen atom. We know that all carbons in furan are sp^2 hybridized. But is the oxygen atom sp^2 hybridized? The oxygen has at least 1 lone electron pair and is attached to an sp^2 hybridized atom, so it is sp^2 hybridized as well. Notice how oxygen has 2 lone pairs of electrons. How many of those electrons are π electrons? An sp^2 hybridized atom only has 1 p orbital, which can only hold 2 electrons, so we know that 1 electron pair is in the p orbital, while the other pair is in an sp^2 orbital. So, only 1 of oxygen's 2 lone electron pairs are π electrons. Furan has 6 π electrons and fulfills the $4n+2$ rule.



1.6- Nomenclature of benzene derivatives

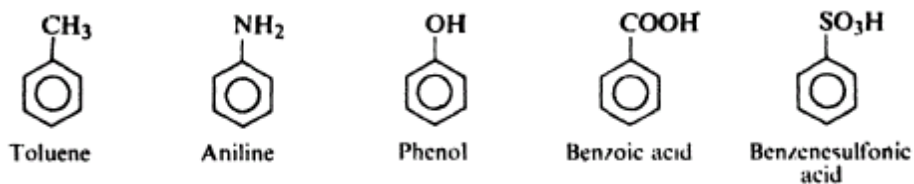


Common Names of Some Aromatic Compounds			
Structure	Name	Structure	Name
	Toluene (bp 111 °C)		Benzaldehyde (bp 178 °C)
	Phenol (mp 43 °C)		Benzoic acid (mp 122 °C)
	Aniline (bp 184 °C)		ortho-Xylene (bp 144 °C)
	Acetophenone (mp 21 °C)		Styrene (bp 145 °C)

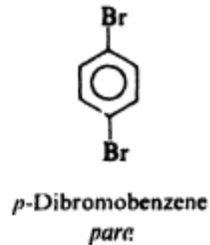
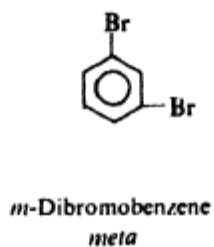
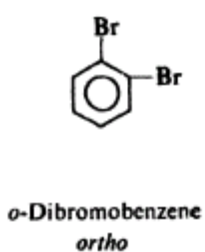
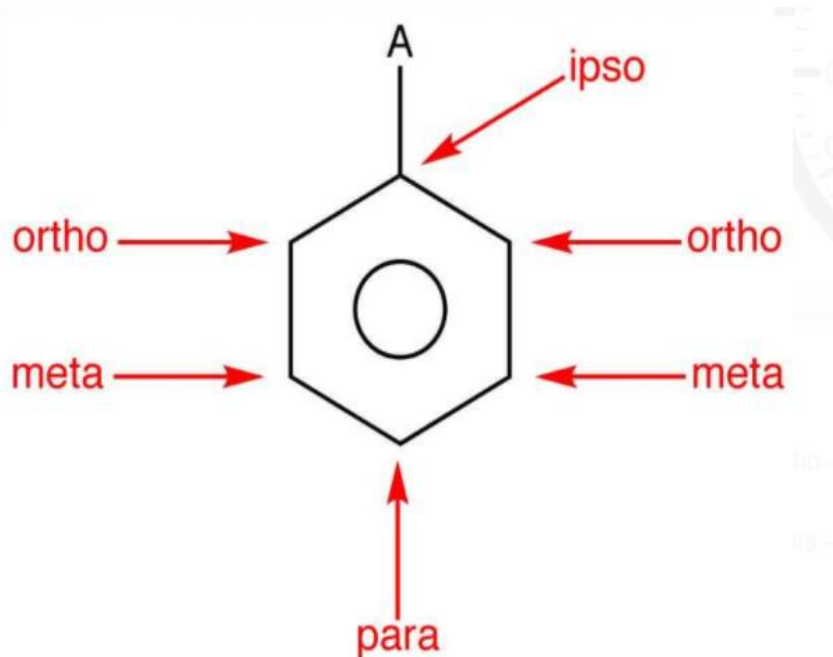
For many of these derivatives we simply prefix the name of the substituent group to the word -benzene, as, for example, in chlorobenzene, bromobenzene, iodobenzene, or nitrobenzene.

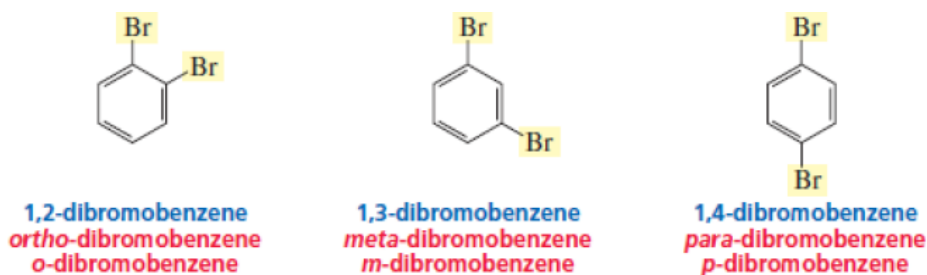
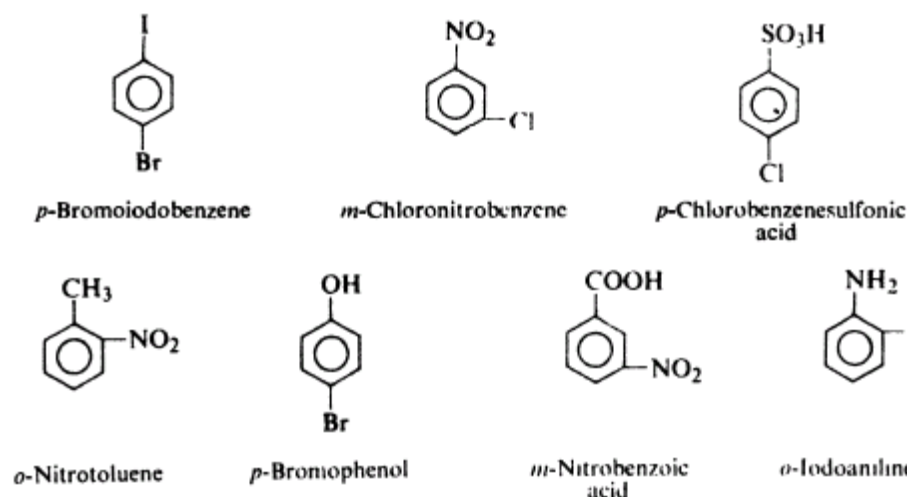


Other derivatives have special names which may show no resemblance to the name of the attached substituent group. For example, methylbenzene is always known as toluene, aminobenzene as aniline, hydroxybenzene as phenol, and so on. The most important of these special compounds are:

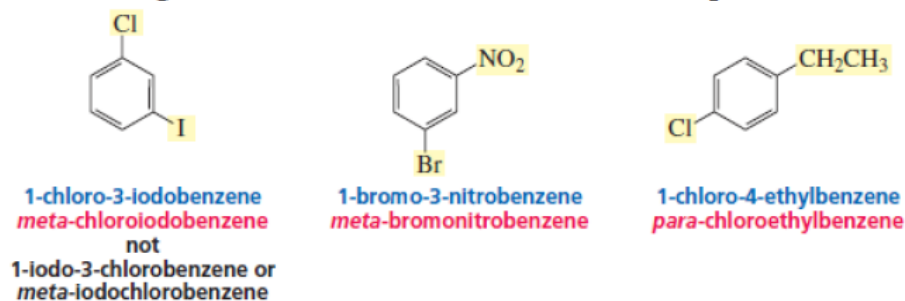


If several groups are attached to the benzene ring, we must not only tell what they are, but also indicate their relative positions. The three possible isomers of a disubstituted benzene are differentiated by the use of the names ortho, meta, and para. For example:

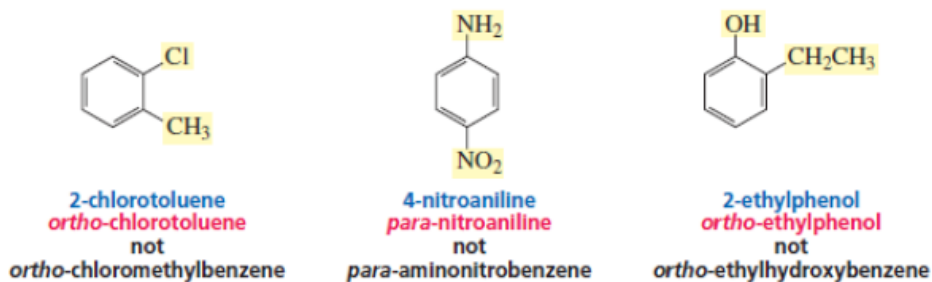




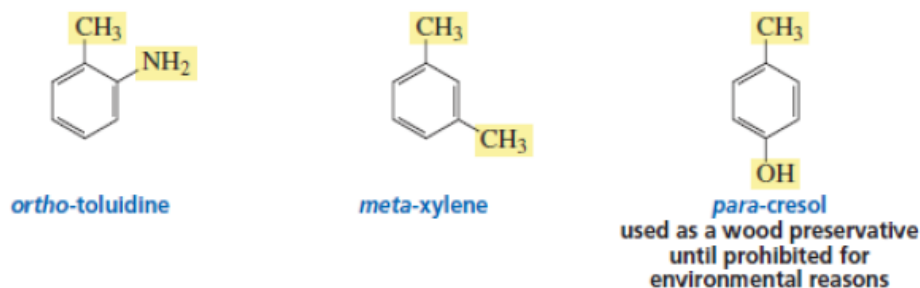
If the two substituents are different, they are listed in alphabetical order. The firststated substituent is given the 1-position, and the ring is numbered in the direction that gives the second substituent the lowest possible number.



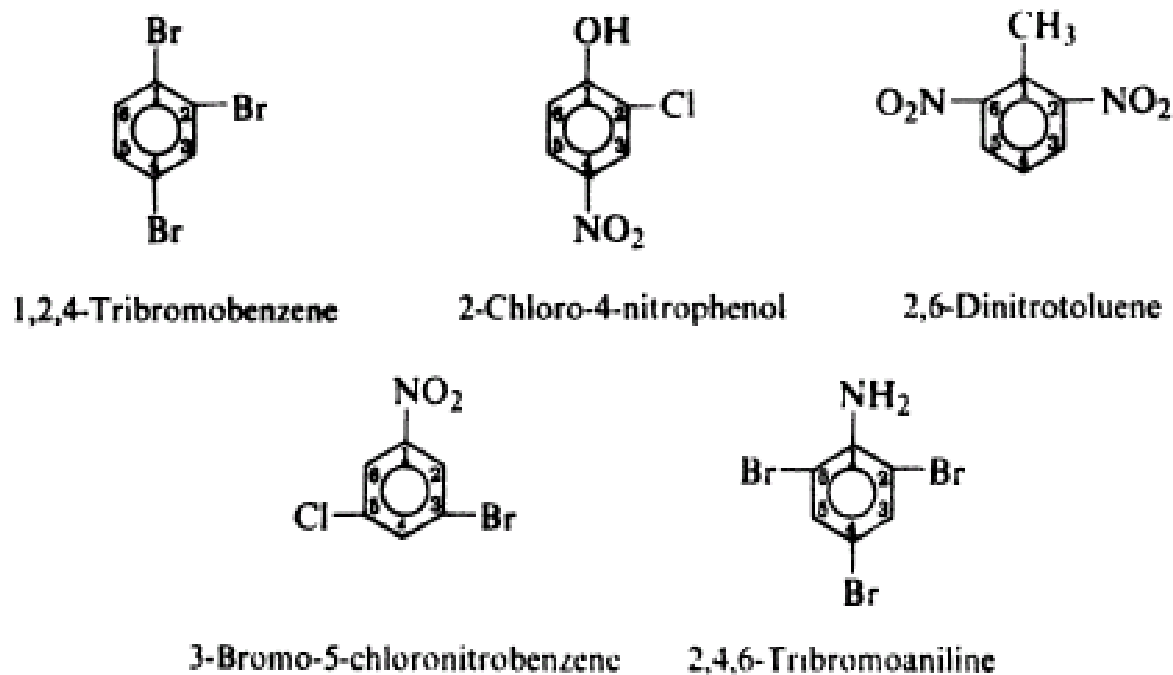
If one of the substituents can be incorporated into a name that name is used and the incorporated substituent is given the 1-position.

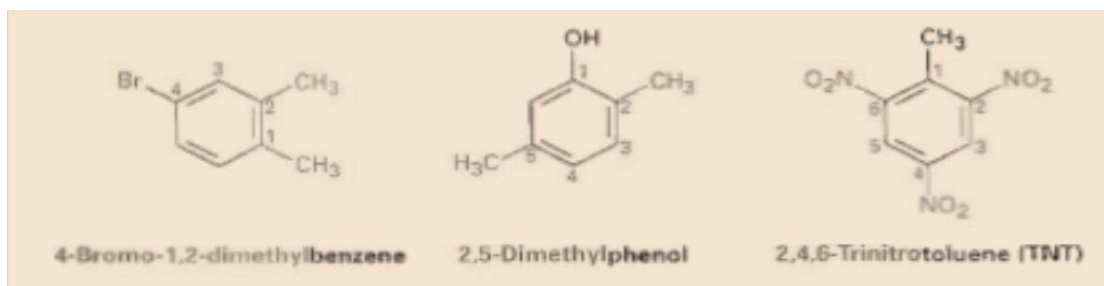
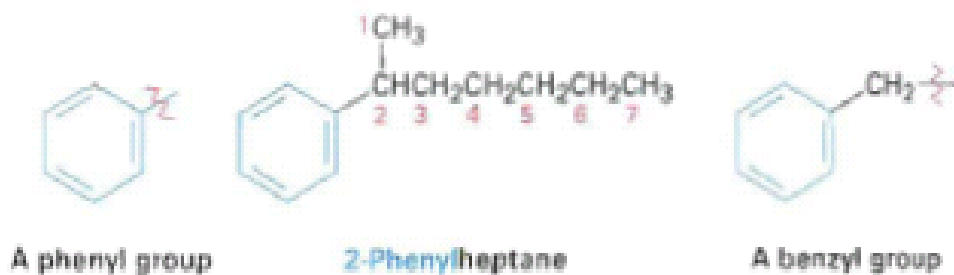


A few disubstituted benzenes have names that incorporate both substituents.



If more than two groups are attached to the benzene ring, numbers are used to indicate their relative positions. For example :





Problem 1 Tell whether the following compounds are ortho-, meta-, or para-disubstituted:

(a)

(b)

(c)

Problem 2 Give IUPAC names for the following compounds:

(a)

(b)

(c)

(d)

(e)

(f)

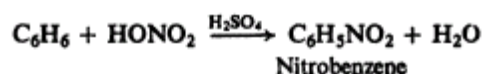
Problem 3 Draw structures corresponding to the following IUPAC names:

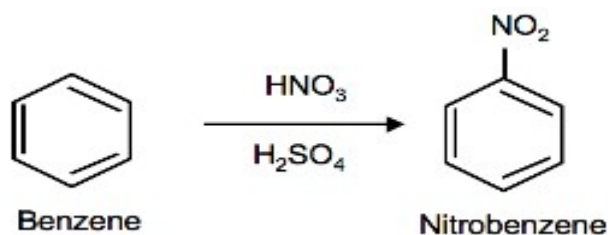
(a) *p*-Bromochlorobenzene (b) *p*-Bromotoluene
 (c) *m*-Chloroaniline (d) 1-Chloro-3,5-dimethylbenzene

1.7- REACTIONS OF BENZENE

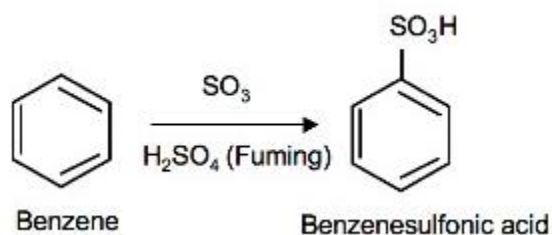
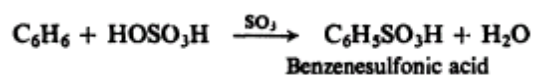
In place of addition reactions, benzene readily undergoes a new set of reactions, all involving **substitution**. The most important are shown below.

1. Nitration.

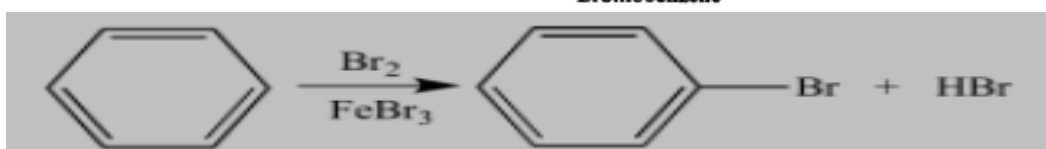
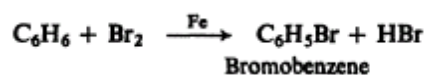




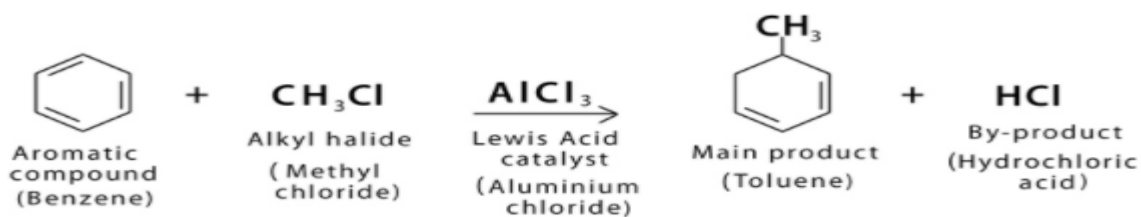
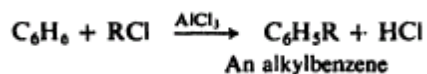
2.Sulfonation.



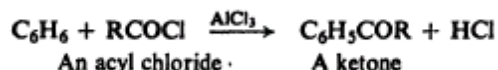
3. Halogenation.



4. Friedel-Crafts alkylation.



5. Friedel-Crafts acylation.



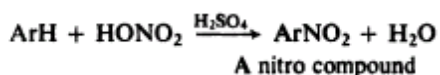
1.8-Electrophilic Aromatic Substitution

The benzene ring serves as a source of electrons, that is, as a base. The compounds with which it reacts are deficient in electrons, that is, are **electrophilic reagents** or acids. Just as the typical reactions of the alkenes are electrophilic addition reactions, so the typical reactions of the benzene ring are electrophilic substitution reactions.

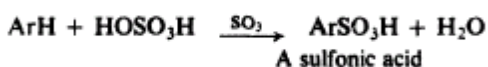
Electrophilic aromatic substitution includes a wide variety of reactions: nitration, halogenation, sulfonation, and Friedel-Crafts reactions, undergone by nearly all aromatic rings.

Ar : aryl, is any aromatic group with attachment directly to ring carbon

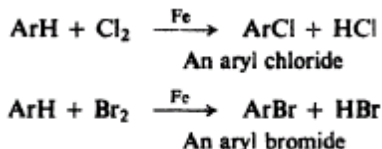
1-Nitration.



