

# ALKYL HALIDES & ARYL HALIDES

## VICTOR GRIGNARD

François Auguste Victor Grignard (1871 - 1935) was a Nobel Prize-winning French chemist.

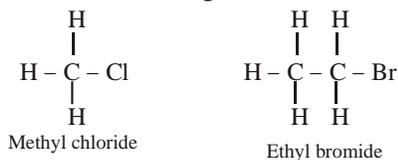
He is most noted for devising a new method for creating carbon-carbon bonds (i.e. an addition reaction) in organic synthesis (Original publication: V. Grignard, Compt. Rend. Vol. 130, p. 1322 (1900)). The synthesis occurs in two steps:

1. Synthesis of the Grignard reagent: an organomagnesium compound (the Grignard reagent) is made reacting an organohalide (R-X, where R stands for some alkyl, acyl, or aryl radical and X is a halogen such as usually bromine or iodine) with magnesium metal dissolved in diethyl ether. The resulting compound, named a Grignard reagent, has the general chemical formula R-Mg-X.
2. Attack on the carbonyl: A ketone or an aldehyde (both contain a carbonyl group) is added to the solution containing the Grignard reagent. The carbon atom that is bonded to the Mg atom bonds to the carbonyl carbon atom by nucleophilic addition, with the formation of a new compound, which is an alcohol.

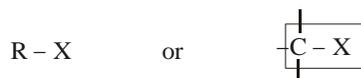
The Grignard reaction is an important means of making larger organic compounds from smaller starting materials. By careful selection of the starting materials, a wide variety of compounds can be made by this reaction. For this work, Grignard was awarded the Nobel Prize in Chemistry in 1912 jointly with fellow Frenchman Paul Sabatier.

## **INTRODUCTION**

Alkyl Halides are compounds in which a halogen atom is attached to carbon. For example,

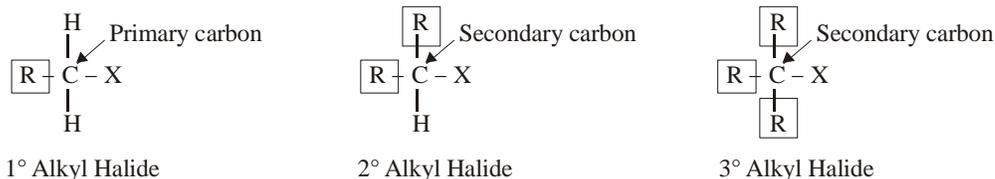


They have the general formula



Where R - alkyl group; X = Cl, Br, I or F. The halogen atom bonded to carbon is the functional group of alkyl halides.

Alkyl halides are classified as Primary ( $1^\circ$ ), Secondary ( $2^\circ$ ), or Tertiary ( $3^\circ$ ), depending upon whether the X atom is attached to a primary, secondary, or a tertiary carbon.



Alkyl halides are among the most useful organic compounds. They are frequently used to introduce alkyl groups into other molecules.

## 5.1 STRUCTURE

Let us consider methyl chloride ( $\text{CH}_3\text{Cl}$ ) for illustrating the orbital make up of alkyl halides in methyl chloride, the carbon atom is  $\text{sp}^3$  hybridized. The chlorine atom has a half-filled  $p$  orbital in valence shell. The  $\text{C}-\text{Cl}$  bond is formed by the overlap of an  $\text{sp}^3$  orbital of carbon and the half-filled  $p$  orbital of chlorine atom shown in figure. Each  $\text{C}-\text{H}$  bond is formed by the overlap of an  $\text{sp}^3$  orbital of carbon

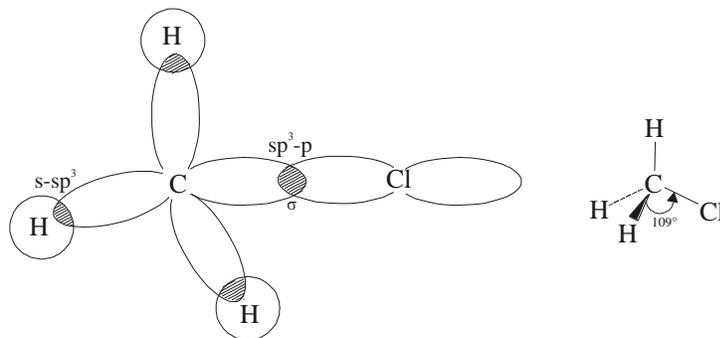


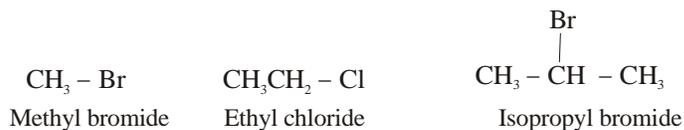
Figure: Orbital structure of Methyl chloride

and the  $s$  orbital of hydrogen. All bonds are  $\sigma$  bonds. The  $\text{H}-\text{C}-\text{H}$  and  $\text{H}-\text{C}-\text{Cl}$  bond angles are approximately tetrahedral.

## 5.2 NOMENCLATURE

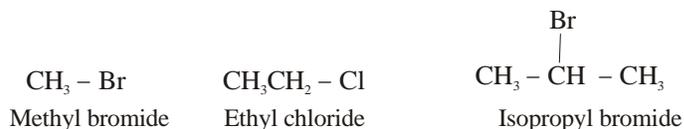
Alkyl halides are named in two ways

(1) **Common system:** In this system the alkyl group attached to the halogen atom is named first. This is then followed by an appropriate word chloride, bromide, or fluoride. Notice that the common names of alkyl halides are TWO-WORD names.



(2) **IUPAC system:** The IUPAC names of alkyl halides are obtained by using the following rules:

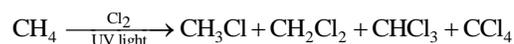
- (a) Select the longest carbon chain containing the halogen atom and name the alkyl halides as a derivative of the corresponding hydrocarbon.
- (b) Number the chain so as to give the carbon carrying the halogen atom the lowest possible number.
- (c) Indicate the position of the halogen atom by a number and by the fluoro-, chloro-, bromo- or iodo-.
- (d) Name other substituents and indicate their positions by numbers. The examples given below show how these rules are applied. Notice that the IUPAC names of alkyl halides are ONE-WORD names.



### 5.3 METHODS OF PREPARATION

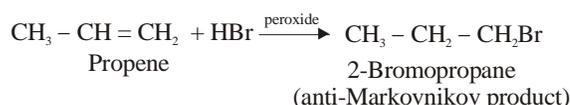
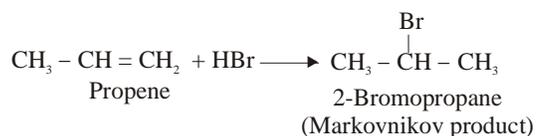
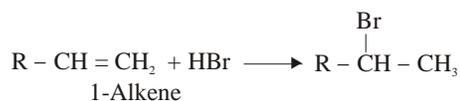
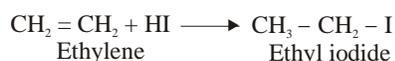
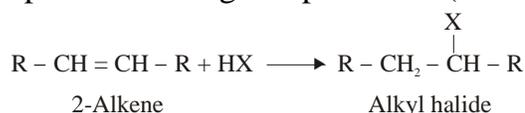
Alkyl halides can be prepared by the following methods:

- (1) **Halogenation of Alkanes:** Alkanes react with  $\text{Cl}_2$  or  $\text{Br}_2$  in the presence of UV light or at high temperature ( $400^\circ\text{C}$ ) to give alkyl halides along with polyhalogen derivatives.

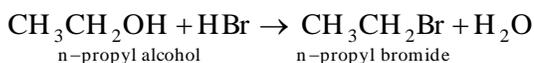
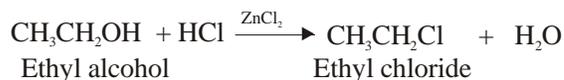
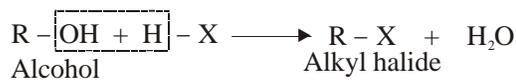


This method is not used in the laboratory because of the difficulty of separating the products.

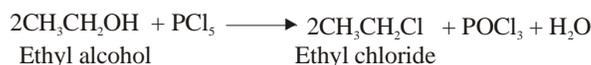
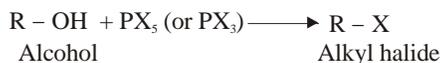
- (2) **Addition of Halogen Acids to Alkenes:** Halogen acids ( $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ) add to alkenes to yield alkyl halides. The mode of addition follows Markovnikov rule, except for the addition of  $\text{HBr}$  in the presence of organic peroxides ( $\text{R-O-O-R}$ ).



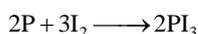
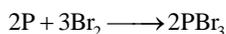
- (3) **Action of Halogen Acids on Alcohols.** Alcohols react with  $\text{HBr}$  or  $\text{HI}$  to produce alkyl bromides or alkyl iodides. Alkyl chlorides are produced by the action of dry  $\text{HCl}$  in the presence of zinc chloride catalyst.



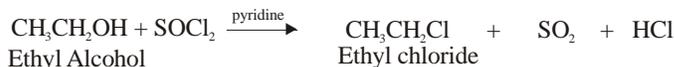
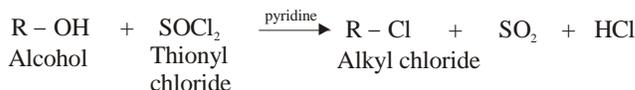
- (4) **Action of Phosphorus Halides on Alcohols.** Alcohols react with phosphorus halides (PX<sub>5</sub> or PX<sub>3</sub>) to form alkyl halides.



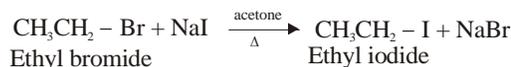
PBr<sub>3</sub> or PI<sub>3</sub> are produced in situ by the addition of Br<sub>2</sub> and I<sub>2</sub> to red phosphorus.



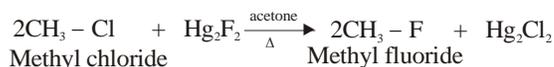
- (5) **Action of Thionyl chloride on alcohols.** Alcohols react with thionyl chloride (SOCl<sub>2</sub>) in the presence of pyridine to produce alkyl chlorides. Pyridine (C<sub>5</sub>H<sub>5</sub>N) absorbs hydrogen chloride as it is formed.



