

# Basics of Organic Chemistry

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## Objectives

At the end of this, we will be able to-

- Know the key terms such as homologous series, functional groups in the systematic learning of organic chemistry
- Explain the basic nomenclature, isomers and synthesis of organic compounds
- Apply the knowledge to explain the basic chemical changes in several reactions of organic compounds

## Contents

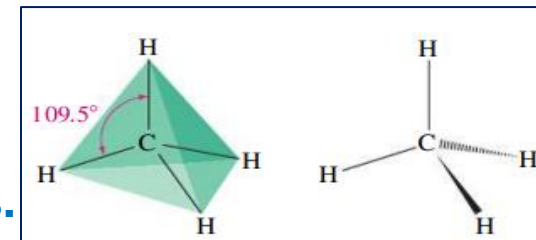
- Introduction of aliphatic and aromatic hydrocarbons
- Nomenclature of various organic compounds
- Synthesis of various hydrocarbons & their derivatives (alkane, alkene, alkyne, alcohol, acid, benzene, phenol, etc.)
- Important organic reactions (addition reaction, elimination reaction, substitution reaction, Friedel craft reactions)
- Selected organic compounds (phenol and its derivatives; alcohols and its derivatives)

# Introduction

Carbon is unique in that, in compounds, it forms strong and stable bonds with other carbon atoms. Carbon forms a vast no. of compounds as its particular ability to form single, double and triple bonds, and to build up molecules with long chains and rings. **Organic compounds are compounds containing carbon and hydrogen atoms, some organic compounds contain other elements, such as oxygen, a halogen or nitrogen. A few contain sulfur.** The simplest organic compounds are those of carbon and hydrogen hydrocarbons and the simplest hydrocarbon is methane, the chief constituent of natural gas.

Based on arrangement of carbon chain, organic compounds are classified-

- Aliphatic compound with straight or branched chain carbon skeleton.
- Alicyclic compound with closed rings, mainly contain single or multiple C-C bonds.
- Arenes - Benzene and its derivatives.



**As there are millions of organic compounds, organic compounds are divided into ‘families’ or homologous series for their systematic study.**







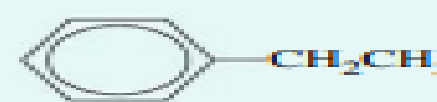

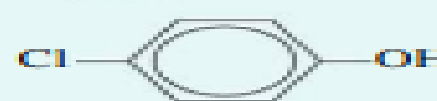
## Homologous series

A series of compounds (make a family) with similar chemical properties, in which members differ from one another by the possession of an additional  $\text{CH}_2$  group, is called a homologous series. **Each homologous series has a particular functional group and general formula. The members of a homologous series show a trend in physical properties, such as melting and boiling temperatures and solubility.**

## Functional group

A functional group is an atom or group of atoms that is typical of a particular organic family and which determines the chemical properties of the molecule. **The functional group has the same distinctive effect on the properties of all molecules in the family. Functional group is also influenced by its environment.**

e.g. as the hydrocarbon chain gets bigger, it has an increasing effect on the chemistry of the molecule and the influence of the functional group gets less as a result.

Class	General Structural Formula <sup>a</sup>	Example	Name of Example
Alkane	$R-H$	$CH_3CH_2CH_2CH_2CH_2CH_3$	Hexane
Alkene		$CH_2=CHCH_2CH_2CH_3$	1-Pentene
Alkyne	$-C\equiv C-$	$CH_3C\equiv CCH_2CH_2CH_2CH_2CH_3$	2-Octyne
Alcohol	$R-OH$	$CH_3CH_2CH_2CH_2OH$	1-Butanol
Alkyl halide	$R-X^b$	$CH_3CH_2CH_2CH_2CH_2CH_2Br$	1-Bromohexane
Ether	$R-O-R'$	$CH_3-O-CH_2CH_2CH_3$	1-Methoxypropane (methyl propyl ether) <sup>c</sup>
Amine	$R-NH_2$	$CH_3CH_2CH_2-NH_2$	1-Aminopropane (propylamine) <sup>c</sup>
Aldehyde		$CH_3CH_2CH_2C(=O)H$	Butanal (butyraldehyde) <sup>c</sup>
Ketone		$CH_3CH_2C(=O)CH_2CH_2CH_3$	3-Hexanone (ethyl propyl ketone) <sup>c</sup>
Carboxylic acid		$CH_3CH_2CH_2C(=O)OH$	Butanoic acid (butyric acid) <sup>c</sup>
Ester		$CH_3CH_2CH_2C(=O)OCH_3$	Methyl butanoate (methyl butyrate) <sup>c</sup>
Amide		$CH_3CH_2CH_2C(=O)NH_2$	Butanamide (butyramide) <sup>c</sup>
Arene	$Ar-H^d$		Ethylbenzene
Aryl halide	$Ar-X^b$		Bromobenzene
Phenol	$Ar-OH$		4-Chlorophenol (p-chlorophenol) <sup>c</sup>

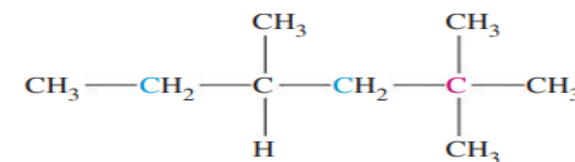
# Nomenclature- Hydrocarbons

The following rules enable us to name branched-chain hydrocarbons unambiguously as long as we apply the rules in sequence.

- Select the longest continuous carbon chain in the molecule and use the hydrocarbon name of this chain as the base name. Except for the common names methane, ethane, propane, and butane, standard Greek prefixes relate the name to the number of C atoms in the chain, as in pentane (C<sub>5</sub>), hexane (C<sub>6</sub>), heptane (C<sub>7</sub>), octane (C<sub>8</sub>)
- Consider every branch of the main branch to be a substituent alkyl group. **Table** gives the names of common alkyl substituents. When the substituent is more complex, we use the rules given previously to name the side group, bearing in mind that we would change the -ane ending to -yl.
- Number the C atoms of the continuous base chain so that the substituents appear at the lowest numbers possible.
- Name each substituent according to its chemical identity and the number of the C atom to which it is attached. For identical substituents use di, tri, tetra, and so on, and write the appropriate carbon number for each substituent.
- Separate numbers from one another with commas but no spaces, and separate numbers from letters with hyphens
- List the substituents alphabetically by name. When determining alphabetical order, the prefixes di-, tri-, sec-, and tert- are ignored. Thus, tert-butyl, precedes methyl in the name 4-tert-butyl-2-methylheptane. However, the prefix iso- is not ignored when deciding the alphabetical order.

## Some Common Alkyl Groups

Common Name	IUPAC Name	Structural Formula
Methyl	Methyl	—CH <sub>3</sub>
Ethyl	Ethyl	—CH <sub>2</sub> CH <sub>3</sub>
Propyl <sup>a</sup>	Propyl	—CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>
Isopropyl	1-Methylethyl	$\begin{array}{c} \text{CH}_3\text{CHCH}_3 \\   \\ \text{—} \end{array}$
Butyl <sup>a</sup>	Butyl	$\begin{array}{c} \text{—CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$
Isobutyl	2-Methylpropyl	$\begin{array}{c} \text{CH}_3 \\   \\ \text{—CH}_2\text{CHCH}_3 \\   \\ \text{CH}_3\text{CHCH}_2\text{CH}_3 \end{array}$
sec-Butyl <sup>b</sup>	1-Methylpropyl	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$
tert-Butyl <sup>c</sup>	1,1-Dimethylethyl	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{CCH}_3 \\   \\ \text{—} \end{array}$



2,2,4-trimethylhexane

C = primary carbon

CH<sub>2</sub> = secondary carbon

C = tertiary carbon

CH<sub>3</sub> = quaternary carbon

# Check List

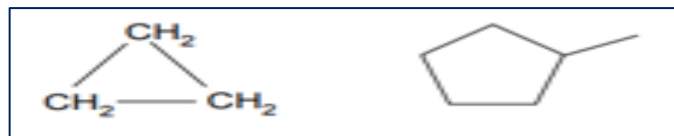
1. Draw the structures for the following compounds: (i) 2-methylpropane (ii) 2,3-dimethylpentane (iii) 3-ethyl-2,4-dimethylhexane

