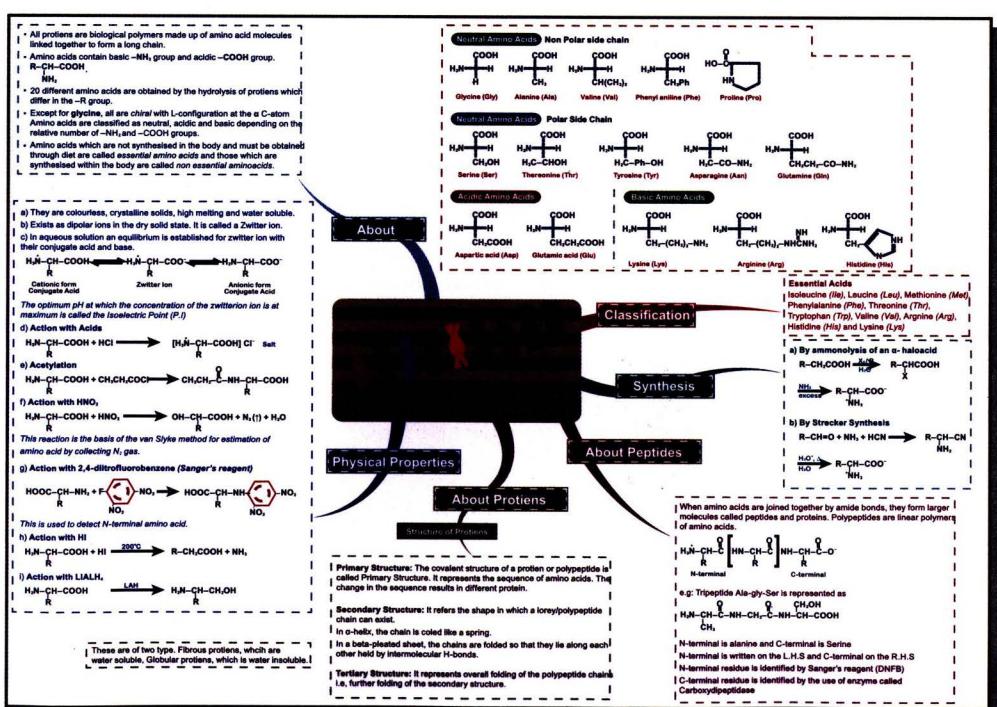


# What is a Concept Map?

A Concept map is a colourful, visual form of representing key concepts covered in a chapter. It can be used as an effective overview, learning and revision tool.

At its heart is a central topic of the chapter. This is then explored by means of branches representing main ideas, which all connect to this central idea.

Concept maps are metacognitive tools that give students awareness towards the process of learning and allow the representation of knowledge structures in thematic fields.



# Why use a Concept Map?

## Students:

Brain is the key to effective learning for a student and more effectively the student uses it, the more successful he/she will be. If the brain of the student is stimulated with correct thinking and effective learning tools, excellent results can be obtained. **Understanding lists, lines, sequences, letters and numbers** is the work of the **LEFT BRAIN**. While **interpreting colour, images, rhythms and spatial awareness** is the work of the **RIGHT BRAIN**. Through a Concept Map both Right & Left parts of the brain would be put into use.

As a learning strategy, concept mapping stimulate learners' **commitment and interest towards the concepts**, which is very important for better learning. Students can use it as tool for effective revision of not just the current class chapters but also the topics covered previously.

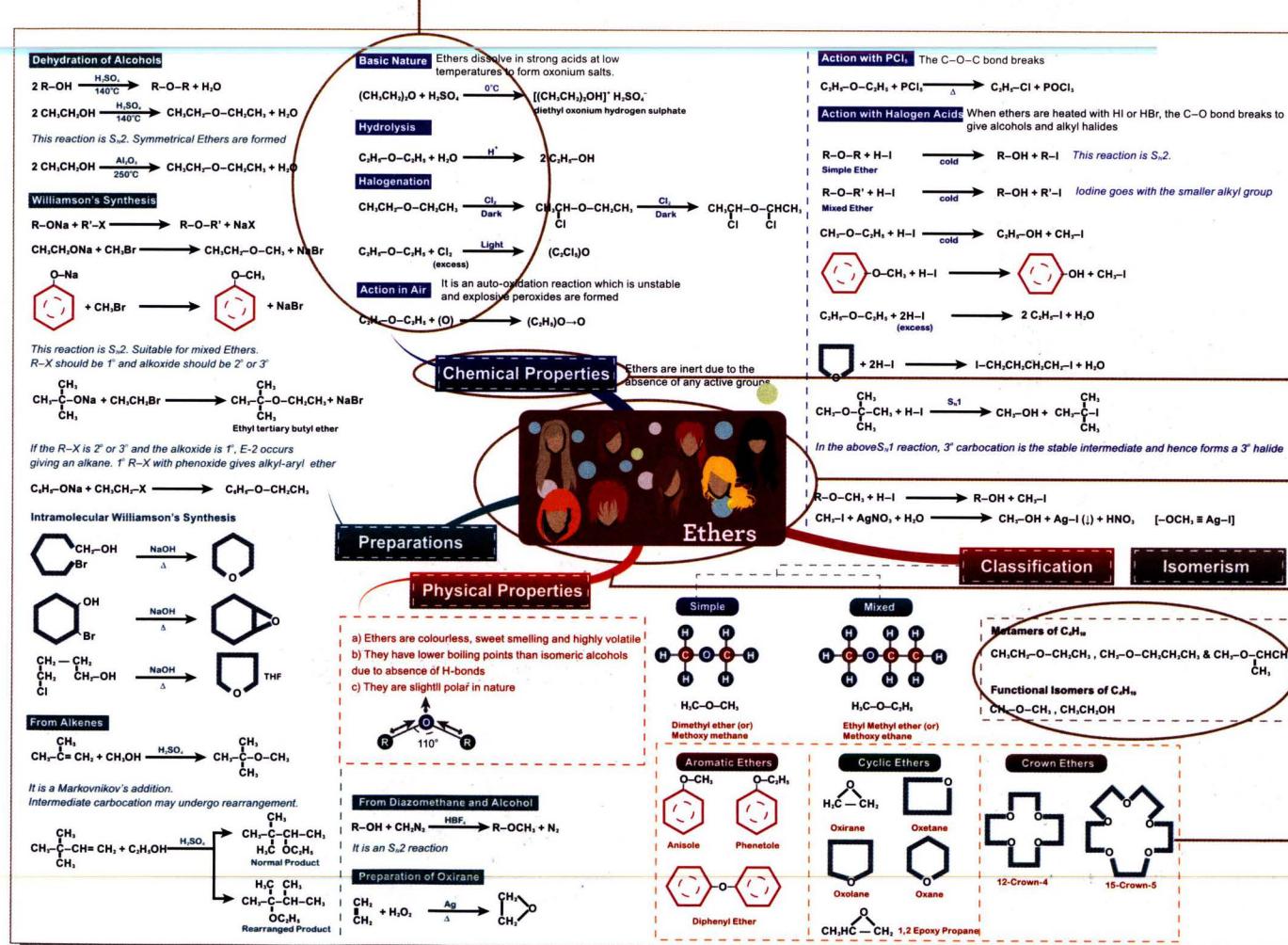
## Teachers:

As a teaching support, concept maps are also helpful, as they permit the establishment of networks of concepts that originate from a central concept in a coherent, structured and integrated manner, **guiding the sequence of teaching**. Concept maps can also be used by teachers for **curriculum planning**. Using this instrument means giving a new meaning to education, as well as a new meaning to the concepts of teaching, learning and assessment of learning.



Each main topic has been transformed into a Map. For example, given below is the map for ETHERS which includes an introduction to the map.

If you take the above branch as an example, we can understand that  
ETHERS has a CHEMICAL PROPERTIES - Basic Nature, Hydrolysis,  
Halogenation, Action in Air



### Important Points

- The sub-concepts and the points under them are colour coded, i.e. each branch is identified with its colour.
- Based on the colour you can identify the sub-concept under which the point will come.
- Refer to the text book and identify the first branch to start with and revise one branch at a time.

Spend some time in understanding the Maps, once you get a hang of them they are a wonderful tool to get ahead in class.

**The Sub-Concept**

**The Central concept of the chapter**

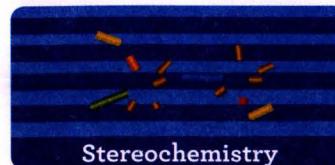
**Branches – Each branch leads to a sub-concept of the chapter**

**These are the important points under each sub-concept & these could be further branched out**

**Image –Image is a mnemonic which will help you remember the concept**



# A to Z of CHEMISTRY



## STEREOCHEMISTRY

<b>Topic</b>	<b>Page no.</b>
Concept map	01, 02
Questions	35
Solutions	41

## ALKANES (PARAFFINS) $C_nH_{2n+2}$

<b>Topic</b>	<b>Page no.</b>
Concept map	03, 04
Questions	35
Solutions	41

## ALKENES (OLEFINS)

<b>Topic</b>	<b>Page no.</b>
Concept map	05, 06
Questions	35
Solutions	41

## ALKYNES

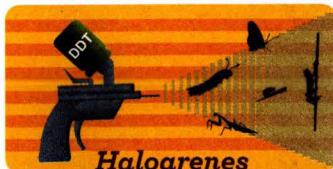
<b>Topic</b>	<b>Page no.</b>
Concept map	07, 08
Questions	35
Solutions	41

## ARENES

<b>Topic</b>	<b>Page no.</b>
Concept map	09, 10
Questions	35
Solutions	41

## ALKYL HALIDES

<b>Topic</b>	<b>Page no.</b>
Concept map	11, 12
Questions	35
Solutions	41



## HALO ARENES

<b>Topic</b>	<b>Page no.</b>
Concept map	13, 14
Questions	35
Solutions	41



## ALCOHOLS

<b>Topic</b>	<b>Page no.</b>
Concept map	15, 16
Questions	35
Solutions	41



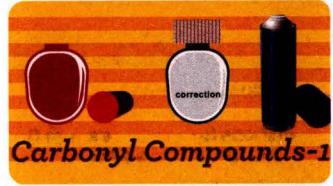
## PHENOLS

<b>Topic</b>	<b>Page no.</b>
Concept map	17, 18
Questions	35
Solutions	41



## ETHERS

<b>Topic</b>	<b>Page no.</b>
Concept map	19, 20
Questions	35
Solutions	41



## CARBONYL COMPOUNDS- I&II

<b>Topic</b>	<b>Page no.</b>
Concept map	21, 22
Questions	35
Solutions	41



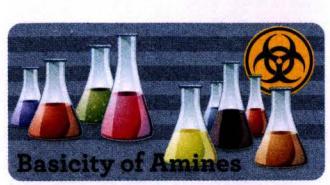
## CARBOXYLIC ACIDS

<b>Topic</b>	<b>Page no.</b>
Concept map	23, 24
Questions	35
Solutions	41



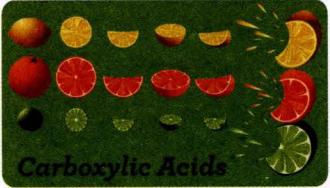
## AMINES

<b>Topic</b>	<b>Page no.</b>
Concept map	26, 27
Questions	35
Solutions	41



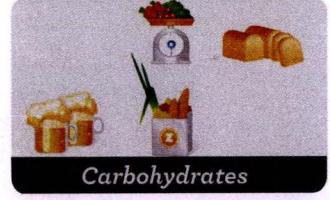
## BASICITY OF AMINES

<b>Topic</b>	<b>Page no.</b>
Concept map	28
Questions	35
Solutions	41



## ACIDITY OF CARBOXYLIC ACIDS

<b>Topic</b>	<b>Page no.</b>
Concept map	29
Questions	35
Solutions	41



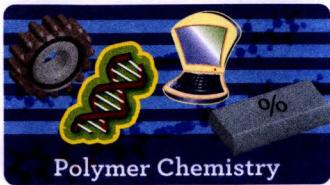
## CARBOHYDRATES

<b>Topic</b>	<b>Page no.</b>
Concept map	05
Questions	35
Solutions	41



## AMINO ACIDS AND PEPTIDES

<b>Topic</b>	<b>Page no.</b>
Concept map	05
Questions	35
Solutions	41



## POLYMER CHEMISTRY

<b>Topic</b>	<b>Page no.</b>
Concept map	05
Questions	35
Solutions	41



**About**

The chemistry of molecules, which deals with the structure in 3 dimensions is called stereochemistry.

The isomers that are different from each other only in the way the atoms are oriented in space are called stereoisomers.

Starch and cellulose are stereoisomers having same Molecular Formula i.e. ( $C_6H_{10}O_5$ ).

They differ only 3 dimensional arrangement of atoms, because of which their chemistry changes.

One axial, one equatorial bond ( $\alpha$ -1,4'-glycoside bond)

Two equatorial bonds ( $\beta$ -1,4'-glycoside bond)

**Calculation of no. of Stereoisomers**

**Case I:** If the molecule is unsymmetrical and contains n chiral carbon atoms, then Number of optical isomers (d&l)= $a=2^n$   
Number of meso forms = m = 0  
Total number of stereoisomers =  $a+m = 2^n+0 = 2^n$   
eg:  $CH_3^*CHClCHCICOOH$  Number of stereoisomers =  $2^2 = 4$

**Case II:** If the molecule is symmetrical and contain even number chiral carbon atoms, then  $a=2^{(n-1)}$ ;  $m=2^{(n-2)}$   
Total number of stereoisomers =  $a+m=2^{(n-1)}+2^{(n-2)}$   
eg: HOOC- $(CHOH)_3-COOH$ ; Glutaric acid, n = 3.  
 $a=2^{(3-1)}=2^{(3/2-1/2)}=2^1=2$   
 $m=2^{(3/2-1/2)}=2^1=2$   
Total number of stereoisomers =  $a+m=2+2=4$

**Case III:** If the molecule is symmetrical and contains odd number of chiral carbon atoms, then  $a=2^{(n-1)} - 2^{(n/2-1/2)}$ ;  $m=2^{(n/2-1/2)}$   
Total number of stereoisomers =  $a+m=2^{(n-1)}$   
eg: HOOC-(CHOH)<sub>3</sub>-COOH; Tartaric acid ; n= 2  
 $a=2^{(2-1)}=2^{(2/2-1)}=2^0=1$   
Total number of stereoisomers =  $a+m = 2+1= 3$

**Entantiomers**

- A particular 3-dimensional arrangement is called configuration and the stereoisomers differ in configuration.
- Stereoisomers have identical IUPAC names except for a prefix and they have same functional groups

**Chiral and Achiral molecules- Enantiomers.**

- A molecule that is not superimposable on its mirror image is called Chiral.
- A molecule that is superimposable on its mirror image is called Achiral.

**Diastereomers**

**Stereoisomers which are not mirror images are called Diastereomers.**

In the compound  $CH_3-CH-CH-CH_3$  there are two different stereogenic centres, giving to 4 stereo isomers.

$CH_3$	$CH_3$	$CH_3$	$CH_3$
H	Br	Br	H
H	Cl	Cl	H
$CH_3$	$CH_3$	$CH_3$	$CH_3$

I                   II                   III                   IV

First enantiomeric pair                   Second enantiomeric pair

I and III are stereoisomers but not mirror images such are called Diastereomers similarly I and IV, II and III, II and IV are Diastereomers.

**Case I:** when number of double bonds (n) is even, then Total number of geometrical isomers =  $2^{(n-1)} + 2^{(n/2-1)}$   
eg:  $CH_3-CH=CH-CH=CH-CH_3$   
Since n=2, Total geometrical isomers =  $2^{(2-1)} + 2^{(2/2-1)} = 3$

**Case II:** When number of double bonds (n) is odd, then Total number of geometrical isomers =  $2^{(n-1)} = 2^{([(n+1)/2]-1)}$   
eg:  $Br-CH=CH-CH=CH-CH=CH-Br$ ; n=3  
Total number geometrical isomers =  $2^{(3-1)}+2^{2-1}=2^2+2^1=6$

**Case III:** If a polyene has same terminal groups, then

**D-Glucose**                  **D-Fructose**

**4-Stereogenic Centres**                  **3-Stereogenic Centres**

**No Stereogenic centre**                  **1-Stereogenic centre.**  
C-atom is bonded to identical alkyl groups that happen to be part of ring.

**A pair of Enantiomers of Lactic acid. \* = Stereogenic centre.**

**Successgyan.in**



A compound that rotates the plane of polarised light is called **optically active**

If the rotation is clockwise, the compound is called **dextrorotatory** and is labelled as d or (+).

If the rotation is anticlockwise, the compound is called **levorotatory** and is labelled as l or (-).

Chiral molecules are optically active and achiral molecules are optically inactive.

d and l isomers are enantiomers and hence the phenomenon is called **enantiomerism** or **optical isomerism**.

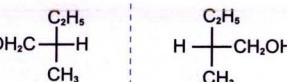
## Optical Activity

### Specific Rotation:

The optical activity of a compound is expressed in terms of specific rotation ( $\alpha$ ), which is a constant.

$$[\alpha]_d^l = \frac{\text{observed rotation (degrees)}}{\text{length(dm)} \times \text{density(g/mL)}}$$

Two enantiomers rotate plane polarised light to an equal extent but in the opposite direction.



d and l isomers of 2-methyl-1-butanol.

(+) or d-isomer  $[\alpha] = +5.90^\circ$

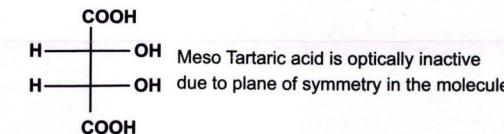
(-) or l-isomer  $[\alpha] = -5.90^\circ$

$$\text{optical purity or enantiomeric excess: } = \frac{\text{observed optical rotation}}{\text{optical rotation of pure sample}} \times 100$$

An equal amount of two enantiomers is called a **racemic mixture** or a **racemate**, which is labelled as dl or ( $\pm$ ). Racemic mixture is optically inactive due to external compensation.

### Meso Compounds:

Compounds containing two or more chiral centres and are optically inactive are called **Meso Compounds**.



In meso compounds, the loss of optical activity is due to internal compensation.

The necessary conditions for optical activity is absence of symmetry in the molecule, due to which the enantiomers are non superimposable (chiral)

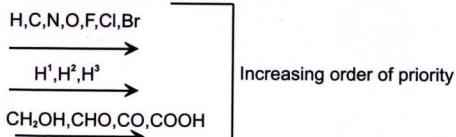
## Racemic Mixture

### The R,S System

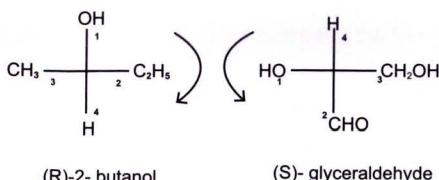
## Labelling Stereoisomers

The four groups present on the chiral centre are assigned a sequence of priority according CIP rules.

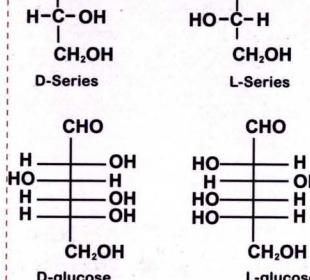
The atom with the highest atomic number gets the highest priority(1) and the one with the lowest atomic number gets the least priority(4)



In a Fisher projection, if the group of the lowest priority(4) is on vertical line and sequence of 1,2,3 groups is clockwise, then it is called 'R', but if it is anticlockwise it is called 'S'.

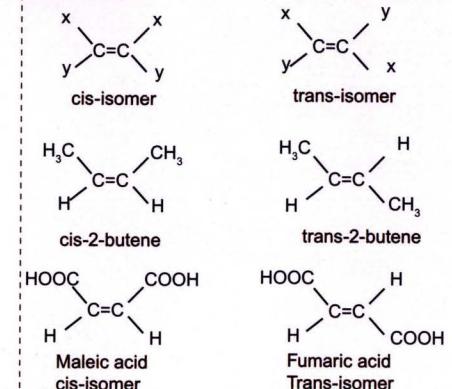


**D,L system:** All sugars whose Fisher projections contains the, -OH group on the right hand side at chiral carbon atom adjacent to the terminal -CH<sub>2</sub>OH group, belong to D-Series and the L-Series contains the -OH on the left hand side.

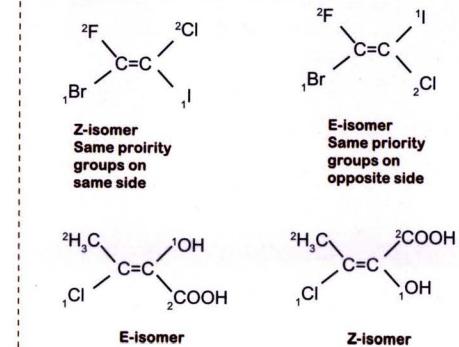


D-glucose and all other naturally occurring sugars are D-sugars.