- (6) **Halogen Exchange reaction:** This reaction is particularly suitable for preparing alkyl iodides. The alkyl bromide or chloride is heated with a concentrated solution of sodium iodide in acetone.



Alkyl fluorides are also prepared by treating an alkyl chloride or bromide with inorganic fluorides.



## 5.4 PHYSICAL PROPERTIES

- (1) CH<sub>3</sub>Cl, CH<sub>3</sub>Br, CH<sub>3</sub>F and CH<sub>3</sub>CH<sub>2</sub>Cl are gases at room temperature. Other alkyl halides upto C<sub>18</sub> are colourless liquids. Those beyond C<sub>18</sub> are colourless solids.

- (2) Alkyl halides are insoluble in water but soluble in organic solvents. The insolubility in water is due to their inability to form hydrogen bonds with water.
- (3) Alkyl bromides and iodides are denser than water. Alkyl chlorides and fluorides are lighter than water.
- (4) Alkyl halides have higher boiling points than alkanes of comparable molecular weight. For a given halogen atom, the boiling points of alkyl halides increase with the increase in the size of the alkyl group. For a given alkyl group, the boiling points of alkyl halides follow the order  $RI > RBr > RCl > RF$ .

## 5.5 CHEMICAL PROPERTIES

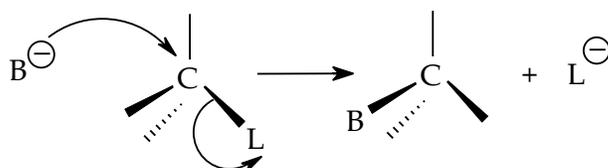
Alkyl halides are very reactive compounds. They undergo substitution, elimination and reduction reactions. Alkyl halides also react with metals to form organometallic compounds.

### HSAB (Hard And Soft Acid-Base) Principle

According to hard and soft acid-base principle of Pearson, hard acids are those species, which have less tendency to accept an electron pair (like  $H^+$ ,  $Li^+$ ,  $Mg^{2+}$ ,  $Cr^{3+}$ ,  $Al^{3+}$ ,  $Al^{3+}$  etc.) and hard bases are those species, which have less tendency to donate electron pair (like  $F^-$ ,  $O^{2-}$  etc.) A hard base prefers a hard acid whereas a soft base prefers a soft acid.

### Basicity And Nucleophilicity

A negatively charged species can function as nucleophile as well as like base but its nucleophilicity and basicity are different. Nucleophilicity of the species is the ability of the species to attack an electrophilic carbon while basicity is the ability of the species to remove  $H^+$  from an acid. Let us have a species,  $B^-$ . Its function as a nucleophile is shown as



and its role as base is indicated as



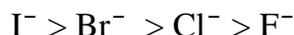
The nucleophilicity is determined by the kinetics of the reaction, which is reflected by its rate constant ( $k$ ) while basicity is determined by the equilibrium constant, which is reflected by its  $K_b$ .

The order of nucleophilicity of different species depends on the nature of solvent used. For instance, let us take  $F^-$ ,  $Cl^-$ ,  $Br^-$  and  $I^-$  with their counter cation as  $Na^+$  and see their nucleophilicity order in different solvents. There are four categories of solvents, namely

non-polar (CCl<sub>4</sub>), polar protic (H<sub>2</sub>O), polar aprotic (CH<sub>3</sub>SOCH<sub>3</sub>) and weakly polar aprotic (CH<sub>3</sub>COCH<sub>3</sub>).

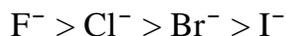
Polar solvents are able to dissociate the salts i.e. ion-pairs can be separated. On the other hand, non-polar and weakly polar solvents are unable to dissociate salts, so they exist as ion-pairs. The ion-pairing is strong when ions are small and have high charge density.

In non-polar and weakly polar aprotic solvents, all the salts will exist as ion-pairs. The ion-pairing will be strongest with the smallest anion (F<sup>-</sup>) and weakest with the largest anion (I<sup>-</sup>), thus the reactivity of X<sup>-</sup> decreases with decreasing size. Thus, the nucleophilicity order of X<sup>-</sup> in such solvents would be



In polar protic solvents, hydrogen bonding or ion-dipole interaction diminishes the reactivity of the anion. Stronger the interaction, lesser is the reactivity of anion. F<sup>-</sup> ion will form strong H-bond with polar protic solvent while weakest ion-dipole interaction will be with I<sup>-</sup> ion. Thus, the nucleophilicity order of X<sup>-</sup> in polar protic solvent would be I<sup>-</sup> > Br<sup>-</sup> > Cl<sup>-</sup> > F<sup>-</sup>.

Polar aprotic solvents have the ability to solvate only cations, thus anions are left free. The reactivity of anions is then governed by their negative charge density (i.e. their basic character). Thus, the order of nucleophilicity of X<sup>-</sup> in polar aprotic solvents would be



On this basis, certain nucleophilicity orders are

- (i) In polar protic solvents, HS<sup>-</sup> > HO<sup>-</sup>
- (ii) In weakly polar aprotic solvents, CsF > RbF > KF > NaF > LiF
- (iii) Bases are better nucleophiles than their conjugate acids. For example, OH<sup>-</sup> > H<sub>2</sub>O and NH<sub>2</sub><sup>-</sup> > NH<sub>3</sub>
- (iv) In non-polar solvents, <sup>-</sup>CH<sub>3</sub> > <sup>-</sup>NH<sub>2</sub> > <sup>-</sup>OH > <sup>-</sup>F
- (v) When nucleophilic and basic sites are same, nucleophilicity parallels basicity. For example, RO<sup>-</sup> > HO<sup>-</sup> > R-CO-O<sup>-</sup>
- (vi) When the atom bonded to nucleophilic site also has an unshared pair of electrons, nucleophilicity of species increases. For example, HOO<sup>-</sup> > HO<sup>-</sup> and H<sub>2</sub> $\ddot{N}$ - $\ddot{N}$ H<sub>2</sub> >  $\ddot{N}$ H<sub>3</sub>

## Nucleophilic Substitution Reactions

### Nucleophilic Displacement By S<sub>N</sub>1 And S<sub>N</sub>2 Mechanisms

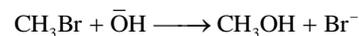
	<b>S<sub>N</sub>1</b>	<b>S<sub>N</sub>2</b>
<b>Steps</b>	Two:	One
	(i) $R:X \xrightarrow{\text{slow}} R^+ + X^-$ <span style="margin-left: 100px;">carbonium</span>	$R:X + Nu^- \longrightarrow RNu$

	(ii) $R^+ + Nu^- \longrightarrow RNu + X^-$	
	or	or
	$R^+ + :Nu$	$R: X + Nu \longrightarrow RNu^+$
	$RNu^+$	$X^-$
<b>Rate</b>	$= K [RX] \text{ (1}^{st} \text{ order)}$	$= K [RX] [ :Nu^- ] \text{ (2}^{nd} \text{ order)}$
<b>TS of slow step</b>		
<b>Stereochemistry</b>	Inversion and racemization	Inversion (backside attack)
<b>Molecularity</b>	Unimolecular	Bimolecular
<b>Reactivity</b>	$3^\circ > 2^\circ > 1^\circ > CH_3$	$CH_3 > 1^\circ > 2^\circ > 3^\circ$
<b>Structure of R</b>	Stability of $R^+$	Steric hindrance in R group
<b>Determining factor</b>		$RI > RBr > RCl > RF$
<b>Nature of X</b>	$RI > RBr > RCl > RF$	With $Nu^-$ there is a large rate increase in polar aprotic solvents.
<b>Solvent effect on rate</b>	Rate increases in polar solvent	
<b>Effect of nucleophile</b>		Rate depends on nucleophilicity $I^- > Br^- > Cl^-$ ; $RS^- > RO^-$
<b>Catalysis</b>	Lewis acid, eg. $Ag^+$ , $AlCl_3$ , $ZnCl_2$	None
<b>Competitive reactoin</b>	Elimination, rearrangement	Elimination

## THE $S_N2$ REACTION

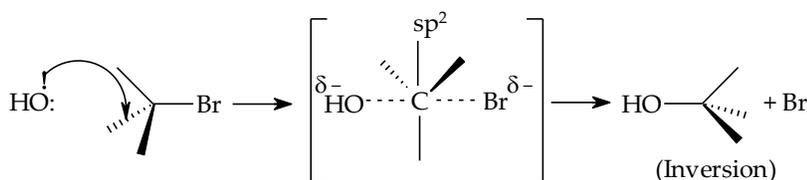
### MECHANISM AND KINETICS

The reaction between methyl bromide and hydroxide ion to yield methanol follows second order kinetics; that is, the rate depends upon the concentration of both reactants.



$$\text{rate} = K[CH_3Br] [OH^-]$$

The simplest way to account for the kinetics is to assume that reaction requires a collision between a hydroxide ion and a methyl bromide molecule. In its attack, the hydroxide ion stays for away as possible from the bromine; i.e. it attacks the molecule from the rear and begins to overlap with the tail of the  $sp^3$  hybrid orbital holding Br. The reaction is believed to take place as shown:



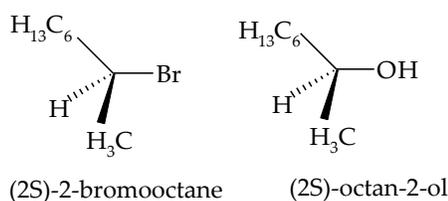
(T.S.)

In the T.S. the carbon is partially bonded to both  $\text{-OH}$  and  $\text{-Br}$ ; the  $\text{C-OH}$  bond is not completely formed, the  $\text{C-Br}$  bond is not yet completely broken. Hydroxide has a diminished  $\text{-ve}$  charge, since it has begun to share its electrons with carbon. Bromine has developed a partial negative charge, since it has partly removed a pair of electrons from carbon. At the same time, of course, ion dipole bonds between hydroxide ion and solvent are being broken and ion-dipole bonds between bromide ion and solvent are being formed.