2. Name the following compounds, all of which have the molecular formula  $C_6H_{14}$

3. Draw the structures for the following compounds: (i) cyclobutene (ii) cyclopentane (iii) 1,3-dimethylcyclohexane

4. Name these compounds:

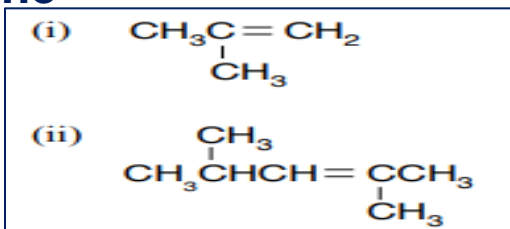
5. Draw the structures for the following compounds:



(i) but-2-ene (ii) 2-methylbut-2-ene (iii) 2,3-dimethylbut-2-ene (iv) 3-ethyl-2-methylpent-1-ene

6. Name these compounds:

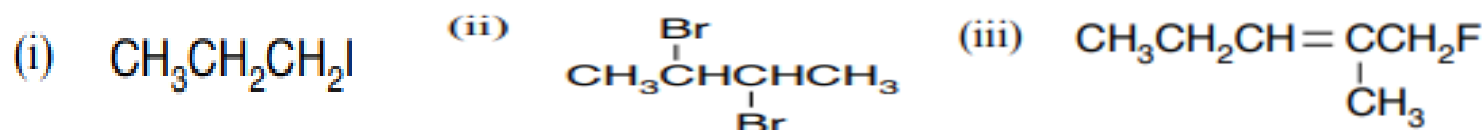
7. Draw the structures for the following compounds:



(i) tetrachloromethane

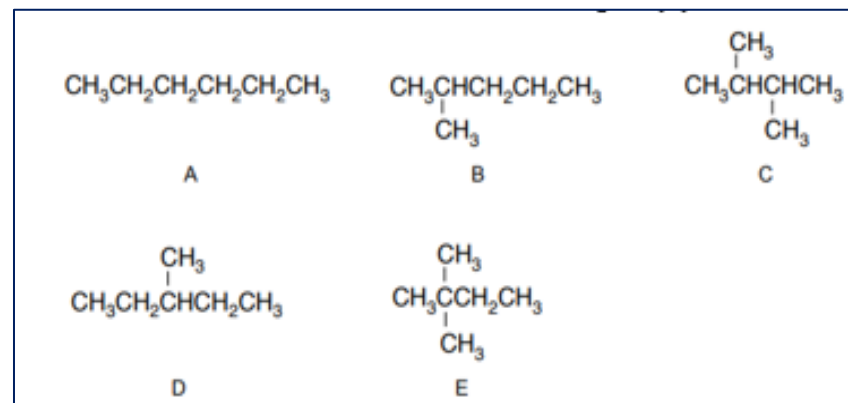
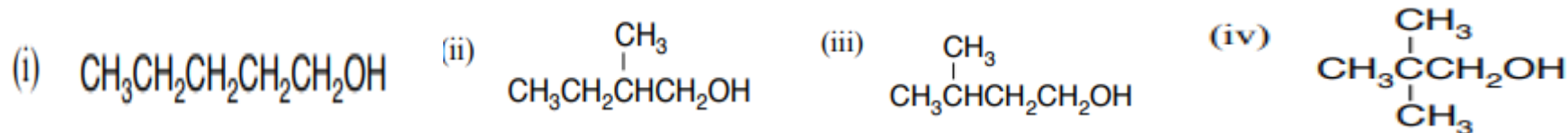
(ii) 1,1-dichloroethene (iii) 1,2-dibromo-2-methylbutane (iv) 1,2-dibromocyclohexane

8. Name these compounds:



9. Draw the structures for the following compounds: (i) ethanol (ii) 2-methylpropan-2-ol (iii) butan-2-ol (iv) but-2-en-1-ol

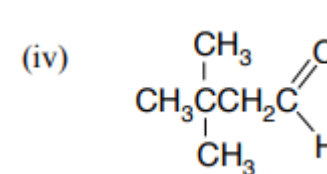
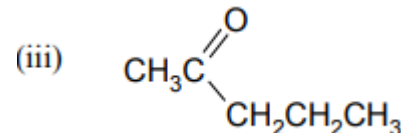
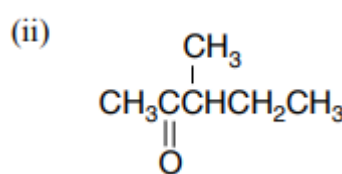
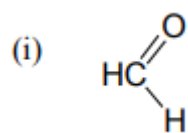
10. Name these compounds:



# Check List

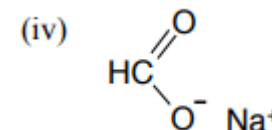
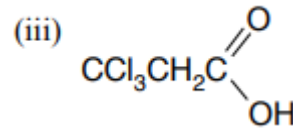
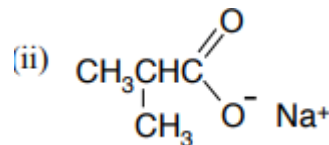
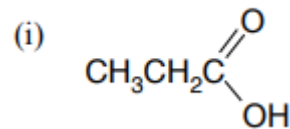
11. Draw the structures for the following compounds: (i) ethanal (ii) butanone (also known as butan-2-one, but the 2 is unnecessary and is often left out) (iii) 2-methylpropanal (iv) 3-methylpentan-2-one

12. Name these compounds:



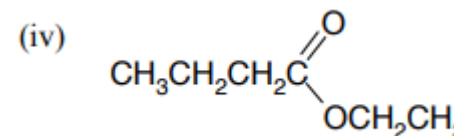
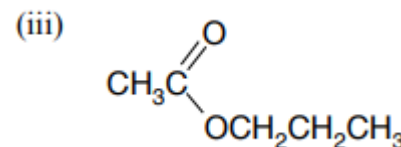
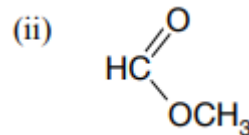
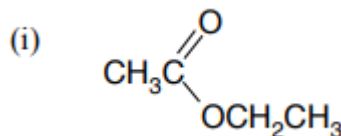
13. Draw the structures of the following compounds: (i) ethanoic acid (ii) potassium ethanoate (iii) 3-chloropropanoic acid (iv) sodium 2,3-dimethylbutanoate

14. Name these compounds:



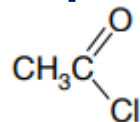
15. Draw the structures of the following compounds: (i) methyl ethanoate (ii) ethyl methanoate (iii) ethyl propanoate (iv) methyl 2-methylpropanoate

16. Name these compounds:



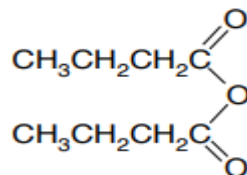
17. Draw the structure for propanoyl chloride.