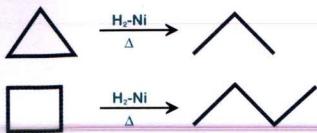
### cis-trans



### E-Z System



## Reduction of Cycloalkanes

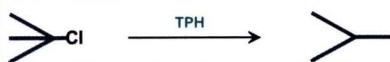


## Reducing of Alkyl Halides



### Reducing Agents:

- a) Zn + dil. HCl
- b) Zn +  $\text{CH}_3\text{COOH}$
- c) Zn + NaOH
- d) Zn + Cu ( $\text{C}_2\text{H}_5\text{OH}$ )
- e) LAH ( $1^\circ$  &  $2^\circ$ )
- f)  $\text{NaBH}_4$  ( $2^\circ$  &  $3^\circ$ )
- g)  $\text{Ph}_3\text{SnH}$  ( $1^\circ$ ,  $2^\circ$  &  $3^\circ$ )
- Triphenyl Tin Hydride
- (TPH)

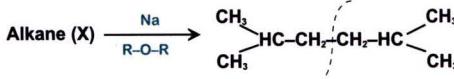


## Wurtz Reaction



A new C-C  $\sigma$  bond is formed and hence this reaction is useful for ascent of series

Symmetrical Alkanes are prepared



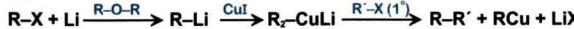
Here, X would be isobutyl chloride  
If Zn is used, it is called Frankland reaction



## Intramolecular Wurtz Reaction



## Corey House Synthesis

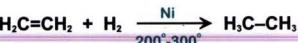


Unsymmetrical Alkanes are also prepared. R-X can be  $1^\circ$ ,  $2^\circ$  or  $3^\circ$  but R'-X should be  $1^\circ$  or  $2^\circ$ . R-CuLi is called Gilman reagent.

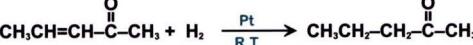


## Catalytic Hydrogenation of Unsaturated Hydrocarbon

### Sabatier-Senderens Reduction



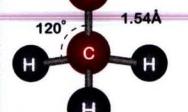
Raney Nickel is an effective catalyst here  
If Pd or Pt are used, the reaction takes place at Room Temperature (R.T.)



C-C Bond Energy = 368 KJ/mol

C-H Bond Energy = 410 KJ/mol

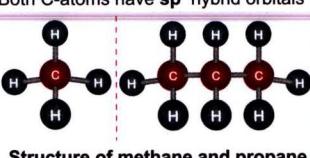
Both C-atoms have  $sp^3$  hybrid orbitals



1.112 Å  
1.54 Å  
120°



Structure of Ethane



Structure of methane and propane

In constitutional isomerism, components of the carbon skeleton are distinctly re-ordered to create different structures.

$\text{C}_2\text{H}_{10} = 2$

$\text{C}_2\text{H}_{12} = 3$

$\text{C}_2\text{H}_{14} = 5$

$\text{C}_2\text{H}_{16} = 9$

$\text{C}_2\text{H}_{18} = 18$

$\text{C}_2\text{H}_{20} = 35$

$\text{C}_{10}\text{H}_{22} = 75$

e.g: Isomers of Pentane







Neopentane

## Preparation

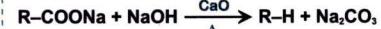
### DANGER

### HIGHLY INFLAMMABLE

## Alkanes (Paraffins) $\text{C}_n\text{H}_{2n+2}$

## Preparation

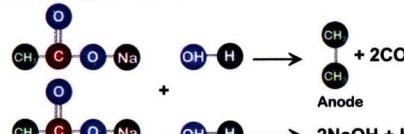
### Decarboxylation of salts of Carboxylic Acids



$3\text{NaOH} + 1\text{CaO} = \text{Soda Lime}$   
(CaO is used for the fusion of the mixture)



### Kolbe's Electrosynthesis

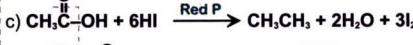
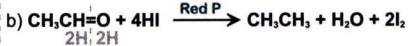


At Anode:  $2\text{CH}_3\text{COO}^- \rightarrow \text{CH}_3-\text{CH}_2 + \text{CO}_2 + 2e^-$  (Oxidation)

At Cathode:



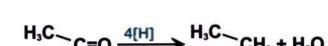
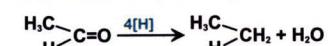
### Reduction using HI / Red Phosphorous



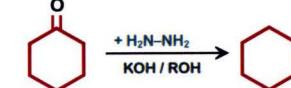
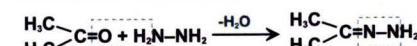
Red Phosphorous is used to remove  $\text{I}_2$   $2\text{P} + 3\text{I}_2 \rightarrow 2\text{PI}_2$

### Clemmensen Reduction: ( $\text{C=O} \rightarrow \text{CH}_2$ )

In presence of  $\text{Hg-Zn} + \text{HCl}$



### Wolff - Kishner Reduction: ( $\text{C=O} \rightarrow \text{CH}_2$ )

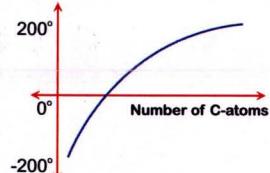


a) Amongst alkanes, C<sub>1</sub> to C<sub>4</sub> are gases; C<sub>5</sub> to C<sub>17</sub> are liquids; C<sub>18</sub> and above are solids.

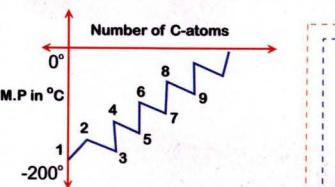
- Natural Gas has 60% - 80% of methane
- Gasoline has C<sub>5</sub>H<sub>12</sub> to C<sub>12</sub>H<sub>26</sub>
- Kerosene has C<sub>12</sub>H<sub>26</sub> to C<sub>16</sub>H<sub>34</sub>
- Diesel Oil has C<sub>15</sub>H<sub>32</sub> to C<sub>18</sub>H<sub>38</sub>

b) Boiling point increases with molecular mass. Greater the surface area more the boiling point. As branching increases, the Boiling point decreases in the isomers.

e.g: n-pentane > iso pentane > neo pentane  
Diesel Oil > Kerosene > Gasoline



c) Alkanes with even number of C-atoms are symmetrical and pack more compactly. Hence they possess higher melting point than the alkanes with odd number of carbon atoms.

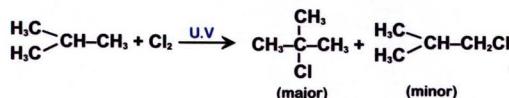
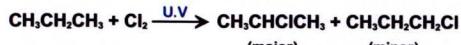
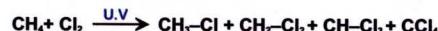


**Saturated Hydrocarbons:** C-C and C-H bonds are non polarised and less reactive.

Free radicals are formed due to homolytic bond fission.  
They undergo substitution through free radicals.

## Substitution Reactions

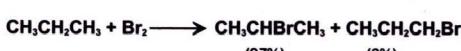
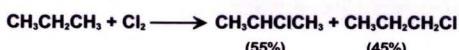
a) **Halogenation:** Substitution of 3° > 2° > 1° H-atoms by halogens in the order F<sub>2</sub> > Cl<sub>2</sub> > Br<sub>2</sub> > I<sub>2</sub>. Free radicals are the intermediates.



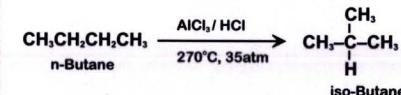
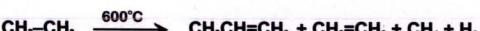
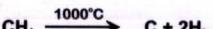
Abstraction of H atoms → 3° > 2° > 1°      Stability of Free Radicals → 3° > 2° > 1°

a) **Reactivity and Selectivity of alkane halogenation:** Reactivity and Selectivity are inversely related according to the Hammond-Leffler postulate.

Reactivity: Cl<sub>2</sub> > Br<sub>2</sub>    Selectivity: Cl<sub>2</sub> < Br<sub>2</sub>

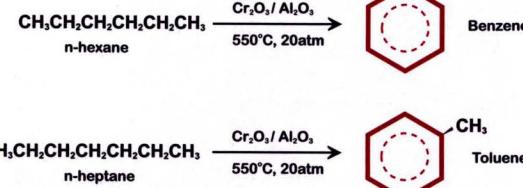


Decomposition of Alkanes into smaller units by heat



## Pyrolysis

## Isomerisation

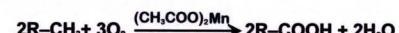
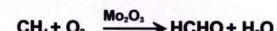
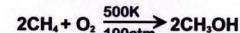


It involves cyclisation and dehydrogenation

## Aromatisation

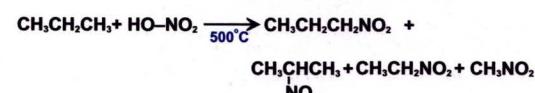
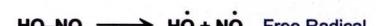
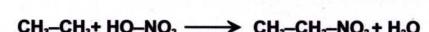
(Catalytic Reforming)

b) **Controlled Oxidation**



## Oxidation Reactions

b) **Nitration:** Substitution of H-atoms by NO<sub>2</sub> group.



It is called vapour phase nitration

c) **Sulphonation:** Substitution of H-atoms by SO<sub>3</sub>H group.



Fuming H<sub>2</sub>SO<sub>4</sub> + SO<sub>3</sub> is the Sulphonating agent

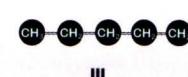
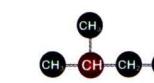
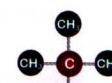
a) **Combustion**



Hence alkanes are used as fuel

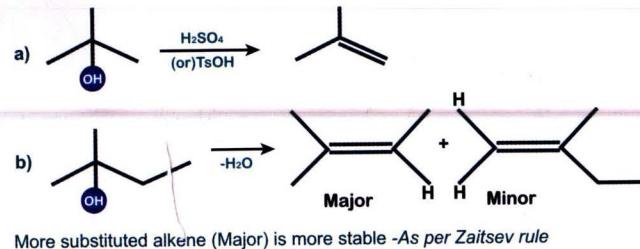
More the number of C-atoms, greater the heat of combustion.

Heat of Combustion is inversely proportional to the surface area.

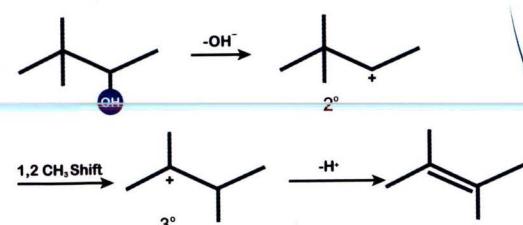


Heat of combustion: I > II > III

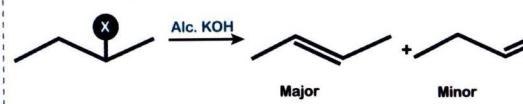
## Dehydration of Alcohols (- H<sub>2</sub>O)



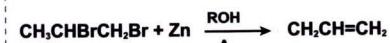
Carbocation is the intermediate. Rearrangement may take place



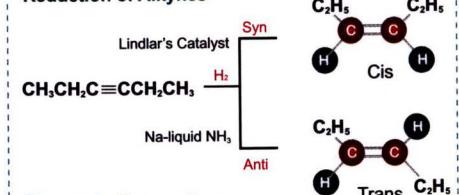
## Dehydrohalogenation of R - X (-H & -X)



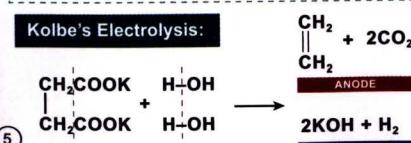
## Dehalogenation (-X)



## Reduction of Alkynes

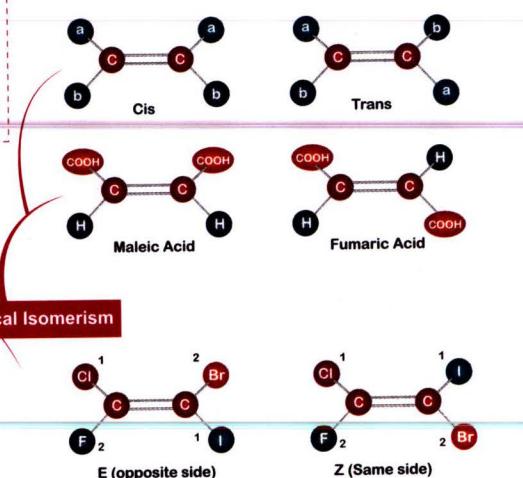
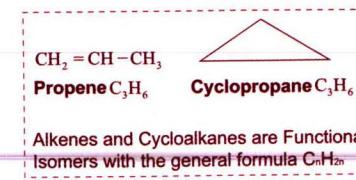
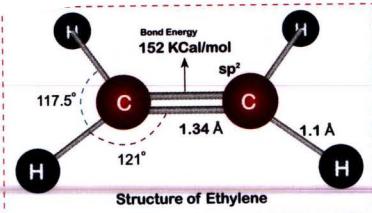


## Kolbe's Electrolysis:



## Physical Properties

- a) Cis isomers have higher boiling points than Trans isomers
- b) Alkenes have higher boiling points than alkanes
- c) Alkenes are less dense as compared to alkanes
- d) C<sub>2</sub> to C<sub>4</sub> in the alkene list are gases  
 C<sub>5</sub> to C<sub>16</sub> in the alkene list are liquids



## Preparations

## Reactivity

### 1. Heats of hydrogenation

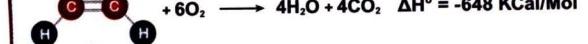


Lower the  $\Delta H^\circ$  greater the stability.  
 Greater the alkyl substitution of a double bond, lower the  $\Delta H^\circ$ .

$\Delta H^\circ$  of its cis isomer is greater than its trans isomer  
 hence its cis isomer is less stable than its trans isomer.

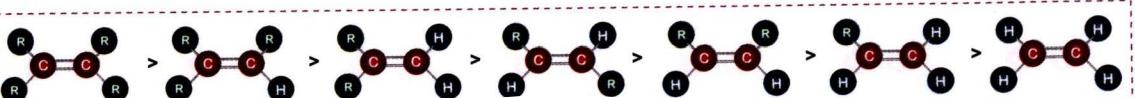
### 2. Heat of Combustion:

**Lower the heat of combustion greater the stability.** The Cis isomer is less stable due to more heat of combustion than its trans isomer.

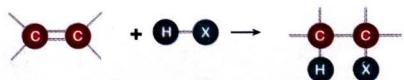


## Stability Chart

Greater the number of attached alkyl groups, the greater is the stability of alkene

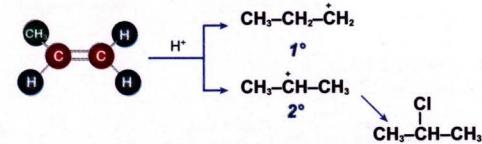


## Hydrohalogenation (+HX) (X = Cl, Br, I)



C - C  $\pi$  & H - X  $\sigma$  are broken. C - X  $\sigma$  & C - H  $\sigma$  are formed. Carbocation is the intermediate.

**Markovnikov's Rule:** E<sup>+</sup> adds on less substituted C-atom to form more stable carbocation

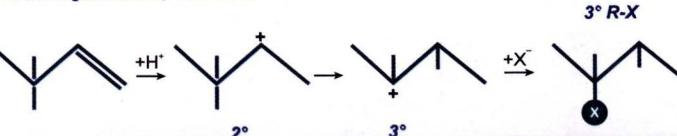


**Stability of carbocations** 3° > 2° > 1°

Undergo Electrophilic Addition

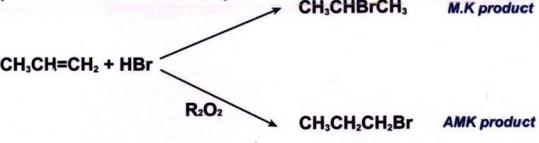
Ozonolysis & Polymerisation

Rearrangement may also occur



**Anti Markovnikov's rule:** It occurs in the presence of organic peroxides

(Kharasch Peroxide Effect)



It is a chain and free radical addition.  
Not possible with HF, HCl, HI.

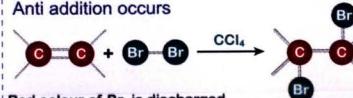
## Addition Reactions

Addition of Halogens & H<sub>2</sub>O  
Hydroxylation (Glycol formation)

## Addition of Halogens (Cl<sub>2</sub> & Br<sub>2</sub>) - Vicinal dihalides are formed.

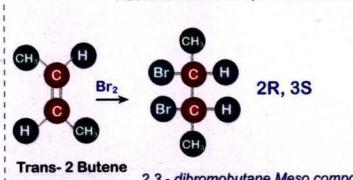
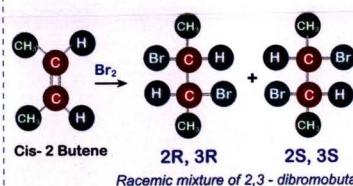
Bridged halonium ion is the intermediate.

Anti addition occurs

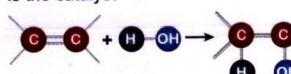


Red colour of Br<sub>2</sub> is discharged.  
Test for unsaturation.

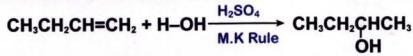
## Stereospecific Reaction



**Addition of H<sub>2</sub>O:** Alcohols are formed, H<sub>2</sub>SO<sub>4</sub> is the catalyst

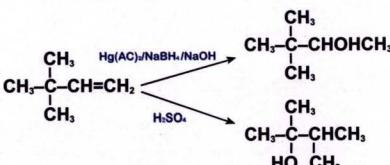


Carbocation is the intermediate.  
Markovnikov's rule is followed



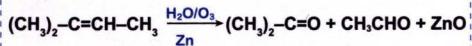
Rearrangement may also occur

In presence of Hg(CH<sub>3</sub>COO)<sub>2</sub> and NaBH<sub>4</sub>/NaOH (Oxy mercuration - demercuration), no rearrangement (no carbocation) occurs. M.K product alone is formed

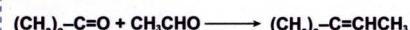


In presence of oxidising agents, aldehydes are oxidised to Carboxylic Acids

In presence of reducing agents aldehydes are reduced to Alcohols

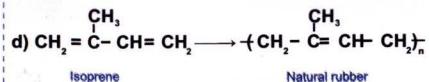
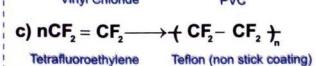
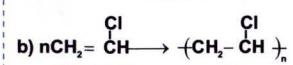


Break at the double bond add O-atom on either side to get the products



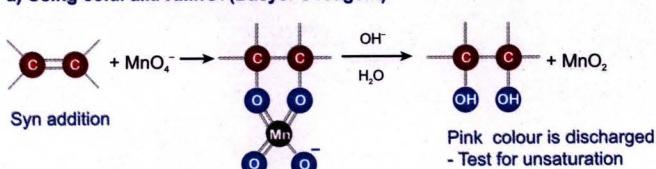
Remove the adjacent O-atoms and place a double bond to get the alkene

## Polymerisation:



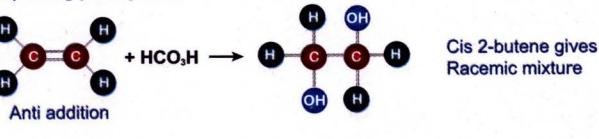
Alkenes are converted to glycols (1,2-diols)

a) Using cold. alk. KMnO<sub>4</sub> (Baeyer's reagent)

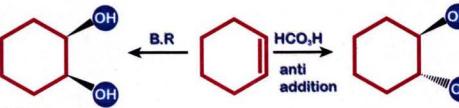


Pink colour is discharged  
- Test for unsaturation

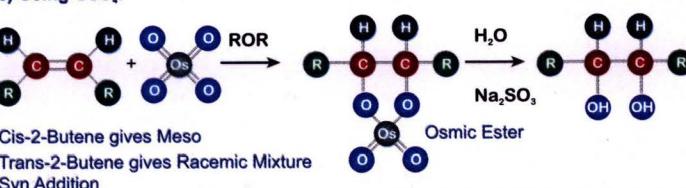
b) Using peroxy acid:



Cis 2-butene gives  
Racemic mixture



c) Using OsO<sub>4</sub>:

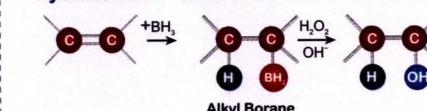


Cis-2-Butene gives Meso

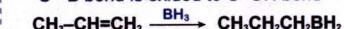
Trans-2-Butene gives Racemic Mixture

Syn Addition

**Hydroboration - Oxidation:** An alcohol is formed

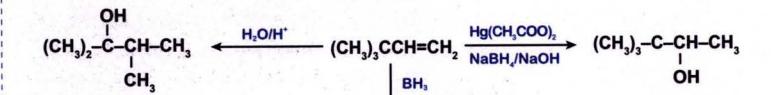


C - B bond is oxidized to C - OH bond



No rearrangement, syn addition.