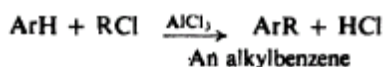
2- Sulfonation.



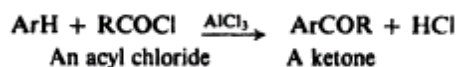
3- Halogenation.



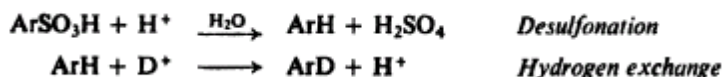
4- Friedel-Crafts alkylation.



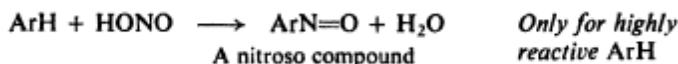
5- Friedel-Crafts acylation.



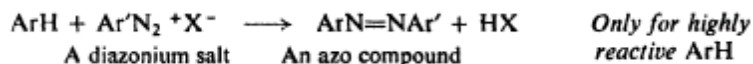
6- Protonation.



7- Nitrosation.

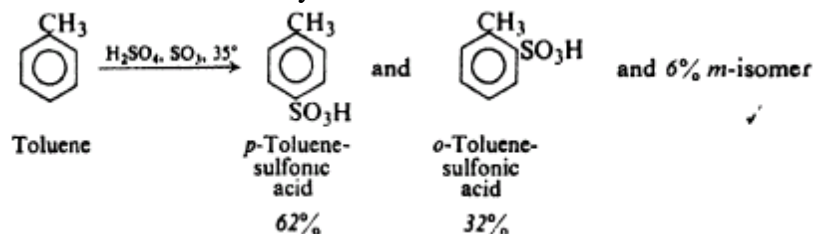


8- Diazo coupling.



1.8- Effect of substituent groups

Like benzene, toluene undergoes electrophilic aromatic substitution: sulfonation, for example. Although there are three possible monosulfonation products, this reaction actually yields appreciable amounts of only two of them: the **o-** and **P-isomers**.



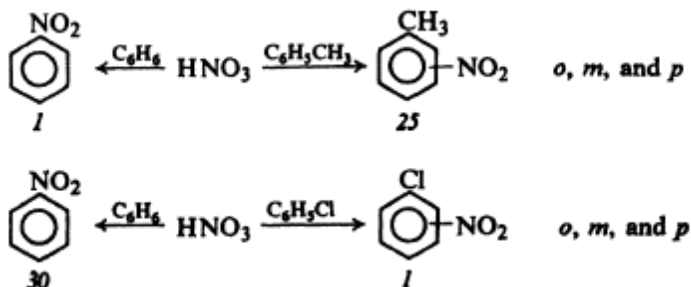
Like methyl or nitro, any group attached to a benzene ring affects the reactivity of the ring and determines the orientation of substitution.

A group that makes the ring more reactive than benzene is called an **activating group**. A group that makes the ring less reactive than benzene is called a **deactivating group**.

A group that causes attack to occur chiefly at positions **ortho** and **para** to it is called an **ortho,para director**. A group that causes attack to occur chiefly at positions **meta** to it is called a **meta director**.

Y		<i>Ortho</i>	<i>Para</i>	<i>Ortho plus para</i>	<i>Meta</i>
O&P directing activators	—OH	50–55	45–50	100	trace
	—NHCOCH ₃	19	79	98	2
	—CH ₃	58	38	96	4
o&p Directing deactivators	—F	12	88	100	trace
	—Cl	30	70	100	trace
	—Br	37	62	99	1
	—I	38	60	98	2
m directing deactivators	—NO ₂	6.4	0.3	6.7	93.3
	—N(CH ₃) ₃ ⁺	0	11	11	89
	—CN	—	—	19	81
	—COOH	19	1	20	80
	—SO ₃ H	21	7	28	72
	—CHO	—	—	28	72

	<i>Ortho</i>	<i>Meta</i>	<i>Para</i>
Nitration	58	4	38
Sulfonation	32	6	62
Bromination	33	—	67



1.9- Classification of substituent groups (Activation& Deactivation)

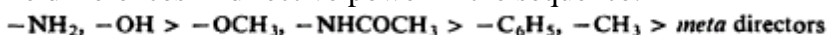
There are two classes: **activating** and *ortho, para* directing, or deactivating and *meta*-directing.

The halogens are in a class by themselves, being deactivating but *ortho,para*-directing.

A group is classified as **activating** if the ring it is attached to is more reactive than benzene (*all activating groups is that they donate electrons to ring*). Hydroxyl, halogen, alkoxy (-OR), and amino substituents, (*donate electrons*) to the aromatic ring by resonance.

Alkyl groups (-R), on the other hand, inductively (*donate electrons*).

The differences in directive power in the sequence:

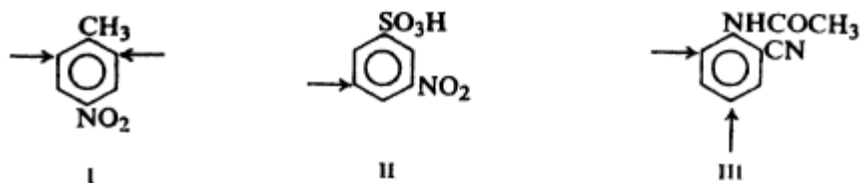


And groups classified as **deactivating** if the ring it is attached to is less reactive than benzene (*all activating groups is that they withdraw electrons from the ring*). Cyano, carbonyl, halogens, and nitro groups are deactivation, inductively withdraw electrons through the σ bond linking the constituent to a benzene ring.

Table EFFECT OF GROUPS ON ELECTROPHILIC AROMATIC SUBSTITUTION	
Activating: <i>Ortho,para</i> Directors	Deactivating: <i>Meta</i> Directors
<i>Strongly activating</i>	-NO ₂
-NH ₂ (-NHR, -NR ₂)	-N(CH ₃) ₃ ⁺
-OH	-CN
<i>Moderately activating</i>	-COOH (-COOR)
-OCH ₃ (-OC ₂ H ₅ , etc.)	-SO ₃ H
-NHCOCH ₃	-CHO, -COR
<i>Weakly activating</i>	Deactivating: <i>Ortho,para</i> Directors
-C ₆ H ₅	-F, -Cl, -Br, -I
-CH ₃ (-C ₂ H ₅ , etc.)	

1.10- Orientation in disubstituted benzenes

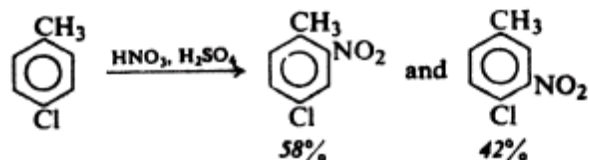
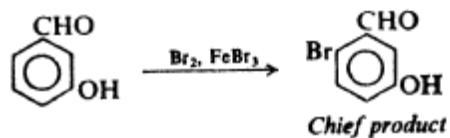
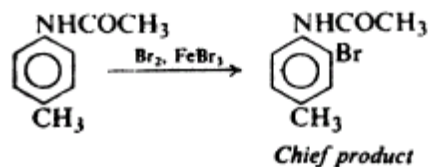
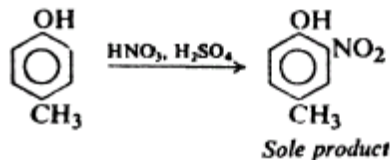
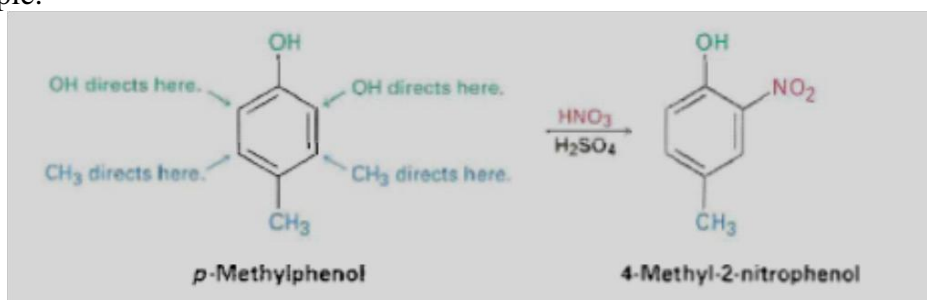
The two substituents may be located so that the directive influence of one *reinforces* that of the other; for example, in I, II, and III the orientation clearly is that indicated by the arrows.



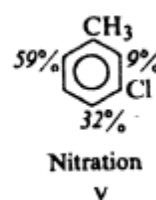
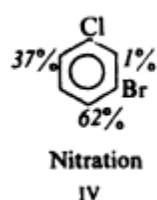
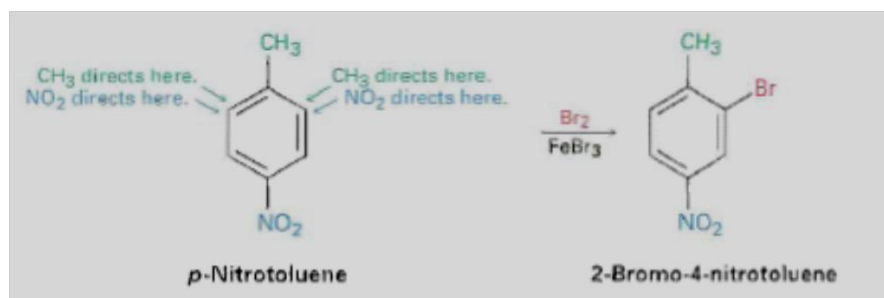
(a) Strongly activating groups generally win out over deactivating or weakly activating groups. The differences in directive power in the sequence:



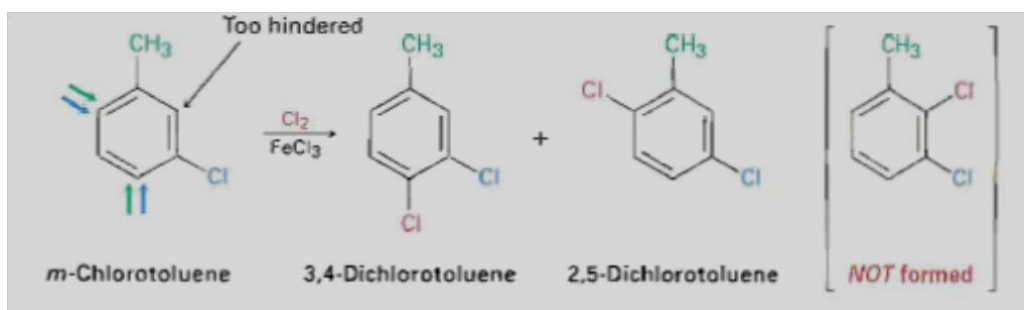
For example:



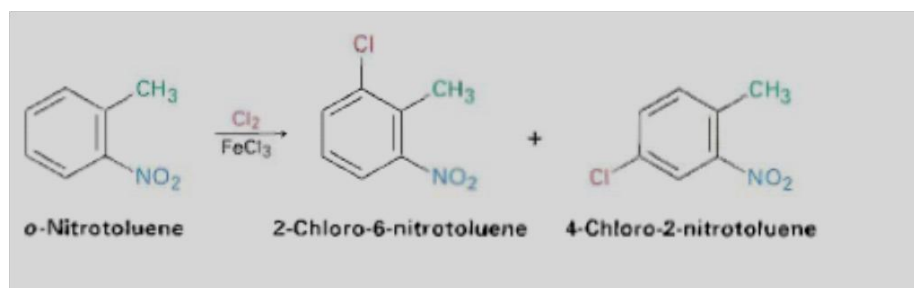
(b) There is often little substitution between two groups that are meta to each other. In many cases it seems as though there just is not enough room between two groups located meta to each other for appreciable substitution to occur there, as illustrated by IV and V:



- (c) Further substitution rarely occur between the two groups in a meta- disubstituted compounds because this site is too hindered. Usually substitution is an ortho-disubstituted compound.

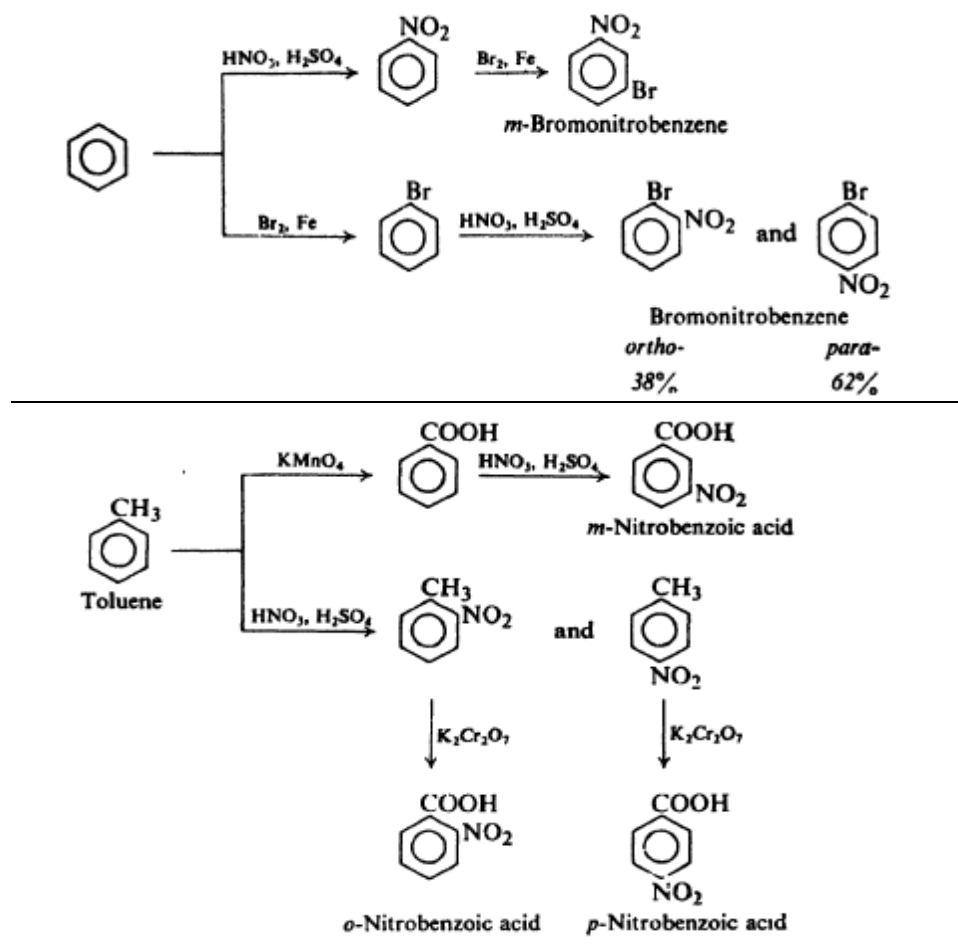


But:



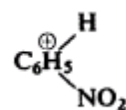
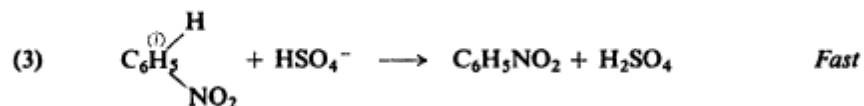
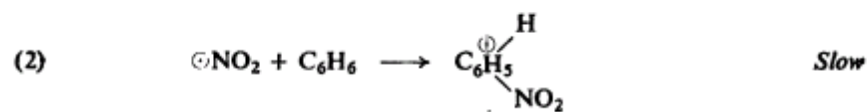
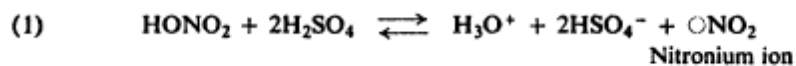
1.11- Orientation and synthesis

In the preparation of the bromonitrobenzenes, for example, it is obvious that if we nitrate first and then brominate, we will obtain the *m*-isomer; whereas if we brominate first and then nitrate, we will obtain a mixture of the *o*- and *p*-isomers. The order in which we decide to carry out the two steps, then, depends upon which isomer we want.



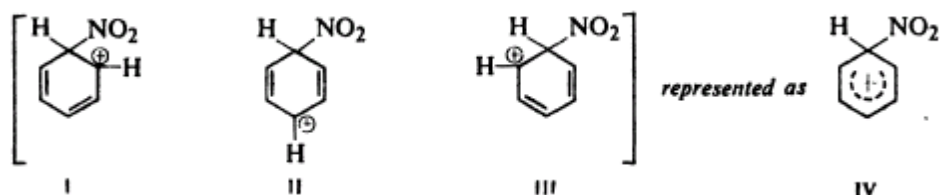
1.12- Mechanism of nitration

The commonly accepted mechanism for nitration with a mixture of nitric and sulfuric acids (the widely used "mixed acid" of the organic chemist) involves the following sequence of reactions:



often called a *benzenonium ion*.

The actual ion must then be a resonance hybrid of these three structures:

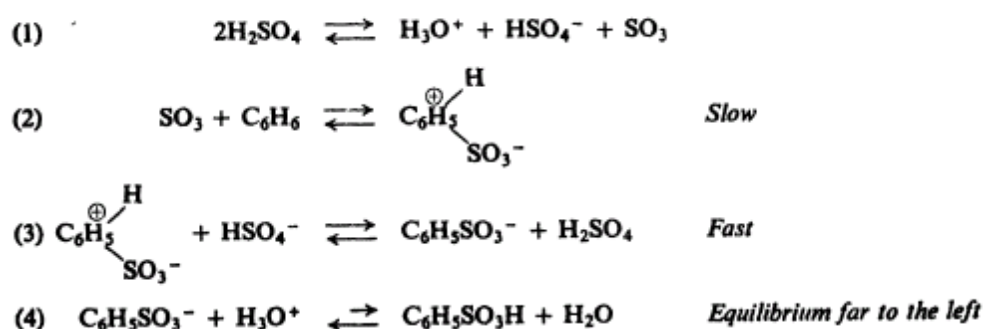


This means, of course, that the positive charge is not localized on one carbon atom, but is distributed over the molecule, being particularly strong on the carbon. The dispersal of the positive charge over the molecule by resonance makes this ion more stable than an ion with a localized positive charge.

Problem Nitration by nitric acid alone is believed to proceed by essentially the same mechanism as nitration in the presence of sulfuric acid. Write an equation for the generation of NO_2^+ from nitric acid alone.