As the  $\text{-OH}$  becomes attached to  $\text{C}$ , 3 bonds are forced apart ( $120^\circ$ ) until they reach the spike arrangement of the T.S; then as bromide is expelled, they move on to the tetrahedral arrangement opposite to the original one.

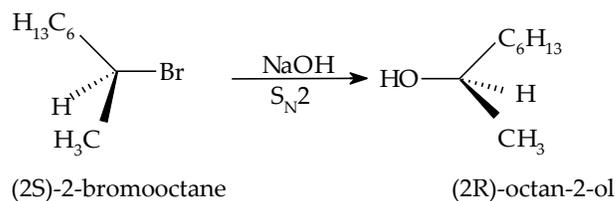
## STEREOCHEMISTRY

Both 2-bromo-octane and 2-octanol are chiral

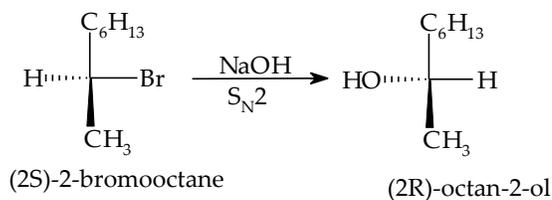


The  $(-)$  bromide and the  $(-)$  alcohol have similar configurations, i.e.  $\text{-OH}$  occupies the same relative position in the  $(-)$  alcohol as  $\text{-Br}$  does in the bromide.

When  $(-)$ -2-bromooctane is allowed to react with sodium hydroxide under  $\text{S}_{\text{N}}2$  conditions,  $(+)$ -2-octanol is obtained



In Fisher projection the above reaction can be represented as follows



We see that  $\text{-OH}$  group has not taken the position previously occupied by  $\text{-Br}$ ; the alcohol obtained has a configuration opposite to the bromide. A reaction that yields a

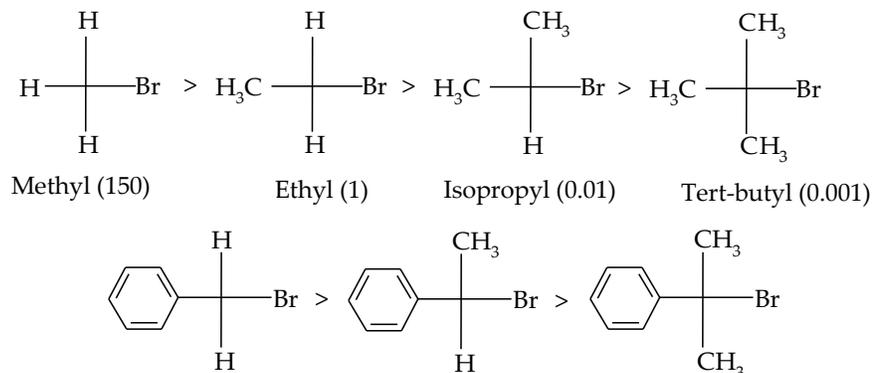
product whose configuration is opposite to that of the reactant is said to proceed with inversion of configuration.

## REACTIVITY

In  $S_N2$  reactions the order of reactivity of  $RX$  is  $CH_3X > 1^\circ > 2^\circ > 3^\circ$ .

Difference in rate between two  $S_N2$  reactions seem to be chiefly due to steric factors (bulk of the substituents) and not due to electronic factors i.e. ability to withdraw or release electrons.

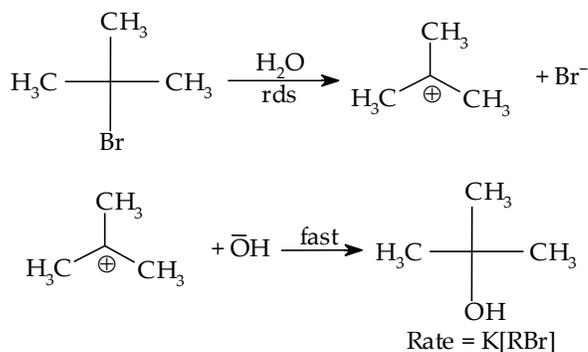
### Relative Reactivity Towards $I^-$



## THE $S_N1$ REACTION

### MECHANISM AND KINETICS

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



$S_N1$  reaction follows first order kinetics

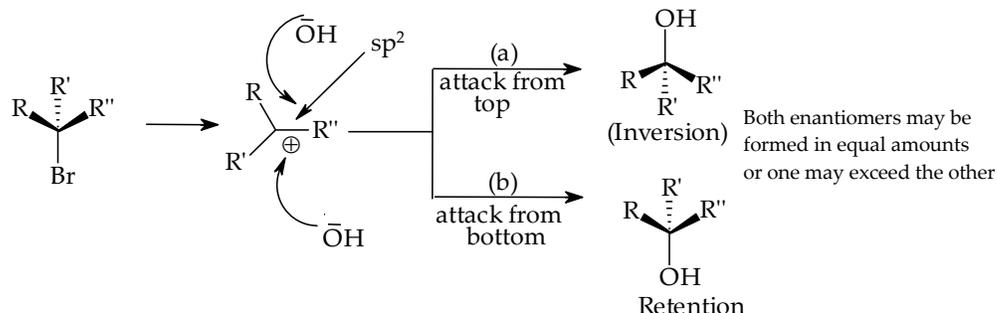
### STEREOCHEMISTRY

When (-)-2-bromo octane is converted into alcohol under conditions where first-order kinetics are followed, partial racemization is observed.

The optically active bromide ionizes to form bromide ion and the flat carbocation. The nucleophilic reagent then attaches itself to carbonium ion from either face of the flat ion.

If the attack were purely random, we would expect equal amounts of two isomers; i.e. we would expect only the racemic modification. But the product is not completely racemized, for the inverted product exceeds its enantiomer.

We can say in contrast  $S_N2$  reaction, which proceeds with complete inversion; an  $S_N1$  reaction proceeds with racemization though may not be complete.



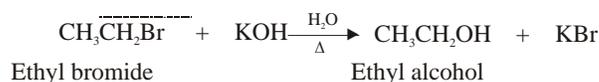
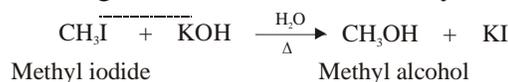
r.d.s □ formation of carbonium ion.

Reactivity of an alkyl halide depends upon the stable carbonium ion it can form.

In  $S_N1$  reactions the order of reactivity of alkyl halides is Allyl, benzyl  $>$   $3^\circ >$   $2^\circ >$   $1^\circ >$   $CH_3X$ .

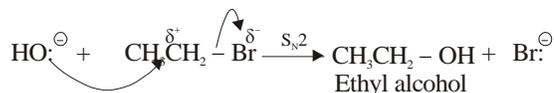
Some of the important nucleophilic substitution reactions of alkyl halides are described below:

(1) **Reaction with aqueous KOH:** Alkyl halides react with aqueous potassium hydroxide to form alcohols. The halogen atom is substituted by -OH group.

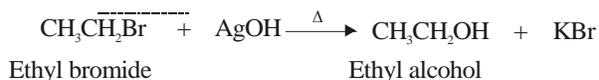
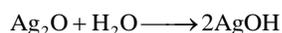


### MECHANISM:

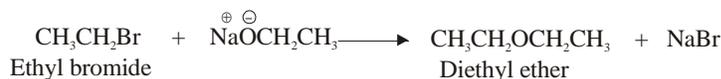
In the above reaction  $\text{OH}^-$  is the nucleophile



(2) **Reaction with Moist Silver Oxide:** Alkyl halides on treatment with a suspension of silver oxide in moist ether produce alcohols. Halogen atom is substituted by -OH group.



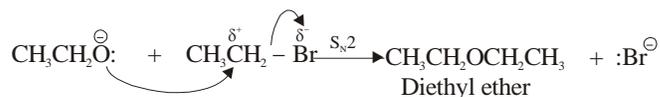
(3) **Reaction with sodium alkoxides:** Alkyl halides react with sodium alkoxides ( $\text{RONa}$ ) to form ethers. Sodium alkoxides are prepared by dissolving metallic sodium in excess of the appropriate alcohol. For example,



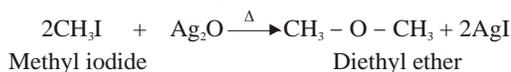
This method of making ethers is called Williamson Ether Synthesis.

### MECHANISM:

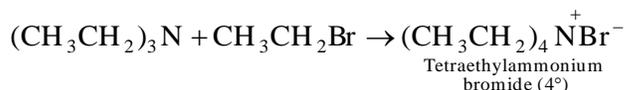
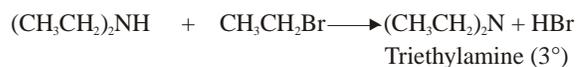
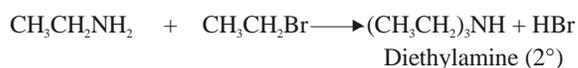
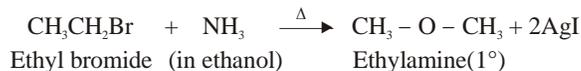
In the above reaction  $\text{CH}_3\text{CH}_2\text{O}^-$  is the nucleophile.



Ethers can also be produced by heating an alkyl halide with dry silver oxide.



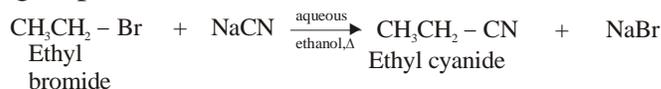
- (4) **Reaction with Ammonia:** When an alkyl halide is heated with an alcoholic solution of ammonia in a sealed tube, alkylation of ammonia takes place. A mixture of different classes of amines results.



Each amine formed exists in equilibrium with its salt. For example,

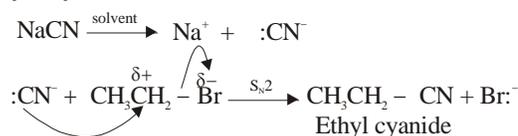


- (5) **Reaction with Sodium Cyanide:** Alkyl halides react with sodium cyanide in a suitable solvent (generally aqueous ethanol) to form alkyl cyanides or nitriles. Halogen atom is replaced by  $-\text{CN}$  group.