Similar to A.M.K addition of H, OH to an alkene



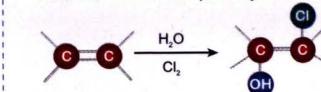
Rearranged Product

Markovnikov Product

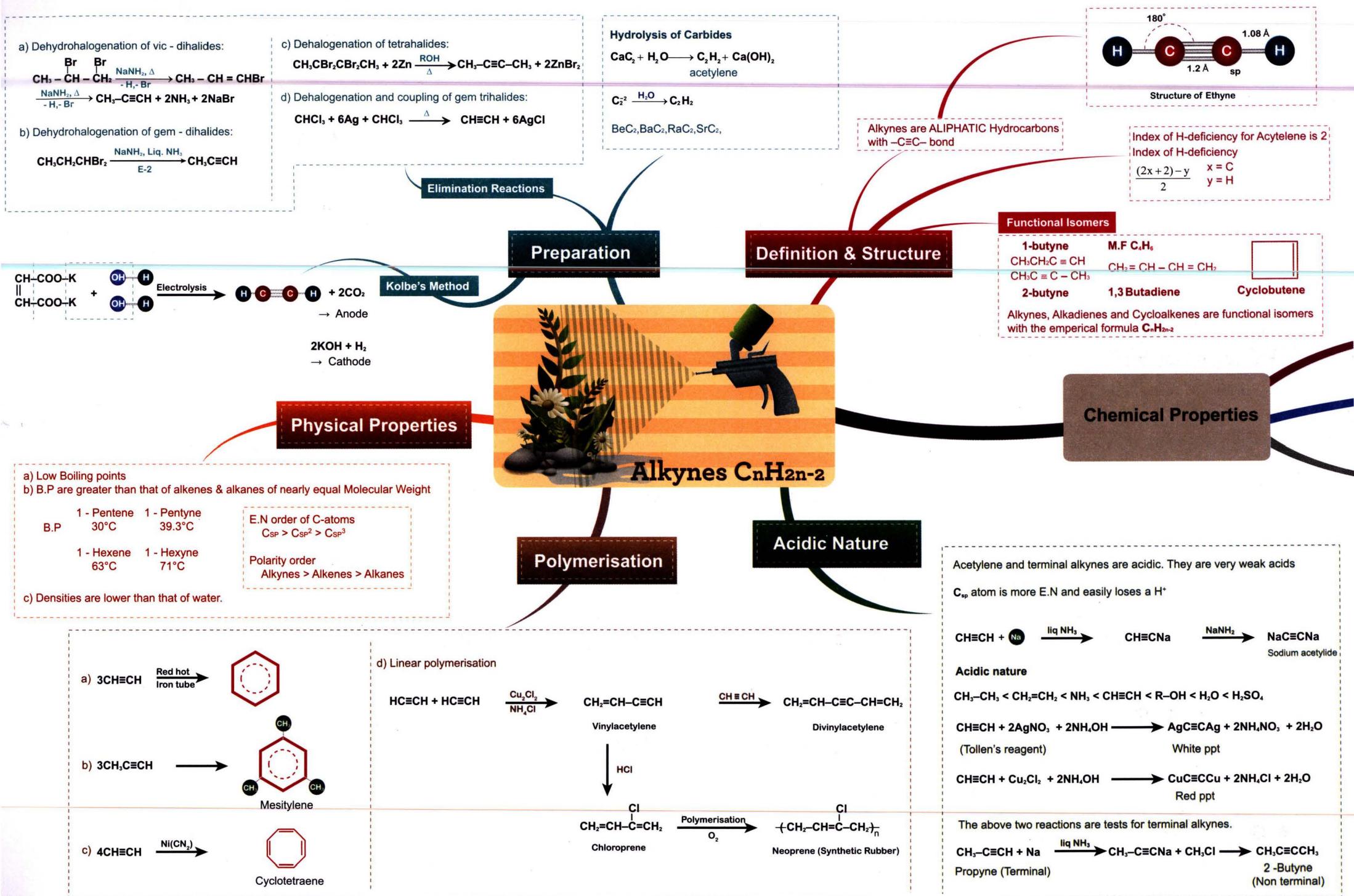


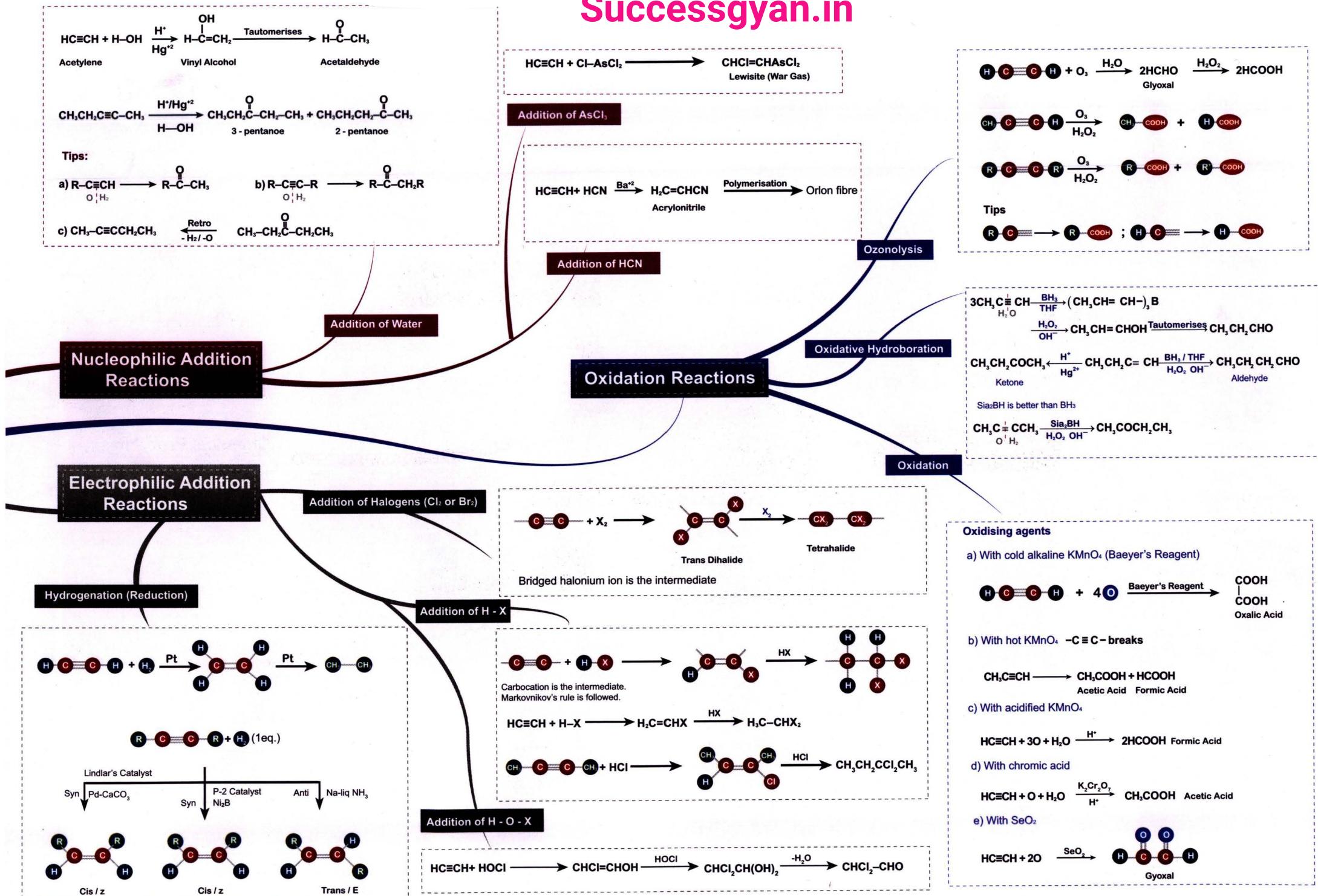
Anti-Markovnikov Product

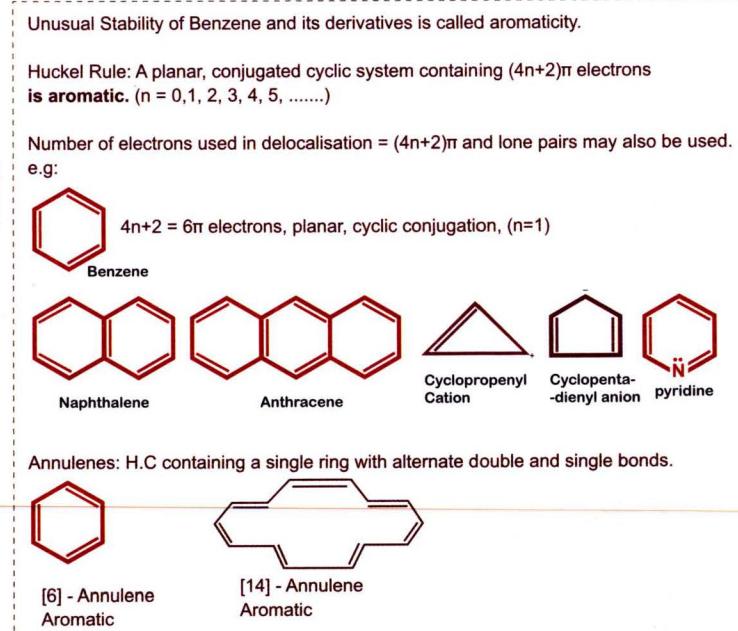
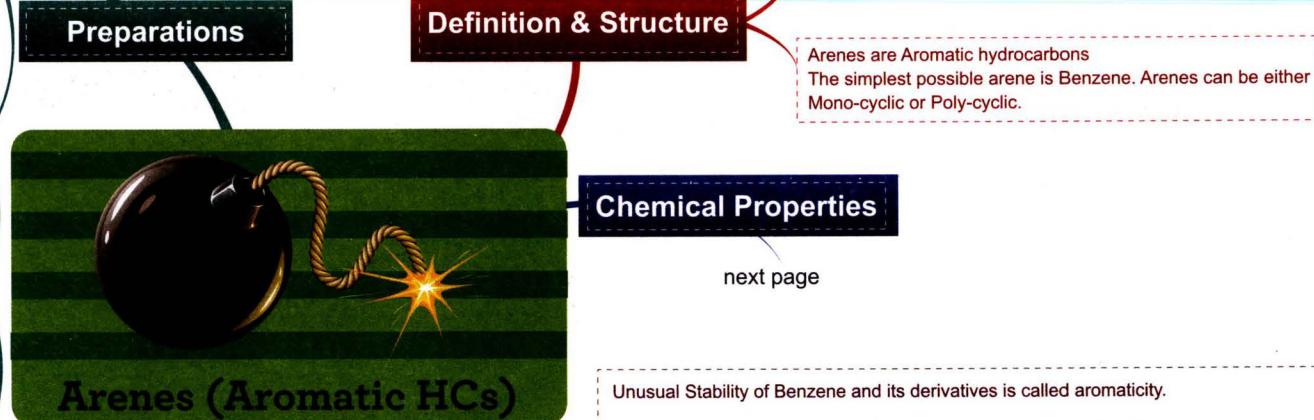
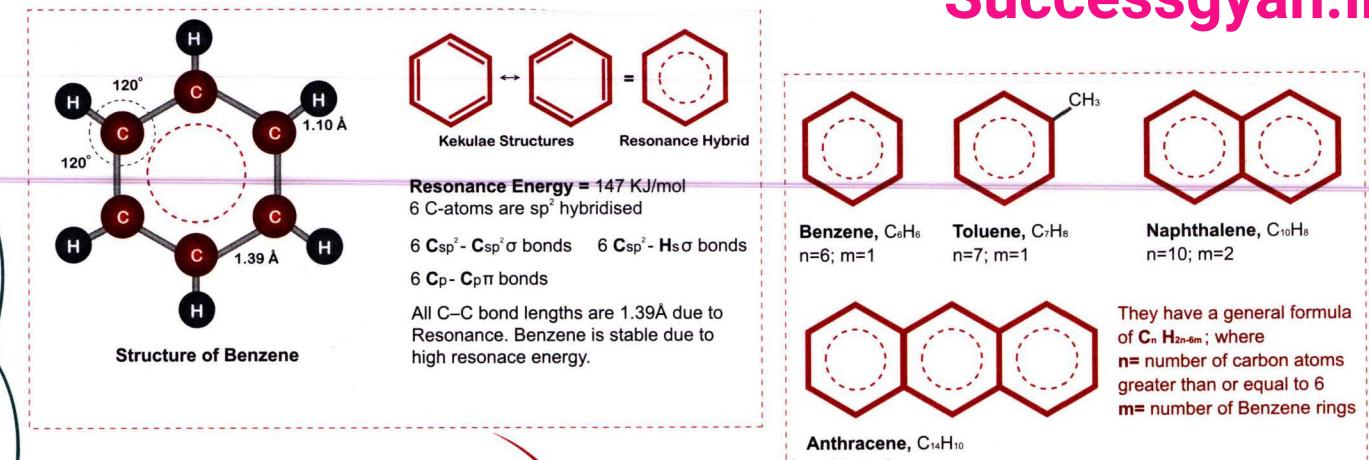
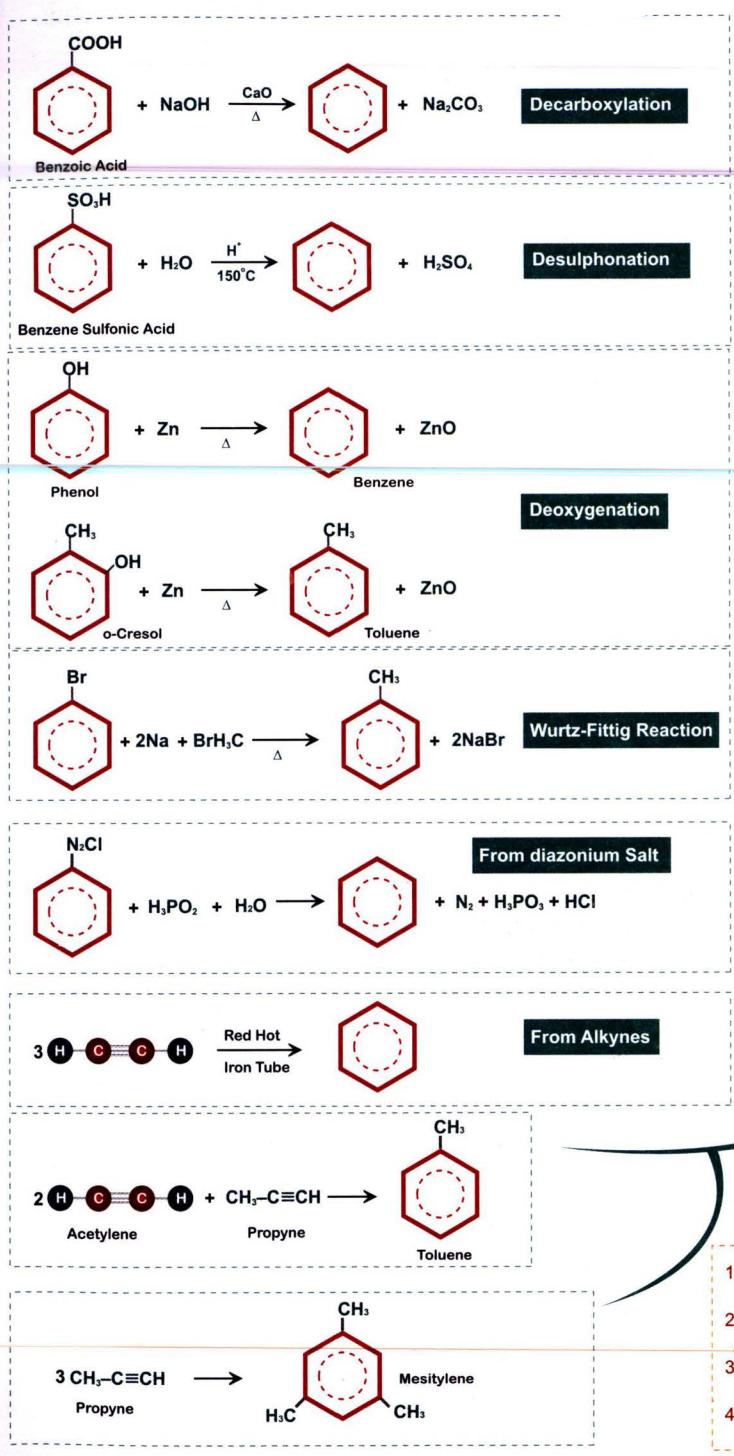
**Addition of X & OH (Halohydrin formation)**



Bridged halonium ion is the intermediate. Anti addition.

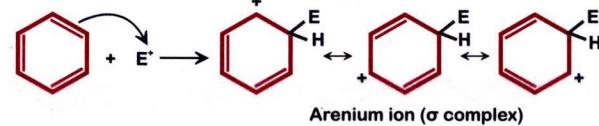




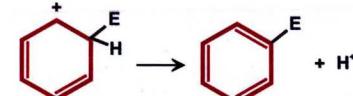


### Step I: Formation of the electrophile (E<sup>+</sup>)

### Step II: Formation of the resonance stabilised Arenium ion ( $\sigma$ complex)



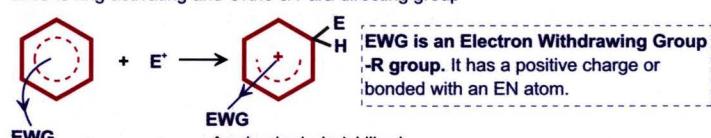
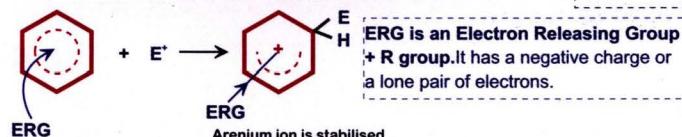
### Step III: Loss of H<sup>+</sup>



### Chemical Properties

### Effect of Substituents

#### Effect of substituents on reactivity and orientation



#### Classification of substituents

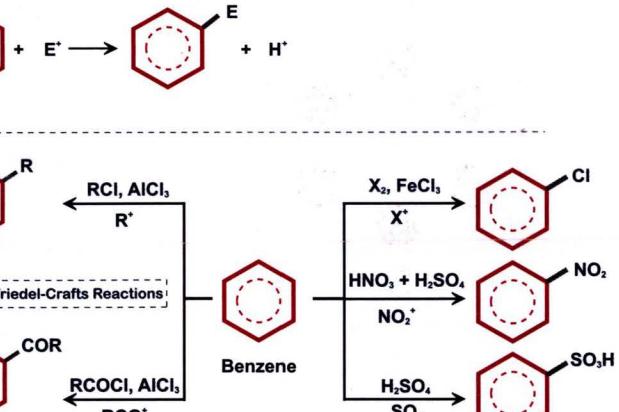
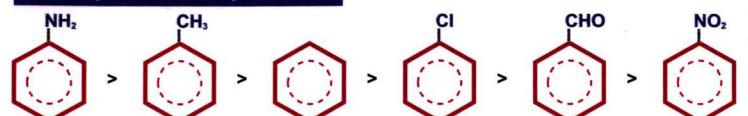
##### I. Ortho, Para directors (+R):

- a)  $-\ddot{\text{N}}\text{H}_2$ ,  $-\ddot{\text{N}}\text{HR}$ ,  $-\text{NR}_2$ ,  $-\text{OH}^-$ ,  $-\text{O}^-$  (Strongly activating)
- b)  $-\text{NHCOCH}_3$ ,  $-\text{HCOR}$ ,  $-\text{OCH}_3$  (Moderately activating)
- c)  $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$ ,  $-\text{R}$ ,  $-\text{C}_6\text{H}_5$  (Weakly Activating)
- d)  $-\text{F}$ ,  $-\text{Cl}$ ,  $-\text{Br}$ ,  $-\text{I}$ ,  $(+\text{R} & -\text{l})$  (Weakly deactivating)

##### II. Meta directors (-R):

- a)  $-\text{NO}_2$ ,  $-\text{CF}_3$ ,  $-\text{CCl}_3$  (Strongly deactivating)
- b)  $-\text{CN}$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{COOH}$ ,  $-\text{COOR}$ ,  $-\text{CHO}$ ,  $-\text{COR}$  (Moderately deactivating)

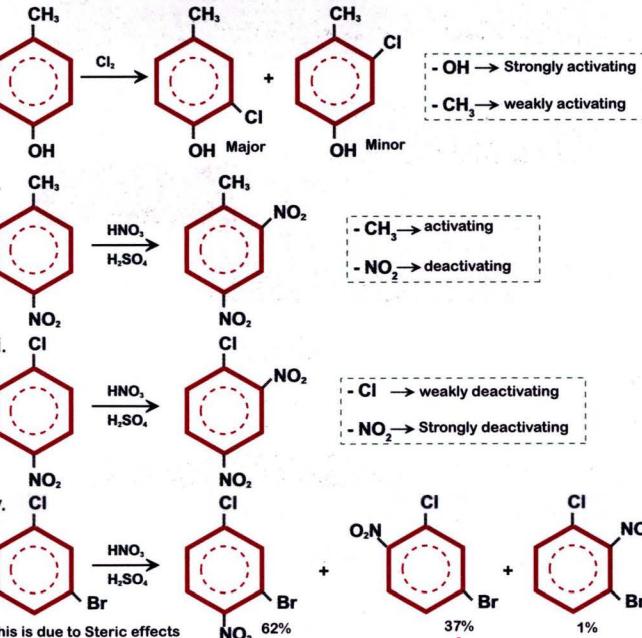
#### Reactivity order with respect to EAS



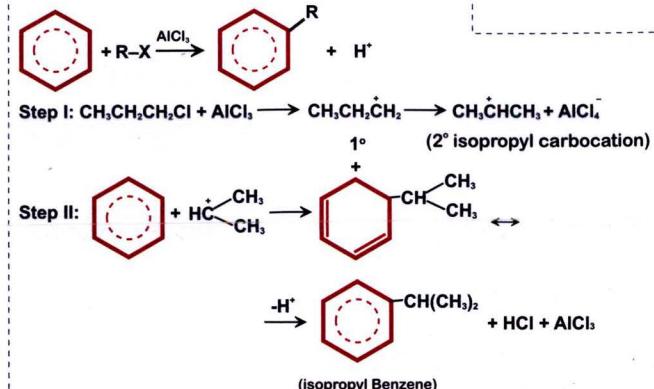
### Electrophilic Aromatic Substitution Reactions

#### Due to high electron density, Arenes (Benzene) react with Electrophilic reagents and undergo substitution (EAS: Electrophilic Aromatic Sub.)