18. Name the compound-



19. Draw the structure for ethanoic anhydride

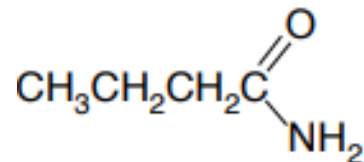
20. Name the compound:



21. Draw the structure for ethanamide.

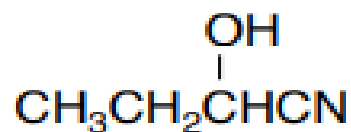
## Check List

22. Name the compound-



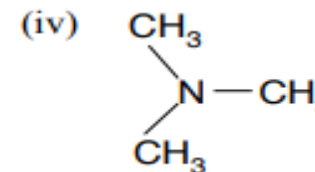
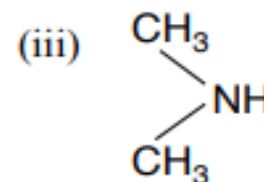
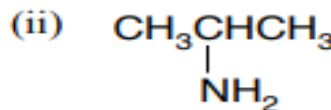
23. Draw the structure for propanenitrile

24. Name the compound-



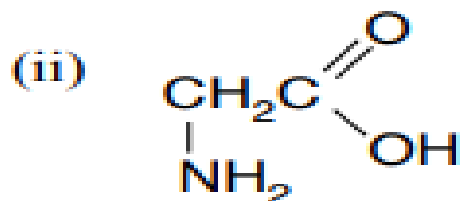
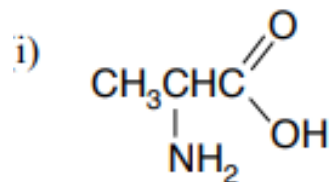
25. Draw the structures for (i) ethylamine (ii) aminoethane (iii) 2-aminobutane (iv) 1,6-diaminohexane (v) diethylamine (vi) triethylamine

26. Name these compounds:



27. Draw the structures for (i) 2-aminobutanoic acid (ii) 3-aminopropanoic acid

28. Name these compounds:





# Representing Molecules

## Molecular formula

The molecular formula of a compound gives the numbers of atoms of each element present in one molecule of the substance. It does not indicate how the atoms are joined together. The molecular formula of ethanol is  $\text{C}_2\text{H}_6\text{O}$  and that of ethene is  $\text{C}_2\text{H}_4$ .

## Empirical formula

The empirical formula is the simplest whole number ratio of the atoms of each element in the compound. The empirical formula of ethanol is the same as its molecular formula; the empirical formula of ethene is  $\text{CH}_2$ .

## Structural formula

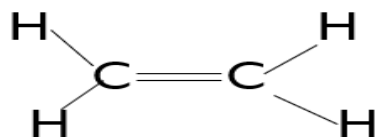
The structural formula of a compound represents the way in which different atoms of the compound are arranged relative to each other. The use of structural formulae overcomes ambiguous molecular formulae such as ethanol and methoxy methane. Both have the same molecular formula as  $\text{C}_2\text{H}_6\text{O}$ , but ethanol has structural formula  $\text{CH}_3\text{CH}_2\text{OH}$  and methoxy methane has structural formula  $\text{CH}_3\text{OCH}_3$ .

The structural formula must include any double bonds that are present in the molecule, the structural formula of ethene is  $\text{H}_2\text{C}=\text{CH}_2$ .

## Displayed or Full structural formula

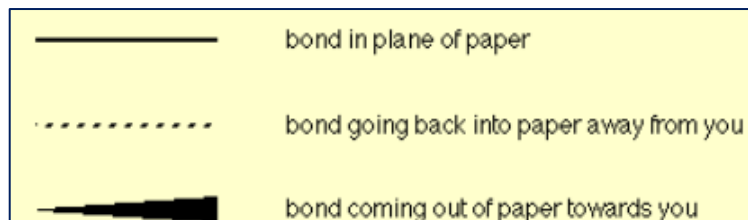
The displayed formula of any organic compound shows both the relative placing of the atoms and the no. of bonds between them. That means, it must show all the atoms separately and all the bonds between them.

The displayed formula for ethene is

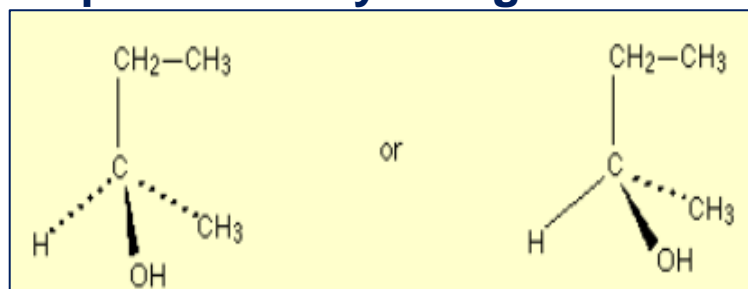


# Representing Molecules

3-D arrangement of some molecules can be presented with the bonds using conventional symbols are shown-



For example, Butan-2-ol has the structural formula 3-D arrangement of the groups around the carbon in butan-2-ol can be represented by using conventional bond notation as-



## Skeletal formula

In skeletal formula the carbon atoms are not drawn.

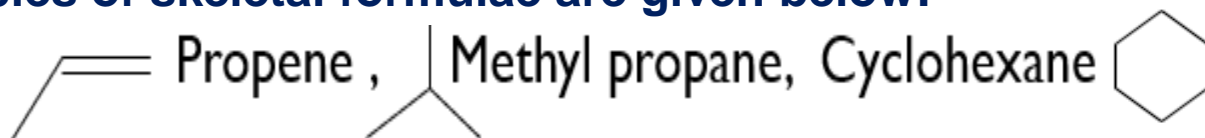
A straight line represents a single bond and a double bond represents a double bond.

A carbon atom is assumed to be at the end of these lines unless another atom except carbon is shown.

Any carbon and hydrogen atoms in the skeletal formula is left in carbon skeleton, with the carbon atoms represented by the junctions between the bonds, only functional groups are shown.

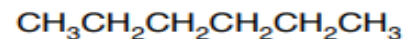
Hydrogen atoms that are bonded to carbon are omitted, but each carbon atom has enough hydrogen atoms joined to it to make a total of four bonds.

Some examples of skeletal formulae are given below:

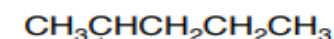


# Check List

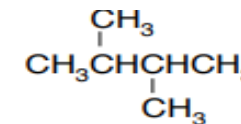
1. Using propane as an example, write formulae or draw diagrams as appropriate to show what is meant by (i) a molecular formula (ii) a structural formula (show the difference between a fully displayed and the more usual simplified version) (iii) a skeletal formula
2. Represent the following compounds with empirical, molecular, structural, full displayed and skeletal formulae: i) Methylpropane ii) Cyclohexane iii) Ethanoic acid iv) 2-methylpropane-2-ol
3. Draw skeletal formulae for the following compounds:



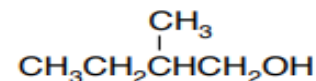
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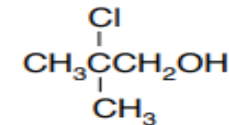
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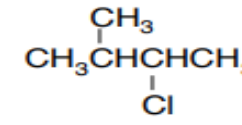
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D

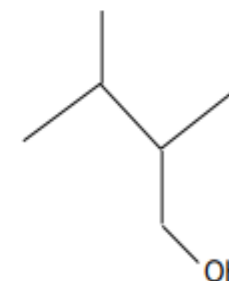
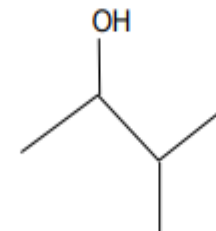
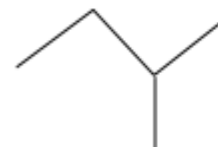


E



F

4. Translate the following skeletal formulae into structural form



# Isomers

## Isomers

Isomers are compounds with the same molecular formula but different structure, i.e. have a different arrangement of the atoms in space. There are two main types of isomers, **constitutional isomers & stereo isomers**

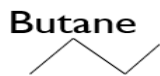
### Constitutional isomers

Structural isomers have the same molecular formula but different molecular structures. This means that the isomers have the same no. of atoms of the same element are arranged differently.

Structural isomers can be divided into three categories, carbon-chain, positional, functional-group.