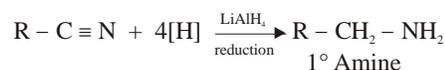
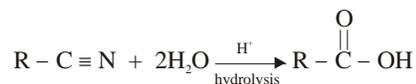


### MECHANISM:

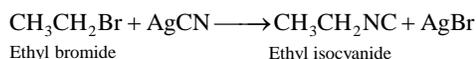
Cyanide ion is an excellent nucleophile. It attacks ethyl bromide by an  $\text{S}_\text{N}2$  mechanism to form ethyl cyanide.



Alkyl cyanides are useful synthetic reagents. They can be easily converted into carboxylic acids and 1° amines.



Alkyl halides react with silver cyanide to form isocyanides

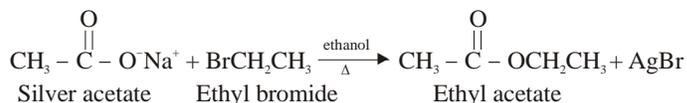


The explanation for this lies in the structure of silver cyanide which is thought to exist in the form of a chain

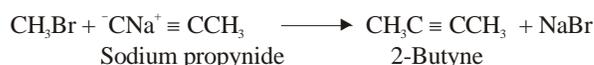


Thus the silver atom is linked to both nitrogen and carbon atom. Accordingly both isomers are possible.

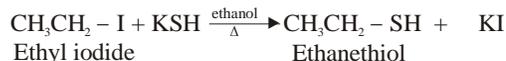
- (6) Reaction with RCOOAg: When an alkyl halide is heated with an alcoholic solution of the silver salt of a carboxylic acid, an ester is formed.



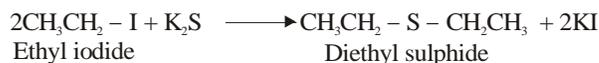
- (7) Reaction with Acetylides: Alkyl halides react with sodium acetylides to form higher alkynes



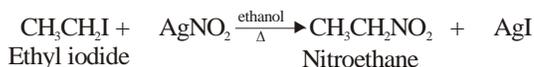
- (8) Reaction with KSH: Alkyl halides react with alcoholic potassium hydrosulphide to form thiols. Halogen atom is substituted by -SH group.



- (9) Reaction with K<sub>2</sub>S. Alkyl halides react with potassium sulphide to form dialkyl sulphides

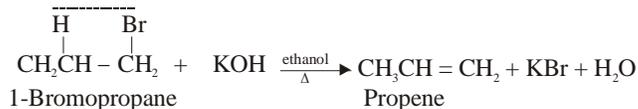
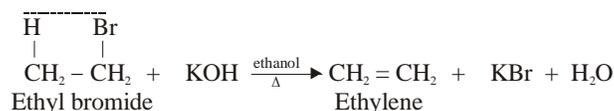


- (10) Reaction with AgNO<sub>2</sub>: Alkyl iodides react with silver nitrite to form nitroalkanes.



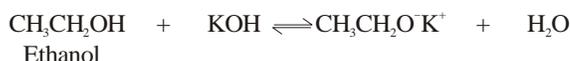
## 5.6 ELIMINATION REACTIONS

- (11) Reaction with alcoholic KOH. Alkyl halides react with alcoholic potassium hydroxide to form alkenes. The reaction involves the elimination of HX from the alkyl halides and is called dehydrohalogenation reaction.



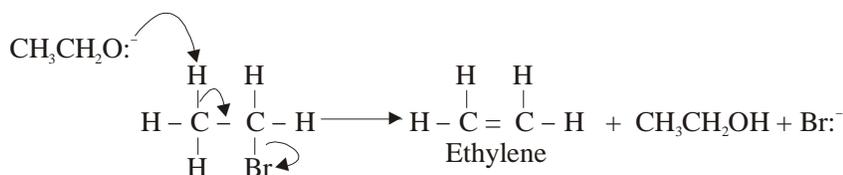
### MECHANISM:

In ethanol an equilibrium occurs between the solvent and potassium hydroxide to produce potassium ethoxide.

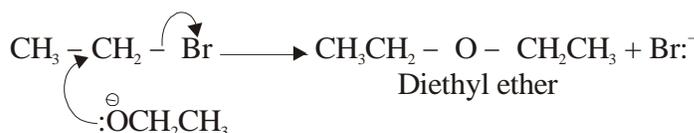


Potassium ethoxide is a strong base. It favours elimination and substitution reactions. There is always a competition between elimination and substitution reactions. For example, ethyl bromide on treatment with alcoholic KOH can give either ethylene or diethyl ether. The attacking nucleophile is  $\text{CH}_3\text{CH}_2\text{O}^-$ :

### ELIMINATION:

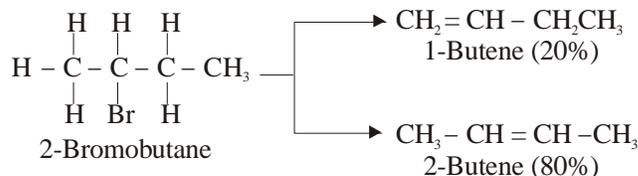


### SUBSTITUTION:



The ratio of the elimination to substitution product depends on the structure of the alkyl halide and experimental conditions. Primary and secondary alkyl halides undergo dehydrohalogenation by E2 mechanism. Tertiary alkyl halides do so by E1 mechanism.

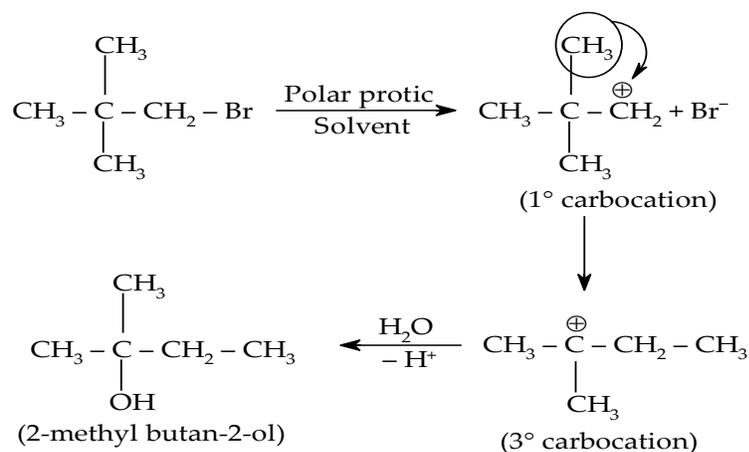
Saytzeff Rule: If the dehydrohalogenation of an alkyl halide can yield more than one alkene, then according to the Saytzeff rule, the main product is the most highly substituted alkene. For example, two alkenes are possible when 2-bromobutane is heated with alcoholic KOH.



Notice that the major product is 2-butene, a disubstituted alkene.

(12) Reaction with Mg-alkyl halides react with magnesium metal in dry ether to form Grignard reagents.

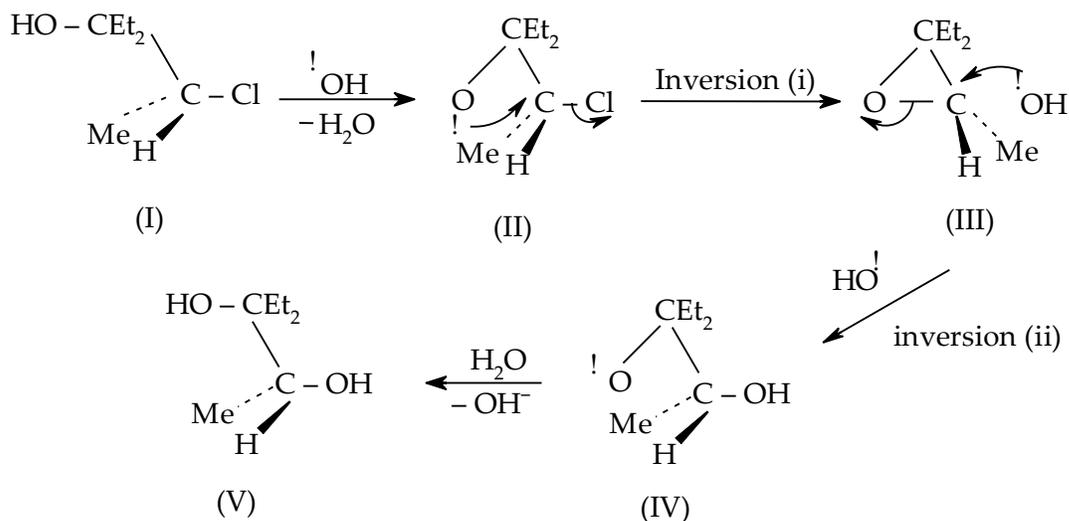




### 5.8 NEIGHBOURING GROUP PARTICIPATION: RETENTION

There are some examples of retention of configuration in nucleophilic displacement reactions. The common feature for such nucleophilic displacements is an atom or group close to the carbon undergoing attack which has at least one electron pair available on it. This neighbouring group can use its electron pair to interact with the 'backside' of the carbon atom undergoing substitution, thus preventing attack by the external nucleophilic reagent. Attack can thus take place only 'from the front side', leading to retention of configuration.

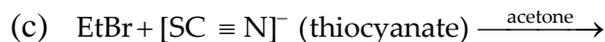
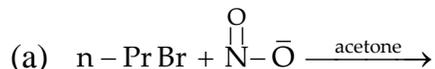
Base hydrolysis of the 1, 2-chlorohydrin is found to yield 1, 2-diol with the same configuration (retention).



## ILLUSTRATIONS

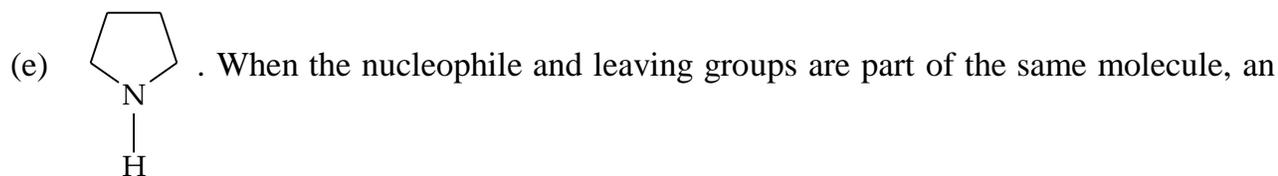
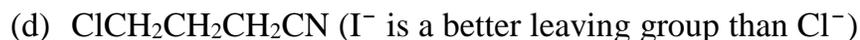
### Illustration 1

Give the organic products of the following reactions



### Solution

The nucleophiles in (a), (b) and (c) are ambident since they each have more than one reactive site. In each case, the more nucleophilic atom reacts even though the other atom may bear a more negative charge.



intramolecular displacement occurs if a three-, or five- or a six-membered ring can form.