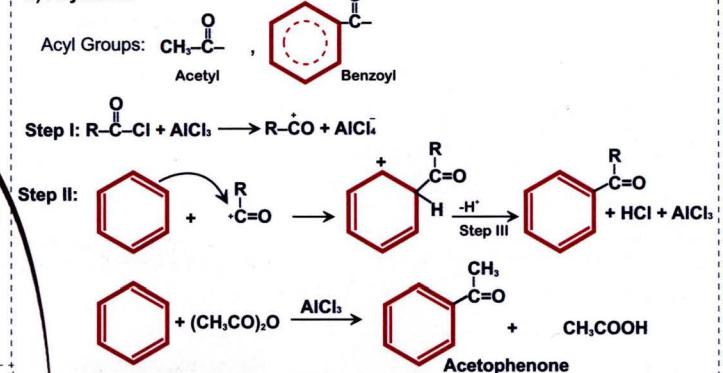
### Orientation in Disubstituted Benzenes



### a) Alkylation:

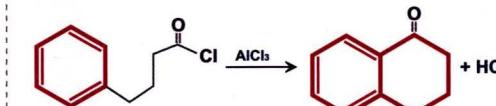


### b) Acylation:

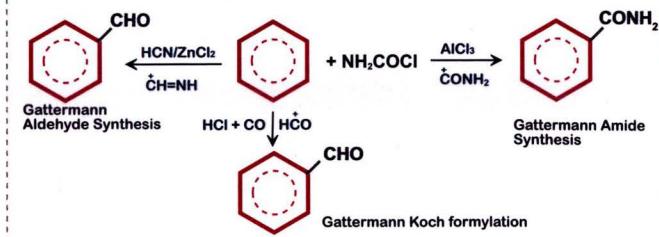


### Limitations of F.C reaction

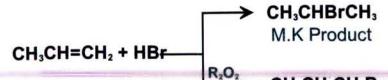
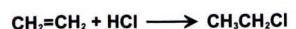
- a) F.C reactions do not occur when benzene is substituted with  $-\text{NO}_2$  (a strong deactivating group) or with  $-\text{NH}_2$ ,  $-\text{NHR}$ ,  $-\text{NR}_2$  (Strong activators).
- b) Aryl or Vinyl halides cannot be used, since they do not form carbocations.
- c) No rearrangements of the carbon chain in acylations in contrast to alkylations.
- d) Intra molecular Friedel Craft's acylation leads to formation of a new ring.



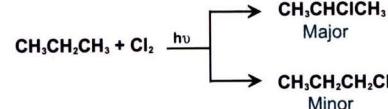
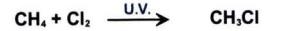
#### Extension of F.C acylation:



1) From Alkenes:



2) From Alkanes:



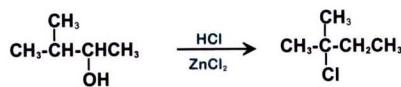
Ease of substitution of H-atoms

$3^\circ > 2^\circ > 1^\circ > \text{CH}_4$

3) From Alcohols:



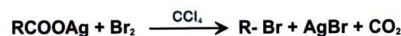
Carbocation is the intermediate. Rearrangement may take place for stable carbocation formation.



Reactivity of alcohols:  $3^\circ > 2^\circ > 1^\circ$

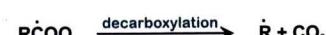
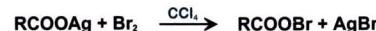
Other Reagents are:  $\text{PCl}_3, \text{PCl}_5, \text{SOCl}_2$

4) Hunsdiecker Reaction:



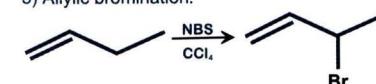
Decarboxylation via radical formation.

Length of C-Chain decreases (descent of series)

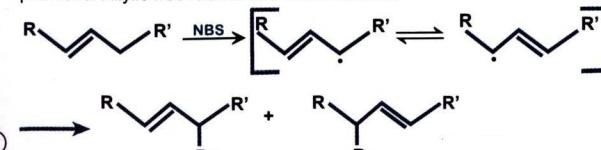


Yield of R-X:  $1^\circ > 2^\circ > 3^\circ$

5) Allylic bromination:



N-Bromosuccinimide is used for bromination at allylic positions. Allylic free radical is the intermediate



1) Nucleophilic substitution reaction ( $S_N$ )



( $\text{NU}^- = \text{OH}^-, \text{CN}^-, \text{OCH}_3^-, \text{NO}_2^-, \text{R}^-, \text{NH}_2^-$  etc)

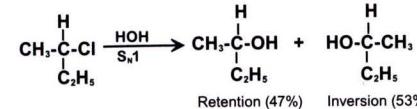
It is of two types.

$S_N1$ : rate =  $K[\text{R-X}]$

I order, unimolecular. Carbocation is intermediate. Racemization occurs.

Reactivity order:  $3^\circ > 2^\circ > 1^\circ > -\text{CH}_3$

Polar, Protic solvent favour  $S_N1$



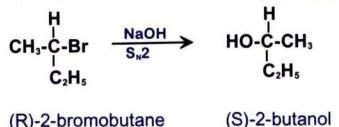
Stereoselective reaction

$S_N2$  : rate =  $K[\text{R-X}][\text{NU}]$

II order, bimolecular reaction. Transition state occurs. Walden Inversion occurs.

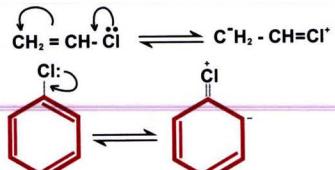
Reactivity Order:  $\text{CH}_3 > 1^\circ > 2^\circ > 3^\circ$

Polar, aprotic solvent favours  $S_N2$



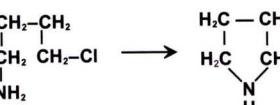
Stereospecific reaction

$S_N$  is difficult in vinyl and phenyl halides due to double bond nature of  $\text{C}=\text{X}$  bond.



Intramolecular  $S_N$

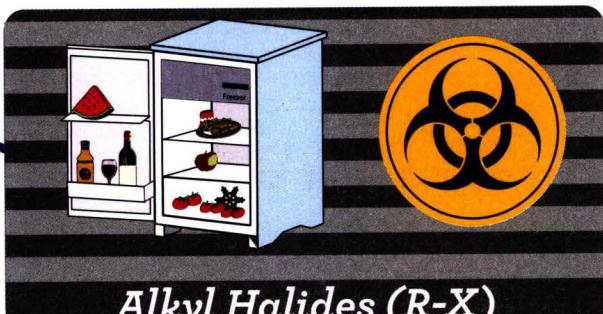
Low concentration of the reactants and formation of 5 or 6 membered ring favour this



$S_N$  Reactions

$\text{aq. KOH}$	$\text{R-CH}_2\text{OH}$
$\text{aq. Ag}_2\text{O}$	$\text{R-CH}_2\text{OH}$
$\text{C}_6\text{H}_5\text{ONa}$ williamson	$\text{R-CH}_2\text{OC}_6\text{H}_5$
$\text{NH}_3$	$\text{RCH}_2\text{NH}_2 + 2^\circ + 3^\circ + 4^\circ$
$\text{KCN/R-OH}$	$\text{RCH}_2\text{CN}$
$\text{AgCN/R-OH}$	$\text{RCH}_2\text{NC}$
$\text{KNO}_2$	$\text{RCH}_2\text{ONO}$
$\text{AgNO}_2$	$\text{RCH}_2\text{NO}_2$
$\text{R'COO}$	$\text{RCH}_2\text{OOCR'}$

## $S_N$ Reactions



## Preparations

## Chemical Properties

## Classification

$1^\circ$	$2^\circ$	$3^\circ$
$\text{R-CH}_2\text{X}$ $\text{CH}_3\text{CH}_2\text{Cl}$ Ethyl chloride	$\text{R-CH}_2\text{X}$ $(\text{CH}_3)_2\text{CHCl}$ Isopropyl Chloride	$\text{R-CH}_2\text{X}$ $(\text{CH}_3)_3\text{CCl}$ Tertiary butyl chloride

### Classification based on Structure

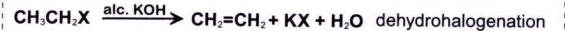
<b>Unsaturated</b>	<b>Aromatic</b>
$\text{CH}_2=\text{CHCl}$ Vinyl Chloride	$\text{CH}_2=\text{CH-CH}_2\text{Cl}$ Alkyl Chloride

Phenyl Chloride      Benzyl Chloride

### Classification based on halogen content

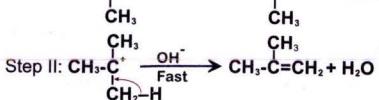
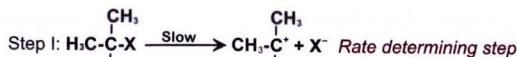
Mono	Di	Tri	Tetra
$\text{CH}_3\text{CH}_2\text{Cl}$		$\text{CHCl}_3$	$\text{CCl}_4$
Vicinal	Geminal		

$\text{CH}_2=\text{CHCH}_2\text{Cl}$        $\text{CH}_2=\text{CH-CH}_2\text{Cl}$



$$\text{E1: rate} = \text{K}[\text{R-X}]$$

Elimination unimolecular, 1 order reaction.  
Carbocation is Intermediate, Two step process



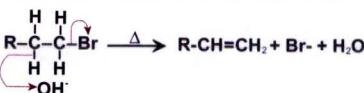
Reactivity order:  $3^\circ > 2^\circ > 1^\circ$

$\text{R-I} > \text{R-Br} > \text{R-Cl} > \text{R-F}$

Similar to  $\text{S}_{\text{N}}1$ . High temperature and strong  $\text{NU}^-$  favours E1 over  $\text{S}_{\text{N}}1$

$$\text{E2: rate} = \text{K}[\text{R-X}][\text{NU}^-]$$

Elimination bimolecular, II order. One step process (concerted process)  $\text{X}^-$  is lost from an  $\alpha$ -C atom and  $\text{H}^+$  from  $\beta$ -C atom (1,2-Elimination) transition state is formed

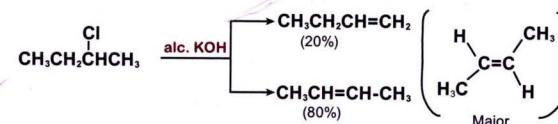


Reactivity order:  $3^\circ > 2^\circ > 1^\circ$

$\text{R-I} > \text{R-Br} > \text{R-Cl} > \text{R-F}$

E2 elimination is stereospecific. Trans-isomer is the major product.

Zaitsev rule.



## Elimination Reactions

### Overall summary of $\text{S}_{\text{N}}1$ , $\text{S}_{\text{N}}2$ , E1, E2 reactions

$\text{CH}_3\text{X}$ Methyl	$\text{RCH}_2\text{X}$ ( $1^\circ$ )	$\text{R}_2\text{CHX}$ ( $2^\circ$ )	$\text{R}_3\text{CX}$ ( $3^\circ$ )
$\text{S}_{\text{N}}2$ only	$\text{S}_{\text{N}}2$ with hindered base $[(\text{CH}_3)_3\text{O}^-]$ Mainly E2	$\text{S}_{\text{N}}2$ with weak bases ( $\text{I}^-$ , $\text{CN}^-$ , $\text{RCOO}^-$ ) E-2 with strong bases ( $\text{RO}^-$ )	$\text{S}_{\text{N}}1$ / E1 or E2 No $\text{S}_{\text{N}}2$ At low temperature- $\text{S}_{\text{N}}1$ At high temperature and strong base- E2

## Physical Properties

a) Insoluble in  $\text{H}_2\text{O}$  but soluble in organic solvents

b) Densities:  $\text{RI} > \text{RBr} > \text{RCI} > \text{RF}$

c) B.P. :  $\text{RI} > \text{RBr} > \text{RCI} > \text{RF}$

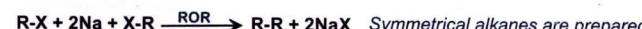
d) B.P. among isomers:  $1^\circ > 2^\circ > 3^\circ$

e) B.P.  $\uparrow$  with number of C-atoms

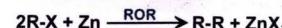
f)  $\text{CH}_3\text{Cl} < \text{CH}_2\text{Cl}_2 < \text{CHCl}_3 < \text{CCl}_4$

$-24^\circ\text{C}$     $40^\circ\text{C}$     $61^\circ\text{C}$     $77^\circ\text{C}$

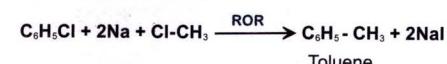
### Wurtz Reaction



### Frankland Reaction

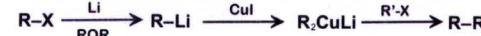


### Wurtz Fittig Reaction



### Corey-House Synthesis

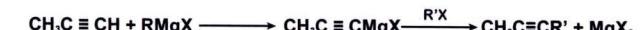
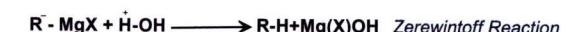
Symmetrical and unsymmetrical alkanes are prepared



### Grignard Reactions



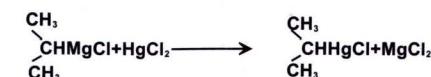
C-Mg bond in polar covalent. Mg-X bond is ionic



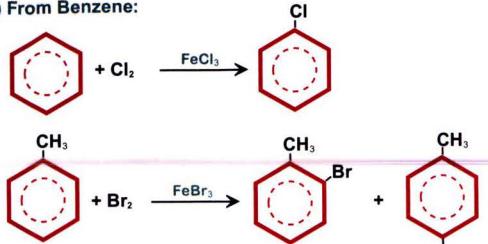
Reactivity of R-X with Mg:  $\text{RI} > \text{RBr} > \text{RCI}$



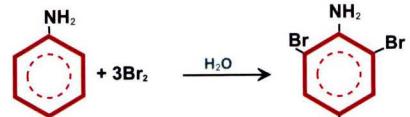
Grignard Reagent can undergo metal-metal exchange reaction



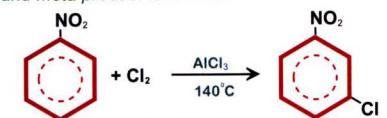
1) From Benzene:



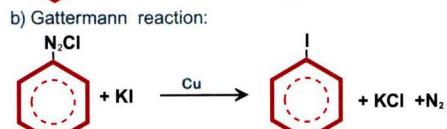
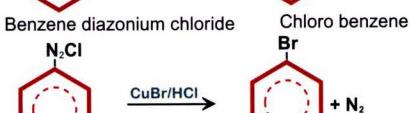
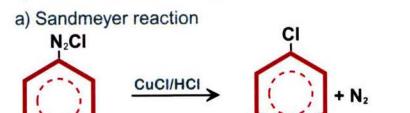
In presence of strongly activating group. Lewis acid is not required



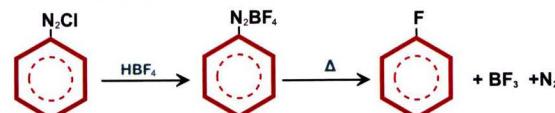
In presence of deactivating group, high temperature is required and Meta product is formed.



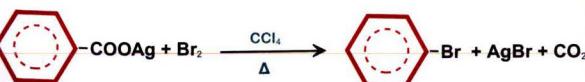
2) From diazonium Chloride:



c) Balz Schiemann reaction:



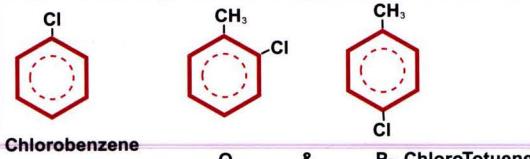
3) Hunsdiecker Reaction



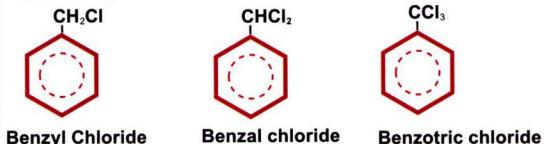
4) Rasching Process(Industrial Method)



Arylhalides: Halogen atom is directly attached to benzene ring



AralKylhalides: Halogen atom is attached to side chain of the benzene ring



Preparation

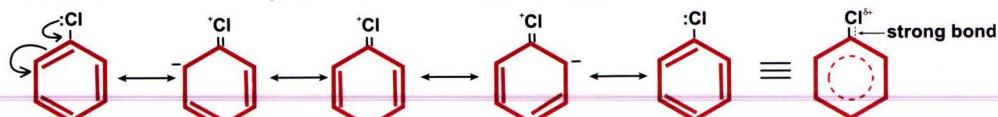
Definition



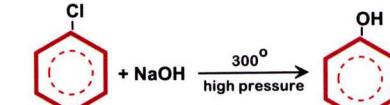
Physical Properties

- 1) Aryl halides are less polar.
- 2) Insoluble in water but soluble in organic solvents.
- 3) p-isomer is more symmetrical and has higher melting point than the o- and m-isomers.

I. Arylhalides, unlike alkylhalides are less reactive towards S<sub>N</sub>-reactions. In Arylhalides the C-X bond is stable and acquired a double bond character due resonance.