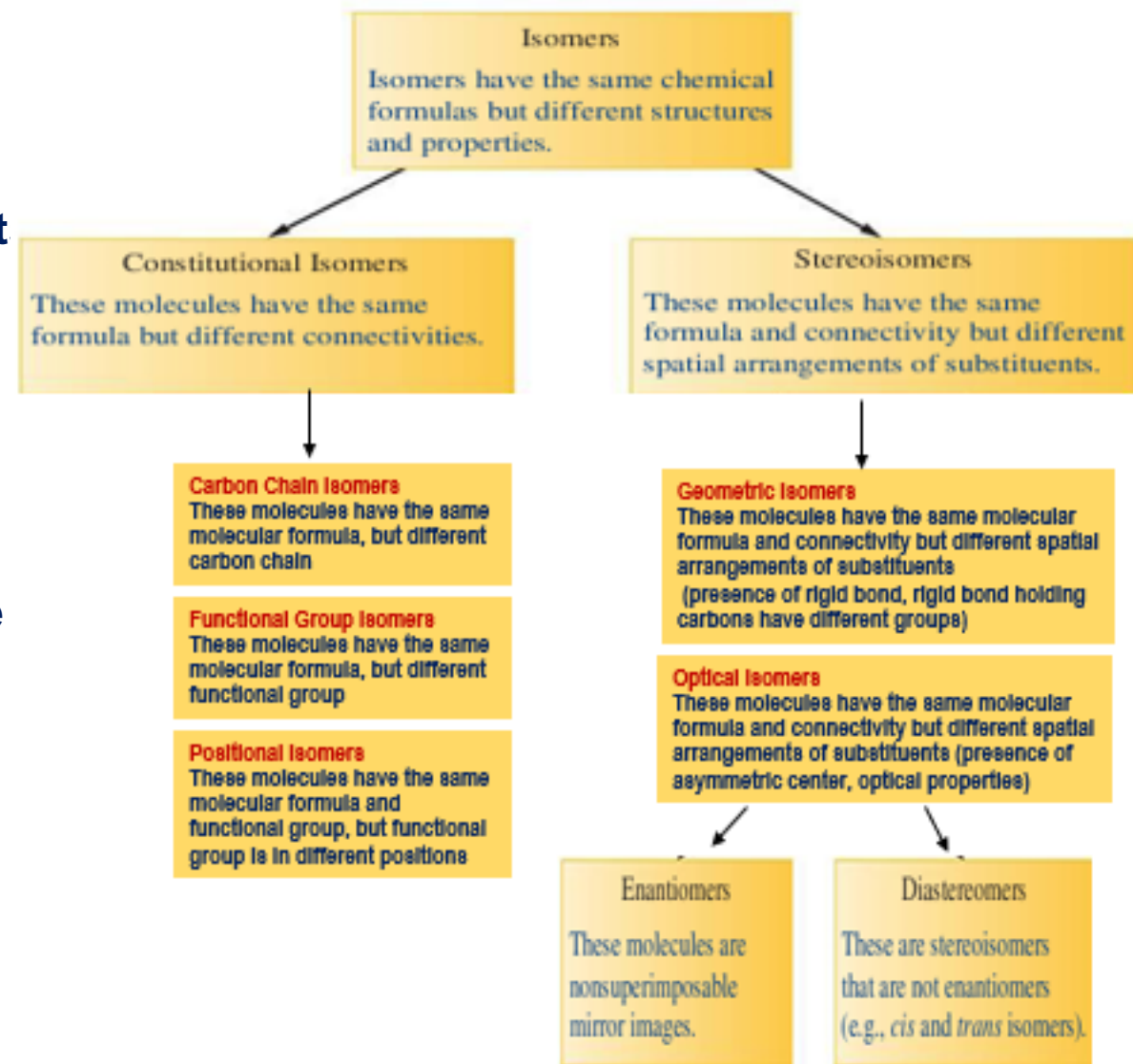
### Carbon-chain isomers

These structural isomers differ in the length of the carbon chain. For example, butane and methyl- propane are carbon chain isomers. The skeletal formulae of these two isomers are:



### Positional isomers

Positional isomers are the structural isomers have the same functional group in different locations on the carbon framework. As for example, propane-1-ol & propane-2-ol both have the molecular formula  $C_3H_8O$  but their structural formula are  $CH_3CH_2CH_2OH$  and  $CH_3CH(OH)CH_3$  respectively.



# Isomers

## Functional-group isomers

Functional group isomerism occurs when two compounds with the same molecular formula are members of different homologous series and have different functional groups.

For example, the ester methyl methanoate,  $\text{HCOOCH}_3$ , is an isomer of ethanoic acid,  $\text{CH}_3\text{COOH}$ . Hex-1-ene & cyclohexane, both have the molecular formula  $\text{C}_6\text{H}_{12}$ , but structural formula are as



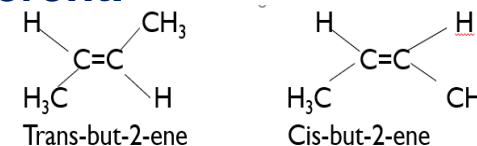
## Stereoisomers

Isomers having the same carbon chain, the position of the groups on the chain and the nature of the functional groups but the arrangement of the atoms in space is different are known as stereoisomers. There are two separate types of stereoisomers-, **geometric isomers**, **optical isomers**.

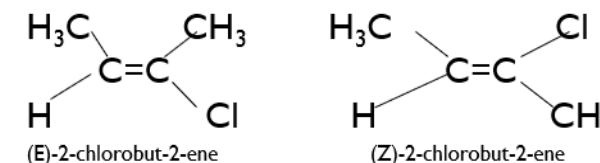
## Geometric isomers

Isomers that differ only in the spatial arrangement of atoms in the planar part of the molecule or above and below a ring. The most common way that this occurs is when a molecule has a  $\text{C}=\text{C}$  group and each of these carbon atoms has two different groups or atoms joined to it. For example, But-2-ene exists as two geometric isomers. The two double bonded carbon atoms and the four atoms joined to them all lie in a plane and can take up different spatial positions in that plane. The geometry of the two isomers is different.

In the trans isomer, the two  $-\text{CH}_3$  groups are staggered at  $180^\circ$  to each other and are on opposite sides of the double bond. In the cis isomer, the two  $-\text{CH}_3$  groups are on the same side of the double bond. Geometric isomers exist as there is restricted rotation around the double bond. Therefore, one isomer cannot spontaneously convert into the other unless sufficient energy is supplied.



**This method of naming geometric isomers breaks down in compounds such as 2-chlorobut-2-ene. Two geometric isomers of this compound are shown as**



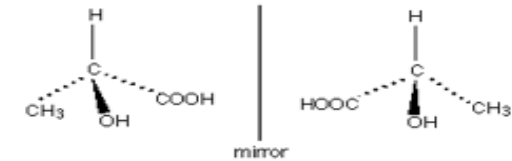
# Isomers

**Optical Isomers-** Compounds that show optical isomerism don't have a plane(or axis or center) of symmetry. They are said to be chiral. The most common cause of chirality in organic chemistry is when a carbon atom has four different groups or atoms attached to it.

For example, the compound  $\text{CHFCIBr}$  is chiral. A chiral centre in a molecule or ion causes it to have two optical isomers. Lactic acid is produced when milk goes sour and in muscles as a result of anaerobic respiration. Its formula is  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$  and its systematic name is 2-hydroxypropanoic acid. The substance exists as two optical isomers.

## Enantiomers

Enantiomers are an optical isomers that are non- superimposable on its mirror image. Enantiomers have identical chemical properties and the same boiling temperatures and solubilities.



They differ in two ways. They rotate the plane of polarization of plane polarized light. A solution of one enantiomer rotates the plane of polarization of plane polarized light in a clockwise direction (+). Lactic acid produced in muscles is a crystalline solid that melts at  $26^\circ\text{C}$  and rotates the plane of polarization clockwise. The other enantiomer rotates it in an anticlockwise direction (-). Lactic acid obtained from the action of microorganisms on milk sugar(lactose) is a crystalline solid, and melts at  $26^\circ\text{C}$ , but rotates the plane of polarization of plane polarized light in an anticlockwise direction.

**Diastereomers,** Stereoisomers that are not mirror images to each other. Diastereomers may or may not be optically active. Diastereomers have different physical properties, such as melting points, boiling points, densities, solubilities, and refractive indices. They also have similar but not identical chemical properties. For example, cis and trans-but-2-ene; meso compound of 2,3-dichlorobutane is not optically active, but its diastereomeric isomer is optically active.

## Racemic mixture

A solution containing equimolar amounts of the two enantiomers is called a racemic mixture. It does not rotate the plane of polarization of plane polarized light. The extent by which an enantiomer rotates the plane of polarization can be measured by using a Polari meter, and it depends on the nature of the enantiomer, and the concentration of the enantiomer in the solution.