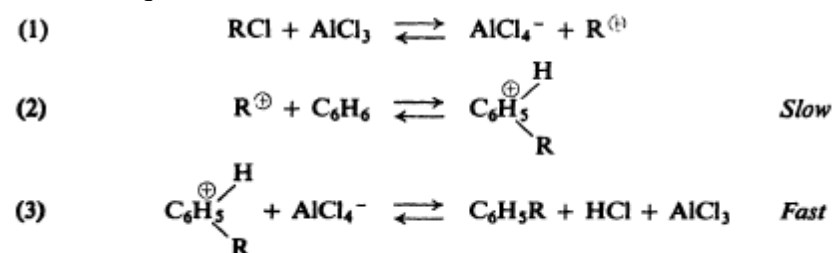
1.13- Mechanism of sulfonation

Sulfonation of many aromatic compounds involves the following steps:



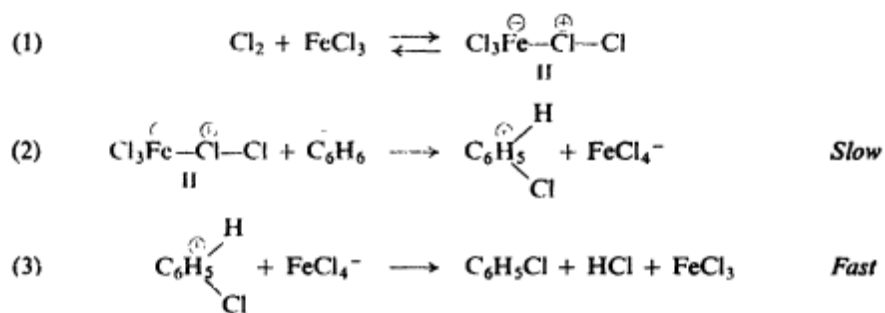
1.14- Mechanism of Friedel-Crafts alkylation

In Friedel-Crafts alkylation, the electrophile is typically a carbonium ion. It, too, is formed in an acid-base equilibrium, this time in the Lewis sense:



6.15- Mechanism of halogenation

Aromatic halogenation, illustrated for chlorination, involves the following steps:



Chapter 2

2. Alkyl halides

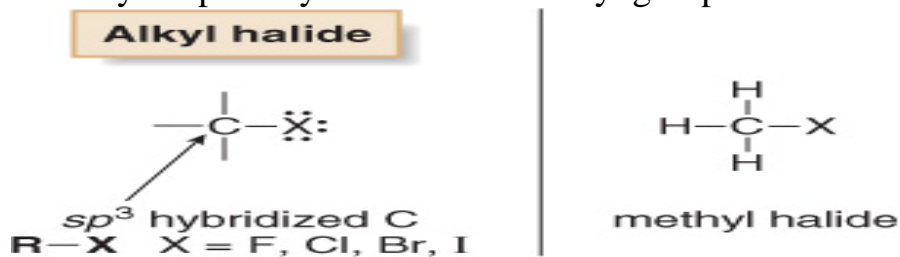
Alkyl halides are organic molecules containing a halogen atom bonded to an sp^3 hybridized carbon atom.

- Alkyl halides are classified as primary (1°), secondary (2°), or tertiary (3°), depending on the number of carbons bonded to the carbon with the halogen atom.
- The halogen atom in halides is often denoted by the symbol “X”

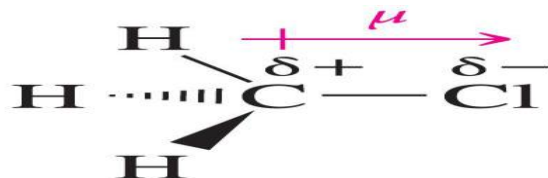
The general formula is RX where R is an alkyl group and X is a halogen.

($X = F, Cl, Br, I$)

R is any simple alkyl or substituted alkyl group.

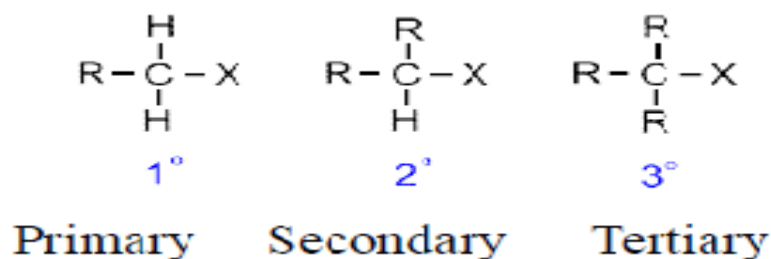


Halogen atoms are more electronegative than carbon atoms, and so the C-Hal bond is polarized.

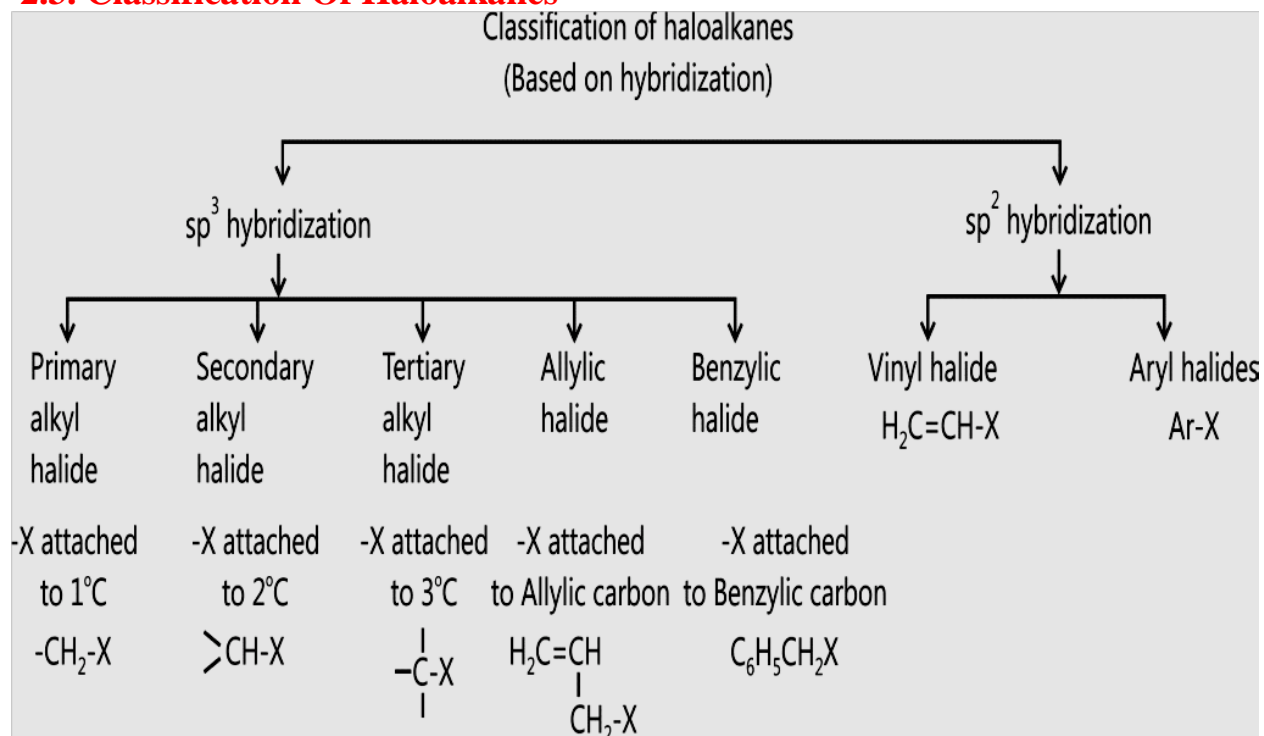


2.2. Classification of alkyl halides

Alkyl halides can be classified according to the class of the carbon that the halogen is attached to.



2.3. Classification Of Haloalkanes


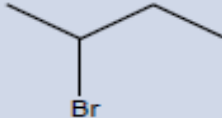
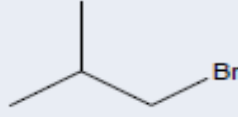
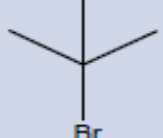


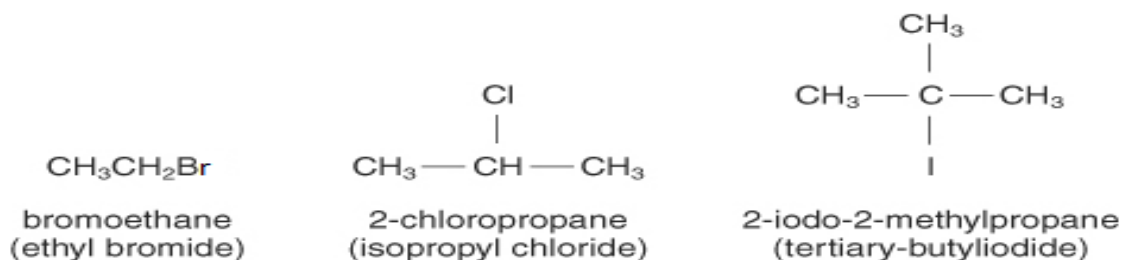
2.4. Nomenclature of Alkyl Halides

1. Common name: replacing **-ane** of alkane by **-yl** and follow by **halide** for longest chain.

2. IUPAC name: prefixing **Halo-**followed by **alkane**, as in alkanes.

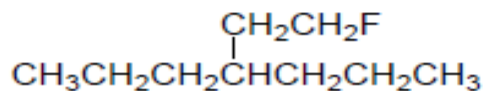
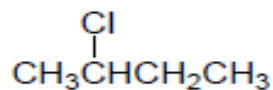
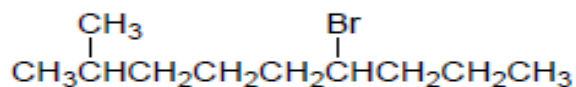
Common name	Structure	IUPAC name	No. of C atom
Methyl bromide		Bromomethane	1
Ethyl bromide		Bromoethane	2
n-Propyl bromide		1-Bromopropane	3
Isopropyl bromide		2-Bromopropane	

n-Butyl bromide		1-Bromobutane
sec-Butyl bromide		2-Bromobutane
Isobutyl bromide		1-Bromo-2-methylpropane
tert-Butyl bromide		2-Bromo-2-methylpropane



Q/ Give the structure and IUPAC name of n-, iso-, sec-, tert- and neo-pentyl chloride.

Q/ Give the common and IUPAC name of the following:



2.5. Physical properties of alkyl halide

Because of greater molecular weight, haloalkanes have considerably higher boiling points than alkanes of the same number of carbons.

n-Pentane (36°C) n-Pentylchloride (108 °C)

•For a given alkyl group, the boiling point increases with increasing atomic weight of the halogen, so that a fluoride is the lowest boiling, an iodide the highest boiling.

•For a given halogen, b.p. rises with increasing number of carbon atoms.

n-Propyl chloride (47) n-Butyl chloride (78.5)

2.6.Mechanism of Elimination Reactions

What is Elimination Reaction?

Elimination reaction is a type of reaction is mainly *used to transform saturated compounds* (organic compounds which contain single carbon-carbon bonds) *to unsaturated compounds* (compounds which feature double or triple carbon-carbon bonds).

Besides, it is an important method for the preparation of alkenes.



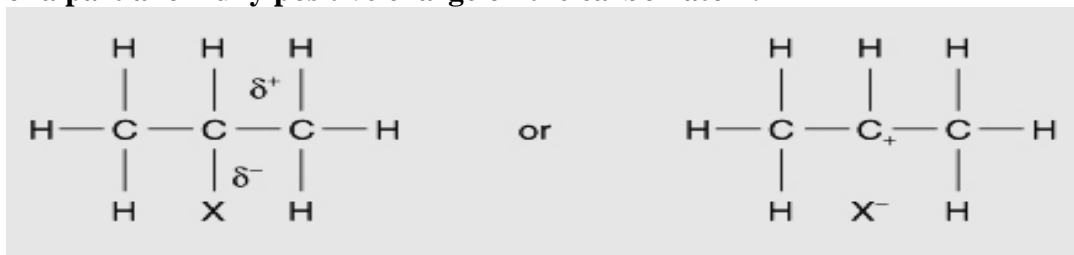
Important Methods of Elimination Reaction

Normally, elimination reactions are distinguished by the kind of atoms or groups of atoms that leave the molecule. Due to this, there are two main methods involved in this type of reaction;

- *Dehydration*
- *Dehydrohalogenation*

In the dehydration method, there is the elimination of a water molecule mostly from compounds such as alcohol. Sometimes, this method is also called Beta elimination reaction where the leaving group and H are placed at neighbor carbon atoms. On the other hand, in dehydrohalogenation, there is a removal of a hydrogen atom and a halogen atom.

As noted earlier, the halogen - carbon bond in an alkyl halide is polarized due to the electronegativity difference between the atoms. This polarization can lead to the formation of a partial or fully positive charge on the carbon atom.

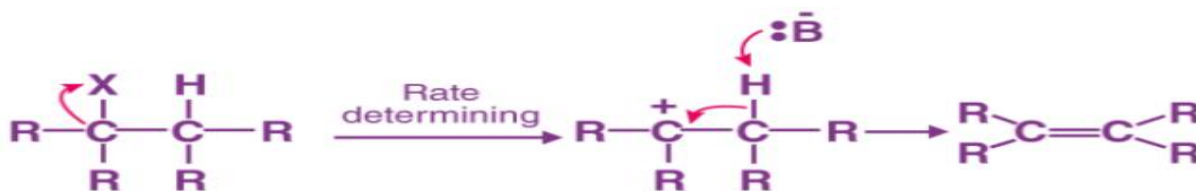


The full or partial positive charge on the carbon atom is delocalized (dispersed) down the carbon chain. This, in turn, makes the hydrogen atoms attached to these carbons very slightly positive and thus very weakly acidic. Therefore, a very strong base can now remove a slightly positive hydrogen with the resulting release of electrons down the chain, forming a π bond between the carbon atoms. The actual mechanism can be one of two types, E1 or E2, depending upon the structure of the activated complex.

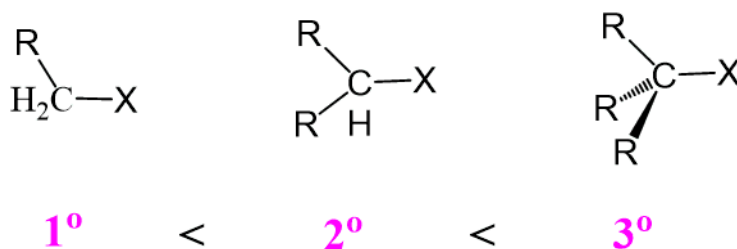
a) E1 mechanism

E1 – A Two-Step Mechanism

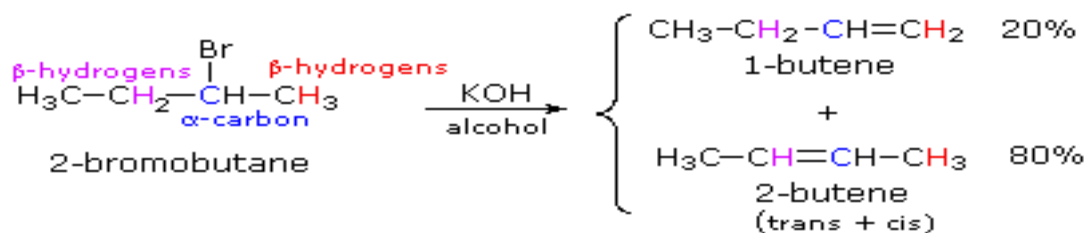
E1= Unimolecular Elimination



Reactivity of Alkyl Halides in the E1 reaction



Increasing rate of E1 reactions



b) E2 mechanism

E1 – A One-Step Mechanism

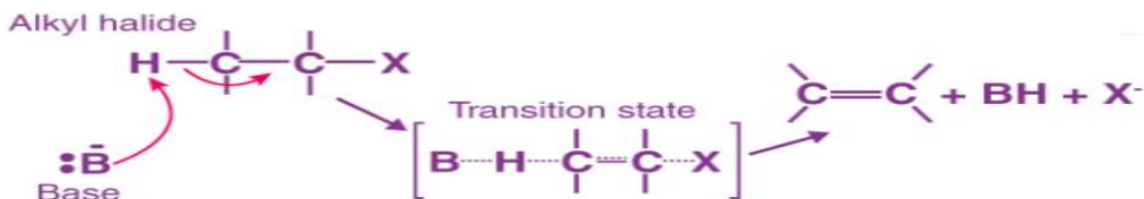
E2= Bimolecular Elimination

- In an E2 mechanism which refers to *bimolecular elimination* is basically a one-step mechanism.
- Here, the carbon-hydrogen and carbon-halogen bonds mostly break off to form a new double bond.

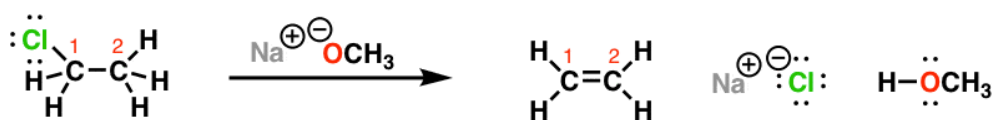
The E2 mechanism can generally be represented as below. In the below-mentioned representation, B stands for base and X stands for the halogen

Effects of R-

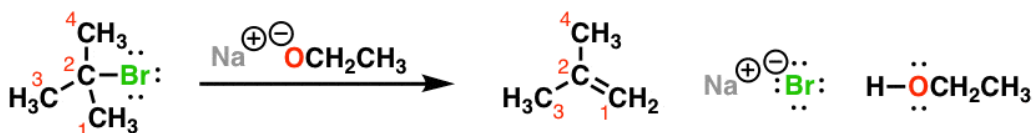
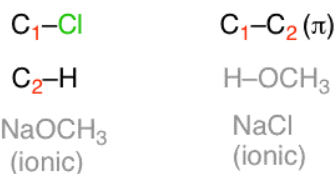
Reactivity order : $(\text{CH}_3)_3\text{C}^- > (\text{CH}_3)_2\text{CH}^- > \text{CH}_3\text{CH}_2^- > \text{CH}_3^-$



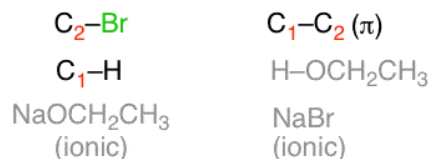
Elimination Reactions



Bonds Broken	Bonds Formed
--------------	--------------



Bonds Broken	Bonds Formed
--------------	--------------



Key pattern of elimination reactions (bonds in bold)

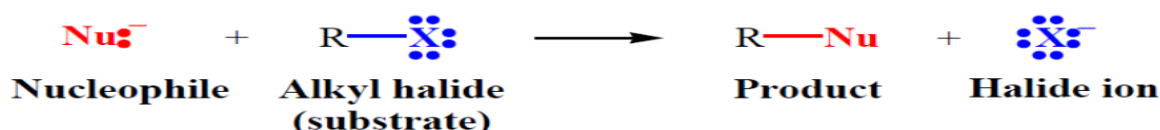
- Formation of a C-C π bond
- Breakage of two single bonds to carbon
[C-H bond and an adjacent C-(atom) single bond]

This is the reverse of addition reactions.

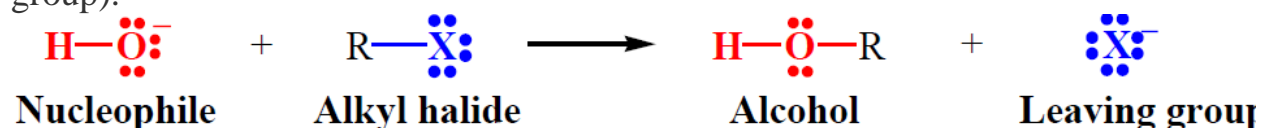
2.7. The nucleophilic substitution reaction of alkyl halides

Nucleophilic substitution reaction is a class of organic reactions where one nucleophile replaces another. It is very similar to the normal displacement reactions which we see in chemistry, where, a more reactive element replaces a less reactive element from its salt solution. The group which takes electron pair and displaced from the carbon is known as “leaving group” and the molecule on which substitution takes place known as “substrate”. The leaving group leaves as a neutral molecule or anion.