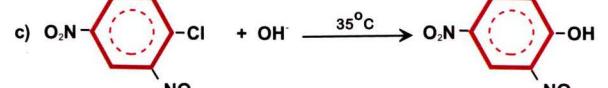
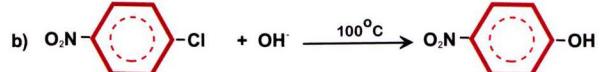
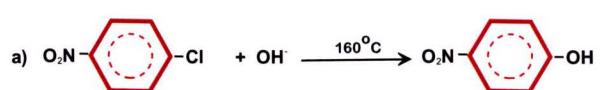
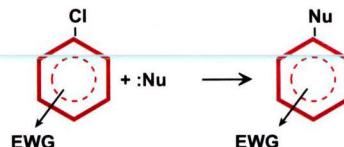


Hence S<sub>N</sub> reactions are not possible under ordinary conditions only under drastic conditions S<sub>N</sub> is possible



Dow Process

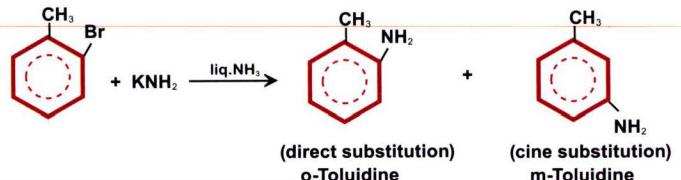
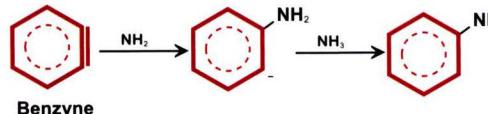
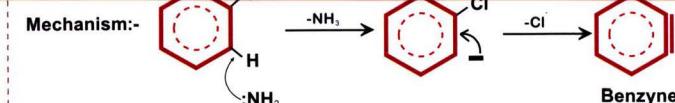
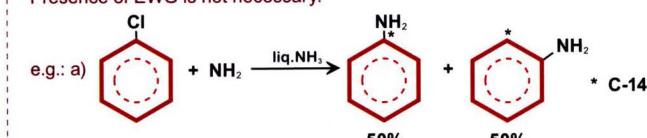
S<sub>N</sub> reactions occur easily when EWG are present in o- and p- positions of the leaving group i.e. halogen



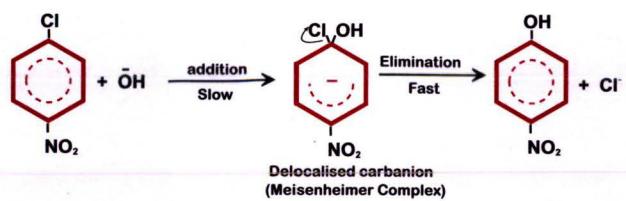
Nucleophilic Substitution Reactions (S<sub>N</sub>)

II. SN-Aromatic by Elimination-Addition (Benzene Concept)

In presence a powerful base elimination addition takes place. Presence of EWG is not necessary.

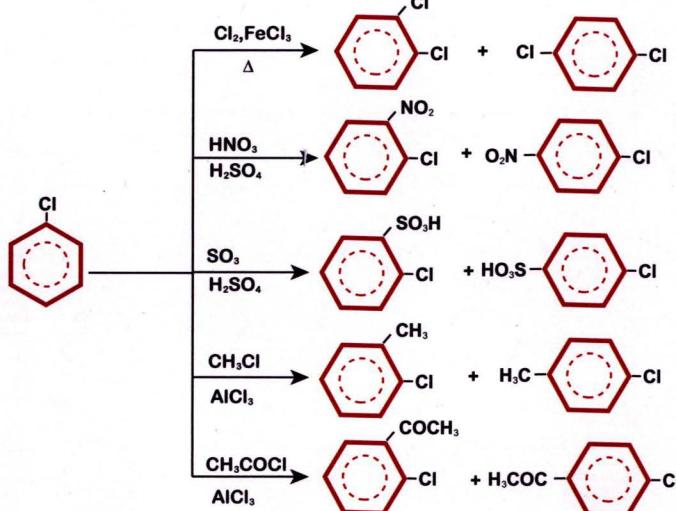


In presence of EWG, the mechanism is called S<sub>N</sub>Aromatic.  
It is an Addition-Elimination reaction

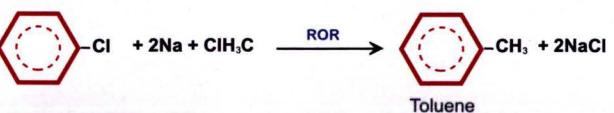


## ii Electrophilic Substitution of Benzene ring: (EAS)

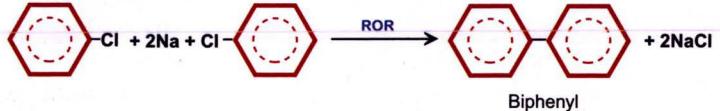
-X group is o- & p- directing and ring deactivation group.



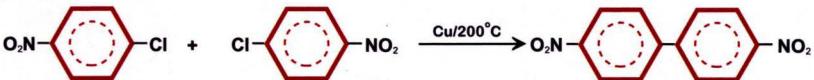
### Wurtz Fittig reaction



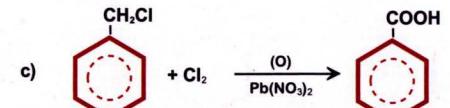
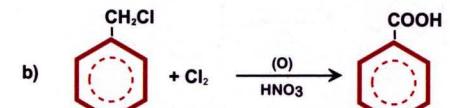
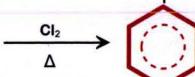
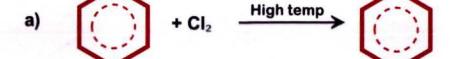
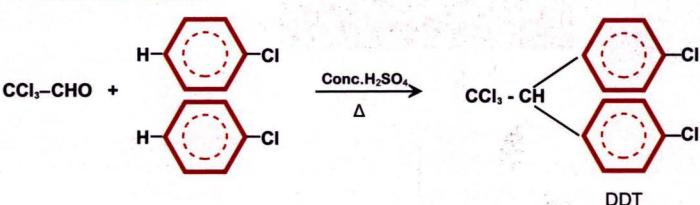
### Fittig reaction



### Ullmann reaction



### Reaction with Chloral:



d) During EAS, o- and p- products are obtained

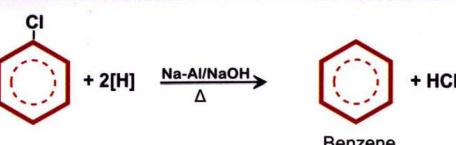
## Reactions

## AralKyl Halides

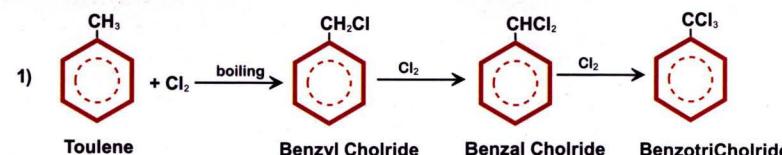
## Preparations

## Chemical Properties

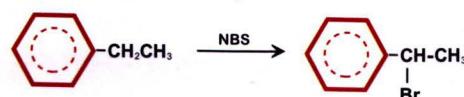
### Reduction



### Preparations of Aralkylhalides



It is free radical side chain halogenation



It is an allylic substitution

## Classification

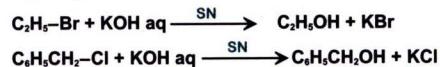
Monohydric (Alcohols)	Dihydric (Glycols)	Trihydric (Glycerols)
--------------------------	-----------------------	--------------------------

CH <sub>3</sub> CH <sub>2</sub> -OH Ethyl alcohol	CH <sub>2</sub> -OH Ethylene Glycol	CH <sub>2</sub> -OH CH-OH CH <sub>2</sub> -OH Glycerol
------------------------------------------------------	----------------------------------------	-----------------------------------------------------------------

## Types of Monohydric alcohols

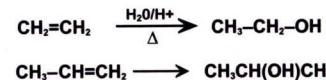
Primary(1°)	Secondary(2°)	Tertiary(3°)
$\begin{array}{c} \text{H} \\   \\ \text{R}-\text{C}-\text{OH} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{R} \\   \\ \text{R}-\text{C}-\text{OH} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{R} \\   \\ \text{R}-\text{C}-\text{OH} \\   \\ \text{R} \end{array}$
CH <sub>3</sub> CH <sub>2</sub> OH Ethyl alcohol Ethanol	CH <sub>3</sub> -C(OH) <sub>2</sub> Isopropyl alcohol Propan-2-ol	CH <sub>3</sub> -C(OH) <sub>2</sub> Tertiary Butyl alcohol 2-Methylpropan-2-ol

## Hydrolysis of R-X



3° R-X gives alkenes in this method

## Addition of water to Alkenes



Markovnikov's Rule is followed

## Hydroboration-Oxidation of Alkenes

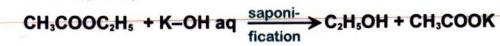


Anti-Markovnikov's product is formed

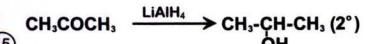
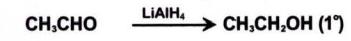
## Action of Grignard's Reagent (G.R) with Carbonyl Compounds:

- G.R + HCHO or Ethylene oxide  $\xrightarrow{\text{H}_3\text{O}^+}$  1° ols
- G.R + Any aldehyde  $\xrightarrow{\text{H}_3\text{O}^+}$  2° ols
- G.R + Any Ketone  $\xrightarrow{\text{H}_3\text{O}^+}$  3° ols

## Ester Hydrolysis



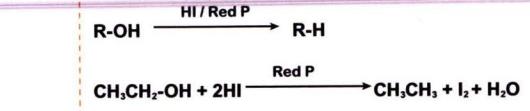
## Reduction of Carbonyl Compounds



Chain Isomerism	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{-OH} \end{array}$ Butyl alcohol	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{CHCH}_2\text{-OH} \end{array}$ Isobutyl alcohol
Positional Isomerism	$\begin{array}{c} \text{OH} \\   \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{-OH} \end{array}$ Propyl alcohol	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{CHCH}_3 \end{array}$ Isopropyl alcohol

Functional Isomerism	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{-OH} \\   \\ \text{CH}_3\text{O-CH}_3 \end{array}$ Butyl alcohol	Dimethyl ether
----------------------	-------------------------------------------------------------------------------------------------------------------	----------------

Optical Isomerism	$\begin{array}{c} \text{C}_2\text{H}_5 \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CH}_3 \end{array}$ R-(+)-Butan-2-ol	$\begin{array}{c} \text{C}_2\text{H}_5 \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{CH}_3 \end{array}$ S-(-)-Butan-2-ol
-------------------	---------------------------------------------------------------------------------------------------------------------------------	---------------------------------------------------------------------------------------------------------------------------------



## Reduction

## Chemical Properties

### a) Action with active Metals: Alkoxides are formed



Order of reactivity: CH<sub>3</sub>OH > 1° > 2° > 3°

Alkoxides are useful in Williamson's Synthesis of Ether

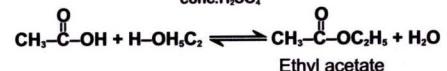
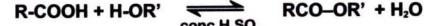


relative acidity order: H<sub>2</sub>O > R-OH > CH≡CH > NH<sub>3</sub> > R-H.

### b) Action with G.R: Alkanes are formed.



### c) Esterification: Alcohols + Acids; organic as well as inorganic (except H-X) gives esters



\*By removing H<sub>2</sub>O equilibrium is shifted to right hand side.

\*Acid Chlorides (RCOCl) or acid anhydrides ((RCO)<sub>2</sub>O) are better than acids for esterification.

\*Presence of bulky alkyl groups near the site of reaction in alcohols or acids, slow down esterification

Acids' Reactivity : HCOOH > CH<sub>3</sub>COOH > RCH<sub>2</sub>COOH > RCHCOOH > R<sub>2</sub>COOH

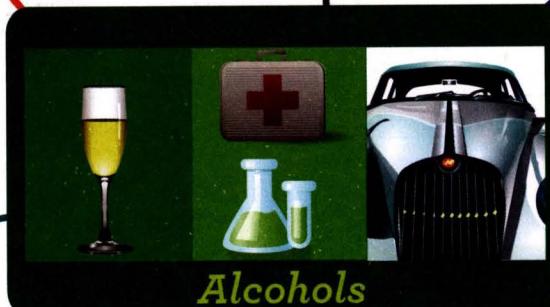
Alcohols' Reactivity: CH<sub>3</sub>OH > 1° > 2° > 3°

alcohol of crystallisation

## Classification

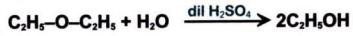
## Isomerism

## Physical Properties

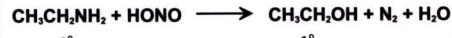


## Preparations

## Hydrolysis of Ethers

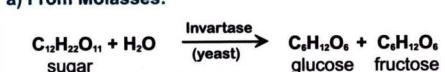


## Hydrolysis of 1° amines



## Industrial Preparations (Fermentation Methods):

### a) From Molasses:



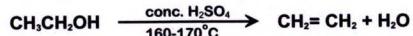
### b) From Starch



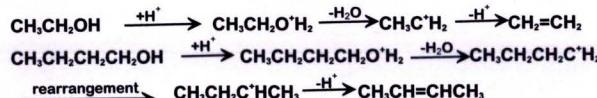
### f) M.P order of isomeric alcohols: 3° < 2° < 1°



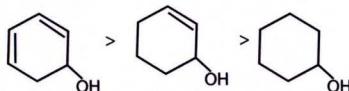
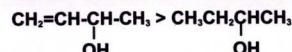
Dehydration using conc.  $H_2SO_4$



Carbocation is the intermediate, E reaction



Order of dehydration of alcohols:  $3^\circ > 2^\circ > 1^\circ$

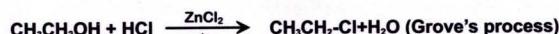
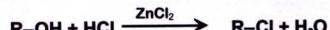


This order is due to conjugated alkene formation

## Dehydration

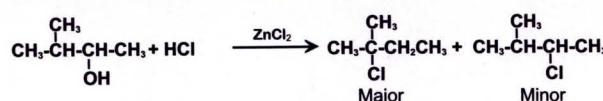
Due to cleavage of C-OH bond

a) Action with conc.  $HCl$  and anhydrous  $ZnCl_2$  (Lucas reagent)

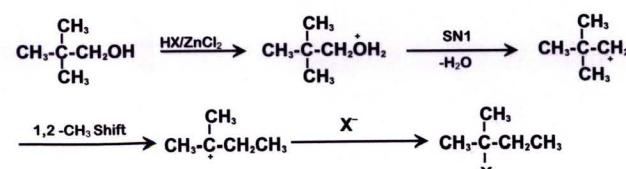


Reactivity order of alcohols:  $3^\circ > 2^\circ > 1^\circ$

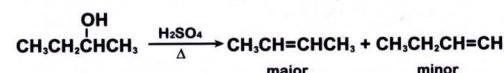
Carbocation is the intermediate, Rearrangement may also take place



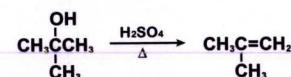
Mechanism:  $R-OH + H^+X^- \rightarrow RO^+H_2 + X^-$



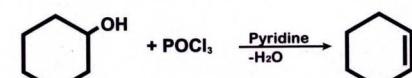
$2^\circ$  ols are dehydrated according to Zaitsev's rule to form more substituted alkene as the major product.



Dehydration of  $3^\circ$  ols:

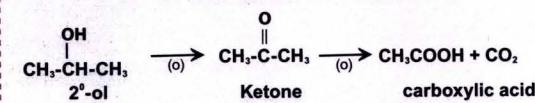
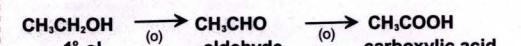


dehydration can be achieved using  $POCl_3$  and Pyridine

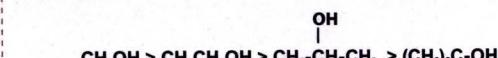


## Oxidation

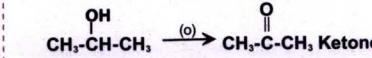
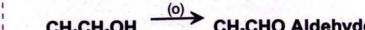
a) With  $KMnO_4/H^+$  or  $K_2Cr_2O_7/H^+$



Reactivity  $\propto$  Number of H-atoms on an  $\alpha$  Carbon atom.



b) with mild oxidising agents.



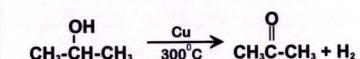
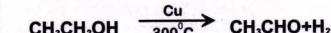
Mild O.A. are

i. Jones reagent (Chromic acid in aq. acetone)

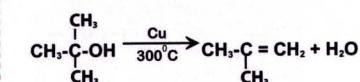
ii. Sarret reagent =  $PCC = C_6H_5NHClCrO_7$

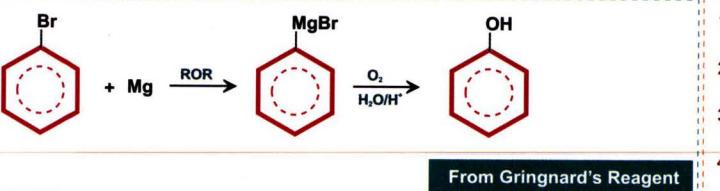
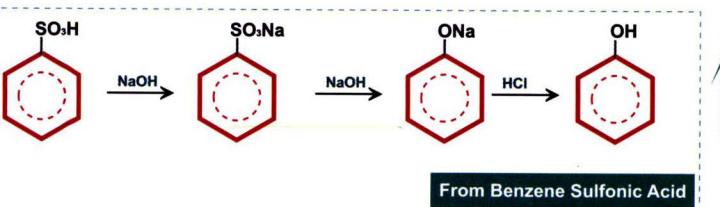
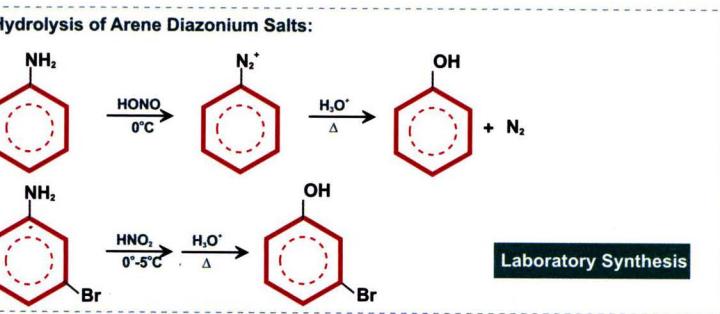
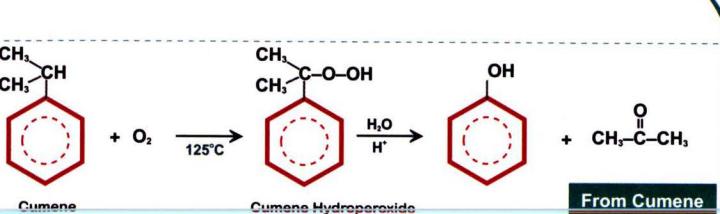
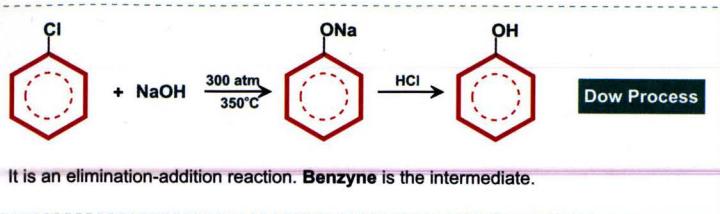
iii. PDC reagent =  $(C_6H_5NH_2)_2Cr_2O_7$

c) Dehydrogenation with Cu



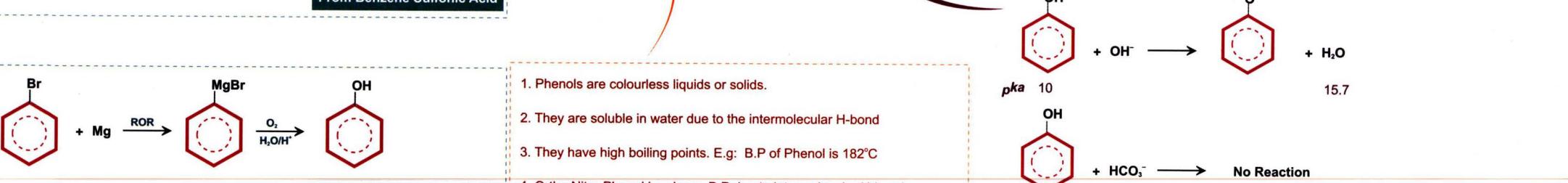
$3^\circ$  - ols undergo dehydration.





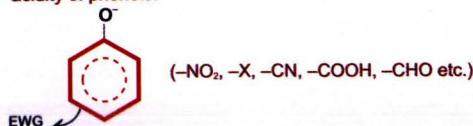
- Phenols are acidic due to resonance stabilization of its conjugate base (Phenoxyde ion)
- Carboxylic Acids > Phenols > Water > Alcohols
- Acid  $pK_a$       Acetic Acid > Phenol > Water > Ethanol  
4.8            10        15.6        16
- Lower the  $pK_a$ , stronger the acid.

d) An acid can be deprotonated by a base that has a conjugate acid with a higher  $pK_a$ .