# Isomers

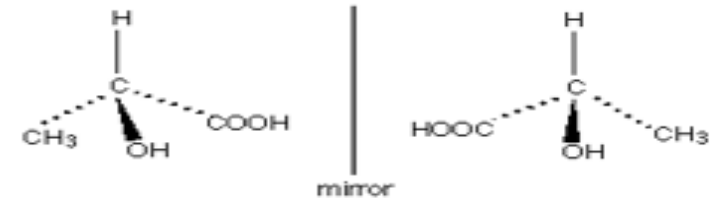
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# Synthesis of Hydrocarbons

## Alkanes

The most important feature of the alkanes is their use as fuels (mixtures of alkanes). The source of these fuels is either crude **petroleum oil or natural gas**. The basic process by which petroleum is turned into useful chemicals with a whole variety of properties is known as **primary distillation ( primary distillation is industrial version of fractional distillation)**.

Petroleum is boiled and the vapors are cooled and liquefied at different range of temperatures. The liquid collected over each range of temperature is known as a fraction. This process provides several fractions which can be used in further, more precise, **fractional distillation process to give a pure yield of a particular alkane**.

**Several laboratory methods are also available for their preparation.**

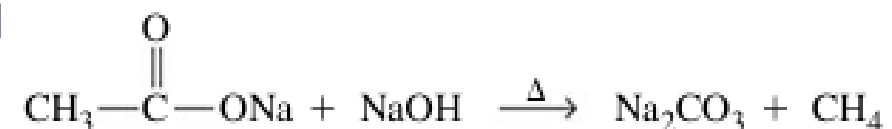
- In the presence of a metal catalyst such as Pt, Pb, or Ni, unsaturated hydrocarbons, whether containing double or triple bonds, may be converted to alkanes by the addition of H atoms to the multiple bond systems (**catalytic hydrogenation**).



- Halogenated hydrocarbons react with alkali metals to produce alkanes of double the carbon content.



- Alkali metal salts of carboxylic acids can be fused with alkali metal hydroxides. Sodium carbonate and an alkane with one carbon fewer than the metal carboxylate are formed



## Principal Petroleum Fractions

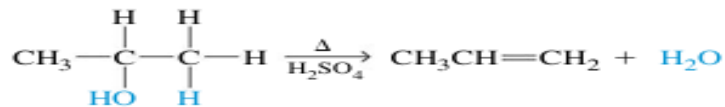
Boiling Range, °C	Composition	Fraction	Uses
Below 0	C <sub>1</sub> to C <sub>4</sub>	Gas	Gaseous fuel
0–50	C <sub>5</sub> to C <sub>7</sub>	Petroleum ether	Solvents
50–100	C <sub>6</sub> to C <sub>8</sub>	Ligroin	Solvents
70–150	C <sub>6</sub> to C <sub>9</sub>	Gasoline	Motor fuel
150–300	C <sub>10</sub> to C <sub>16</sub>	Kerosene	Jet fuel, diesel oil
Over 300	C <sub>16</sub> to C <sub>18</sub>	Gas-oil	Diesel oil, cracking stock
—	C <sub>18</sub> to C <sub>20</sub>	Wax-oil	Lubricating oil, mineral oil, cracking stock
—	C <sub>21</sub> to C <sub>40</sub>	Paraffin wax	Candles, wax paper
—	above C <sub>40</sub>	Residuum	Roofing tar, road materials, waterproofing



# Synthesis of Hydrocarbons

## Alkenes

The general laboratory preparation of alkenes uses an elimination reaction, a reaction in which atoms are removed from adjacent positions on a carbon chain.



**Alkenes-** Ethene in particular, are of immense importance to the chemical in very small

quantities but are obtained from crude oil by the process of

cracking and catalytic reforming. Ethene is the starting point for a

great many synthetic processes. It is used for the production of polymers, detergents, solvents and many other chemicals. Ethene has a number of effects on plant growth. It is also a plant hormone, which has the effect of ripening fruit.

## Alkynes

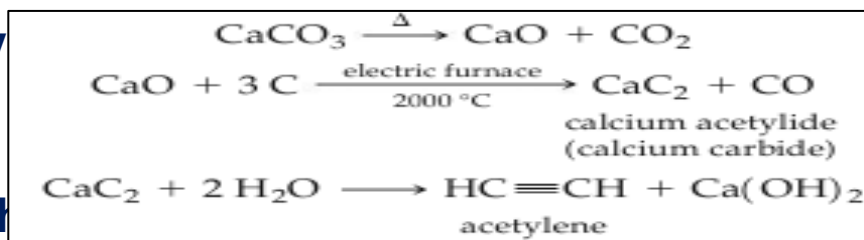
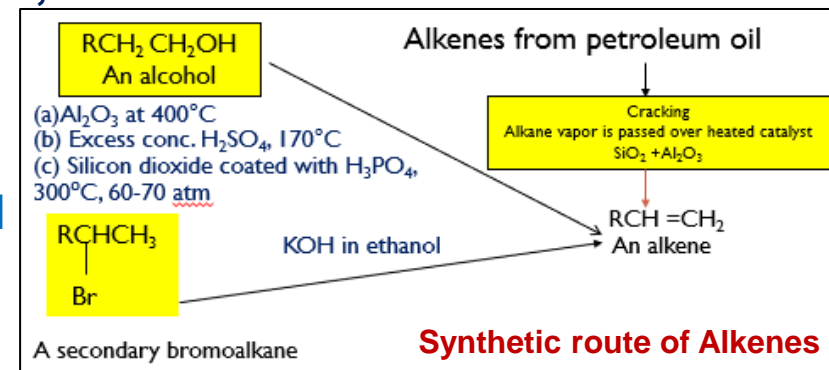
The simplest alkyne is ethyne (acetylene), which can be prepared from coal, water, and limestone in a three-step process:

Most other alkynes are prepared from acetylene by taking advantage of the acidity of the C-H bond.

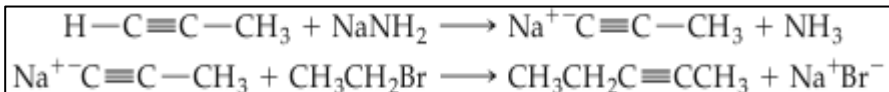
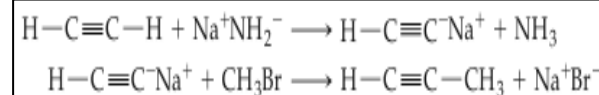
In the presence of a very strong base, such as sodium amide (NaNH<sub>2</sub>), the amide anion removes the

sodium acetylide. The acetylide can then react with an alkyl halide, such as CH<sub>3</sub>Br:

By continuing this reaction, the triple bond can be positioned as desired in the chain, as in the synthesis of 2-pentyne,



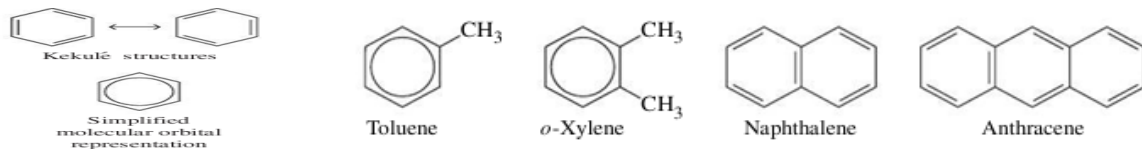
onia and the salt



# Synthesis of Hydrocarbons

## Benzene

Aromatic hydrocarbons have ring structures with unsaturation (multiple bond character) in the carbon-to-carbon bonds in the rings. Most aromatic hydrocarbons are based on the molecule benzene,  $C_6H_6$ .



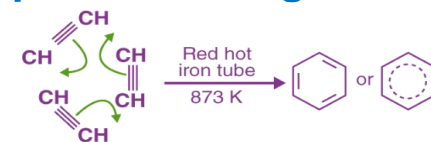
- They are planar (flat), cyclic molecules.
- They have a conjugated bonding system- a bonding scheme among the ring atoms that consists of alternating single and double bonds. The system must extend throughout the ring, and the electron clouds associated with the double bonds must involve  $(4n+2)$  electrons where,  $n = 2, 3, 4, \dots$ .