A Nucleophilic substitution reaction in organic chemistry is a type of reaction where a nucleophile gets attached to the positive charged atoms or molecules of the other substance.



A nucleophile, a species with an unshared electron pair (lone-pair electrons), reacts with an alkyl halide (substrate) by replacing the halogen substituent (leaving group).



Mechanism of Nucleophilic substitution reaction:

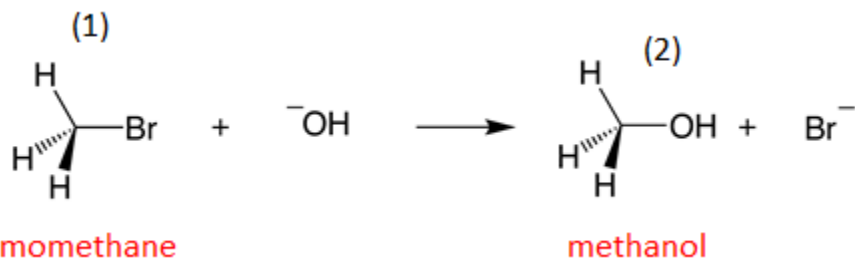
Two mechanisms of nucleophilic substitution reaction are discussed here. **S_N1** reaction and the **S_N2** reaction, where S represents chemical substitution, N represents nucleophilic, and the number stands for the kinetic order of a reaction.

Difference Between Sn1 and Sn2:

Sn1	Sn2
Sn1 is a unimolecular reaction	Sn2 is a bimolecular reaction
It follows a 1st order kinetic mechanism.	It follows the 2nd order Kinetic mechanism.
Sn1 involves two steps	Sn2 is a single-step process
In Sn1, the rate of reaction depends on the concentration of the substrate.	In Sn2, the rate of reaction depends on the concentration of both the substrate and the nucleophile.
In Sn1 as the leaving group leaves, the substrate forms a carbocation intermediate.	In Sn2, the reaction happens in a single transition state.
Optically active substrate becomes optically inactive and half of the optically active substrate becomes similar.	Sn2 involves inversion reaction.

a) S_N2 Reaction – Mechanism of S_N2 Reaction

In this reaction, the elimination of the leaving group and the addition of the nucleophile occur simultaneously. S_N2 takes place where the central carbon atom has easy access to the nucleophile

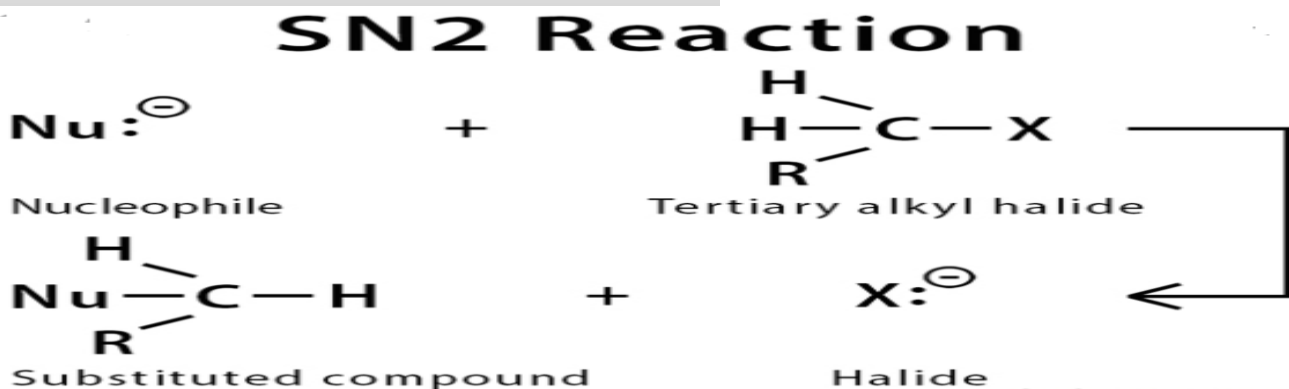


this reaction is an example of a S_N2 reaction.

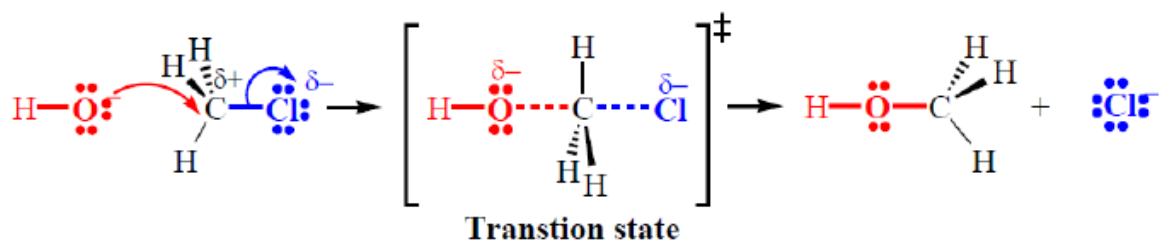
S stands for **substitution**

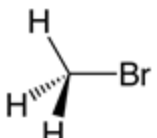
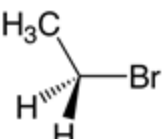
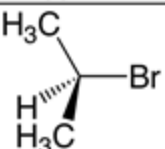
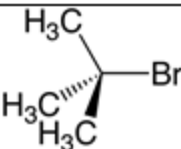
N stands for **nucleophilic**

2 stands for **bimolecular**



Mechanism:



Alkyl halide	Relative rate
	1200
	40
	1
	≈ 0

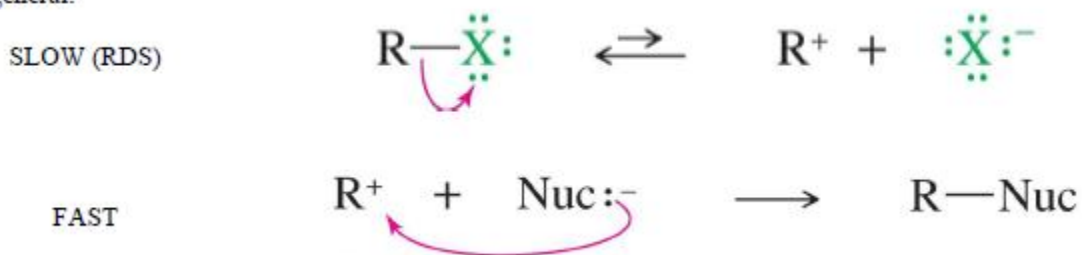
Factor Affecting SN2 Reactions

The leaving group

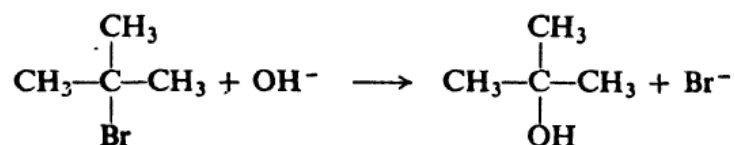
		relative rates of reaction	pK _a HX	
HO ⁻	+ RCH ₂ I	→ RCH ₂ OH + I ⁻	30 000	-10
HO ⁻	+ RCH ₂ Br	→ RCH ₂ OH + Br ⁻	10 000	-9
HO ⁻	+ RCH ₂ Cl	→ RCH ₂ OH + Cl ⁻	200	-7
HO ⁻	+ RCH ₂ F	→ RCH ₂ OH + F ⁻	1	3.2

b) S_N1 Reaction – Mechanism of S_N1 Reaction

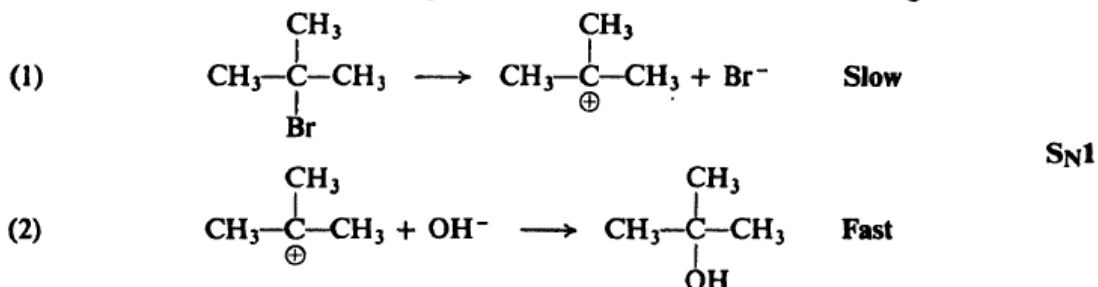
In general:

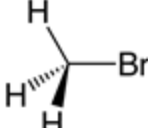
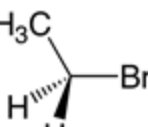
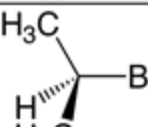
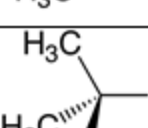


The reaction between *tert*-butyl bromide and hydroxide ion to yield *tert*-butyl alcohol follows first-order kinetics; that is, the rate depends upon the concentration of only one reactant, *tert*-butyl bromide.

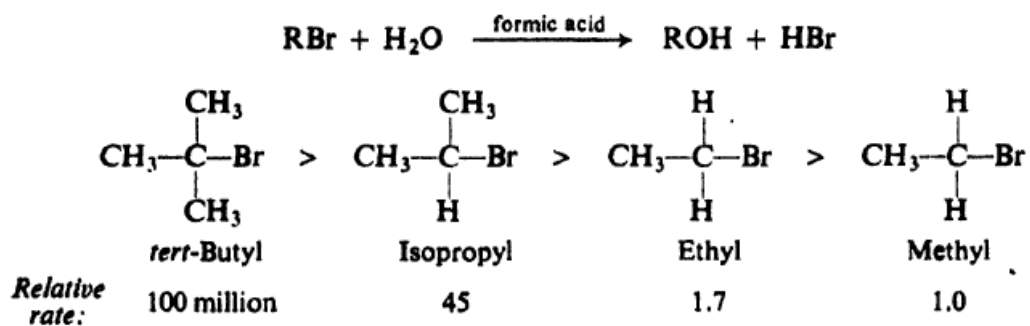


These observations are quite consistent with the following mechanism.



Alkyl halide	Relative rate
	≈ 0 *
	≈ 0 *
	12
	1 200 000

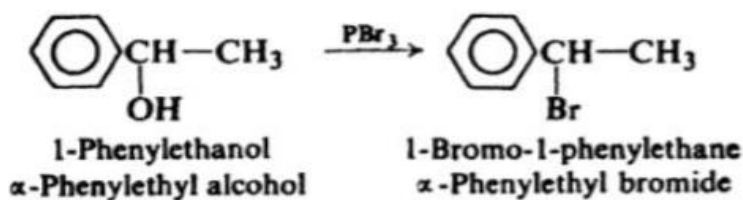
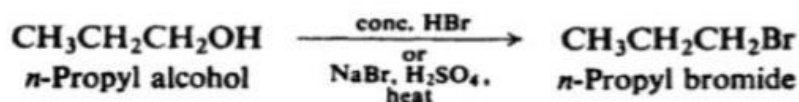
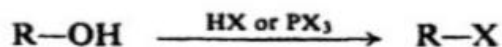
The following example gives some idea of how much the rate of an S_N1 reaction can be changed by changes in structure:



Preparation

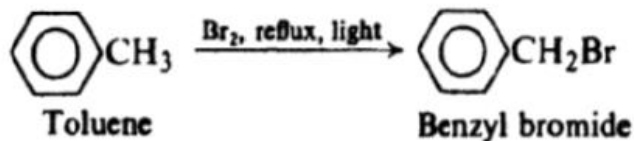
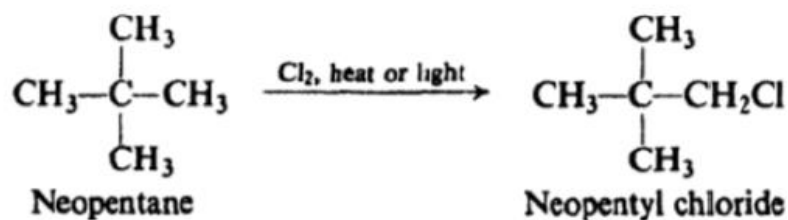
1- From alcohols

Alcohols react with hydrogen halides or phosphorus halides.



2- Halogenation of certain hydrocarbons.

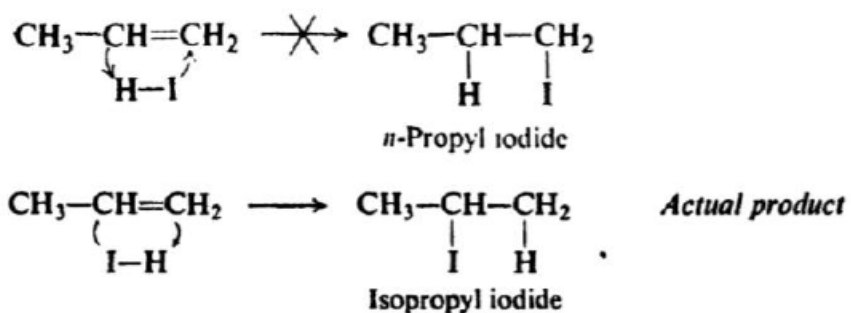
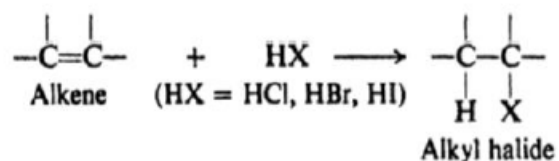
Under the influence of ultraviolet light, or at 250-400, chlorine or bromine converts alkanes into chloroalkanes (alkyl chlorides) or bromoalkanes (alkyl bromides).



3- Addition of hydrogen halides to alkenes.

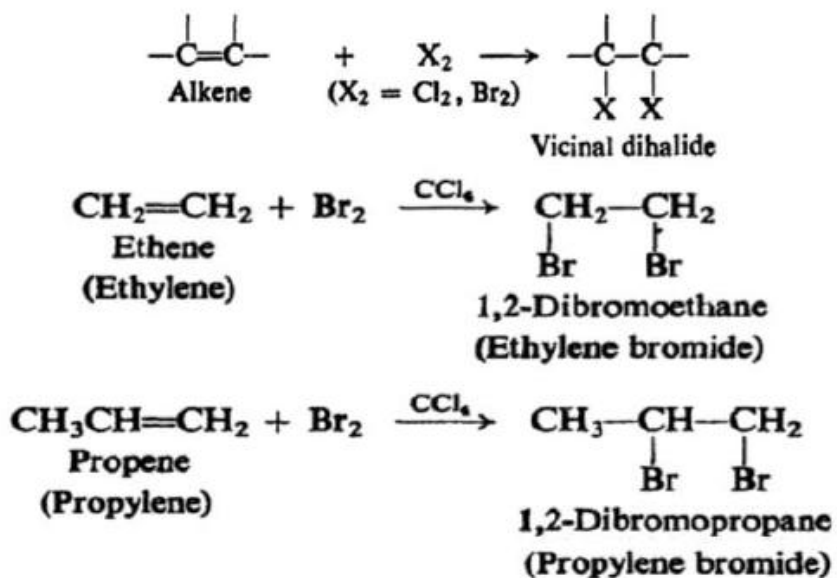
Markovnikov's rule

An alkene is converted by hydrogen chloride, hydrogen bromide, or hydrogen iodide into the corresponding alkyl halide.



4- Addition of halogens to alkenes and alkynes

Alkenes are readily converted by chlorine or bromine into saturated compounds that contain two atoms of halogen attached to adjacent carbons.



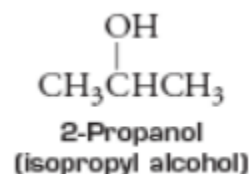
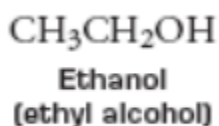
Chapter three

3. Alcohols

1. Structure

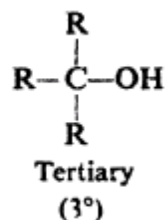
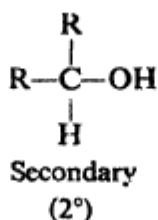
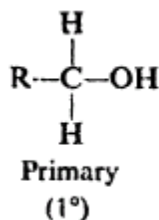
Alcohols are compounds of the general formula **ROH**, where **R** is any alkyl or substituted alkyl group. Alcohols have a hydroxyl (OH) group bonded to a saturated carbon atom. The group may be primary, secondary, or tertiary; it may be open-chain or cyclic; it may contain a double bond, a halogen atom, or an aromatic ring.

For example:



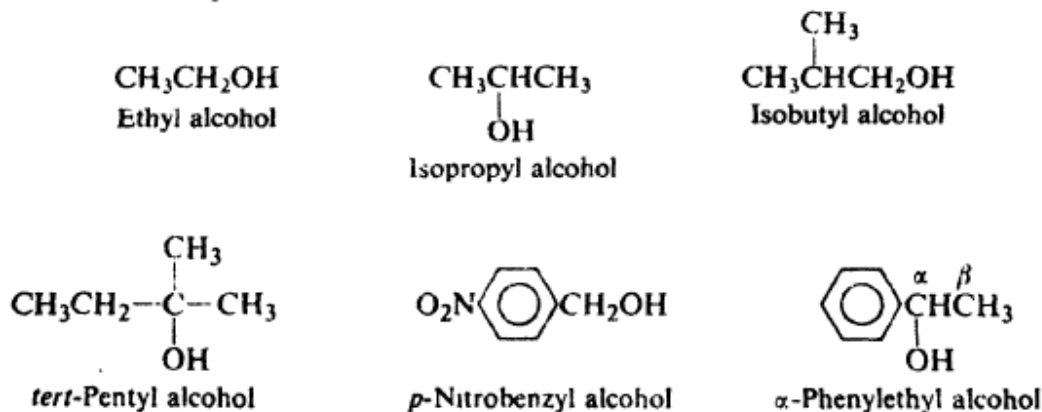
2. Classification

We classify a carbon atom as primary, secondary, or tertiary according to the number of other carbon atoms attached to it. An alcohol is classified according to the kind of carbon that bears the **OH** group:



3. Nomenclature of Alcohols

Alcohols are named by the different systems. For the simpler alcohols, the common names can be used. These consist simply of the name of the alkyl group followed by the word alcohol. For example:

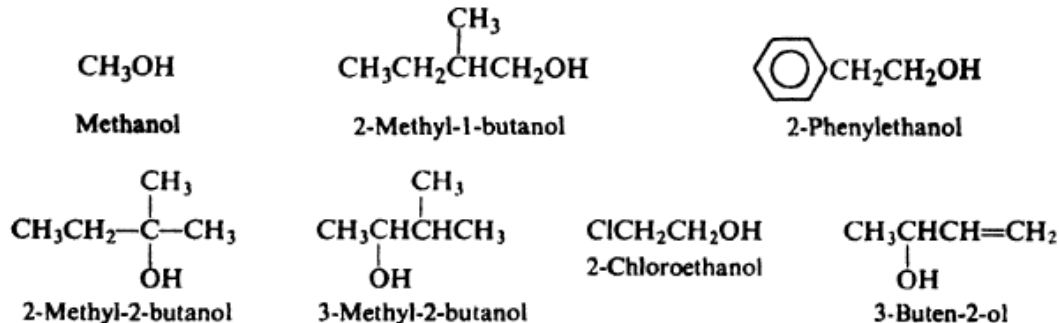


IUPAC System for Naming

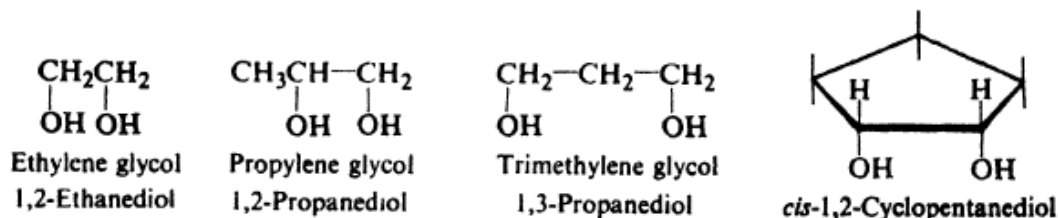
(1) Select as the parent structure the longest continuous carbon chain that contains the OH group then consider the compound to have been derived from this structure by replacement of hydrogen by various groups. The parent structure is known as ethanol, propanol, butanol, etc., depending upon the number of carbon atoms; each name is derived by replacing the terminal -e of the corresponding alkane name by **-ol**.