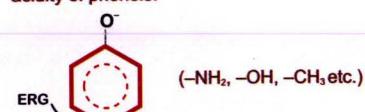


1. Phenols are colourless liquids or solids.
2. They are soluble in water due to the intermolecular H-bond
3. They have high boiling points. E.g: B.P of Phenol is 182°C
4. Ortho Nitro Phenol has lower B.P due to intramolecular H-bond.
5. Order of Boiling Points:  
 $p\text{-nitrophenol} > m\text{-nitrophenol} > o\text{-nitrophenol}$   
 $p\text{-chlorophenol} > m\text{-chlorophenol} > o\text{-chlorophenol}$

f) Electron withdrawing groups (EWG) stabilize the phenoxide ion and hence increase acidity of phenols.

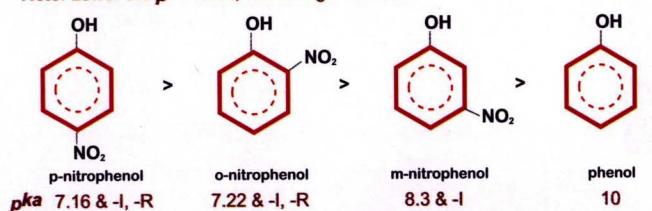


g) Electron releasing groups (ERG) destabilize the phenoxide ion and hence decrease acidity of phenols.



Case I: Nitrophenol is more acidic than phenol. (-NO<sub>2</sub> is EWG by -I & -R)

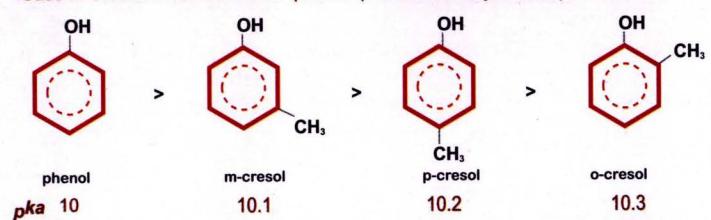
Note: Lower the pKa value, the stronger the acid



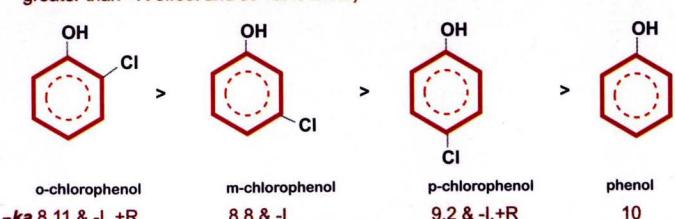
Hence nitrophenols are more acidic than phenol. Due to intramolecular H-bond, acidity of o-isomer is lower than p-isomer

## EAS Reactions

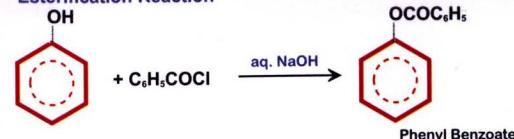
Case II: Cresol is less acidic than phenol. (-CH<sub>3</sub> is ERG by +I & +R)



Case III: Chlorophenol is more acidic than phenol. (-Cl has -I & +R effects and -I is greater than +R effect and so -Cl is EWG)

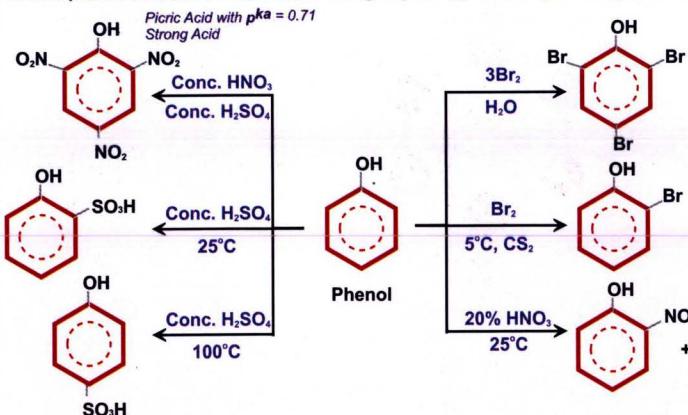


### Esterification Reaction

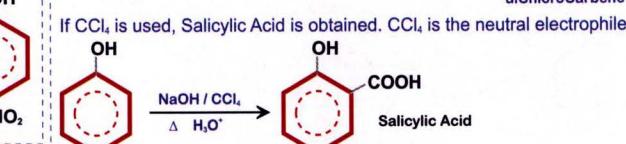
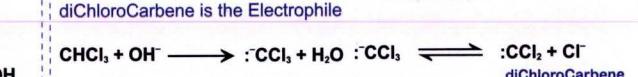
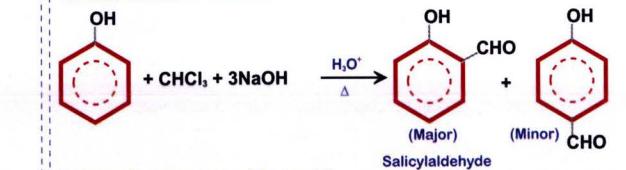


It is called Schotten-Baumann reaction.

Electrophilic Aromatic Substitution: -OH group is o-, p- directing and ring activating

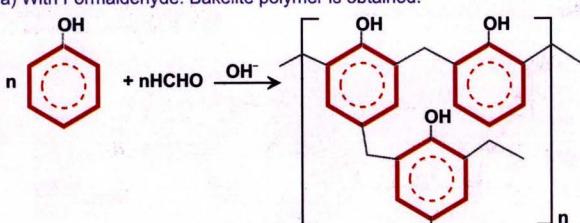


### Reimer Tiemann Reaction:

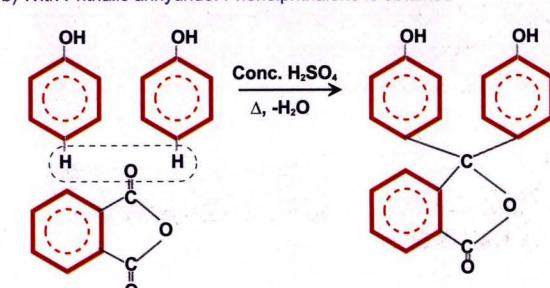


### Condensation Reactions:

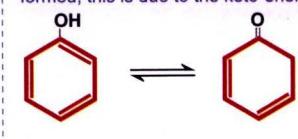
a) With Formaldehyde: Bakelite polymer is obtained.



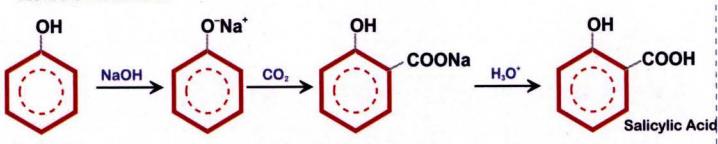
b) With Phthalic anhydride: Phenolphthalein is obtained



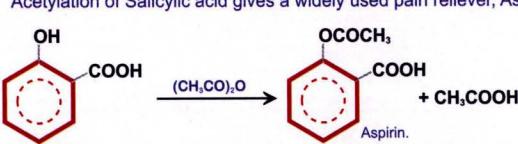
Action with neutral FeCl<sub>3</sub>: (Test for Phenol) Violet coloured Iron(III) complex is formed, this is due to the keto-enol forms. Alcohols donot give this test.



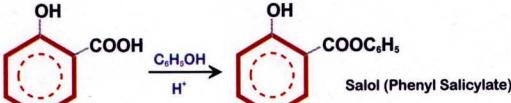
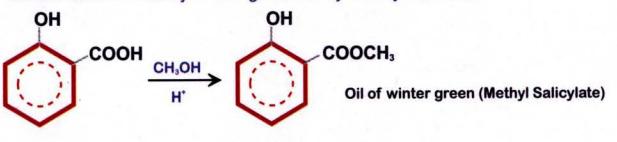
### Kolbe's Reaction:



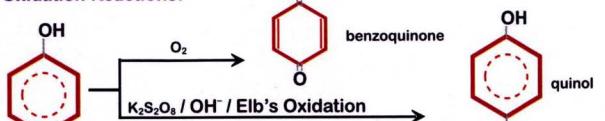
Acetylation of Salicylic acid gives a widely used pain reliever, Aspirin.



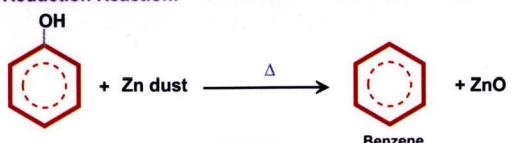
Esterification of Salicylic acid gives Methyl Salicylate / Salol



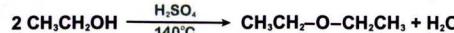
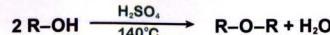
### Oxidation Reactions:



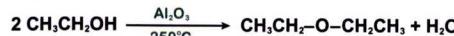
### Reduction Reaction:



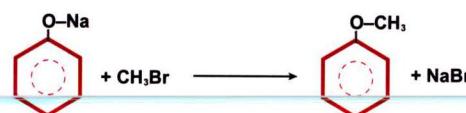
## Dehydration of Alcohols



This reaction is  $S_{N}2$ . Symmetrical Ethers are formed



## Williamson's Synthesis



This reaction is  $S_{N}2$ . Suitable for mixed Ethers.

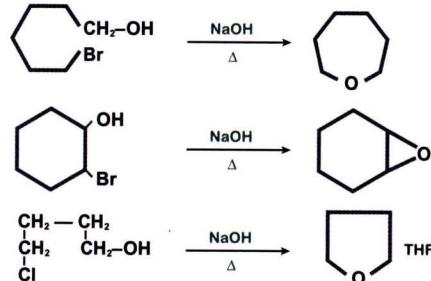
$\text{R-X}$  should be  $1^\circ$  and alkoxide should be  $2^\circ$  or  $3^\circ$



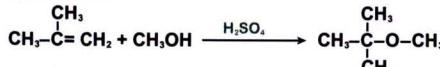
If the  $\text{R-X}$  is  $2^\circ$  or  $3^\circ$  and the alkoxide is  $1^\circ$ ,  $E-2$  occurs giving an alkane.  $1^\circ \text{R-X}$  with phenoxide gives alkyl-aryl ether



## Intramolecular Williamson's Synthesis

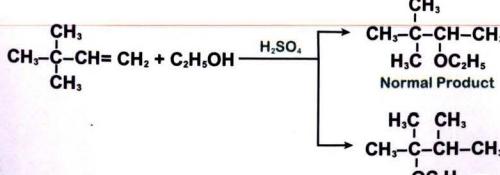


## From Alkenes

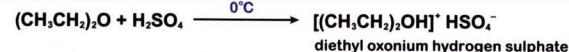


It is a Markovnikov's addition.

Intermediate carbocation may undergo rearrangement.



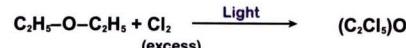
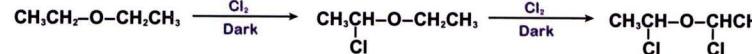
**Basic Nature** Ethers dissolve in strong acids at low temperatures to form oxonium salts.



## Hydrolysis



## Halogenation

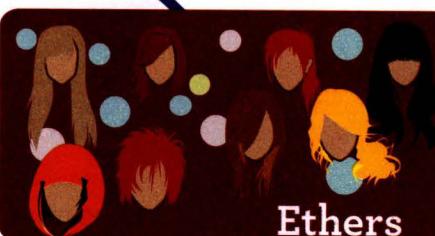


**Action in Air** It is an auto-oxidation. Unstable and explosive peroxides are formed



## Chemical Properties

Ethers are inert due to the absence of any active groups



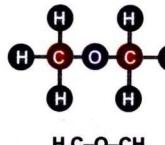
## Preparations

## Physical Properties

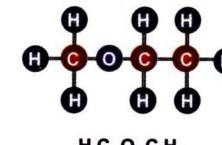
- a) Ethers are colourless, sweet smelling and highly volatile
- b) They have lower boiling points than isomeric alcohols due to absence of H-bonds
- c) They are slightly polar in nature



### Simple



### Mixed



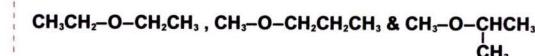
### Etheric

### Ethyl Methyl ether (or) Methoxy ethane

## Classification

## Isomerism

### Metamers of $\text{C}_4\text{H}_10\text{O}$



### Functional Isomers of $\text{C}_2\text{H}_6\text{O}$

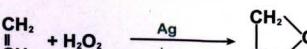


## From Diazomethane and Alcohol

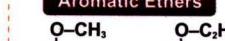


It is an  $S_{N}2$  reaction

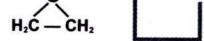
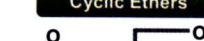
## Preparation of Oxirane



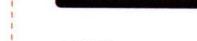
### Aromatic Ethers



### Cyclic Ethers



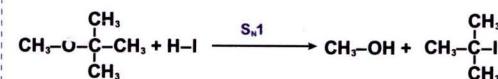
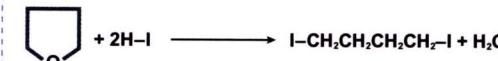
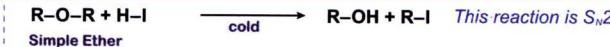
### Crown Ethers



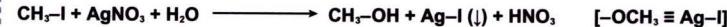
## Action with $\text{PCl}_5$



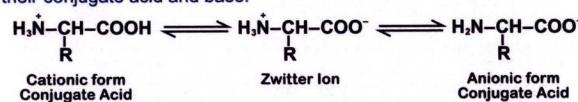
**Action with Halogen Acids** When ethers are heated with  $\text{HI}$  or  $\text{HBr}$ , the C–O bond breaks to give alcohols and alkyl halides



In the above  $S_N1$  reaction,  $3^\circ$  carbocation is the stable intermediate and hence forms a  $3^\circ$  halide  
The reaction of ethers with  $\text{HI}$  forms the basis of ziesel method for the detection and estimation of alkoxy group in a compound.

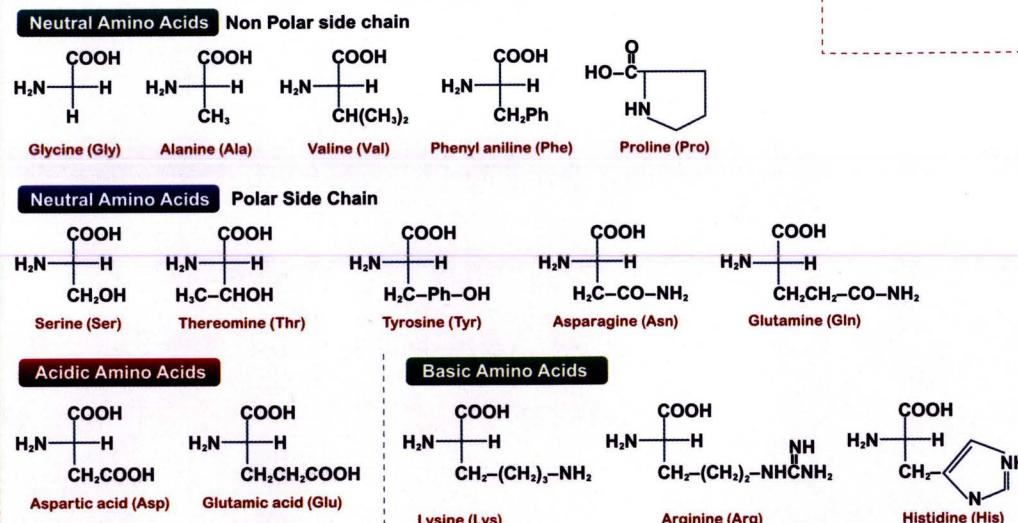


- All proteins are biological polymers made up of amino acid molecules linked together to form a long chain.
  - Amino acids contain basic  $\text{--NH}_2$  group and acidic  $\text{--COOH}$  group.  
 $\text{R--CH--COOH}$   
 $\text{NH}_2$
  - 20 different amino acids are obtained by the hydrolysis of proteins which differ in the  $\text{--R}$  group.
  - Except for **glycine**, all are *chiral* with L-configuration at the  $\alpha$ -C-atom  
 Amino acids are classified as neutral, acidic and basic depending on the relative number of  $\text{--NH}_2$  and  $\text{--COOH}$  groups.
  - Amino acids which are not synthesised in the body and must be obtained through diet are called *essential amino acids* and those which are synthesised within the body are called *non essential aminoacids*.



The optimum pH at which the concentration of the zwitter ion is at maximum is called the Isoelectric Point (P.I).

About



## Classification

## Synthesis

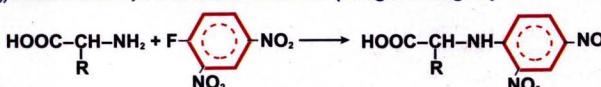
## Amino Acids and Peptides

## Properties

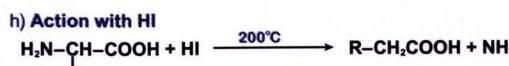
## About Peptides

## About Proteins

These are of two types. Fibrous proteins, which are water soluble; Globular proteins, which are water insoluble.



This is used to detect N-terminal amino acids.



**Primary Structure:** The covalent structure of a protein or polypeptide is called Primary Structure. It represents the sequence of amino acids. The change in the sequence results in different protein.

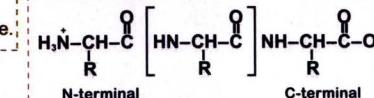
**Secondary Structure:** It refers to the shape in which a long polypeptide chain can exist.

In  $\alpha$ -helix, the chain is coiled like a spring.

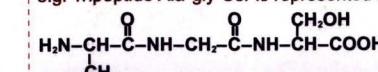
In a beta-pleated sheet, the chains are folded so that they lie along each other held by intermolecular H-bonds.

**Tertiary Structure:** It represents overall folding of the polypeptide chain i.e. further folding of the secondary structure.

When amino acids are joined together by amide bonds, they form larger molecules called peptides and proteins. Polypeptides are linear polymers of amino acids.



e.g: Tripeptide Ala-gly-Ser is represented as

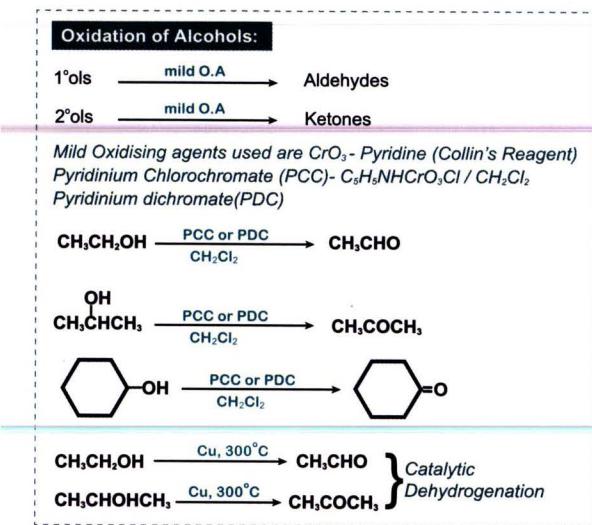


N-terminal is alanine and C-terminal is Serine

N-terminal is written on the L H S and C-terminal on the R H S

N-terminal residue is identified by Sanger's reagent (DNFB)

N-terminal residue is identified by Sanger's Reagent (DNB-Cl), C-terminal residue is identified by the use of enzyme called Carboxypeptidase.



## Preparations

### Reduction of Acid chlorides and Esters

### 4. Reduction of Nitriles: (stephen reduction)

## From Alkynes

### a) By Hydration:

### b) By Hydroboration-Oxidation

## Physical Properties

1) Aldehydes and Ketones are polar and hence they have higher Boiling Point than non-polar compounds like alkanes, ethers etc.



2) They have lower Boiling Point than alcohols and carboxylic acids due to absence of intermolecular H-bond.

Propionic acid: 141 °C	n-butraldehyde: 75 °C
n-butyl alcohol: 118 °C	n-pentane: 36 °C
Ethyl methyl Ketone: 80 °C	diethyl ether: 35 °C

## Carbonyl Compounds-1

## Preparations

### From Grignard Reagents

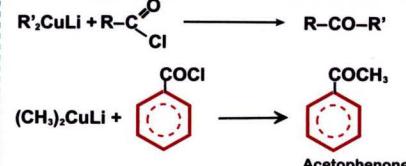
### Hydrolysis of Gem-dihalides

### Wacker Process

Alkenes are oxidised to aldehydes & ketones.