### Illustration 2

Compare the rates of  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  reactions of cyclopropyl and cyclopentyl chloride.

### Solution

Cyclopropyl chloride is much less reactive than cyclopentyl chloride in each type of reaction because the  $\text{sp}^2$  hybridised carbon ( $120^\circ$  bond angle) created in each transition state augments the ring strain.

### Illustration 3

Explain the fact that a small amount of NaI catalyzes the general reaction



### Solution

With  $I^-$  ion, the overall reaction occurs in two steps, each of which is faster than the uncatalyzed reaction.

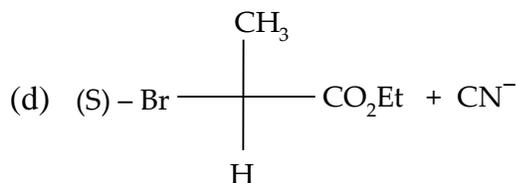
**Step 1.**  $R - Cl + I^- \longrightarrow R - I + Cl^-$ . This step is faster because  $I^-$ , a soft base has more nucleophilicity than  $OR^-$ , a hard base.

**Step 2.**  $R - I + R' O: ^- \longrightarrow R - OR' + I^-$ . This step is faster because  $I^-$  is a better leaving group than  $Cl^-$ .

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### PRACTICE EXERCISE

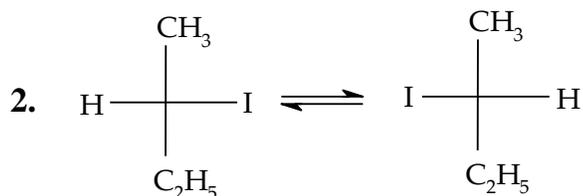
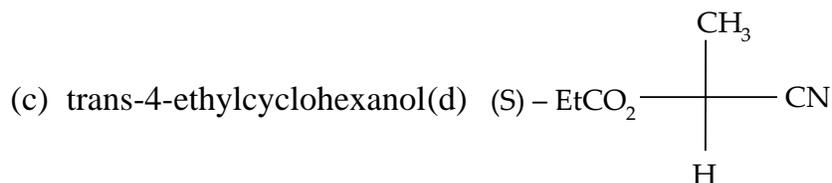
1. Give the products of the following displacement reactions.



2. Optically active 2-iodobutane on treatment with NaI in acetone gives a product, which does not show optical activity. Explain why?

### Answers

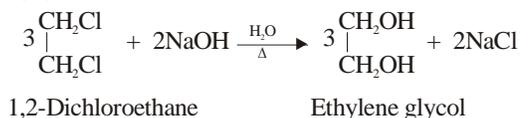
1. (a)  $(S) - CH_3CH(OMe)CH_2CH_3$  (b)  $(R) - CH_3CH(OEt)CH_2CH_3$



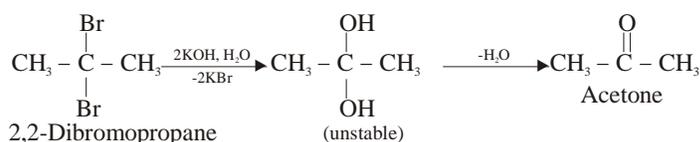
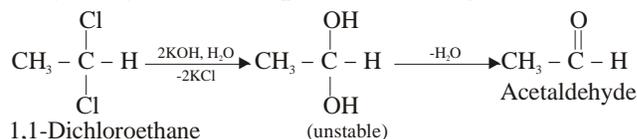


Thus they undergo both substitution and elimination reactions.

- (1) Hydrolysis with aqueous NaOH or KOH, vic-Dihalides on heating with aqueous sodium hydroxide give glycols.

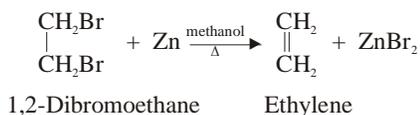


gem-Dihalides on hydrolysis with aqueous KOH gives an aldehyde or a ketone.

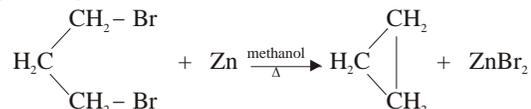


This reaction is used to distinguish vic-dihalides from gem-halides. Notice that vic-dihalides on hydrolysis give glycols while gem-dihalides give aldehydes or ketones.

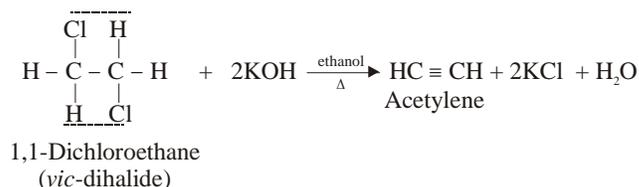
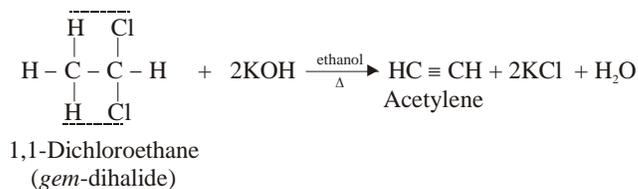
- (2) Reaction with zinc: Dehalogenation vic-Dihalides and gem-dihalides on treatment with zinc dust in methanol give alkenes.



1,3- to 1,6-Dihalides give cycloalkanes.

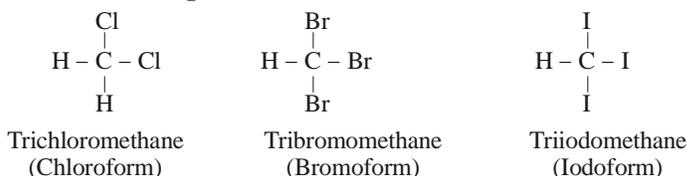


- (3) Reaction with Alcoholic KOH: Dehydrohalogenation, vic-Dihalides and gem-dihalides on treatment with alcoholic potassium hydroxide give alkynes.



## 5.11 TRIHALOGEN DERIVATIVES

Trihalogen derivatives are compounds obtained by replacing three hydrogen atoms of a hydrocarbon by three halogen atoms. The presence of three identical halogen atoms is indicated by the prefix *tri*- and the position numbers.



### CHLOROFORM

Trichloromethane,  $\text{CHCl}_3$

Chloroform is an important trihalogen derivative of methane. In the past of chloroform was extensively used as a great anesthetic for surgery but it is rarely used for this purpose now because it causes extensive liver damage.

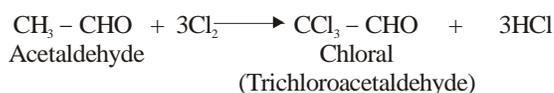
Preparation, Chloroform is prepared

(1) From Ethyl Alcohol (or Acetone) and Bleaching powder. By heating ethyl alcohol or acetone with bleaching powder,  $\text{Ca}(\text{OCl}_2)$ . The bleaching powder acts as source of chlorine and calcium hydroxide. This method is used to make chloroform in the laboratory and on commercial scale. Reaction of ethyl alcohol with bleaching powder takes place by the following three steps.

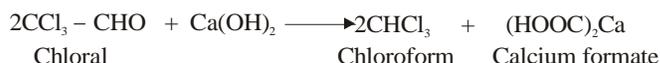
#### Step 1: Oxidation



#### Step 2: Chlorination



#### Step 3: Hydrolysis



Reaction of acetone with bleaching powder takes place by the following two steps.

#### Step 1: Chlorination

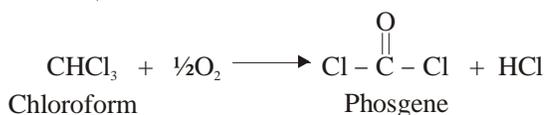


#### Step 2: Hydrolysis



Chemical Properties: The chemical properties of chloroform are as follows:

(1) Oxidation: Chloroform undergoes oxidation the presence of light and air to form phosgene (carbonyl chloride).





Uses: Chloroform is used:

- (1) as a solvent for fats, waxes and rubber and
- (2) in the preparation of chloropicrin and chloretone.

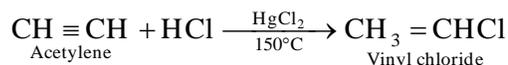
## 5.12 UNSATURATED HALIDES

**VINYL CHLORIDE**, *Chloroethene*,  $\text{CH}_2 = \text{CH} \square \text{Cl}$

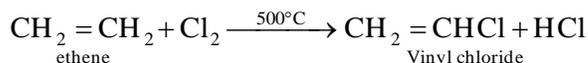
Vinyl chloride is the most important of the unsaturated halides.

Preparation: Vinyl chloride is obtained

- (1) By the controlled addition of hydrogen chloride to acetylene,  $\text{HgCl}_2$  is used as a catalyst.



- (2) By the action of chlorine on ethylene at  $500^\circ\text{C}$ .

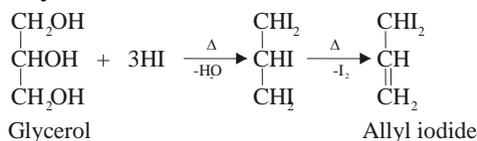


**ALLYL IODIDE**, *3-Iodo-1-propene*,  $\text{CH}_2 \square \text{CHCH}_2\text{I}$

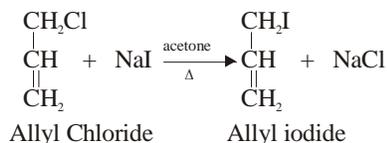
Allyl iodide is widely used in organic synthesis.