(2) Indicate by a number the position of the OH group in the parent chain, generally using the lowest possible number for this purpose.

(3) Indicate by numbers the positions of other groups attached to the parent chain.

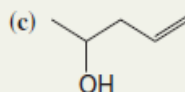
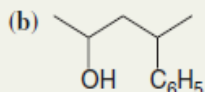
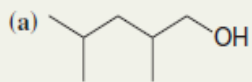


Alcohols containing two hydroxyl groups are called glycols. They have both common names and IUPAC names.

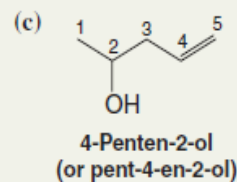
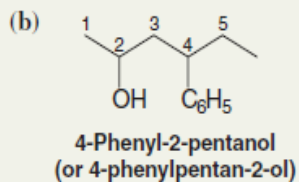
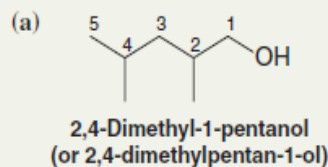


Solved Problem

Give IUPAC substitutive names for the following alcohols:



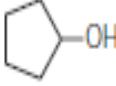
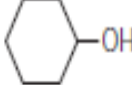
ANSWER The longest chain *to which the hydroxyl group is attached* gives us the *base name*. The ending is -ol. We then number *the longest chain from the end that gives the carbon bearing the hydroxyl group the lower number*. Thus, the names, in both of the accepted IUPAC formats, are



4,Physical properties

Alcohols, in contrast, contain the very polar OH group. In particular, this group contains hydrogen attached to the very electronegative element, oxygen, and therefore permits hydrogen bonding .

Physical Properties of Alcohols

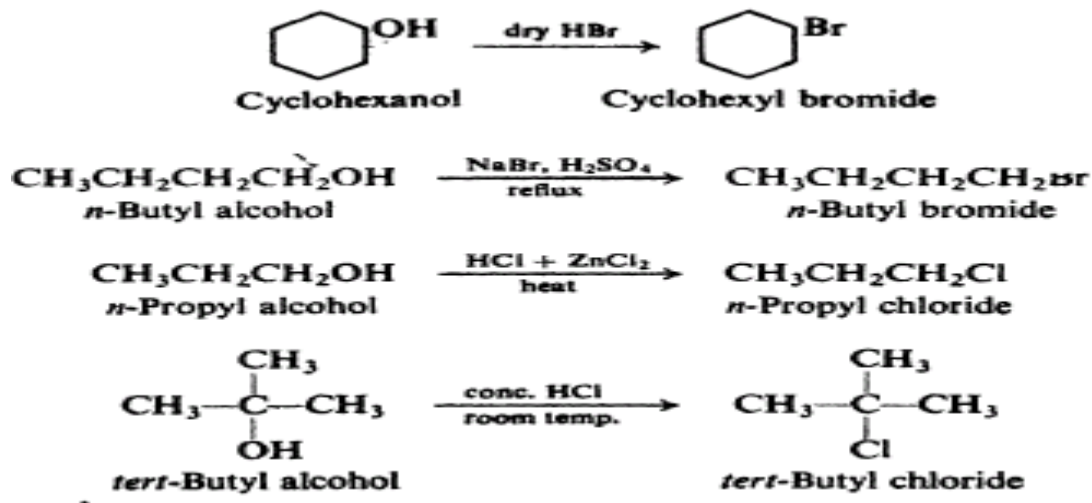
Name	Formula	mp (°C)	bp (°C) (1 atm)	Water Solubility (g/100 mL H ₂ O)
Monohydroxy Alcohols				
Methanol	CH ₃ OH	-97	64.7	∞
Ethanol	CH ₃ CH ₂ OH	-117	78.3	∞
Propyl alcohol	CH ₃ CH ₂ CH ₂ OH	-126	97.2	∞
Isopropyl alcohol	CH ₃ CH(OH)CH ₃	-88	82.3	∞
Butyl alcohol	CH ₃ CH ₂ CH ₂ CH ₂ OH	-90	117.7	8.3
Isobutyl alcohol	CH ₃ CH(CH ₃)CH ₂ OH	-108	108.0	10.0
sec-Butyl alcohol	CH ₃ CH ₂ CH(OH)CH ₃	-114	99.5	26.0
tert-Butyl alcohol	(CH ₃) ₃ COH	25	82.5	∞
Pentyl alcohol	CH ₃ (CH ₂) ₃ CH ₂ OH	-78.5	138.0	2.4
Hexyl alcohol	CH ₃ (CH ₂) ₄ CH ₂ OH	-52	156.5	0.6
Heptyl alcohol	CH ₃ (CH ₂) ₅ CH ₂ OH	-34	176	0.2
Octyl alcohol	CH ₃ (CH ₂) ₆ CH ₂ OH	-15	195	0.05
Cyclopentanol		-19	140	
Cyclohexanol		24	161.5	3.6
Benzyl alcohol	C ₆ H ₅ CH ₂ OH	-15	205	4
Diols and Triols				
Ethylene glycol	CH ₂ OHCH ₂ OH	-12.6	197	∞
Propylene glycol	CH ₃ CHOHCH ₂ OH	-59	187	∞
Trimethylene glycol	CH ₂ OHCH ₂ CH ₂ OH	-30	215	∞
Glycerol	CH ₂ OHCHOHCH ₂ OH	18	290	∞

5. Reactions**1. Reaction with hydrogen halides**

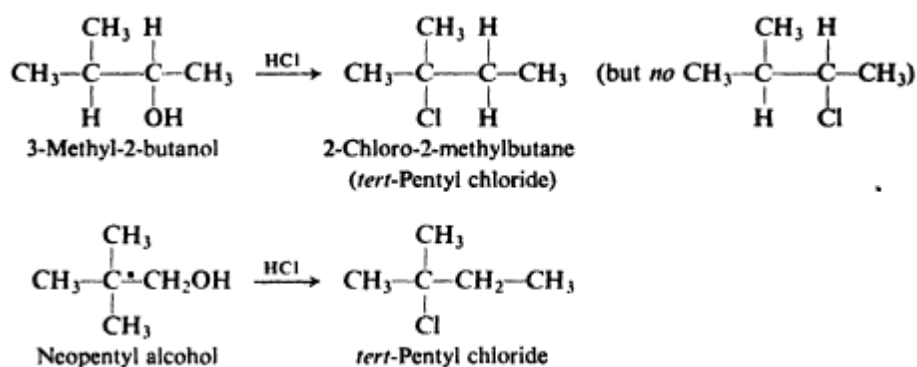
Alcohols react readily with hydrogen halides to yield alkyl halides and water. The reaction is carried out either by passing the dry hydrogen halide gas into the alcohol, or by heating the alcohol with the concentrated aqueous acid. Sometimes hydrogen bromide is generated in the presence of the alcohol by reaction between sulfuric acid and sodium bromide.



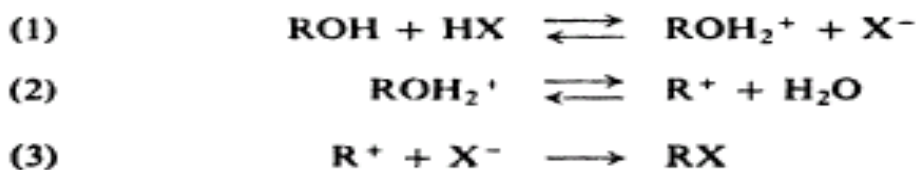
The least reactive of the hydrogen halides, HCl, requires the presence of zinc chloride for reaction with primary and secondary alcohols; on the other hand, the very reactive tert-butyl alcohol is converted to the chloride by simply being shaken with concentrated hydrochloric acid at room temperature. For example:



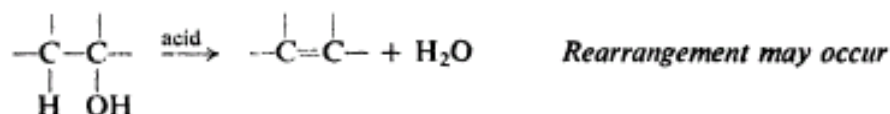
Rearrangement of the alkyl group occurs, except with most primary alcohols.



- Mechanism

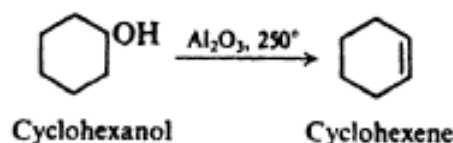
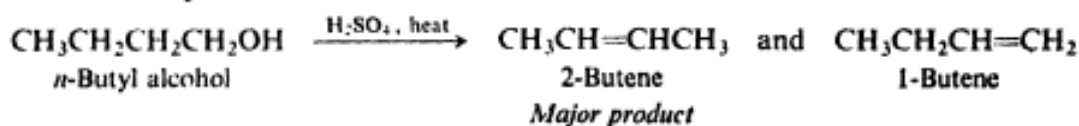


2- Dehydration



Reactivity of ROH: 3° > 2° > 1°

Examples:

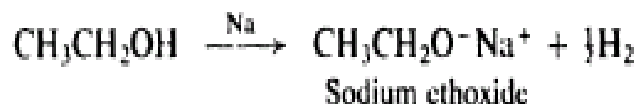


3- Reaction as acids: reaction with active metals

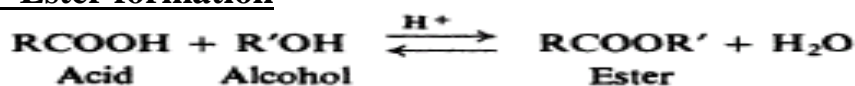


Reactivity of ROH: CH₃OH > 1° > 2° > 3°

Examples:



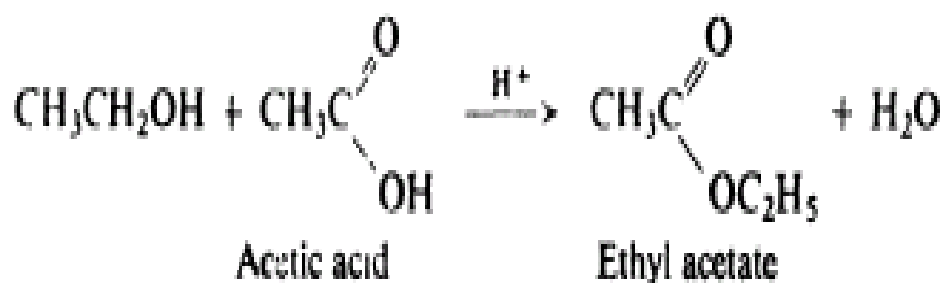
4- Ester formation



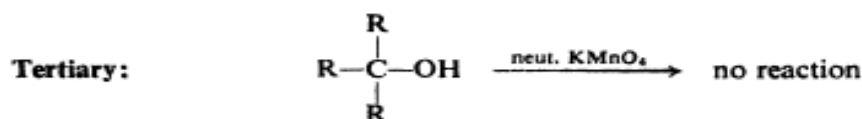
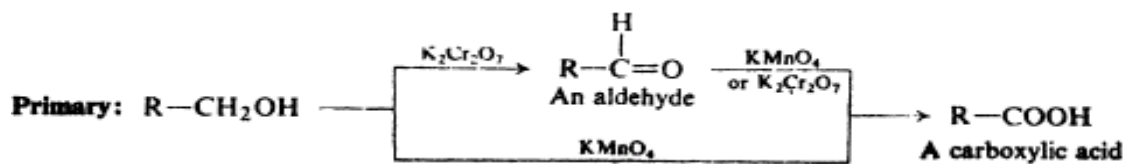
Reactivity in esterification: CH₃OH > 1° > 2° (> 3°)

HCOOH > CH₃COOH > RCH₂COOH > R₂CHCOOH > R₃CCOOH

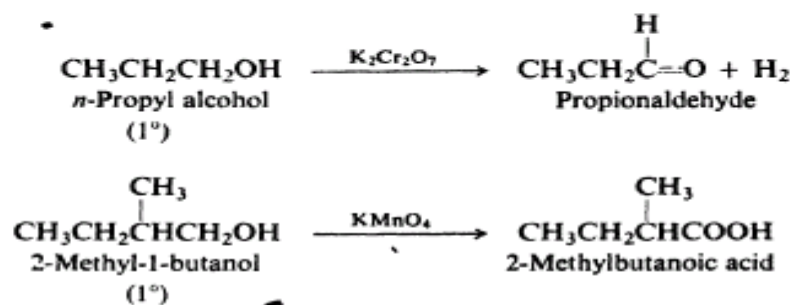
Example:



5- Oxidation

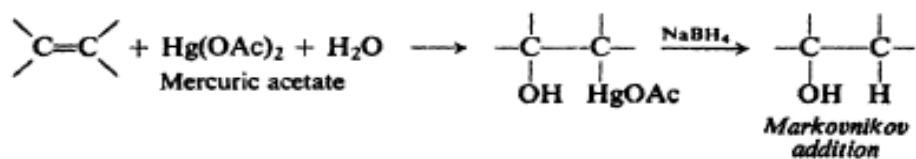


Examples:

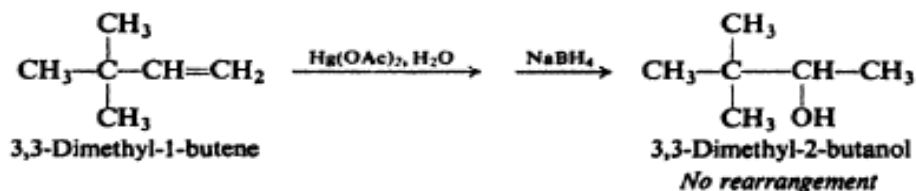


6.Preparation of alcohols

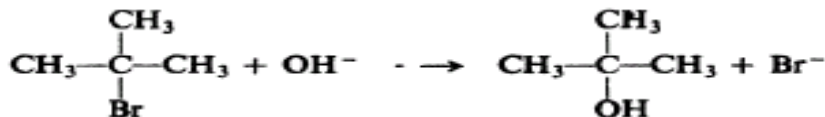
1. Oxymercuration-demercuration



Examples:



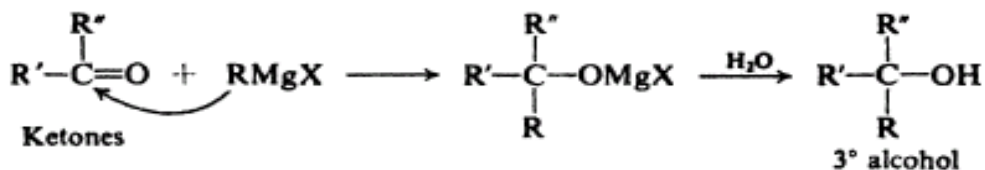
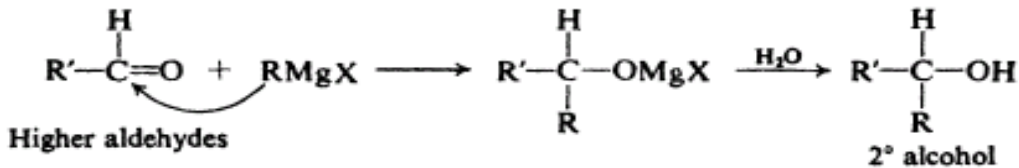
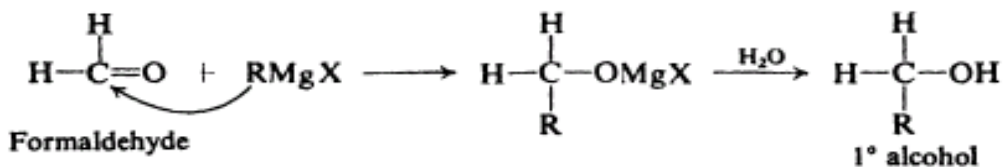
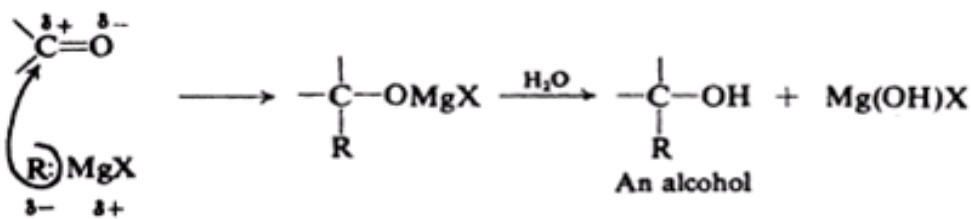
2-Hydrolysis of alkyl halides



3- Grignard synthesis of alcohol

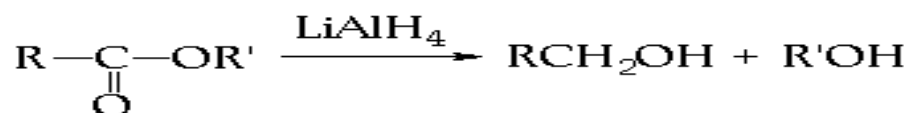
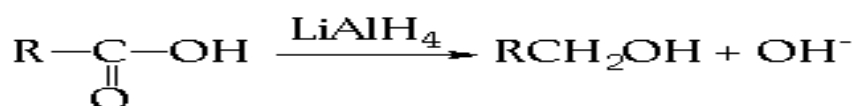
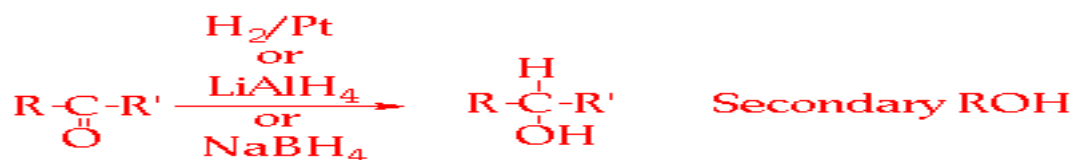
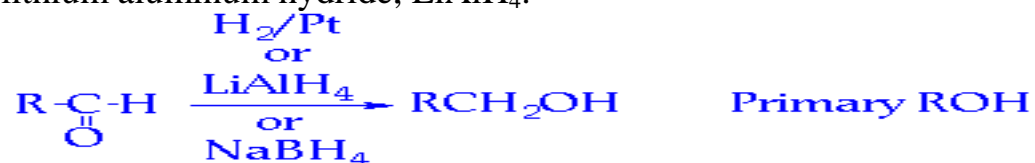


One of the most important uses of the Grignard reagent is its reaction with aldehydes and ketones to yield alcohols. Aldehydes and ketones have the general formulas:



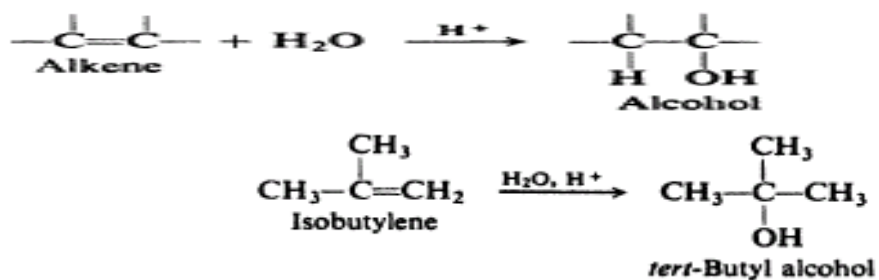
4- Reduction of carbonyl compounds

Aldehydes can be reduced to primary alcohols, and ketones to secondary alcohols, either by catalytic hydrogenation or by use of chemical reducing agents like lithium aluminum hydride, LiAlH₄.