### Decarboxylation of calcium salts of carboxylic acids

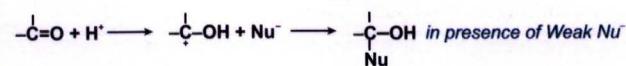
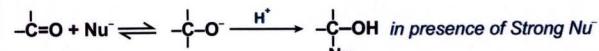
### From organo copper compounds: Ketones are prepared



### Aromatic Hydrocarbons are prepared in

- Freidel-Crafts reaction
- Gattermann reaction
- Reimer Tiemann reaction

Aldehydes and Ketones carry partial +ve charge on C-atom of  $\text{C}=\text{O}$  group. Hence they undergo nucleophilic addition reactions.

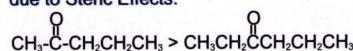


Due to +I effect of alkyl group the reactivity decreases in the order

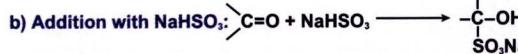
$$\therefore \text{reactivity} \propto \frac{1}{\text{MW}} \propto \frac{1}{\text{+I Effect}}$$



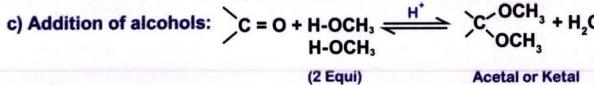
In Ketones, more hindered ketone is less reactive than a less hindered ketone due to Steric Effects.



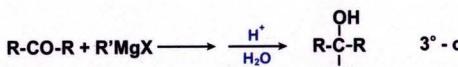
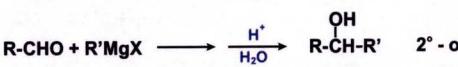
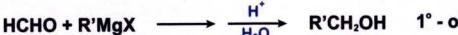
Due to Resonance Effect Aromatic Carbonyl Compounds are less reactive than aliphatic Carbonyl Compounds.



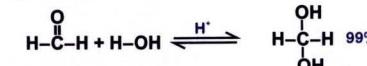
All types of aldehydes and only aliphatic methyl ketones give this reaction. Hence this reaction is used for differentiation.



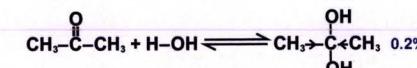
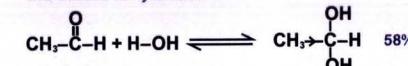
d) Addition of Grignard's reagent:



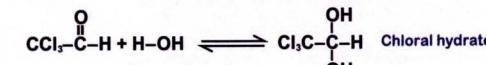
e) Addition with  $\text{H}_2\text{O}$ : Gem-diols are formed



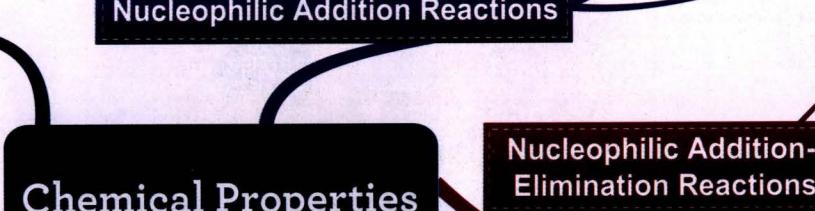
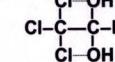
+I groups decreases the stability of gem-diols and hence decreases the extent of hydration



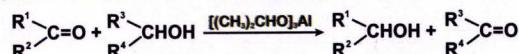
Presence of -I group on  $\alpha$ -C-atom increases the stability of the gem diols and hence increases the extent of hydration.



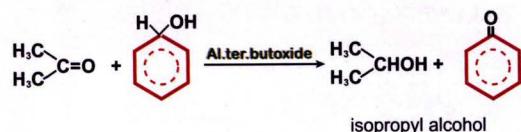
Chloral hydrate is highly stable due to intramolecular H-bond & -I Effect of Cl atoms



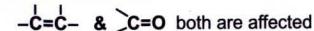
c) Meerwein panndorf verdey (MPV) reduction 1:



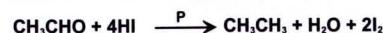
The reverse reaction is called Oppenauer oxidation



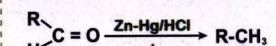
d) Reduction in presence of  $\text{H}_2 / \text{Ni}$ :



e) Reduction with  $\text{HI} / \text{Red P}$ :



a) Reduction  $\text{C=O}$  to  $-\text{CH}_2-$  group

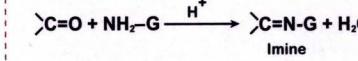
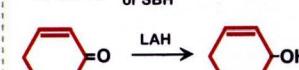
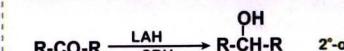
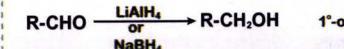


Clemmenson's Reduction

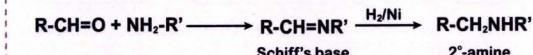


The above reduction in presence of  $\text{NH}_2-\text{NH}_2/\text{OH}^-$  is called Wolff Kischner Reduction

b) Reduction of  $\text{C=O}$  to  $-\text{CHOH}-$  group



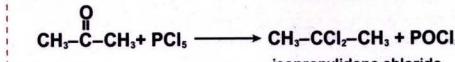
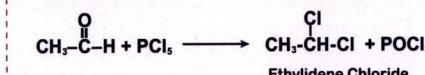
-G = H, R, OH,  $\text{NH}_2$ ,  $\text{NHC}_6\text{H}_5$  etc



$\text{HCHO}$  reacts with  $\text{NH}_3$  to form Urotropine(Hexamethylene tetramine)



Action with  $\text{PCl}_5$ : Gem-dichlorides are formed



Action with  $\text{Cl}_2$ :



Mild O.A. As oxidise only aldehydes to carboxylic acids

Tollens reagent (Ammonical silver nitrate) gives silver mirror



Fehling's Solution (alkaline  $\text{Cu}^{2+}$  + Tartrate ions) oxidize aliphatic aldehydes only and gives red precipitate of  $\text{Cu}_2\text{O}$ .



Benedict Solution (alkaline  $\text{Cu}^{2+}$  + Citrate ions) also oxidises in a similar way to give red ppt. of  $\text{Cu}_2\text{O}$

Ketones are not oxidised by these mild O.A.

Hence these reactions are used to distinguish (tests) aldehydes and ketones.

#### Baeyer-Villiger oxidation

Organic peroxides oxidises aldehydes to Carboxylic acids and Ketones to Esters.

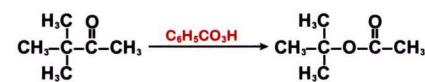


O-atom is inserted between C-atom and H-atom in aldehydes



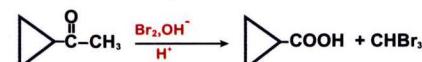
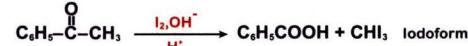
In case of unsymmetrical Ketones preference of insertion of O-atom in decreasing order is

$\text{H} > 3^\circ\text{R} > 2^\circ\text{R} > \text{Ph} > 1^\circ\text{R} > \text{CH}_3$

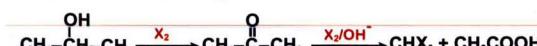


#### Halform Reaction

Aldehydes and Methyl Ketones react with  $\text{X}_2$  ( $\text{Cl}_2, \text{Br}_2, \text{I}_2$ ) in presence of alkali and forms Haloform.

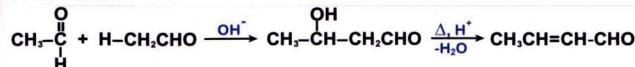


$\text{CH}_3-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-$  and  $\text{CH}_3-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2$  give Haloform reaction

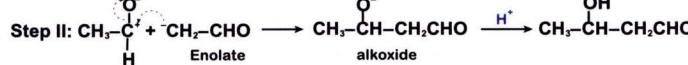
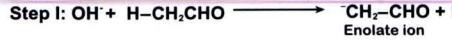


$\text{CH}_3\text{OH}$  &  $\text{CH}_3\text{CH}_2\text{OH}$  are distinguished by this reaction

Aldol Condensation: Compounds containing  $\alpha$ -H atoms undergo Self-Condensation in presence of mild (dilute) bases to form  $\beta$ -hydroxy carbonyl compounds called aldols.



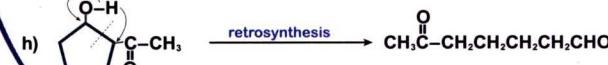
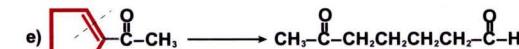
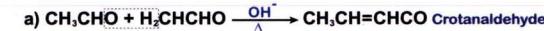
Mechanism:



Carbonyl Compounds containing  $\alpha$ -H atoms form the enolate ion in presence of base. It is a nucleophilic addition of an enolate ion on another carbonyl compound.

A new C-C  $\sigma$  bond is formed between  $\alpha$ -C-atom and carbonyl carbon of another molecule.

Dehydration of Aldol is favourable due to extended conjugate system



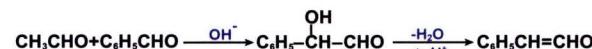
Tips

#### Oxidation Reaction

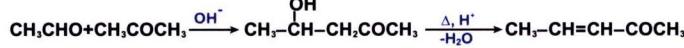
#### Aldol Condensation

## Carbonyl Compounds-2

#### Crossed Aldol Condensation

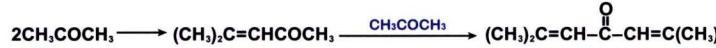


Acetaldehyde containing  $\alpha$ -H atoms forms enolate ion

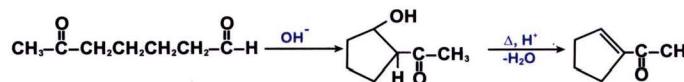


Acetaldehyde is more reactive for nucleophilic addition. Hence acetone forms the enolate ion

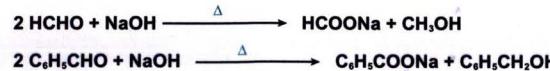
In presence of dry  $\text{HCl}$  gas, Acetone gives Mesyl oxide and then phorone



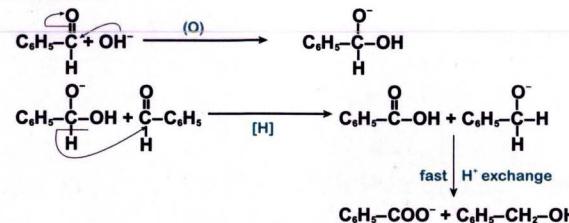
#### Intramolecular Aldol Condensation:



Aldehydes having no  $\alpha$ -H atoms, undergo simultaneous oxidation and reduction (disproportionation) in presence of conc. NaOH to form a salt of carboxylic acid and an alcohol.

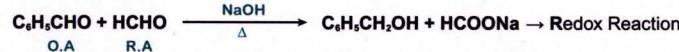


Mechanism:



Therefore rate = K [Ald]<sup>2</sup> [OH<sup>-</sup>] → 3rd order reaction

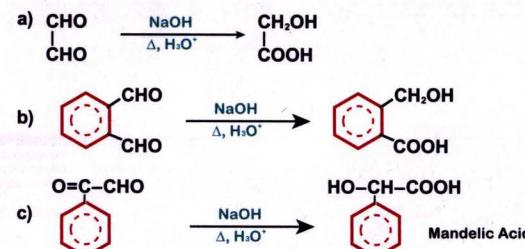
Crossed C.R.:



b/s HCHO is more reactive for nu<sup>-</sup> addition and undergoes oxidation.

Intramolecular C.R.:

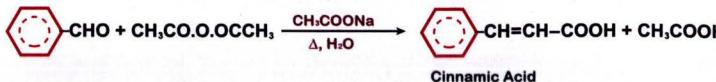
Dialdehydes and  $\alpha$ -ketoaldehydes undergo intramolecular C.R.



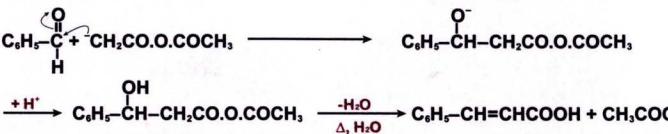
Keto group is reduced and aldehyde group is oxidised.

### Canizzaro Reaction

Aromatic Aldehydes, when heated with an anhydride of an aliphatic acid in the presence of sodium salt of the same acid gives  $\alpha, \beta$  - unsaturated acid.

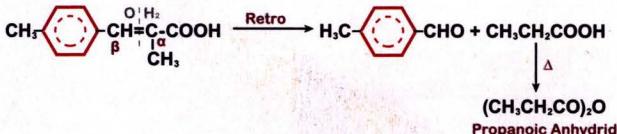
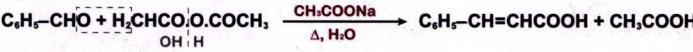


Mechanism:

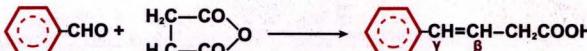


It is nucleophilic addition of carbanion intermediate on the carbonyl carbon of aromatic aldehyde

Tips:

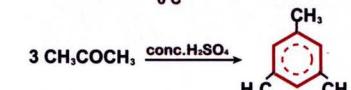
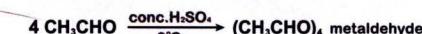
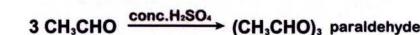


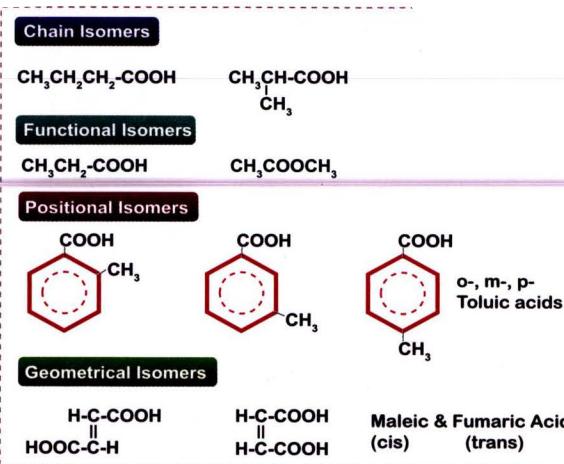
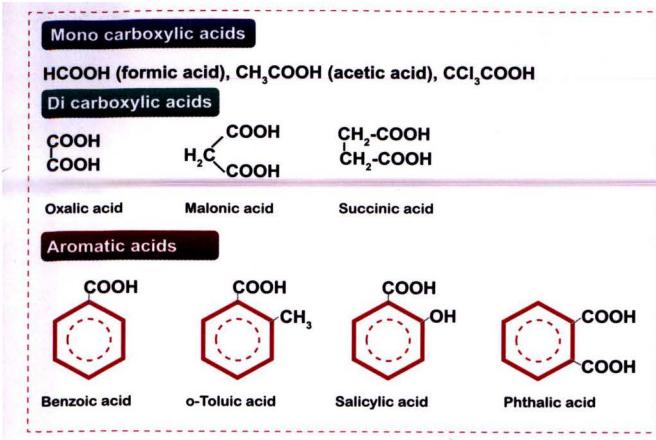
with cyclic anhydrides,  $\beta, \gamma$  - unsaturated acid is formed



### Perkin Reaction

### Polymerisation Reactions





- 1) Carboxylic acids are polar
- 2) First four members are miscible with water and higher ones are insoluble in water.
- 3) B.P. of acids are higher than that of alcohols  
e.g. B.P. of CH<sub>3</sub>CH<sub>2</sub>COOH(MW=74)=141°C & B.P. of CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH(MW=74)=118°C  
This is due to presence of two H.bond between two carboxylic acids(dimer)



- 4) Even members have higher M.P. than odd members preceding or following it.

## Physical Properties

## Classification

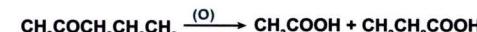
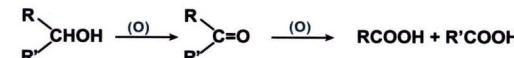
## Isomerism

## Preparations

Oxidation of Alcohols, Aldehydes and Ketones

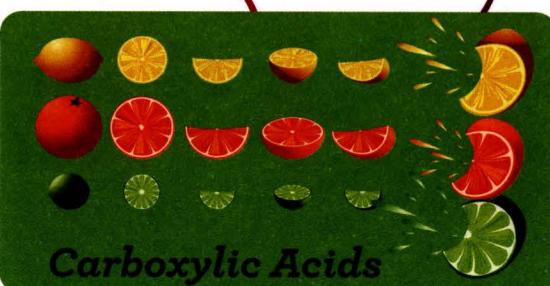
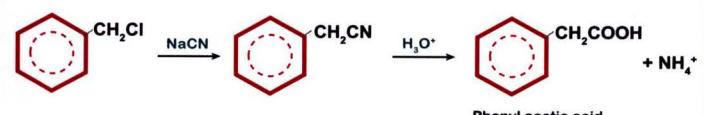
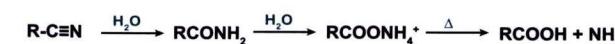


O.A = alkaline KMnO<sub>4</sub>, acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>



Ketonic group remains with smaller alkyl group

Hydrolysis of Cyanides:

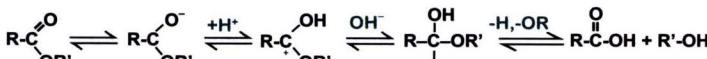


## Hydrolysis of Esters

Acidic or alkaline hydrolysis of esters yield carboxylic acid and alcohol.



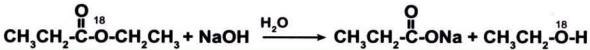
Acidic hydrolysis is reversible and I order reaction



Alkaline hydrolysis is irreversible and II order reaction



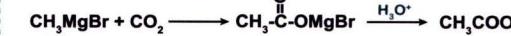
Carboxylate ion can not attack Nu<sup>-</sup> and hence it is irreversible.