Benzene and its homologues are similar to other hydrocarbons in being insoluble in water but soluble in organic solvents. The boiling points of the aromatic hydrocarbons are slightly higher than those of the alkanes of similar carbon content. Two important aromatic functional groups are the phenyl and benzyl groups. A phenyl group is obtained when one of the six equivalent H atoms of a benzene molecule is removed. A benzyl group is obtained by replacing one of the H atoms in a methyl group with a phenyl group.

### Synthesis of Benzene

Benzene is prepared from ethyne by the process of cyclic polymerization. In this process, Ethyne is passed through a red-hot iron tube at 873 K. The ethyne molecule then undergoes cyclic polymerization to form benzene.

Benzene can be prepared from aromatic acids through decarboxylation reaction. In this process, the sodium salt of the benzoic acid (sodium benzoate) is heated with soda lime to produce benzene along with sodium carbonate.



Benzene can be prepared from phenols too through their reduction. In this process vapors of phenol are passed over heated zinc dust. Zinc dust reduces them to form benzene.

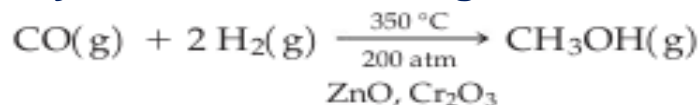


# Synthesis of Derivatives of Hydrocarbons

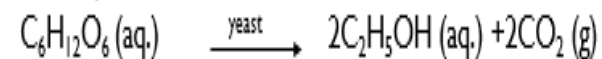
## Alcohols

Two methods by which alcohols can be synthesized are by the hydration of alkenes and the hydrolysis of alkyl halides. Hydration of alkenes is an example of an addition reaction and hydrolysis of alkyl halides is an example of substitution reaction.

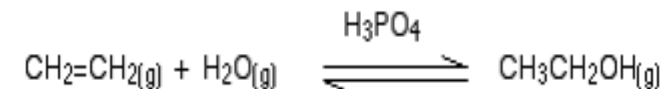
**Methanol (wood alcohol) is the simplest alcohol. It is a highly toxic substance that can lead to blindness or death if ingested. Most methanol is manufactured from carbon monoxide and hydrogen. Methanol is the most extensively produced alcohol. It is used in the synthesis of other organic chemicals and as a solvent, but potentially its most important use may be as a motor fuel.**



Ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ , is grain alcohol, which is found in alcoholic beverages. It is easily produced by the fermentation of the juices of sugarcane or other materials that contain natural sugars.



The industrial method involves the hydration of ethylene. Ethanol is manufactured by the hydration of ethene. The catalyst used is solid silicon dioxide coated with phosphoric(V) acid at  $300^\circ\text{C}$  and 60 to 70 atm. The reaction is reversible. Only 5% of the ethene is converted into ethanol at each pass through the reactor. By removing the ethanol from the equilibrium mixture and recycling the ethene, it is possible to achieve an overall 95% conversion.

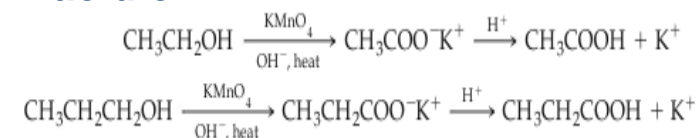


## Carboxylic acid

Carboxylic acids can be obtained in the laboratory by the oxidation of a primary alcohol or an aldehyde. For this purpose, the oxidizing agent is generally  $\text{KMnO}_4\text{(aq.)}$  in an alkaline medium. Because the medium is alkaline, the product is the potassium salt, but the free carboxylic acid can be regenerated by making the medium acidic.

**Carboxylic acids can also be prepared by the hydrolysis of nitriles. The hydrolysis of a nitrile can be carried out in either acidic or basic**

**Solution.**

$$\text{R}-\text{C}\equiv\text{N} + 2 \text{H}_2\text{O} \xrightarrow[\Delta]{\text{H}^+ \text{ or } \text{OH}^-} \text{RCOOH} + \text{NH}_3$$


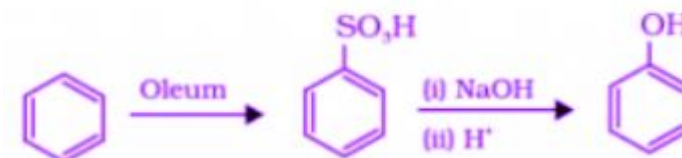
# Synthesis of Derivatives of Hydrocarbons

## Phenol

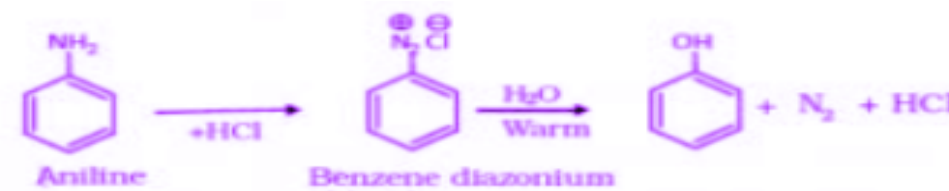
Chlorobenzene is an example of a haloarene which is formed by the monosubstitution of the benzene ring. When chlorobenzene is fused with sodium hydroxide at 623K and 320 atm, sodium phenoxide is produced. Finally, sodium phenoxide on acidification gives phenol.



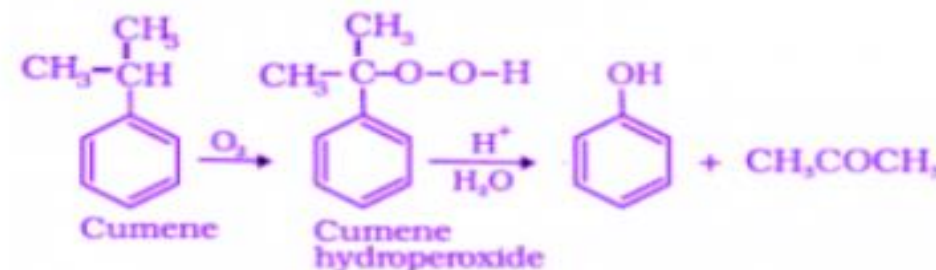
Benzene sulphonic acid can be obtained from benzene by reacting it with oleum. This benzene sulphonic acid can be treated with molten sodium hydroxide at high temperatures to encourage the formation of sodium phenoxide. Finally, sodium phenoxide on acidification gives phenol.



When an aromatic primary amine is treated with nitrous (NaNO<sub>2</sub> + HCl) acid at 273 – 278 K, diazonium salts are obtained. These diazonium salts are highly reactive in nature. Upon warming with water, these diazonium salts finally hydrolyze to phenols. Phenols can also be obtained from diazonium salts by treating it with dilute acids.



Cumene is an organic compound obtained by Friedel-Crafts alkylation of benzene with propylene. Upon oxidation of cumene (isopropyl benzene) in the presence of air, cumene hydroperoxide is obtained. Upon further treatment of cumene hydroperoxide with dilute acid, phenols are obtained. Acetone is also produced as one of the by-products of this reaction in large quantities. Hence, phenols prepared by these methods need purifications.

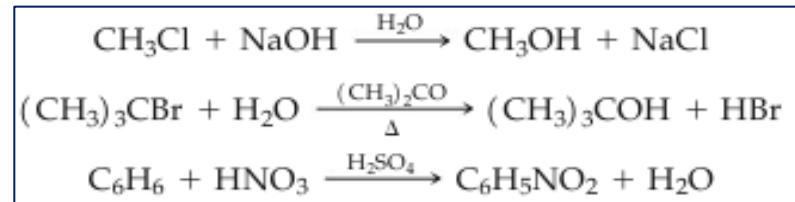
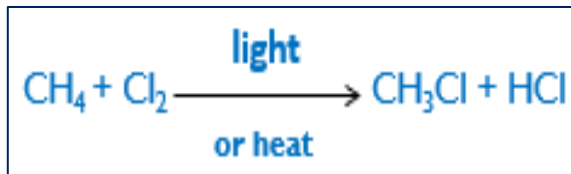


# Organic Reactions

Organic compounds undergo a variety of different reactions, including substitution, addition, elimination, and rearrangement reactions.