5- Hydroxylation of alkenes

Water adds to the more reactive alkenes in the presence of acids to yield alcohols.



PROBLEMS

1. (a) Draw the structures of the eight isomeric pentyl alcohols, $C_5H_{11}OH$. (b) Name each by the IUPAC system and by the carbinol system.
(c) Label each as primary, secondary, or tertiary, (d) Which one is isopentyl alcohol? *tert*-Pentyl alcohol? (e) Give the structure of a primary, a secondary, and a tertiary alcohol of the formula $C_6H_{13}OH$.
2. Arrange the following compounds in order of decreasing boiling point: (a) 3-hexanol; (b) n-hexane; (c) n-octyl alcohol; (e) n-hexyl alcohol.
3. Write equations to show how isopropyl alcohol might be prepared: (a) from an olefin; (b) from an alkyl halide; (c) by a Grignard reaction.
- 4- Give structures of the Grignard reagent and the aldehyde or ketone that would react to yield each of the following alcohols.
 - (i) 1-phenyl-1-propanol
 - (j) 2-phenyl-2-propanol
 - (k) 1-phenyl-2-propanol
 - (n) cyclohexylcarbinol
 - (o) 1-cyclohexylethanol
 - (p) 2,4-dimethyl-3-pentanol

Chapter four

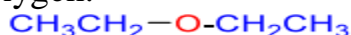
4. Ethers and Epoxides

1. Structure

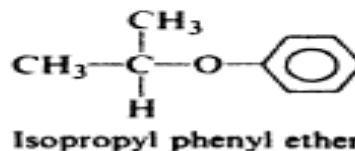
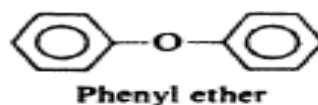
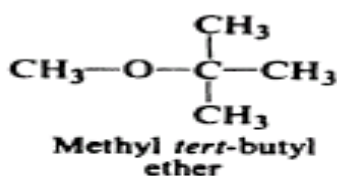
An ether has two organic groups (alkyl, aryl, or vinyl) bonded to the same oxygen atom, $R-O-R'$, $Ar-O-R$, or $Ar-O-Ar$.

2. Nomenclature of ethers

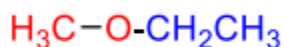
Common names of (symmetrical) ethers add the suffix ether after naming the groups on either side of the oxygen.



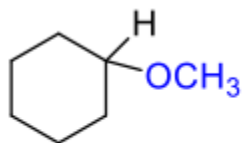
Ethyl Ether
(Diethyl Ether)



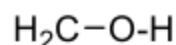
IUPAC names ethers by taking the more complex alkyl group as the root name, and naming the remaining part as an alkoxy group.



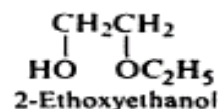
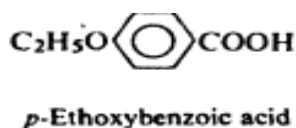
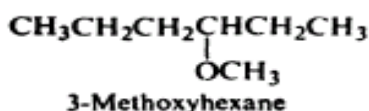
methoxyethane



methoxycyclohexane



2-ethoxyethanol



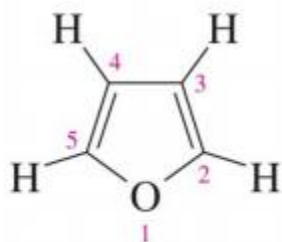
The simplest aryl alkyl ether has the special name of anisole.



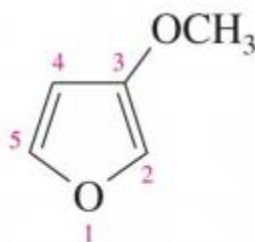
Cyclic Ethers

Naming these heterocyclic compounds depends on the ring size and number of oxygens.

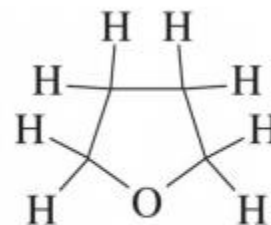
a- Furans



furan

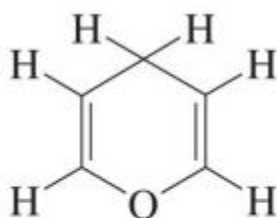


3-methoxyfuran

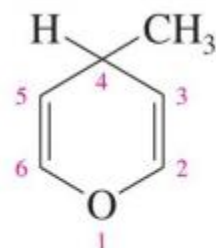


tetrahydrofuran (THF)
(oxolane)

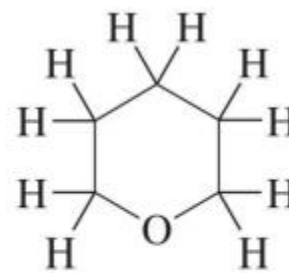
b-Pyrans



pyran



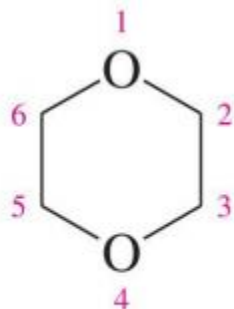
4-methylpyran



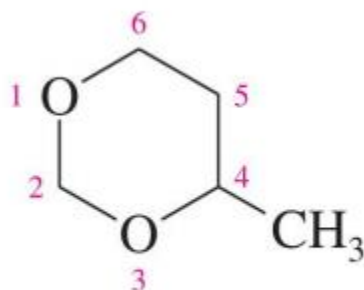
tetrahydropyran (THP)
(oxane)

c- Dioxanes

These are six membered rings with two oxygens.



1,4-dioxane



4-methyl-1,3-dioxane

3. Physical properties of ethers

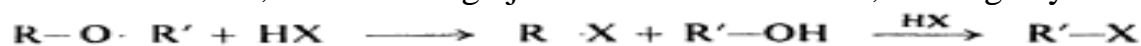
This weak polarity does not appreciably affect the boiling points of ethers, which are about the same as those of alkanes having comparable molecular weights, and much lower than those of isomeric alcohols. Compare, for example, the boiling points of n-heptane (98), methyl n-pentyl ether (100), and n-hexyl

alcohol (157). The hydrogen bonding that holds alcohol molecules strongly together is not possible for ethers, since they contain hydrogen bonded only to carbon .

Name	M.p., °C	B.p., °C	Name	M.p., °C	B.p., °C
Methyl ether	-140	-24	Anisole	-37	154
Ethyl ether	-116	34.6	Propylene glycol (Ethyl phenyl ether)	-33	172
<i>n</i> -Propyl ether	-122	91	Phenyl ether	27	259
Isopropyl ether	-60	69	1,4-Dioxane	11	101
<i>n</i> -Butyl ether	-95	142	Tetrahydrofuran	-108	66
Vinyl ether		35			
Allyl ether		94			

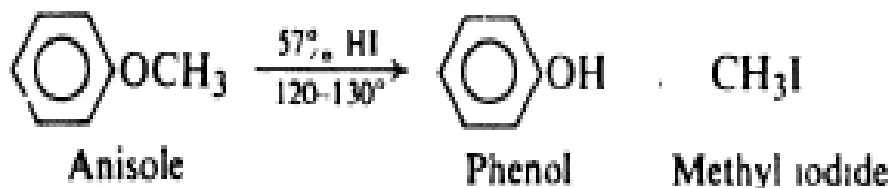
4. Reactions of ethers. Cleavage by acids

Ethers are comparatively unreactive compounds. The ether linkage is quite stable toward bases, oxidizing agents, and reducing agents. In so far as the ether linkage itself is concerned, ethers undergo just one kind of reaction, cleavage by acids :

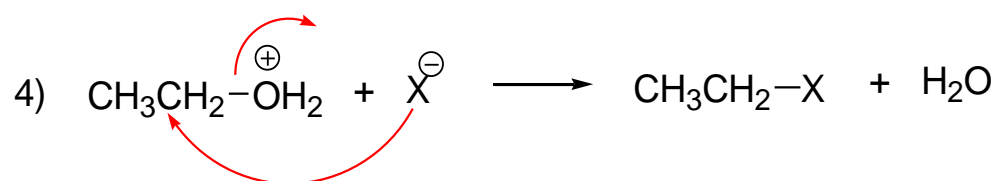
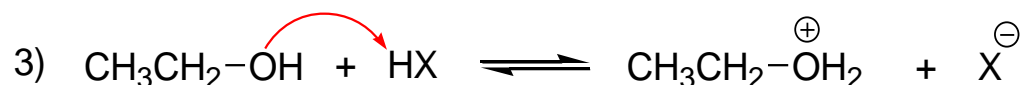
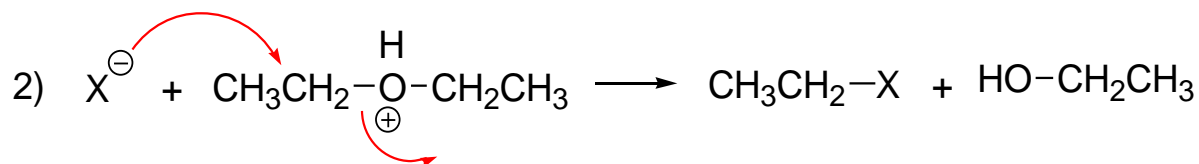
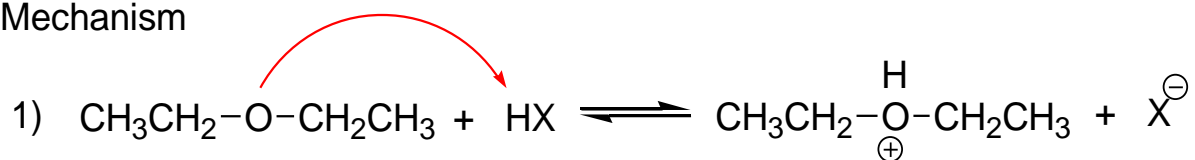


Reactivity of HX: HI > HBr > HCl

Cleavage takes place only under quite vigorous conditions: concentrated acids (usually HI or HBr) and high temperatures.



Mechanism

**5. Industrial sources of ethers. Dehydration of alcohols**

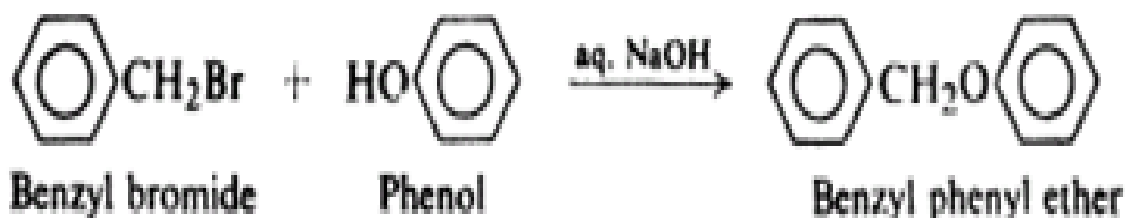
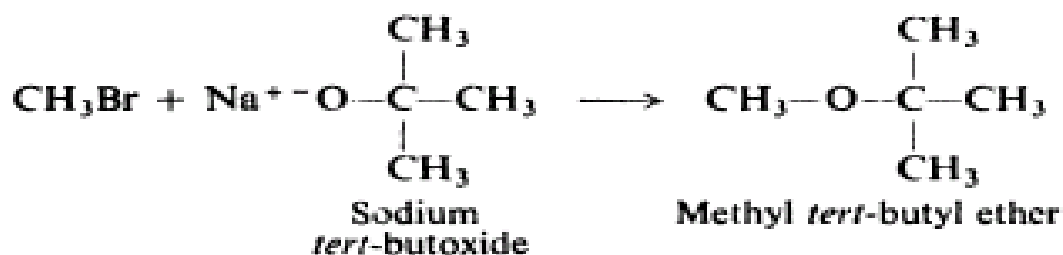
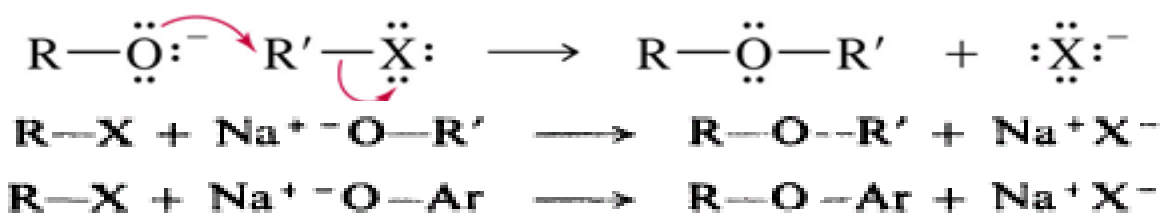
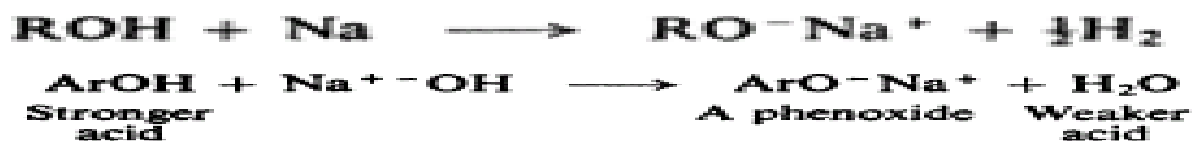
A number of symmetrical ethers containing the lower alkyl groups are prepared on a large scale, chiefly for use as solvents. The most important of these is **ethyl ether**, the familiar anesthetic and the solvent we use in extractions and in the preparation of **Grignard reagents**; others include isopropyl ether and n-butylether. These ethers are prepared by reactions of the corresponding alcohols with sulfuric acid. Since a molecule of water is lost for every pair of alcohol molecules, the reaction is a kind of dehydration. Dehydration to ethers, rather than alkenes.



6. Preparation of ethers

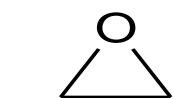
Williamson synthesis S_N2

In the laboratory, the Williamson synthesis of ethers is important because of its versatility: it can be used to make unsymmetrical ethers as well as symmetrical ethers, and aryl alkyl ethers as well as dialkyl ethers. In the Williamson synthesis an alkyl halide (or substituted alkyl halide) is allowed to react with a sodium alkoxide or a sodium phenoxide.

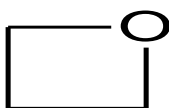


EPOXIDE

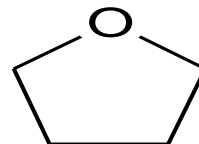
- Epoxides are cyclic ethers
- Three-membered ring compound
- Also known as oxiranes



oxirane



oxetane



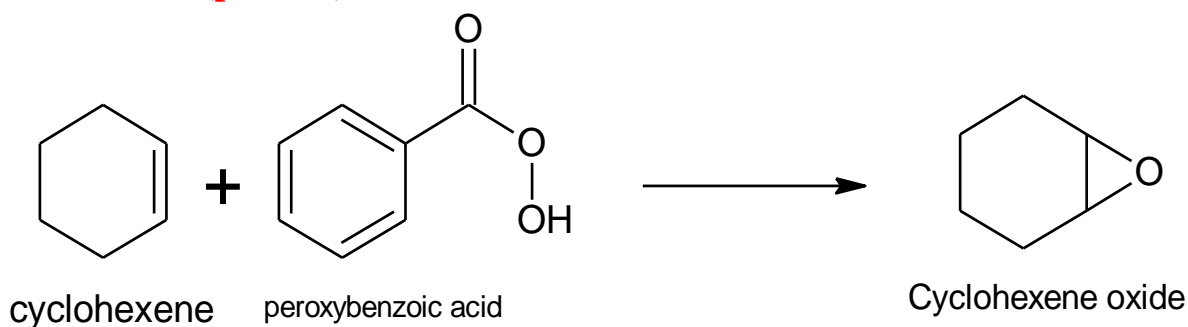
oxalane

Preparation

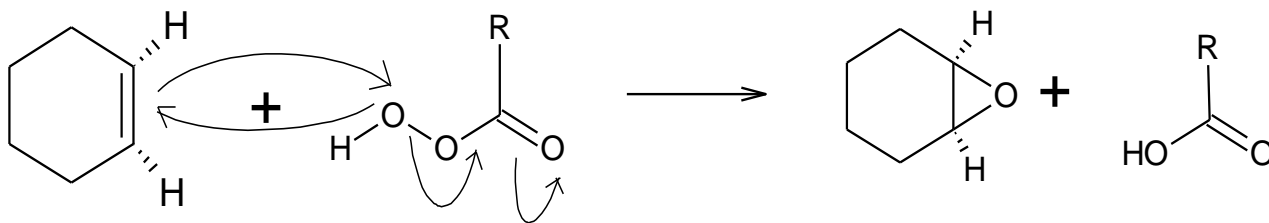
1. Peroxy oxidation of alkenes
2. Base promoted cyclization of vicinal halohydrins

Oxidation of Alkene

Most widely used method Reaction of an alkene with an organic **peroxy acid (peracid)**.