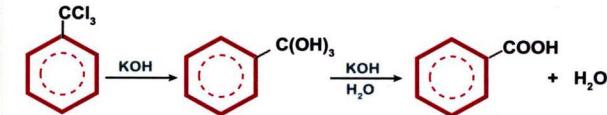
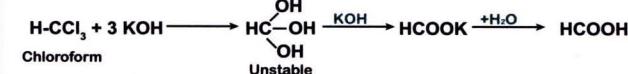
Relative reactivity of acyl compounds towards hydrolysis



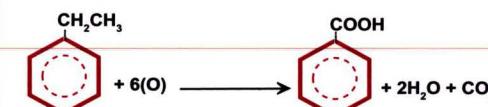
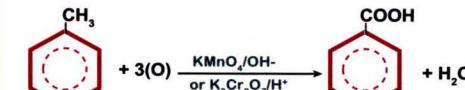
## From Grignard Reagents



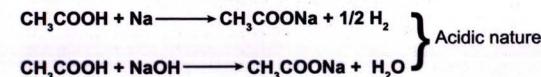
## Hydrolysis of trihalides



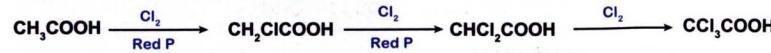
## Oxidation of alkyl benzene



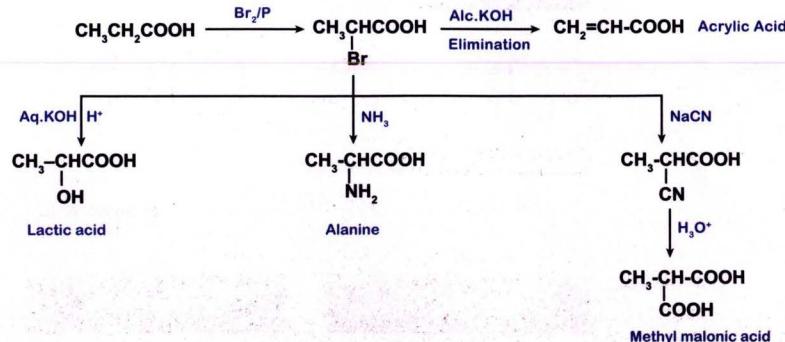
### Reactions due to H-atoms of-COOH group



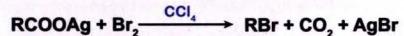
### Reactions due to $\alpha$ -H-atoms: (HVZ reaction)



The function of phosphorous is to convert a little of the acid into acid halide  
HVZ reaction provides a path for the preparation of substituted carboxylic acids by  $S_N$  reaction

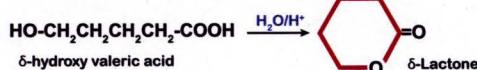
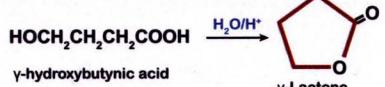


### Hunsdiecker reaction (decarboxylation)

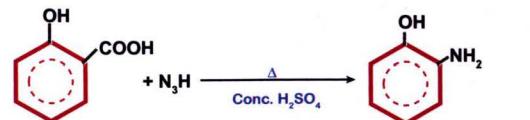
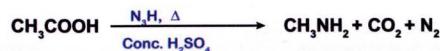


### Intramolecular Esterification:

Hydroxy acids form cyclic esters called Lactones  
This spontaneous **intramolecular esterification** is favourable when five or six membered ring is formed

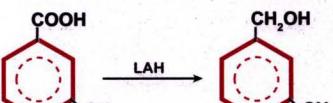
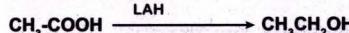


### Schmidt Reaction:



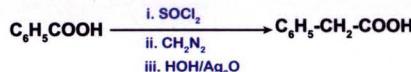
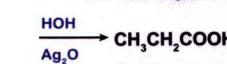
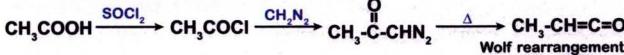
## Chemical Properties

### Reduction Reactions

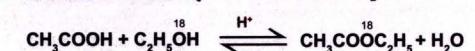
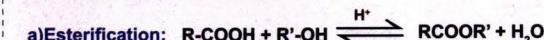


### Arndt - Eistert reaction

R-COOH is converted into R-CH<sub>2</sub>COOH (higher homologue)

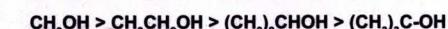


### Reactions due to -OH group

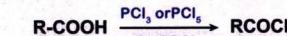


The presence of bulky groups near the site of reaction ,slows down esterification

Hence the decreasing order of esterification of acids and alcohols is  
 $\text{HCOOH} > \text{CH}_3\text{COOH} > (\text{CH}_3)_2\text{CHCOOH} > (\text{CH}_3)_3\text{C-COOH}$



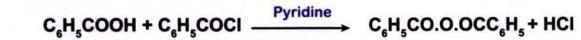
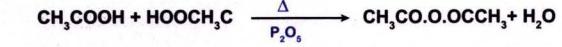
### b) Formation of Acid Chlorides:



### c) Formation of Amides:



### d) Formation of Acid anhydrides:



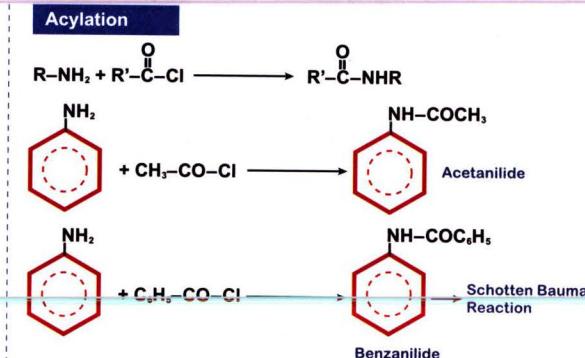
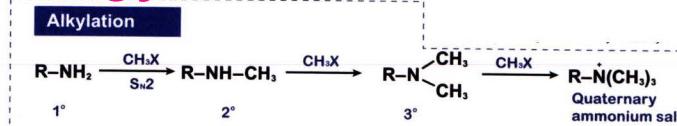
Chain Isomers	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-\text{NH}_2$ n-Butyl amine	$\text{CH}_3\text{CHCH}_2-\text{NH}_2$ isoButyl amine
Positional Isomers	$\text{CH}_3\text{CH}_2\text{CH}_2-\text{NH}_2$ n-Propyl amine	$\text{NH}_2$ $\text{CH}_3-\text{CH}-\text{CH}_3$ , isoPropyl amine
Metamers	$\text{CH}_3\text{CH}_2-\text{NH}-\text{CH}_2\text{CH}_3$ diEthyl amine	$\text{CH}_3\text{CH}_2\text{CH}_2-\text{NH}-\text{CH}_3$ Methyl-propyl amine
Functional Isomers	$\text{CH}_3\text{CH}_2\text{CH}_2-\text{NH}_2$ n-Propyl amine	$\text{CH}_3\text{CH}_2-\text{NH}-\text{CH}_3$ Ethyl Methyl amine
		$(\text{CH}_3)_3-\text{N}$ Trimethyl amine

Aliphatic Amines		
$\text{R}-\text{NH}_2$ (1°)	$\text{R}-\text{NH}-\text{R}$ (2°)	$\text{R}_3\text{N}$ (3°)
$\text{CH}_3-\text{NH}_2$ Methyl amine	$\text{CH}_3-\text{NH}-\text{CH}_3$ Dimethyl amine	$(\text{CH}_3)_3-\text{N}$ Trimethyl amine

Aromatic Amines		
$\text{NH}_2$ Aniline	$\text{NH}-\text{CH}_3$ Methyl Aniline	$\text{N}(\text{CH}_3)_2$ Dimethyl Aniline

- a) Lower amines (1° & 2°) are soluble in  $\text{H}_2\text{O}$  due to intermolecular H-bond. Solubility decreases with increase in MW.
- b) Amines are polar and can form intermolecular H-bond like  $\text{NH}_3$  (except 3° amines)
- c) Amines have higher B.P than non polar compounds of the same molecular weight but lower than that of alcohols and carboxylic acids.
- d) Due to presence of a lone pair of electrons on N-atom, amines acts as nucleophiles (bases)



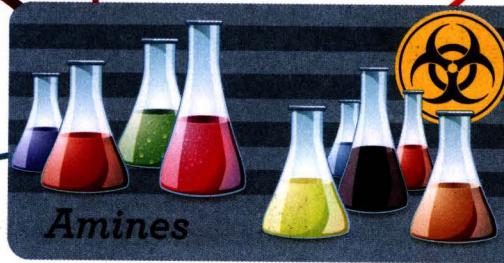
## Isomerism

## Classification

## Physical Properties

## Chemical Properties

## Preparations

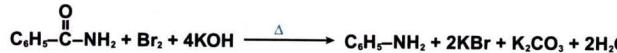


## Preparations

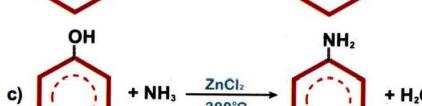
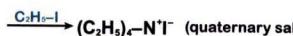
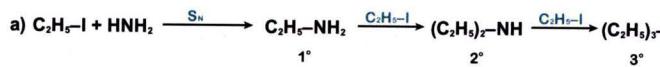
### Hoffmann degradation of Amides



Carbonyl Carbon atom of the amide is lost as  $\text{CO}_3^{2-}$



### By Ammonolysis Reaction



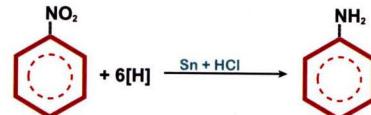
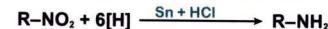
### By Reduction

Almost any Nitrogen containing organic compound can be reduced to an amine

#### a) Reduction of Nitriles (Mendius Reaction):



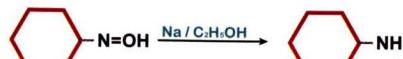
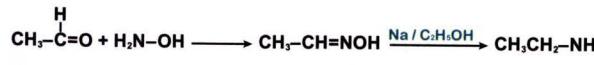
#### b) Reduction of Nitro Compounds:



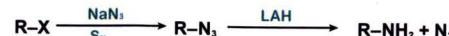
#### c) Reduction of Acid Amides:



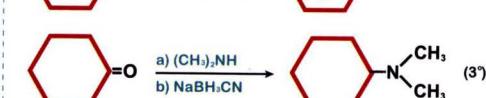
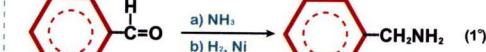
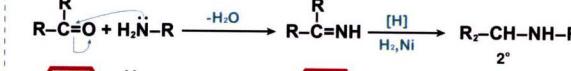
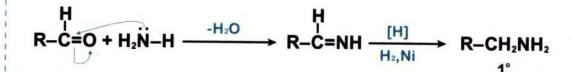
#### d) Reduction of Oximes:



#### e) Reduction of Azides:

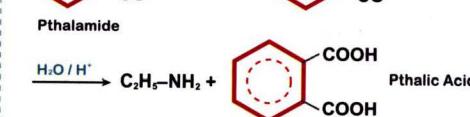
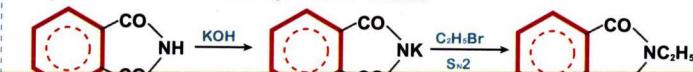


### By Reductive Amination of Aldehydes or Ketones



### Gabriel Pthalimide Synthesis

Alkyl Halides combine with  $\text{NH}_3$  to form 1° amines

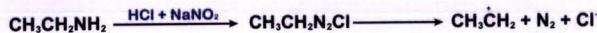


Reaction stops here and hence no more alkylation to form 2° & 3° amines mixture

## Action with Nitrous Acid



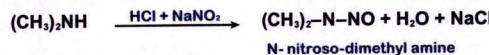
1° amines evolve  $N_2$  with  $HNO_2$ . The unstable diazonium salt changes into carbocation, which gives a variety of products like Alkenes, Alcohols, Alkyl Halides etc.



Aryl diazonium salts are stable in cold aqueous solutions.



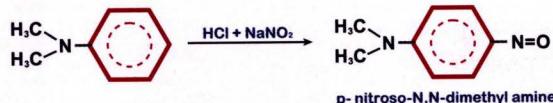
2° amines yield N-Nitrosoamines, a oily yellow liquid (insoluble in water)



3° amines (aliphatic) yield amine salt and N-Nitrosoammonium halide.

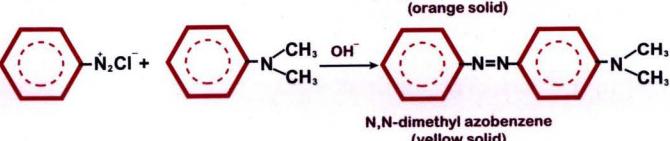
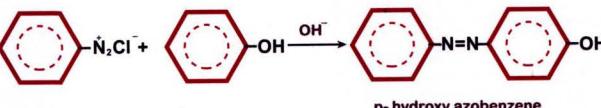


Aromatic 3° amines undergo Electrophilic aromatic substitution called Nitrosation reaction at para position.



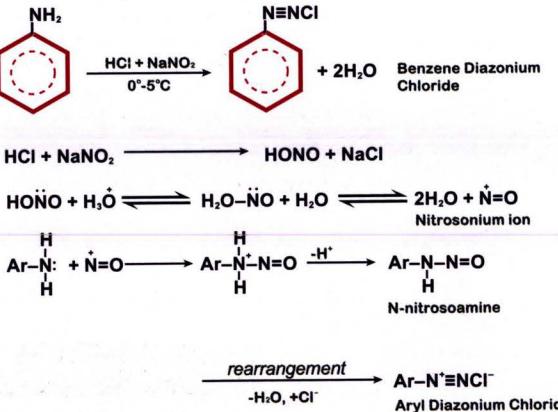
## Physical Properties

- a) Crystalline solid, colourless, turns brown in air
- b) Unstable and explode when warmed
- c) Freely soluble in water
- d) Aqueous solution is neutral but conducts electricity indicating the presence of ions



If para position is not available, then the coupling takes place at the ortho position.

Conversion of aryl 1° amines into a diazonium salt is called diazotisation.



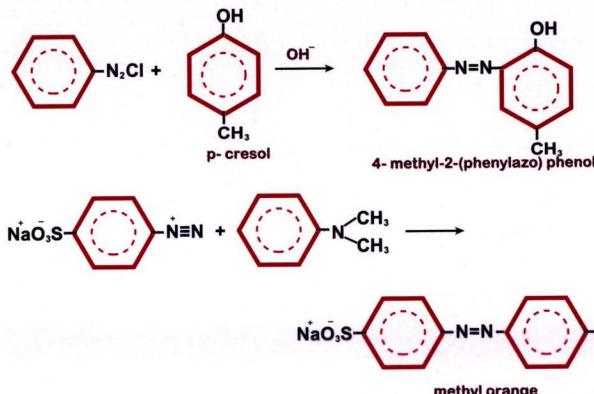
## Diazotisation

## Aryl Diazonium Salts

## Chemical Properties

### Coupling Reactions

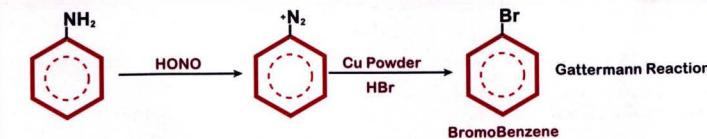
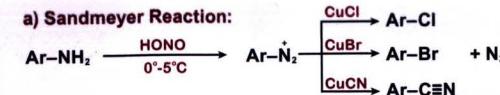
- It is an Electrophilic Aromatic Substitution
- $ArN_2^+$  is the electrophile
- $N_2$  is not lost



Azo compounds are intensely coloured because the azo linkage ( $-N=N-$ ) brings two aromatic rings into conjugation. This extended system of delocalised  $\pi$  electrons allows absorption of light in the visible region.

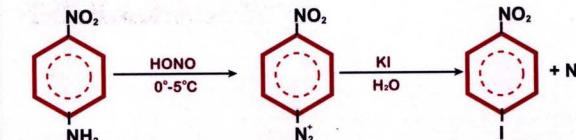
## Substitution Reactions

Diazo ( $-N=N$ ) group is replaced by a nucleophile

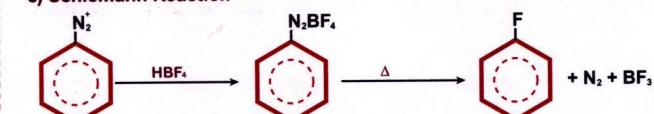


Presence of ERG at o- and p- position increases while EWG decreases the rate of the substitution.

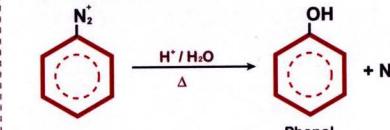
### b) Replacement of -I



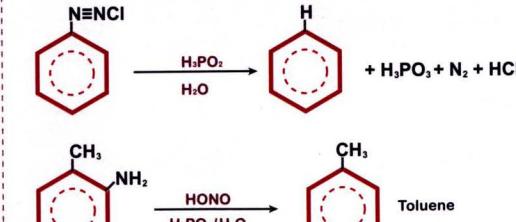
### c) Schiemann Reaction



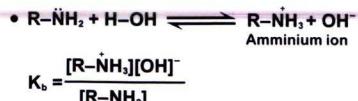
### d) Replacement by -OH



### e) Replacement by -H (deamination):



- Amines are relatively weak bases
- They are stronger bases than water but weaker bases than  $\text{-OH}^-$ ,  $\text{-OCH}_3$  and  $\text{-CH}_3$



- Greater the  $K_b$ , lower the  $pK_b$ , stronger the base
- Thus lone pair of N-atom is used for protonation and hence the basic nature
- The basic nature order of amines is  
Aliphatic Amines > Aralkylamines > Ammonia > Arylamines

- The alkyl groups stabilises the amminium ion due to  $+I$  effect



- With the increase in alkyl substitution the basic nature increases  
 $(\text{CH}_3)_3\text{-N} > (\text{CH}_3)_2\text{-NH} > \text{CH}_3\text{-NH}_2 > \text{NH}_3$  - in gas phase  
 $3^\circ > 2^\circ > 1^\circ$

In aqueous solution the order is

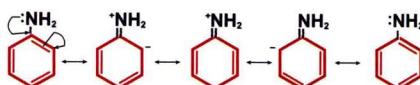


$pK_b = 3.28 \quad 3.36 \quad 4.30 \quad 4.74$

The lower basic nature of  $3^\circ$ -amine is due to

- a) steric hindrance b) poorer solvation of amminium ion

- Aryl amines are weaker bases than Aliphatic amines and  $\text{NH}_3$ . This is due to the fact that lone pair on N-atom is used in delocalisation of  $\pi$  electrons and are less available for protonation



- This resonance stabilisation is lost on protonation

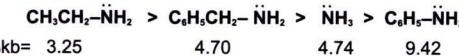


In anilinium ion, N-atom has no more electron pair to interact with the  $\pi$  system of aromatic ring

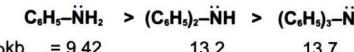
- Aralkyl amines ( $\text{Ar.C}_6\text{H}_5\text{-NH}_2$ ) resemble aliphatic amines because N-atom is not in conjugation with  $\pi$  system of aromatic ring



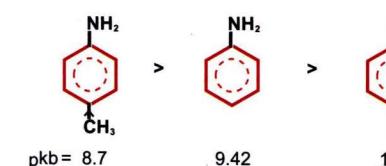
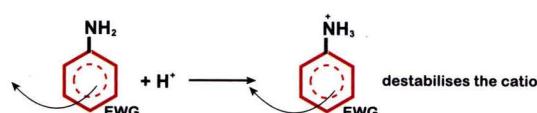
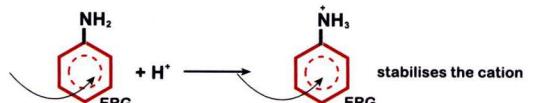
Hence the order is



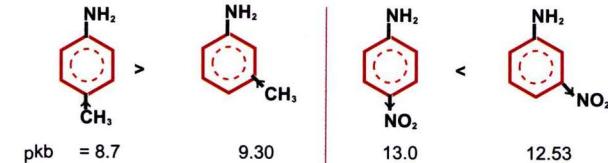
Conjugation of the amino group of an arylamine with second aromatic ring, then a third reduces its basicity even further



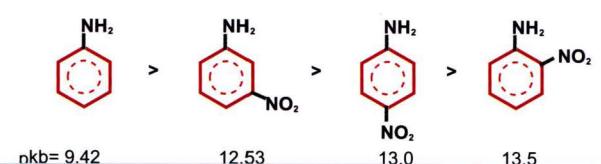
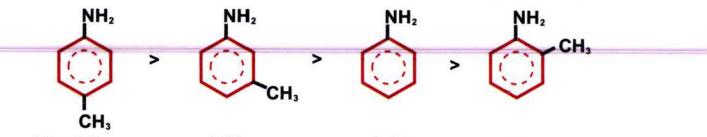
ERG (-CH<sub>3</sub>, -OCH<sub>3</sub>, -NH<sub>2</sub> etc) increases the basic nature while EWG(-X, -NO<sub>2</sub>, -CN) decreases the basic nature of Aniline



The base strengthening or weakening effect is more marked when the substituent is present at p-position than at m-position



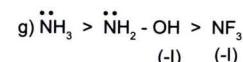
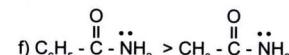
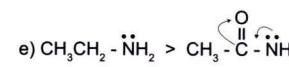
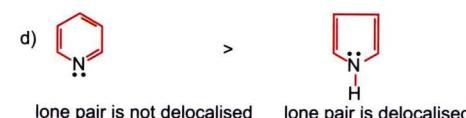
o-substituted anilines (having ERG or EWG) are less basic than aniline. It is due to combined effects of steric and electronic, called ortho effect



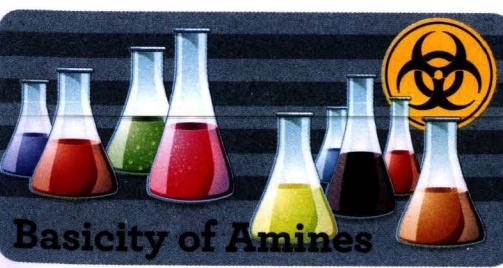
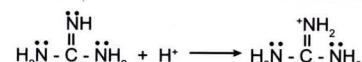
N-methyl anilines are more basic than Aniline  
 $\text{C}_6\text{H}_5\text{-N}(\text{CH}_3)_2 > \text{C}_6\text{H}_5\text{-NHCH}_3 > \text{C}_6\text{H}_5\text{-NH}_2$

#### Basicity of other Nitrogen containing compounds

- a)  $\text{R}-\ddot{\text{N}}\text{H}_2 > \text{R}-\text{CH}=\ddot{\text{N}}\text{H} > \text{R}-\text{C}\equiv\ddot{\text{N}}$   
 $\text{Sp}^3 \quad \text{Sp}^2 \quad \text{Sp}$
- b)  $\text{CH}_3\text{CH}_2\text{CH}_2-\ddot{\text{N}}\text{H}_2 > \text{CH}_3\text{CH}=\text{CH}-\ddot{\text{N}}\text{H}_2 > \text{CH}_3\text{C}\equiv\ddot{\text{N}}\text{H}_2$   
 $\text{Sp}^3 \quad \text{Sp}^2 \quad \text{Sp}$
- c)  $\text{R}-\ddot{\text{N}}\text{H}_2 > \text{HO}-\ddot{\text{N}}\text{H}_2$   
 $+I \quad -I$



h) Guanidine ( $pK_b = 0.40$ ) is the strongest base among neutral organic compounds



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