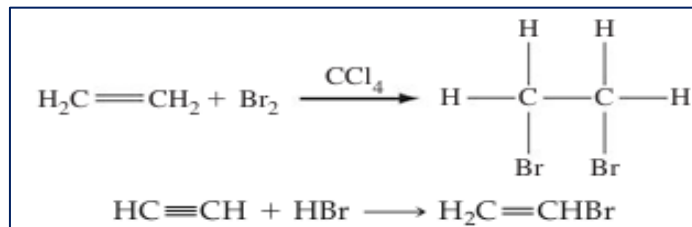
## Substitution

In a substitution reaction, an atom, an ion, or a group in one molecule is replaced by (substituted with) another. Here are a few examples of substitution reactions:



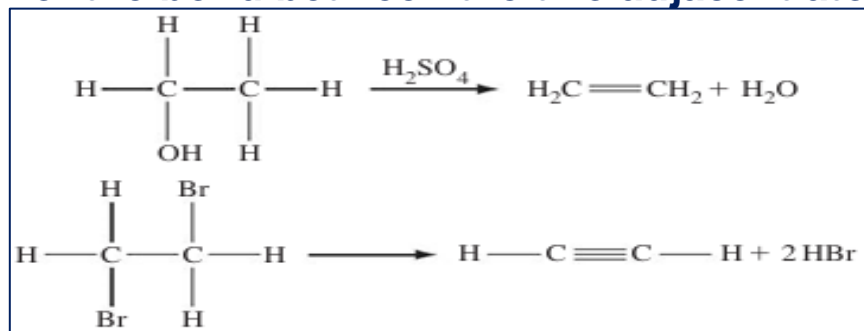
## Addition

In an addition reaction, a molecule adds across a double or triple bond in another molecule. Here are two examples:



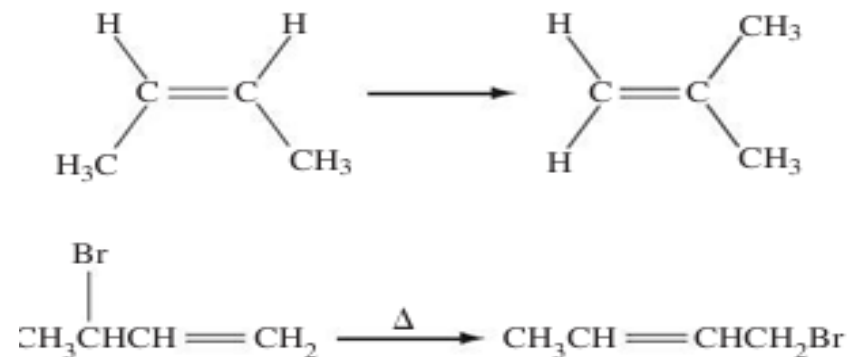
## Elimination

In an elimination reaction, atoms or groups that are bonded to adjacent atoms are eliminated as a small molecule. Typically, the order of the bond between the two adjacent atoms increases as a result of the elimination, as shown in the examples below:



## Rearrangement

Rearrangement reaction (or an isomerization reaction), the carbon skeleton of a molecule is rearranged.



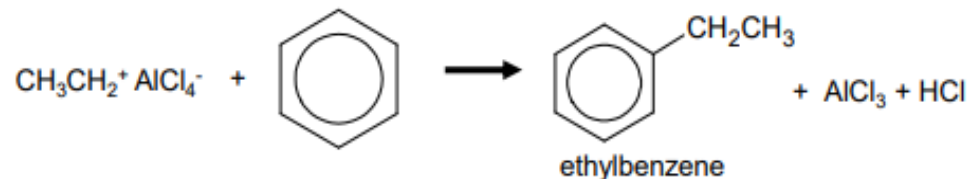


# Organic Reactions

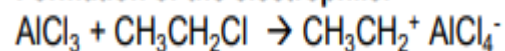
## Friedel Crafts Alkylation

**Change in functional group:** benzene  $\longrightarrow$  Alkylbenzene. Any chloroalkane can be used  $\text{RCl}$  where  $\text{R}$  is any alkyl group e.g.  $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$ . **The electrophile is the  $\text{R}^+$ .** **Reagents:** chloroalkane in the presence of anhydrous aluminium chloride catalyst.

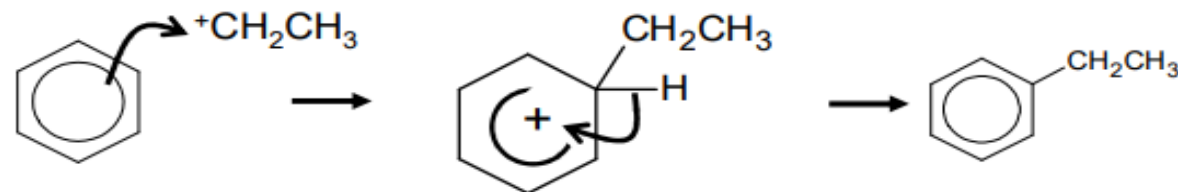
Overall Equation for reaction



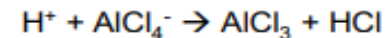
Formation of the electrophile.



Mechanism



The  $\text{H}^+$  ion reacts with the  $\text{AlCl}_4^-$  to reform  $\text{AlCl}_3$  catalyst and  $\text{HCl}$ .



## Friedel Crafts Acylation

**Change in functional group:** benzene  $\longrightarrow$  phenylketone. **Reagents:** acyl chloride in the presence of anhydrous aluminium chloride catalyst. **Conditions:** heat under reflux ( $50^\circ\text{C}$ ). **Mechanism:** Electrophilic Substitution  
**Any acyl chloride can be used  $\text{RCOCl}$  where  $\text{R}$  is any alkyl group e.g.  $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$ . The electrophile is the  $\text{RCO}^+$**

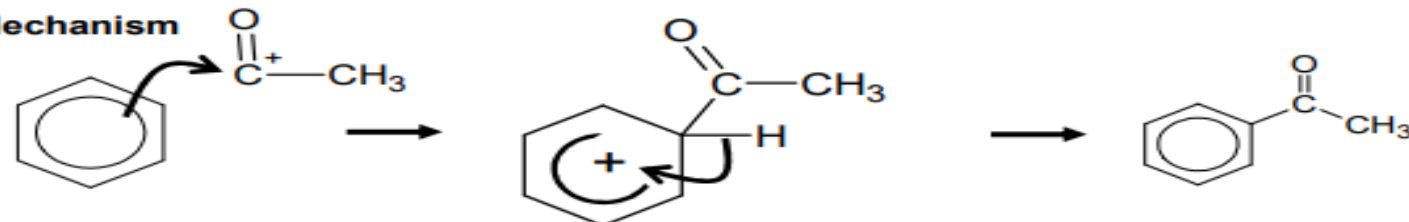
Generic example:



Equation for Formation of the electrophile.



Mechanism



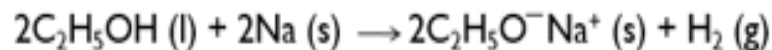
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# Derivatives of Alcohols

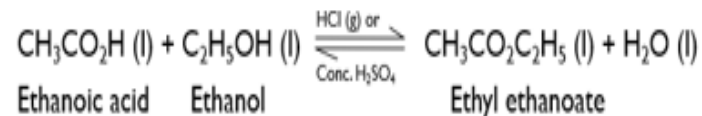
## Reaction with sodium

Alcohol reacts with sodium to give hydrogen and a sodium alkoxide. The reaction is much slower than the reaction of water and sodium



## Reaction with carboxylic acid- Esterification

Alcohols and carboxylic acids react to give esters. Esterification takes place much faster in the presence of a catalyst, such as hydrogen chloride or concentrated sulphuric acid. Acid anhydrides and acid chlorides also react with alcohols to give ester

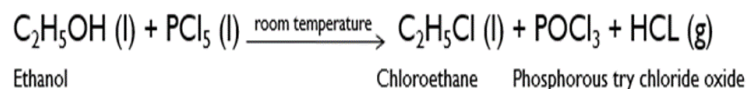
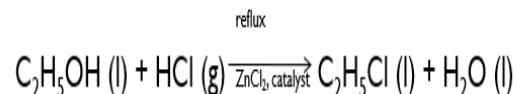


## Halogenation

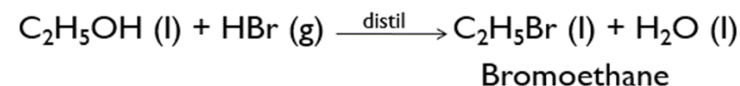
Dry hydrogen chloride is bubbled through the anhydrous alcohol in the presence of anhydrous zinc chloride as catalyst.