Preparation. It is prepared:

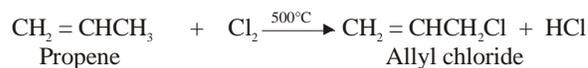
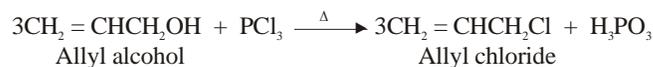
- (1) By heating glycerol with hydriodic acid



- (2) By heating allyl chloride with sodium iodide in acetone.



This halogen-exchange reaction is called **Finkelstein Reaction**. Allyl chloride used in the reaction may be obtained by heating allyl alcohol with  $\text{PCl}_3$  or chlorination of propene at  $500^\circ\text{C}$ .



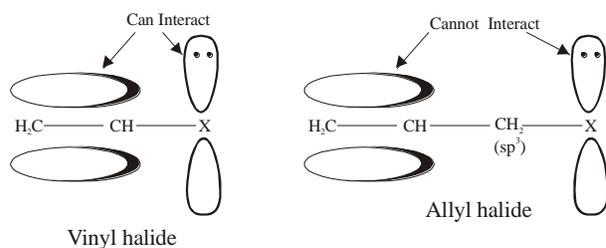
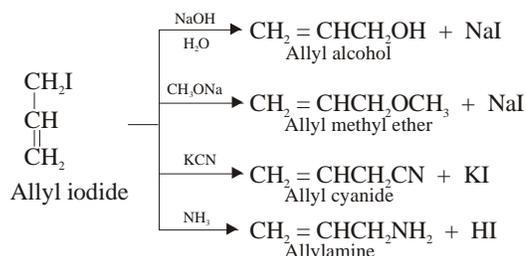
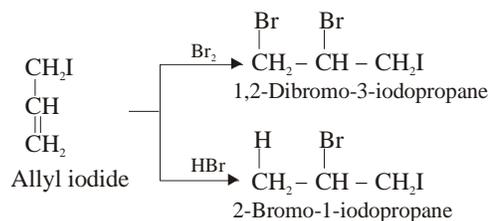


Figure: In allyl halides, the p-orbital of the halogen atom cannot interact with the  $\pi$  MO of the C-C double bond. This is because they are separated by a saturated  $sp^3$  hybridized carbon atom.

(1) **Substitution Reactions.** Following are some of the important nucleophilic substitution reactions of allyl iodide.

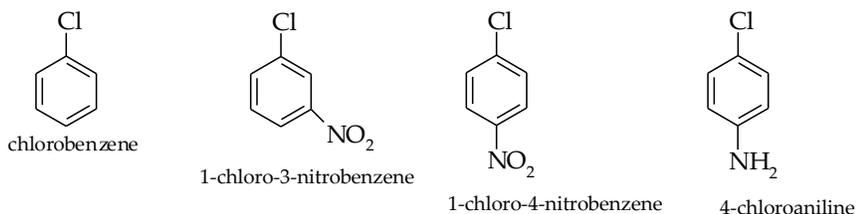


(2) **Addition Reactions.** The carbon-carbon double bond in allyl iodide shows the usual electrophilic addition reaction. Markovnikov rule is followed.



### 5.13 ARYL HALIDES

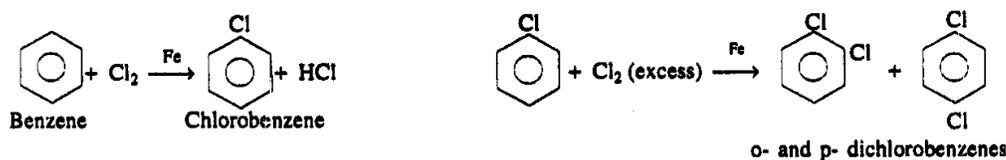
Aryl halides are the compounds that contain halogen atom directly attached to the benzene ring. They have general formula  $\text{ArX}$ .



Any halogen compound that contains a benzene ring is not classified as aryl halide. e.g. Benzyl chloride is not an aryl halide, but is a substituted alkyl halide.

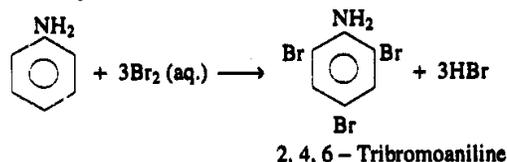
#### Preparation:

(i) By direct halogenation in presence of a halogen carrier such as Fe, chlorine or bromine readily replaces nuclear hydrogen of aromatic hydrocarbons. Mono-, di- and trichloro or bromo derivatives are obtained, depending upon the proportion of halogen to hydrocarbon. *o*- and *p*- di- chloro di- bromo benzenes are formed on further halogenation.

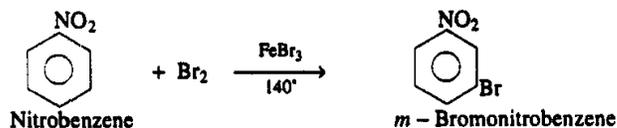


Similarly, toluene on chlorination gives *o*- and *p*- chlorotoluenes.

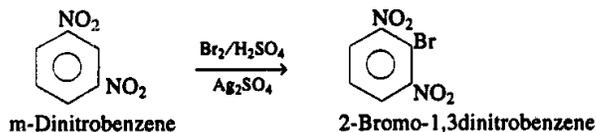
- (ii) **Nuclear halogenation** of highly activated compounds, like amines and phenols do not require any Lewis acid catalyst,



- (iii) **Strongly deactivated aromatic compounds** require high **temperature** for the reaction.



- (iv) **Halogens in presence of silver sulphate**- This is very reactive halogenating agent for strongly deactivated compounds.



- (v) **Decomposition of diazonium salts**- When aqueous benzene diazonium chloride is warmed at about 60°C with cuprous chloride (catalyst) in HCl, chlorobenzene is formed. The reaction is known as **Sandmeyer's Reaction (1884)**.



- (vi) **Reaction of PCl<sub>5</sub> on phenols**-  $\text{C}_6\text{H}_5\text{OH} + \text{PCl}_5 \rightleftharpoons \text{C}_6\text{H}_5\text{Cl} + \text{POCl}_3 + \text{HCl}$

- (vii) **Action of HOBr** -



## PROPERTIES

- (i) Aryl halides are heavier than water. Among the halides, the melting points and boiling points follow the order.

**Aryl Iodides > Bromides > Chlorides > Fluorides**

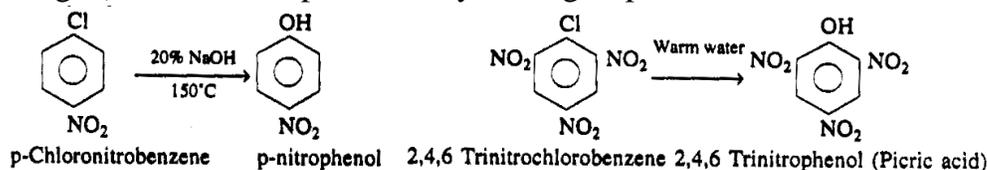
- (ii) Among the isomeric halides (*o*-, *m*-, *p*-), the differences in their melting points are much wider than those in their boiling points. The m.p. of *o*-, *m*-, *p*- dichlorobenzenes,

for example, are 17\*, - 25", and - 55"C respectively, whereas their boiling points are 180\*, 174\* and 175'C respectively. The p-isomer usually has the highest m.p. presumably due to its more symmetrical structure.

**(iii) Reactions involving halogen atom-**

(a) **Aromatic Nucleophilic substitution reactions-** *Because of resonance, the halogens do not have a tendency to ionise in aryl halides. Thus aryl halides normally do not undergo S<sub>N</sub>1 or S<sub>N</sub>2 type of reactions. For example, phenyl halides do not normally react with nucleophiles such as -OH, CN etc. Such reactions take place when halogen is activated under drastic conditions. For example,*

**Electron withdrawing groups** (- NO<sub>2</sub>, - CN, - SO<sub>3</sub>H, - COOH, - CHO, - COR etc.) when present in *o*- and or *p*- positions to the halogen atom, makes the latter (halogen) active and replaceable by other groups.



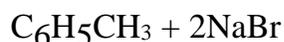
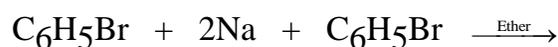
**Electron releasing groups** (- NH<sub>2</sub>, - OH, - OR, - R etc.) deactivate the nuclear halogens towards nucleophilic aromatic substitution in the order, - NH<sub>2</sub> > - OH > - OR > - R

(b) **Reduction-**



(c) **Formation of Grignard reagent**  $\text{C}_6\text{H}_5\text{Br} + \text{Mg} \xrightarrow{\text{Ether}} \text{C}_6\text{H}_5\text{MgBr}$

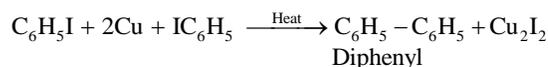
(d) **Wurtz Fittig reaction**



Toluene

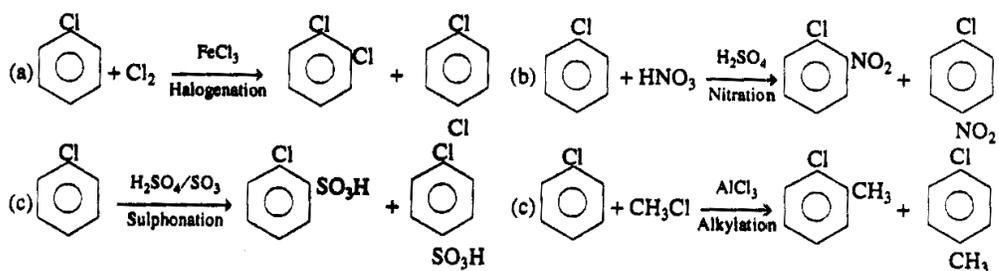
When only aryl halides are used, the reaction is called Fittig reaction, while Wurtz reaction involves only the alkyl halides,

(e) **Ulmann reaction-** When iodobenzene is heated with finely divided copper at 200°C diphenyl is formed. The reaction is called **Ulmann reaction**.



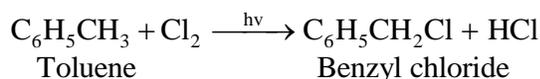
Aryl chlorides and bromides do not react unless electron withdrawing groups like - NO<sub>2</sub> are present at *o*- and/or *p*- positions to the halogen. Aryl **fluorides do not react at all in Ulmann reaction**.