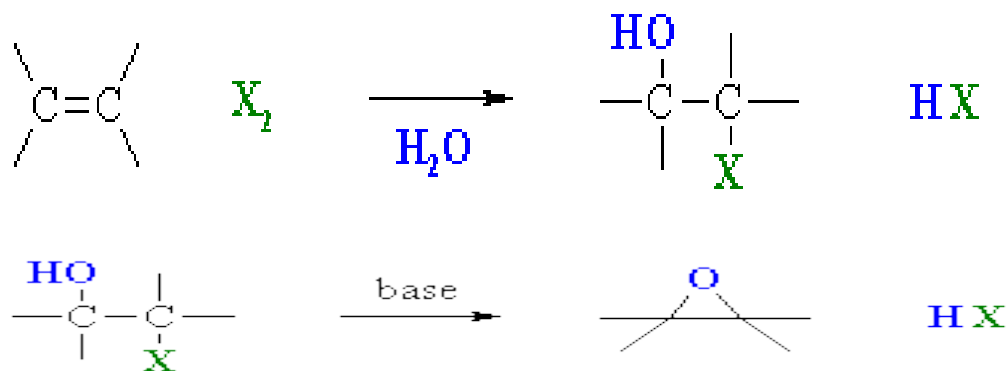


Mechanism



Base promoted cyclization of vicinal halohydrins

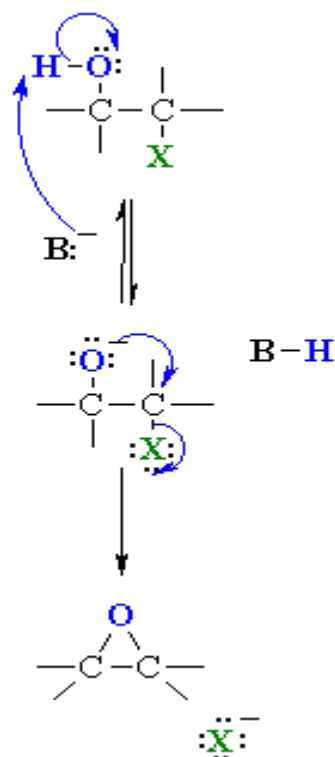
Reaction type: Electrophilic Addition then Nucleophilic Substitution



MECHANISM OF HALOHYDRIN TO EPOXIDE

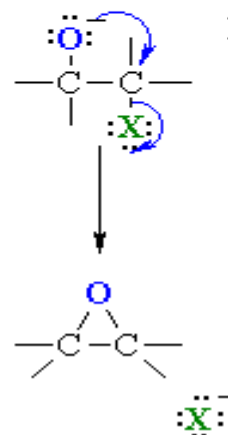
Step 1:

An acid/base reaction. The base deprotonates the alcohol forming an alkoxide intermediate that has enhanced nucleophilicity.



Step 2:

An intramolecular S_N2 reaction where the alkoxide nucleophile attacks the electrophilic C displacing the leaving group, the halide ion. The nucleophile has to attack *anti* to the $C-X$ bond.



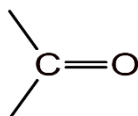
Chapter 5

ALDEHYDES AND KETONES

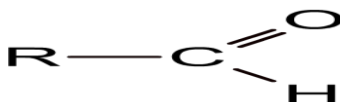
Aldehydes and ketones are simple compounds which contain a *carbonyl group* - a carbon-oxygen double bond **C=O**.

The carbonyl group

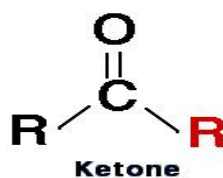
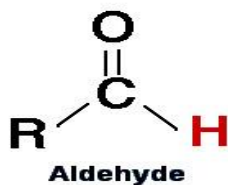
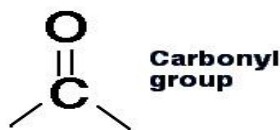
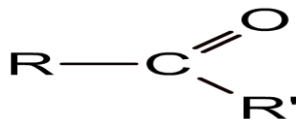
The *carbonyl group* (>C=O) is the functional group found in compounds such as aldehydes, ketones, and carboxylic acids.



In **aldehydes** the carbonyl group is at the end of the carbon chain and so has at least one hydrogen attached to it.



In **ketones** the carbonyl group is in the middle of a carbon chain and so has two alkyl groups attached to it.



(R and R` =alkyl or aryl).

Some Common Classes Carbonyl Compounds

Class	General Formula	Class	General Formula
ketones	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{R}' \end{array}$	aldehydes	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$
carboxylic acids	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} \end{array}$	acid chlorides	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{Cl} \end{array}$
esters	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{O}-\text{R}' \end{array}$	amides	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{NH}_2 \end{array}$

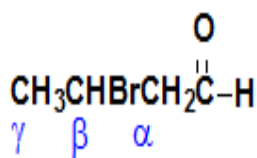
Common Names of Aldehydes

In the common system, aldehydes are named from the common names of the corresponding carboxylic acid.

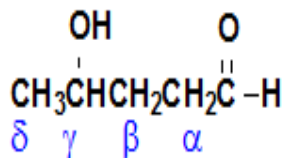
- The '**ic acid**' ending is replaced with '**aldehyde**'.
- The aldehyde group is always at the end of a chain (**terminal**).

Structure	IUPAC name	Common name	Structure	IUPAC	Common name
HCO ₂ H	methanoic acid	formic acid	HCHO	methanal	formaldehyde
CH ₃ CO ₂ H	ethanoic acid	acetic acid	CH ₃ CHO	ethanal	acetaldehyde
CH ₃ CH ₂ CO ₂ H	propanoic acid	propionic acid	CH ₃ CH ₂ CHO	propanal	propionaldehyde
CH ₃ (CH ₂) ₂ CO ₂ H	butanoic acid	butyric acid	CH ₃ (CH ₂) ₂ CHO	butanal	butyraldehyde
CH ₃ (CH ₂) ₃ CO ₂ H	pentanoic acid	valeric acid	CH ₃ (CH ₂) ₃ CHO	pentanal	valeraldehyde
CH ₃ (CH ₂) ₄ CO ₂ H	hexanoic acid	caproic acid	CH ₃ (CH ₂) ₄ CHO	hexanal	caproaldehyde

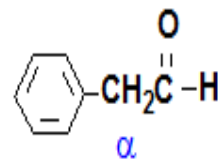
- Substituents locations are given using Greek letters (α, β, γ, δ) beginning with the carbon *next to* the carbonyl carbon, the a-carbon.**



β -bromobutyraldehyde

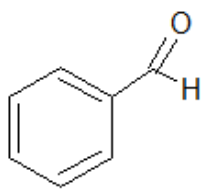


γ -hydroxyvaleraldehyde

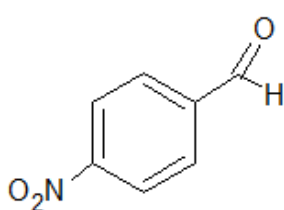


α -phenylacetaldehyde

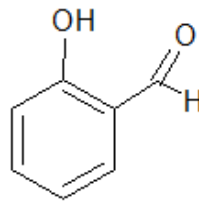
- Aromatic aldehydes are usually designated as derivatives of the simplest aromatic aldehyde, **Benzaldehyde**



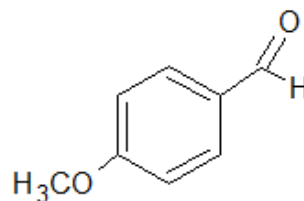
Benzaldehyde



p-Nitrobenzaldehyde



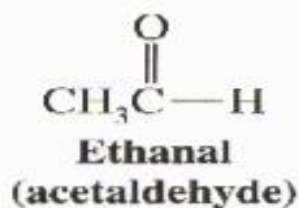
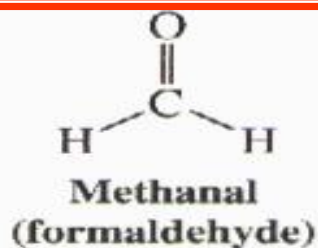
o-Hydroxybenzaldehyde
Salicylaldehyde

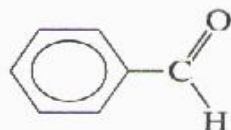
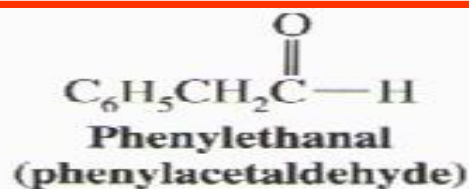


p-Methoxybenzaldehyde
Anisaldehyde

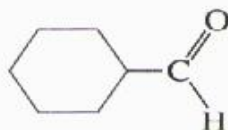
IUPAC Nomenclature of Aldehydes

- Select the longest continuous carbon chain that contains the C=O group and replace the ending **-e** by the suffix **-al**
- The **CHO** group is assigned the number **"1"** position and takes precedence over other functional groups that may be present such as **-OH, C=C**
- If the **CHO** group is bonded to a ring, name the ring and add the suffix **-carbaldehyde**

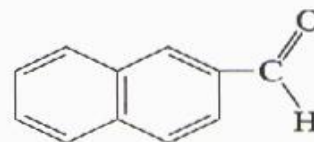




Benzenecarbaldehyde
(benzaldehyde)



Cyclohexanecarbaldehyde

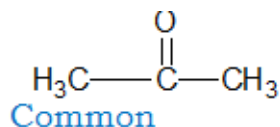


2-Naphthalenecarbaldehyde

Nomenclature of Ketones

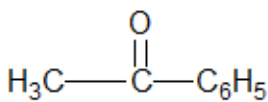
❖ Common name:

- ❑ listing the alkyl substituents attached to the carbonyl group **alphabetically**, followed by the word **ketone**. As with aldehydes, substituents locations are given in common names using Greek letters (α , β , γ , δ .) beginning with the α -carbon.



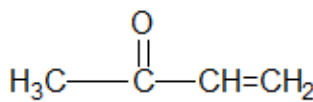
Dimethyl ketone

Acetone

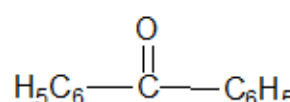


Methyl phenyl ketone

Acetophenone



Methyl vinyl ketone

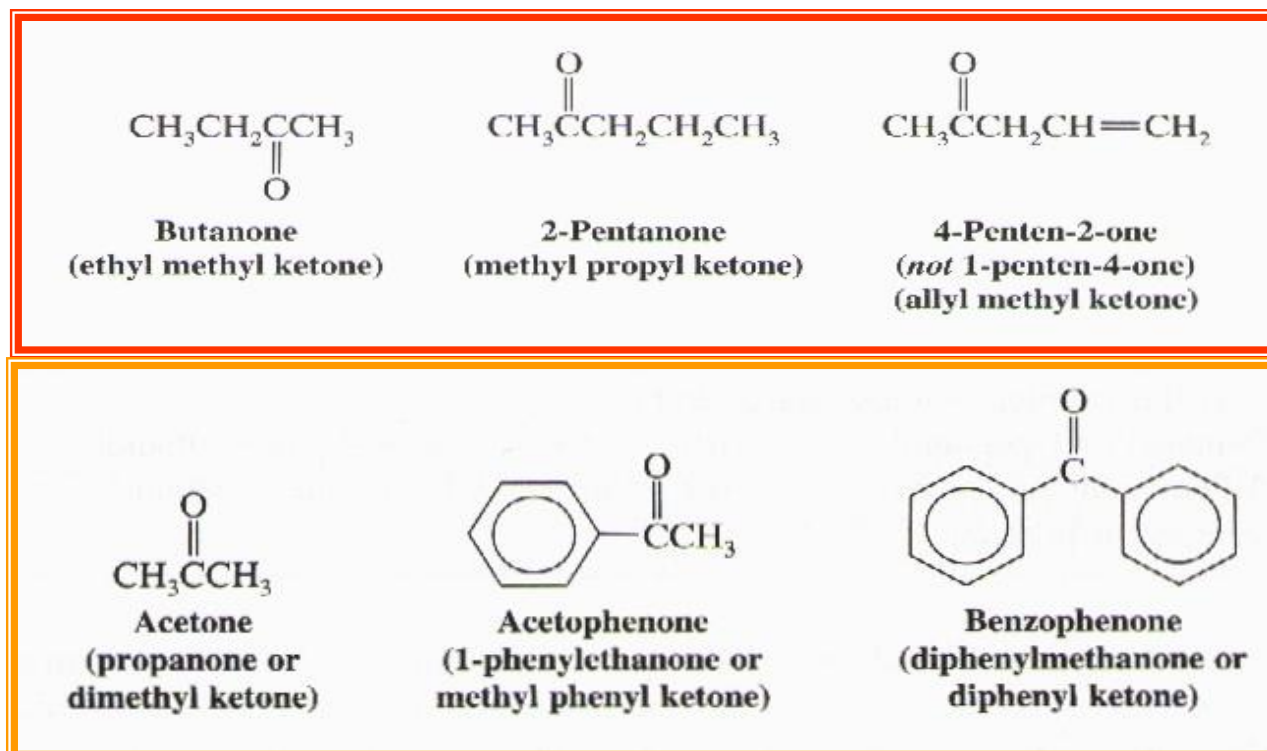


Diphenyl ketone

Benzophenone

❖ IUPAC system:

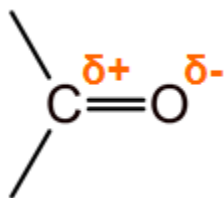
- Find the **longest chain** containing the **carbonyl group**, and change the **-e** ending of the parent alkane to the suffix **-one**.
- Number the carbon chain to **give the carbonyl carbon the lower number**. Apply all of the other usual rules of nomenclature.



Physical Properties

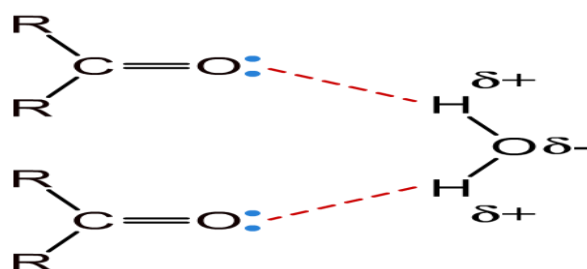
The carbonyl group is a polar group; therefore, aldehydes and ketones have higher boiling points than hydrocarbons of the same molecular weight.

The carbonyl group is polar due to the greater electronegativity of oxygen (3.4) than carbon (2.6). This influences the properties of aldehydes and ketones, such as solubility .



Small aldehydes and ketones are soluble in water due to hydrogen bonding between a lone pair on the oxygen of the carbonyl group and the hydrogen of the water. borderline solubility is reached at about five carbons .

- Polarization of group creates Dipole-dipole attractions between the molecules of aldehydes and ketones, resulting in higher boiling points than nonpolar alkanes and ether.



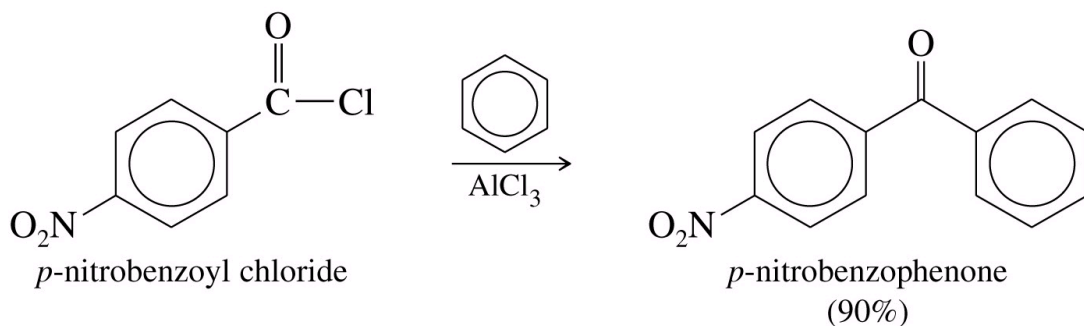
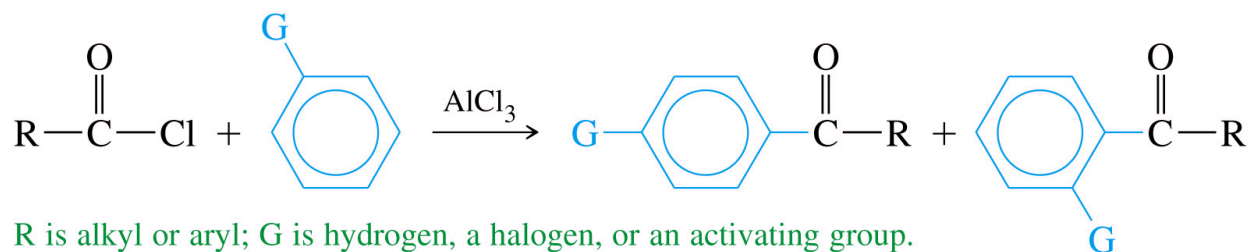
Aldehydes and ketones are soluble in the usual organic solvents.

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ Butane bp -0.5°C (MW = 58)	$\text{CH}_3\text{CH}_2\overset{\text{O}}{\parallel}\text{CH}$ Propanal bp 49°C (MW = 58)	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_3$ Acetone bp 56.1°C (MW = 58)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ 1-Propanol bp 97.2°C (MW = 60)
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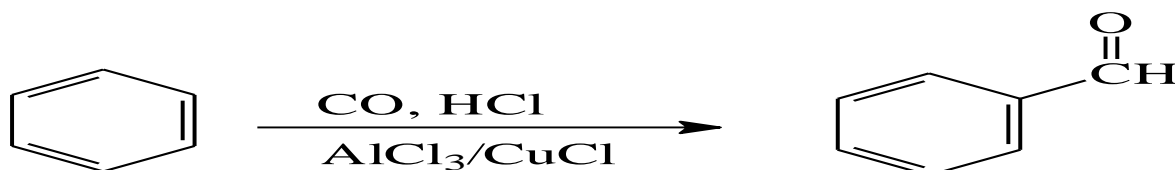
Preparation of Ketones and Aldehydes

1. Friedel-Crafts Acylation (ketones)
2. Gatterman-Koch Formylation (aldehydes)
3. Hydration of Alkynes (ketones with oxymercuration, aldehydes with hydroboration)
4. Ozonolysis of Alkenes (aldehydes and ketones depending on substitution)
5. Gilman Reaction (ketones)
6. Reduction of acids, acid chlorides and nitriles
7. Oxidation of primary alcohols (aldehydes)