When the solution is saturated, it is refluxed on a water bath. For secondary and tertiary alcohols concentrated hydrochloric acid can be used. For tertiary alcohols, zinc chloride catalyst is not needed. Order of rates of reaction is

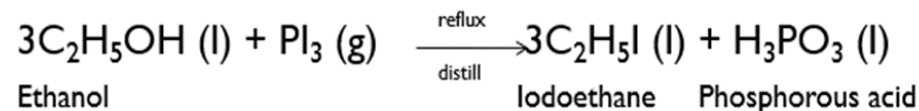
Tertiary > secondary > primary alcohol. Phosphorous (V) chloride reacts in the cold with alcohols. Phosphorous (III) chloride cannot be used. The sulphur dichloride oxide reacts with alcohols at room temperature to produce a chloroalkane. Sulphur dioxide and hydrogen chloride are given off. Care would have to be taken because both of these are poisonous.



Bromination is carried out by sodium bromide and concentrated sulphuric acid (as source of hydrogen bromide). PBr<sub>3</sub> or red phosphorous and bromine (to generate PBr<sub>3</sub> in the reaction mixture) are also used for bromination. Alcohol and PBr<sub>3</sub> mixture is refluxed on a water bath, and then halogenoalkane is distilled over.



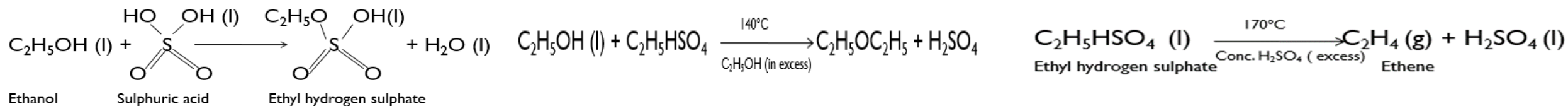
Iodination is carried out by red phosphorous and iodine (as a source of hydrogen iodide). Conc. H<sub>2</sub>SO<sub>4</sub> can not be used because it oxidizes HI to I<sub>2</sub>. Phosphorous (III) iodide (by the addition of iodine to red phosphorous) is also used for iodination. Alcohol and PI<sub>3</sub> mixture is refluxed on a water bath, and then halogenoalkane is distilled over.



# Derivatives of Alcohols

## Dehydration

A primary alcohol reacts with cold concentrated sulphuric acid to form an alkyl hydrogen sulphate. With excess alcohol if reaction mixture is warmed to 140°C, dehydration results an ether. With excess conc. H<sub>2</sub>SO<sub>4</sub> and 170°C; elimination of water results an alkene



The gases produced are passed through sodium hydroxide solution to remove the carbon dioxide and sulphur dioxide produced from side reactions. The ethene is collected over water.

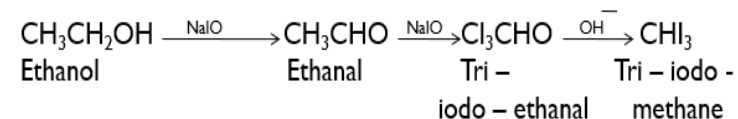
Al<sub>2</sub>O<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> at 300°C also act as a dehydrating agents. Phosphoric(V) acid tends to be used in place of sulphuric acid because it is safer and produces a less messy reaction. Phosphoric(V) acid isn't a strong oxidizing agent.

## Oxidation

Primary alcohols are oxidized to aldehydes, can be further oxidized to carboxylic acids. Secondary alcohols are oxidized to ketones. Tertiary alcohols are resistant to oxidation. A powerful acidic oxidizing agent converts them into a mixture of carboxylic acids. A number of oxidizing agents can be used. Acidified Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution at room temperature is used as oxidizing agents. The dichromate solution turns from the orange color of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> (aq.) to the green color of Cr<sup>3+</sup>. Acidified potassium manganate (VII) solution is too powerful oxidizing agent, it oxidizes primary alcohol to acids and secondary alcohol to ketones.

## Haloform

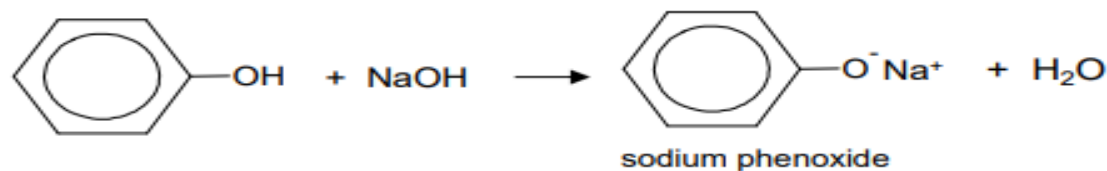
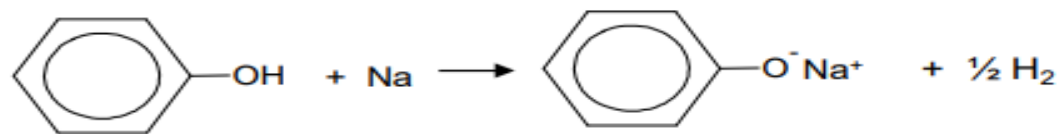
All secondary alcohols and one primary alcohol, ethanol give a pale yellow precipitate or crystal of haloform with characteristic smell when reacts with halogen and alkali (except fluorine). This means, alcohols of formula CH<sub>3</sub>CH(OH)R are oxidized by sodium iodate (I) to CH<sub>3</sub>COR and therefore give a (+) ve iodoform test.





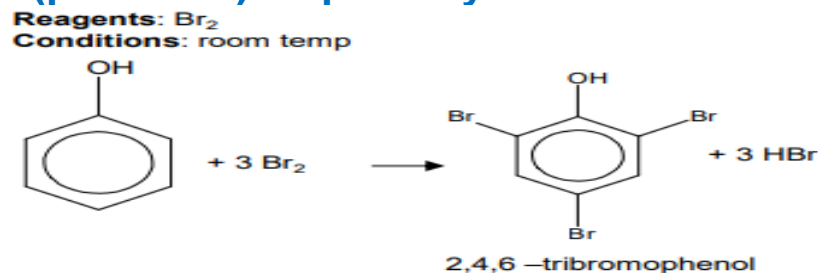
# Derivatives of Phenols

Phenols are very weakly acidic. They are weaker acids than carboxylic acids. Like carboxylic acids, phenols react with sodium metal and sodium hydroxide.



The sodium phenoxide compound is more soluble than the original phenol. So the solid phenol dissolves on addition of NaOH

Phenol does not need a  $\text{FeBr}_3$  catalyst like benzene in substitution reaction with bromine, and undergoes multiple substitution whereas benzene will only add one Br. The product in this reaction is a white solid. In phenol the lone pair of electrons on the oxygen (p-orbital) is partially delocalized into the ring. The electron density increases and the  $\text{Br}_2$  is more polarized.



In comparison with benzene, phenol does not need concentrated nitric acid or the concentrated sulphuric acid catalyst in the substitution reaction with nitric acid.

With 4M  $\text{HNO}_3$  single substitution occurs (in comparison to the conc.  $\text{HNO}_3$  needed for benzene). Reagent: 4M  $\text{HNO}_3$   
Conditions: room temp.