(iv) **Reactions of benzene ring** -Aryl halides undergo typical electrophilic substitution reactions, though less readily than benzene, because halogens have a deactivating influence on the aromatic ring. For example,

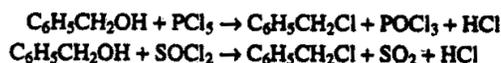


## 5.14 ARYL ALKYL HALIDE

**Preparation** - (i) Phenyl chloromethane or benzyl chloride,  $C_6H_5CH_2Cl$  is prepared by passing dry chlorine gas into boiling toluene in presence of light.

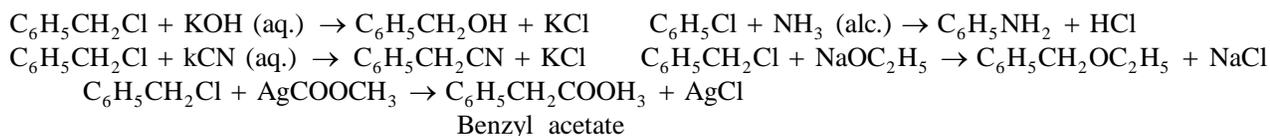


(ii) Industrially it is prepared by chloromethylating benzene with formaldehyde and HCl.

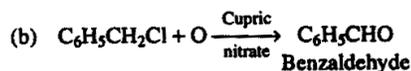
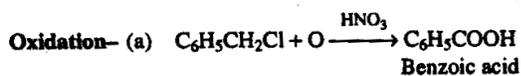
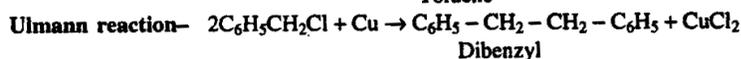
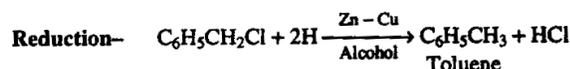


### Properties - (a) Reactions involving halogenation

#### i) Nucleophilic substitution reactions

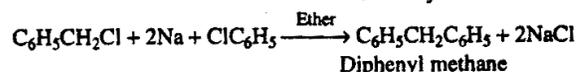
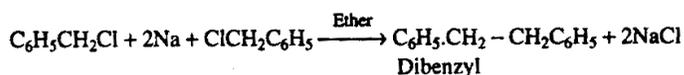


In all the above reactions H-atom of the benzyl chloride has been replaced by groups like -OH, -NH<sub>2</sub>, -CN etc.

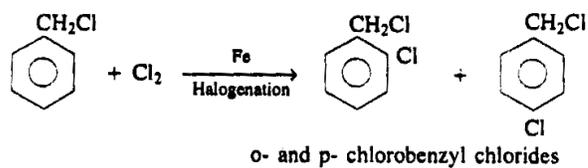
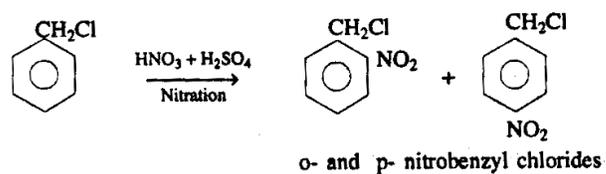


Lead nitrate also gives benzaldehyde.

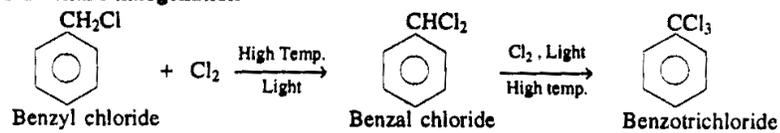
#### (ii) Wurtz reaction



(b) **Reaction of benzene ring-** Side chain halogen derivatives undergo usual **electrophilic substitution reaction**. The new substituents enter at o- and p-positions. For example



(c) Side chain halogenation-



The nuclear halogenation takes place in cold, dark and in presence of a halogen carrier.

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## MISCELLANEOUS PROBLEMS

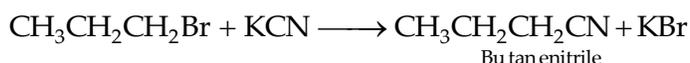
### OBJECTIVE TYPE

#### Example 1

In which case formation of butane nitrile is possible?

- (a)  $C_3H_7Br + KCN$  (b)  $C_4H_9Br + KCN$   
(c)  $C_3H_7OH + KCN$  (d)  $C_4H_9OH + KCN$

#### Solution



Ans. (a)

#### Example 2

Which represents nucleophilic aromatic substitution reaction?

- (a) Reaction of benzene with  $Cl_2$  in sunlight  
(b) Benzyl bromide hydrolysis with water  
(c) Reaction of NaOH with dinitrofluoro benzene  
(d) Sulphonation of benzene.

#### Solution

Two nitro groups make the nucleophilic substitution in benzene easy.

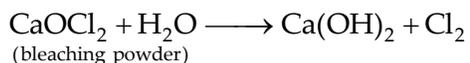
Ans. (c)

#### Example 3

The product formed on reaction of ethyl alcohol with bleaching power is

- (a)  $CH_3OH$  (b)  $CH_3 - CH_2 - OH$  (c)  $CHCl_3$  (d) Both (a) and (b).

#### Solution



$Cl_2$  is the halogen and  $Ca(OH)_2$  is the base for chloroform reaction with ethanol.

Ans. (c)

#### Example 4

An optically active 3-bromo-3-methyl hexane on hydrolysis gives

- (a) 3-methyl-3-hexanol with retention of configuration  
(b) 3-methyl-3-hexanol with inversion of configuration  
(c) a mixture of optically active 3-methyl-3-hexanol and 3-methyl-3-hexene  
(d) optically inactive 3-methyl-3-hexanol

**Solution**

3-bromo-3-methyl hexane, on ionization gives a 3° carbocation, which can be attacked by nucleophile (H<sub>2</sub>O) to give 3-methyl-3-hexanol (optically active) as well as it can lose a proton to H<sub>2</sub>O to give 3-methyl-3-hexene.

**Ans.** (c)

**Example 5**

Which of the following statements about benzyl chloride is incorrect?

- (a) it is less reactive than alkyl halides
- (b) it can be oxidized to benzaldehyde by boiling with copper nitrate solution
- (c) it is a chymator liquid and answers Beilstein's test
- (d) it gives a white precipitate with alcoholic silver nitrate.

**Solution**

C<sub>6</sub>H<sub>5</sub> – CH<sub>2</sub>Cl (benzyl chloride) is as reactive as allyl halide as the halogen in both cases is bonded with sp<sup>3</sup> carbon atom and both of them are more reactive than alkyl halide.

**Ans.** (a)

**Example 6**

Tertiary alkyl halides are practically inert to substitution by S<sub>N</sub><sup>2</sup> mechanism because of

- (a) insolubility
- (b) instability
- (c) inductive effect
- (d) steric hindrance

**Solution**

Steric hindrance due to bulky alkyl group prevents the backside attack of S<sub>N</sub><sup>2</sup>.

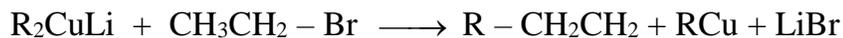
**Ans.** (d)

**Example 7**

Alkyl halides react with lithium dialkyl copper reagents to give

- (a) insolubility
- (b) alkyl copper halides
- (c) alkanes
- (d) alkenyl halides

**Ans.** (c)

**Solution****Example 8**

Which of the following undergoes nucleophilic substitution exclusively by S<sub>N</sub><sup>1</sup> mechanism?

- (a) Benzyl chloride
- (b) Ethyl chloride
- (c) Chlorobenzene
- (d) Isopropyl chloride

**Solution**

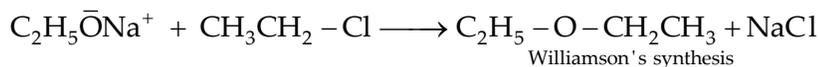
Benzyl chloride forms resonance stabilized benzyl carbocation for S<sub>N</sub><sup>1</sup> reaction.

**Ans.** (a)

**Example 9**

In which of the following reactions, the product is an ether?

- (a)  $C_6H_6 + CH_3COCl$ /anhydrous  $AlCl_3$                       (b)  $C_2H_5Cl + aq.KOH$   
 (c)  $C_6H_6 + C_6H_5COCl$ /anhydrous  $AlCl_3$                       (d)  $C_2H_5Cl + C_2H_5ONa$

**Solution**

**Ans. (d)**

**Example 10**

The halide, which undergoes nucleophilic substitution (by  $S_NAr$  mechanism) most readily is

- (a) p -  $MeC_6H_4Cl$                       (b) p -  $MeOC_6H_4Cl$       (c) p -  $ClC_6H_4Cl$                       (d) p -  $O_2NC_6H_4Cl$

**Solution**

The reaction proceeds by carbanion formation, which can be stabilized by electron-withdrawing groups present at ortho or para positions. The most electron- withdrawing group amongst all is -  $NO_2$ .

**Ans. (d)**

**SUBJECTIVE TYPE****Example 1**

- (a) Account for the trend in relative rates observed for the formation of alcohols from the listed  $RX$ 's in  $H_2O$  /  $EtOH$  at  $25^\circ C$  :  $MeBr$ , (2140 unit);  $MeCH_2Br$  (171 unit),  $Me_2CHBr$  (4.99 unit),  $Me_3CBr$  (1010 unit).  
 (b) Why is  $EtOH$  added to the water?

**Solution**

- (a) The first three halides react mainly by the  $S_N2$  pathway and their rate decline as  $Me$ 's replace  $H$ 's on the attacked  $C$ , because of steric hindrance.  $H_2O$  is the nucleophile. A change to the  $S_N1$  pathway accounts for the sharp rise in the reactivity of  $Me_3CBr$ .  
 (b) Water is a poor solvent for alkyl halides and  $EtOH$  is added to acid in their solution.

**Example 2**

- (a) Compare the rates of (i)  $S_N1$  and (ii)  $S_N2$  reactions of allyl chloride and n-Pr chloride. Explain your answers.