1. Friedel-Crafts Acylation



2. Gatterman-Koch Formylation

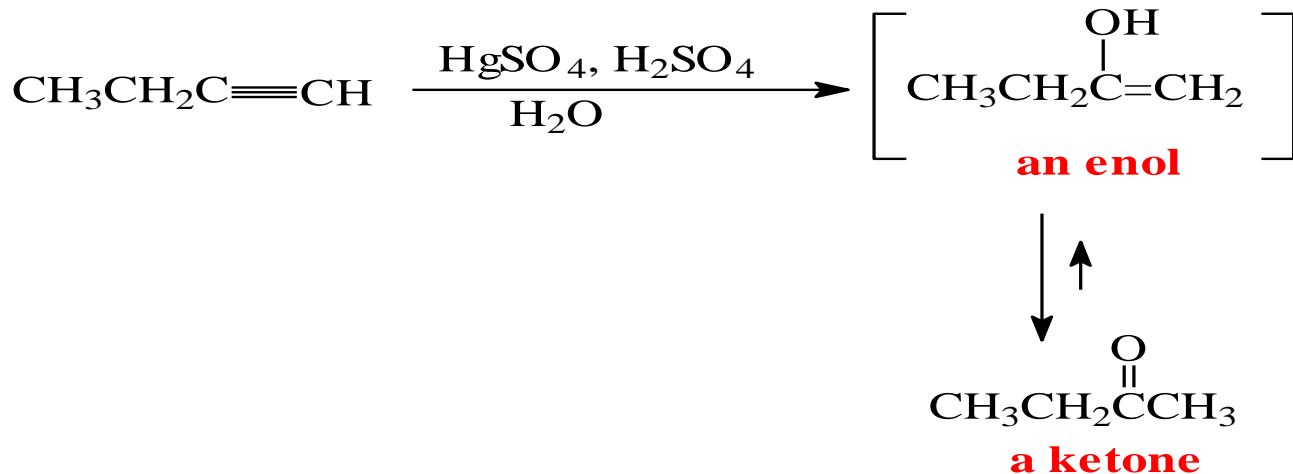


benzene or activated benzene needed

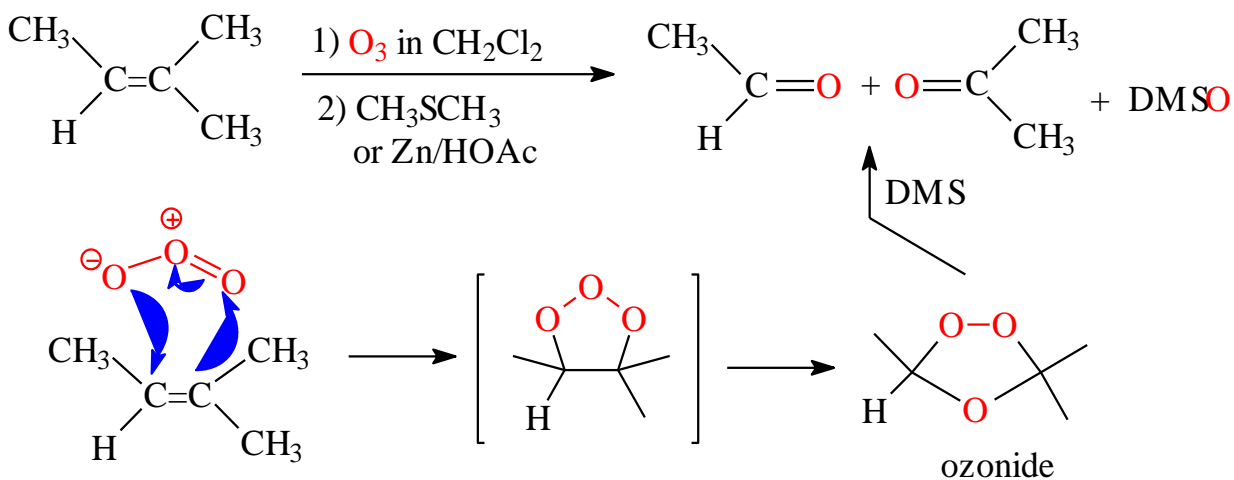
in situ preparation of formyl chloride



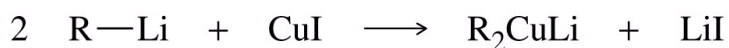
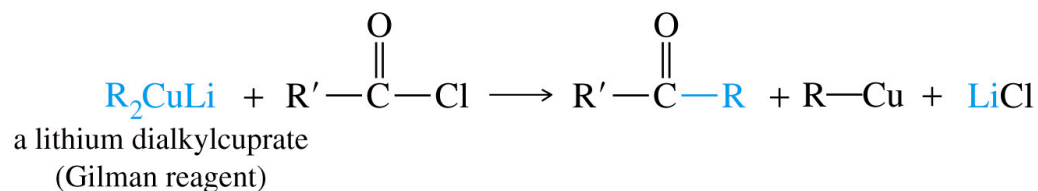
3. Oxymercuration Hydration (Markovnikov)



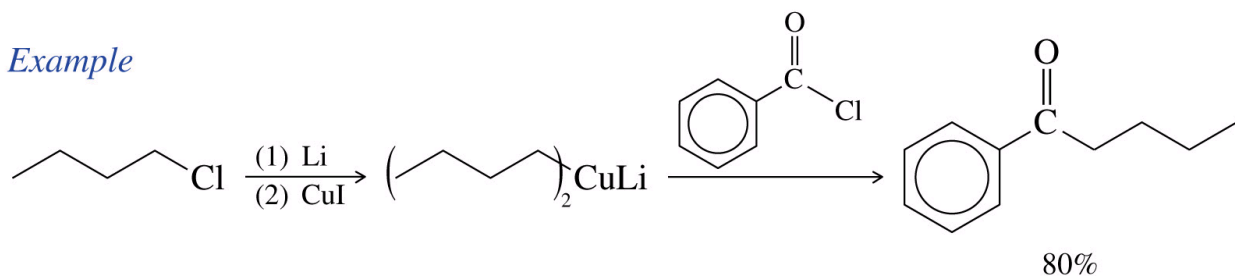
4. Ozonolysis (Alkene Cleavage)



5. Gilman Reagent with Acid Chlorides

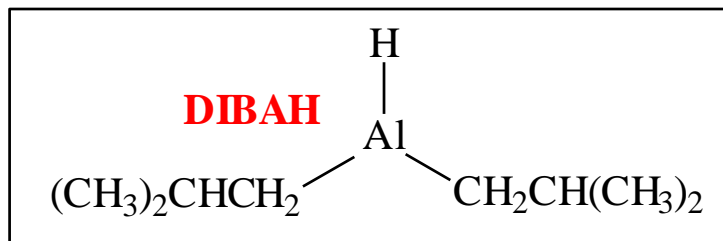
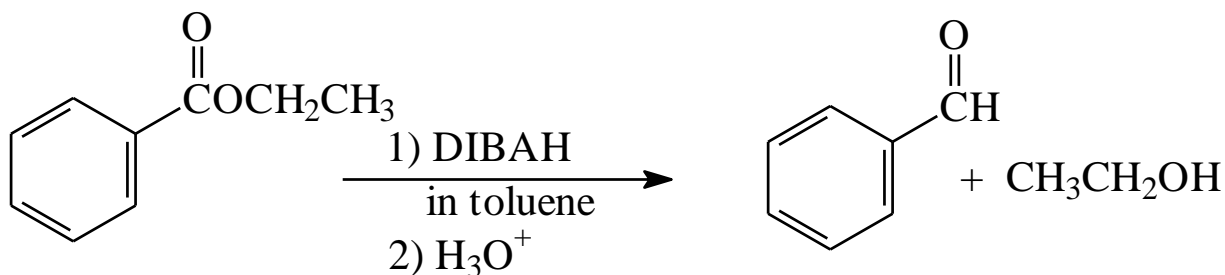


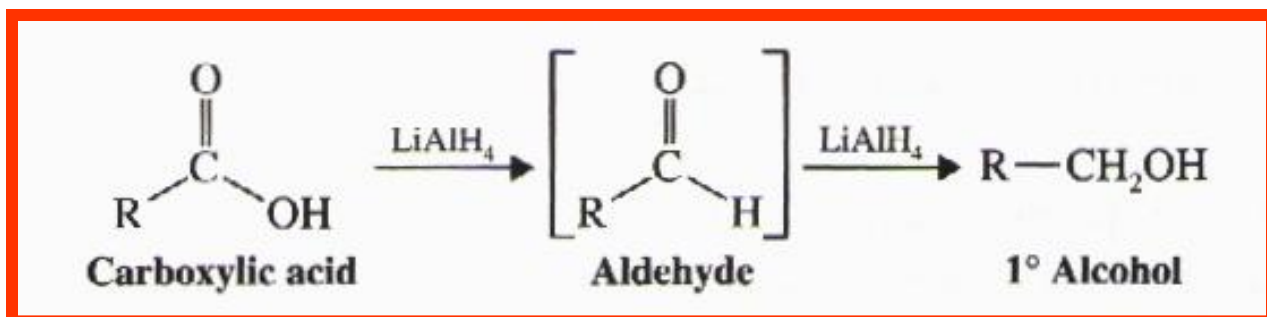
Example



6. DIBAH (Diisobutyl Aluminum Hydride)

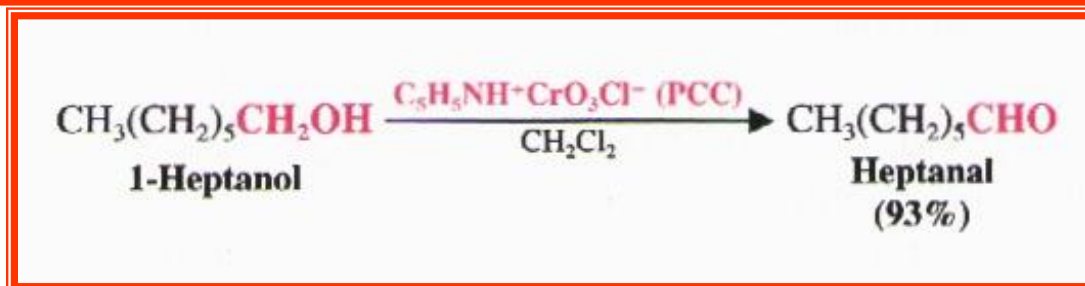
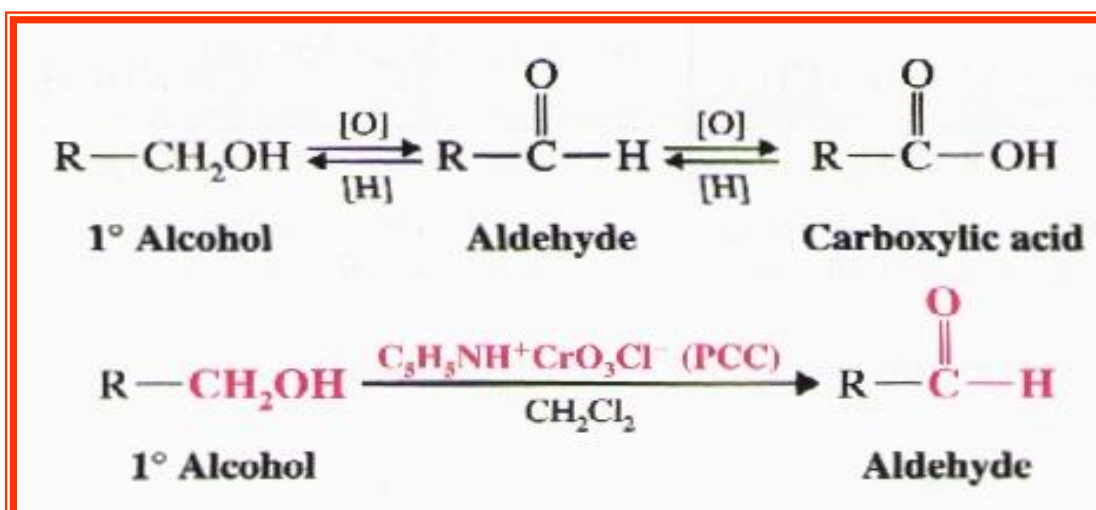
Reduction of an **Ester** to an **Aldehyde**





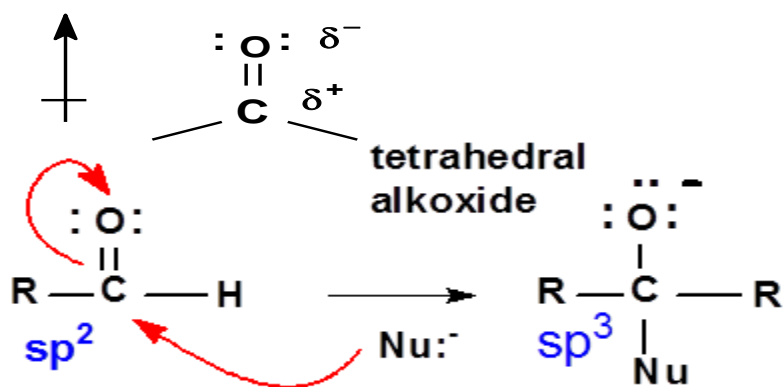
7. Oxidation of primary alcohols (Aldehydes by Oxidation of 1° Alcohols)

Aldehydes can be prepared from 1° alcohols by oxidation with pyridinium chlorochromate (PCC):



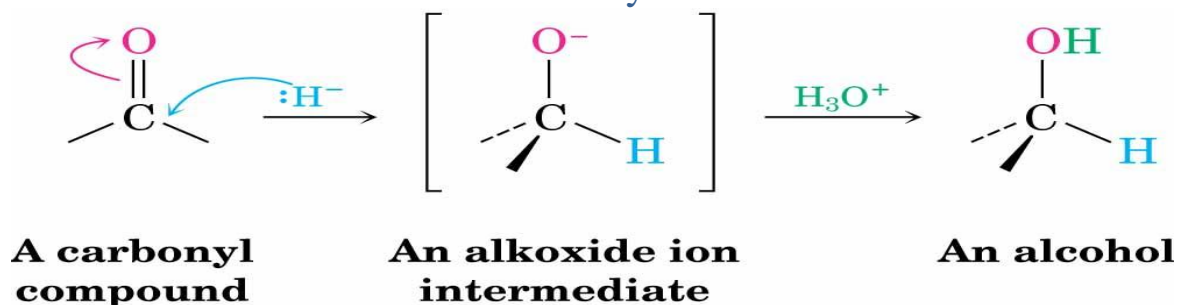
REACTIONS OF ALDEHYDES AND KETONES

Nucleophilic Addition Reactions: Strong Nucleophiles

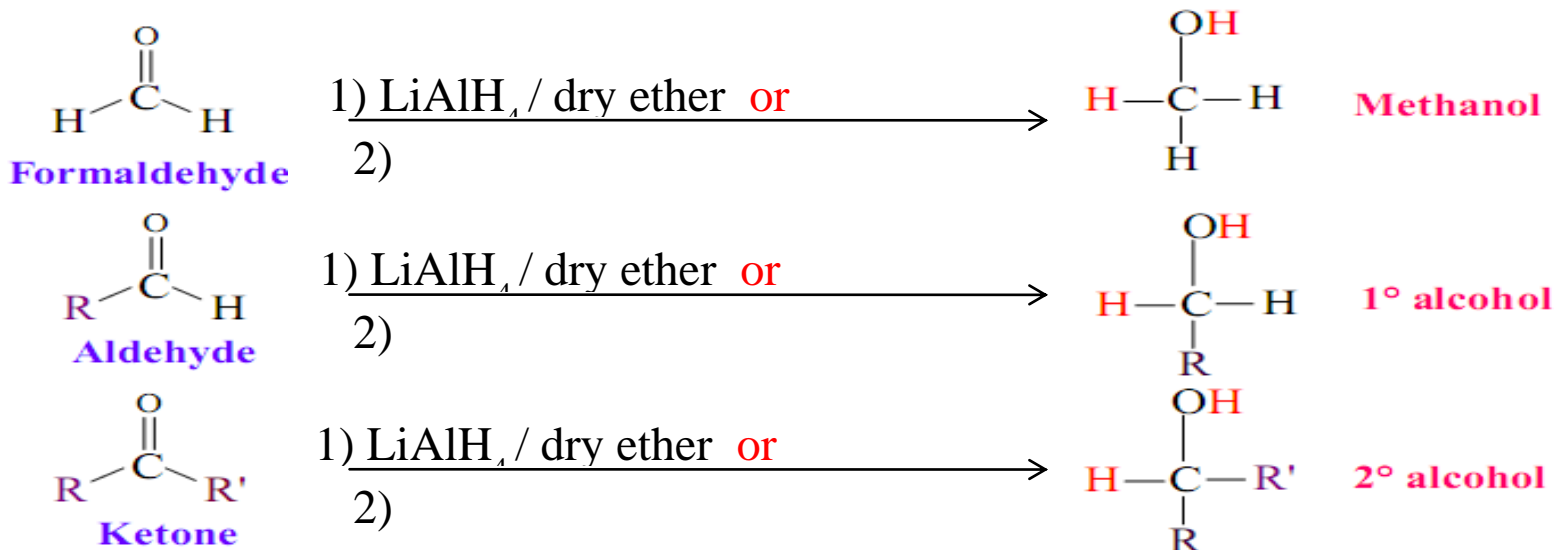


1-Reduction of carbonyl group

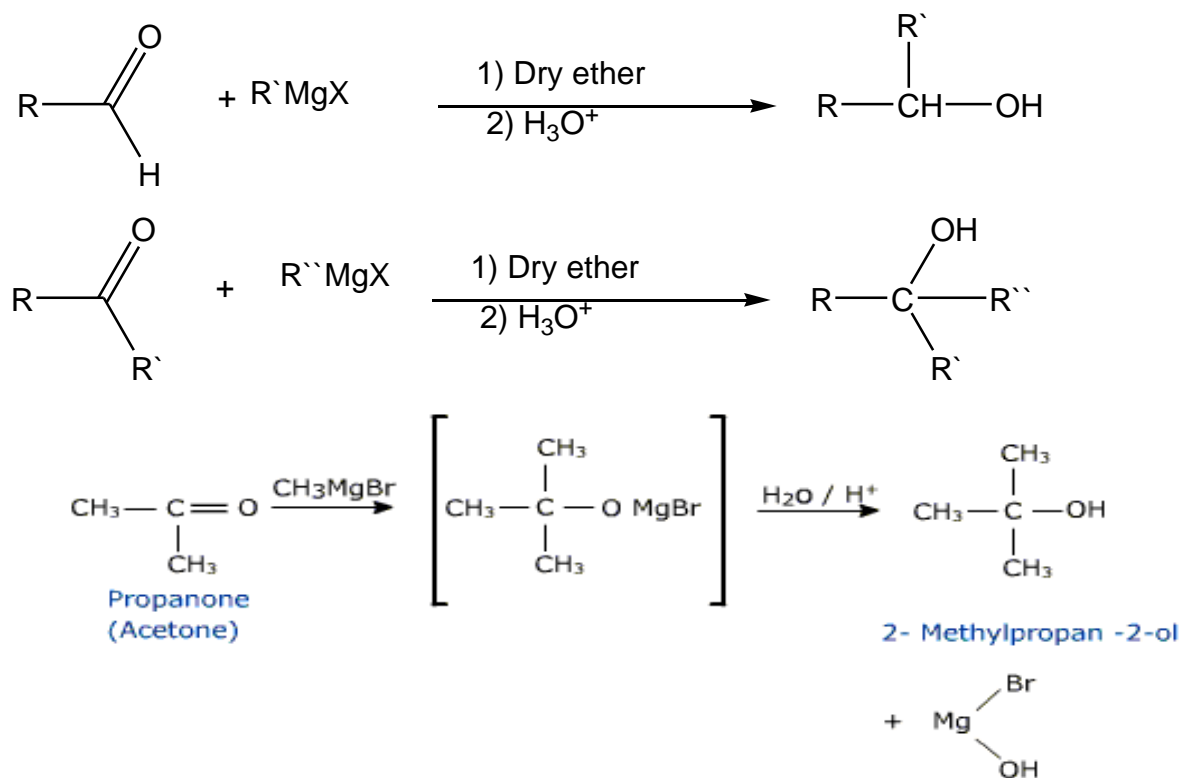
Addition of metal hydrides: Formation of alcohols.



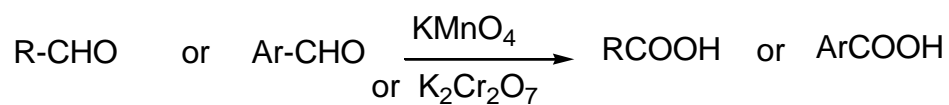
Reduction by hydride reagents, Lithium aluminium hydride
LiAlH₄ or Sodium boron hydride NaBH₄.



2- Addition of Grignard Reagents: Formation of alcohols



3-Oxidation reaction



Tollens Test

Using to distinguish between aldehyde and ketone

- Add ammonia solution to AgNO_3 solution until precipitate dissolves.
- Aldehyde reaction forms a silver mirror.