(b) Account for the formation of  $\text{HOCH}_2\text{CH}=\text{CHMe}$  from the hydrolysis of  $\text{H}_2\text{C}=\text{CHCH}(\text{Me})\text{Cl}$ .

### Solution

(a) Allyl chloride is much more reactive than  $n\text{-PrCl}$ , although it is also a  $1^\circ \text{RX}$ . The + charge of its intermediate  $\text{R}^+$  is stabilized by resonance. Allyl halides show  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  mechanism but  $n\text{-propyl chloride}$  shows only  $\text{S}_{\text{N}}2$  mechanism.

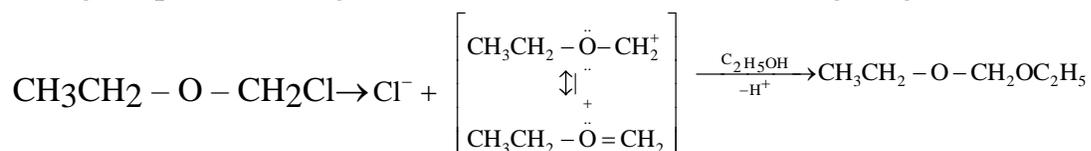
(b) The intermediate  $\text{R}^+$ , can react with  $\text{H}_2\text{O}$  at either  $\text{C}^1$  or  $\text{C}_3$ , each of which has charge. Reaction at the  $1^\circ \text{C}_1$  affords the more substituted alkenol although  $2^\circ \text{C}_3$  has more  $\delta^+$ . This reaction is an example of an allylic rearrangement.

### Example 3

Account for the rapid rate of ethanolsis of  $\text{ClCH}_2\text{OCH}_2\text{CH}_3$ , although the substrate is  $1^\circ$  halide.

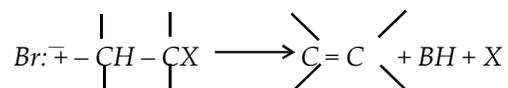
### Solution

The rapidity of this  $\text{S}_{\text{N}}1$  reaction is attributed to the stability of a  $\text{C}^+$  bonded to  $\ddot{\text{O}}^-$ . The empty p AO on  $\text{C}^+$  can overlap sidewise with a filled p AO on O, thereby delocalizing and stabilizing the positive charge. The  $\text{C}^+$  then reacts with  $\text{EtOH}$ , giving an ether.



### Example 4

(a) Suggest three logical ways for the following general elimination to occur:



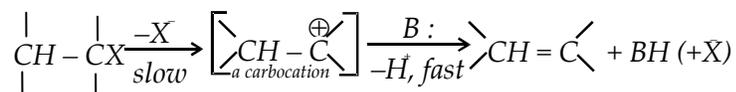
(Disregard the viability in terms of actual chemistry).

(b) Predict the rate expressions, orders, and molecularities of the reactions in part (a) Justify your predictions.

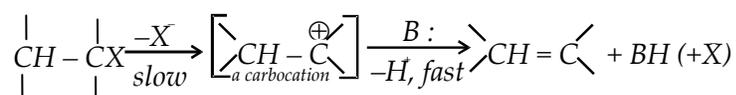
(c) What symbols are used to denote the three elimination pathways based on their molecularities ?

### Solution

(a) Two steps :  $\text{X}^-$  leaves first, then the remaining  $\text{R}^+$  loses an adjacent  $\text{H}^+$  to  $:\text{B}^-$

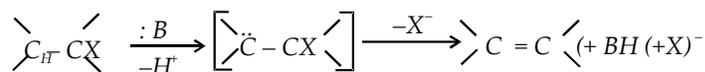


The first step is slow because it is an ionization giving the very high energy R



Two steps : H<sup>+</sup> leaves first followed by X<sup>-</sup> from the intermediate carbanion.

Except for those few cases where the substrate has a very acidic H<sup>+</sup>, the first step is slow.



A one step concerted departure of X<sup>-</sup> and H<sup>+</sup>.

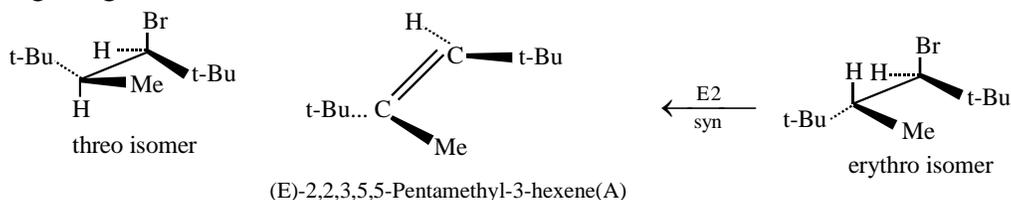
- (b) 1. The slow step has only one species, the substrate, and the first order rate = k<sub>1</sub>[RX] for the unimolecular reaction.
2. Regardless of which step is rate-controlling, the second-order rate = k<sub>2</sub>[RX][:B<sup>-</sup>]. However, if the first step is slower, the reaction is bimolecular because both reactants are involved. If the second step is lower, only the carbanion is involved and the reaction is unimolecular.
3. Both reactants participate in the single step, and the second order rate = k<sub>2</sub>[RX][:B<sup>-</sup>] for this bimolecular reaction.
- (c) E1 (elimination, unimolecular)  
 E1<sub>cb</sub> (elimination, unimolecular of the conjugate base).  
 E2 (elimination, bimolecular).

### Example 5

Account for the formation of the same product from an E2 reaction of both threo- and erythro-2,2,3,5,5-pentamethyl-4-bromohexane.

### Solution

In the diastereomer. H and Br can be anti-coplanar with the bulky t-Bu's anti to each other. The TS is unencumbered by any steric hindrance from the t-Bu's. The product is the alkene with trans-t-Bu's. In the erythro isomer anti-coplanarity of Br and H can only be attained if the bulky t-Bu's are cis-like in a prohibitively high enthalpy TS. However, syn-coplanarity of Br and H can be attained with trans-like bulky t-Bu's in a much lower enthalpy TS, giving A

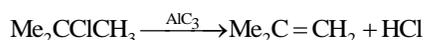


### Example 6

- (a) Why do even 3° alkyl halides rarely undergo E1 reactions?  
(b) How can the E1 reaction be promoted?  
(c) Account for the different yields of the same two products when CH<sub>3</sub>CHBrCH<sub>3</sub> reacts with  
(i) EtO<sup>-</sup>Na<sup>+</sup>/EtOH and (ii) EtOH.

### Solution

- (a) 3° RX's react by E1 only when the base is weak or has a very low concentration. As the base gets stronger or more concentrated, the E2 mechanism prevails. If the base is too weak or too dilute, either R<sup>+</sup> reacts with the nucleophilic solvent to give the S<sub>N</sub>1 product or, in nonplanar solvents, RX fails to react.  
(b) Electrophilic catalysis, e.g. with Ag<sup>+</sup>, aids in the ionization of C - X. Even here the counter anion (An<sup>-</sup>) of Ag<sup>+</sup> can bond to R<sup>+</sup> to give R-Abn or can act as a base and remove the H to give the alkene. Ideally An<sup>-</sup> should be basic, yet a poor nucleophile. AlCl<sub>3</sub> in benzene avoids this problem.



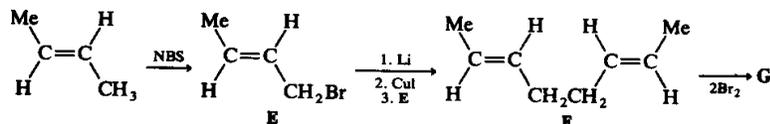
- (c) (i) EtO<sup>-</sup> is a strong base and with 2° RX's the E2 product, CH<sub>3</sub>CH = CH<sub>2</sub> predominates over the S<sub>N</sub>2 product, CH<sub>3</sub>CH(OEt)CH<sub>3</sub>. (ii) EtOH is weakly basic but nucleophilic, and S<sub>N</sub>1 is favoured to give mainly CH<sub>3</sub>(OEt)CH<sub>3</sub>.

### Example 7

- (a) From E-2-butene prepare CH<sub>3</sub>CHBrCHBrCH<sub>2</sub>CH<sub>2</sub>CHBrCHBrCH<sub>3</sub> (G).  
(b) Which diastereoisomers of G are products of this synthesis? (c) Which diastereomers of G are obtained if Z-2-butene is used? To simplify drawing all the structures, describe them in terms of R/S designations of the stereocenters.

### Solution

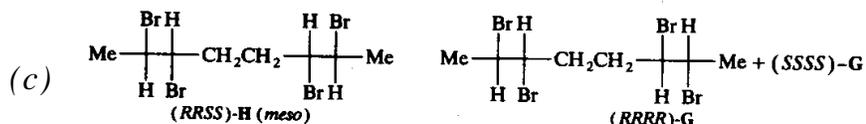
- (a) To go from a 4-carbon to a 8-carbon compound requires a coupling of alkyl halide.



- (b)  $\begin{array}{c} \text{Br} & \text{H} & & \text{H} & \text{Br} \\ | & | & & | & | \\ \text{H}-\text{C}-\text{C}-\text{CH}_2\text{CH}_2-\text{C}-\text{C}-\text{H} \\ | & | & & | & | \\ \text{Me} & \text{Br} & & \text{Br} & \text{Me} \end{array} \quad \begin{array}{c} \text{Br} & \text{H} & & \text{Br} & \text{Me} \\ | & | & & | & | \\ \text{H}-\text{C}-\text{C}-\text{CH}_2\text{CH}_2-\text{C}-\text{C}-\text{H} \\ | & | & & | & | \\ \text{Me} & \text{Br} & & \text{H} & \text{Br} \end{array} + (\text{RSSR})-\text{G}$   
(SRSR)-G (meso) (SRRS)-G

Br<sub>2</sub> adds *anti* to each double bond in F, engendering four stereocenters. Going from left to right, to get the diastereomer shown, the Br's add from top, bottom, bottom, top giving the *meso* (SRSR) isomer. Adding the Br's in the sequence bottom, top, top, bottom, gives the same *meso* isomer. Adding the Br's in the sequence top, bottom, top, bottom gives an enantiomer (SRRS), while the sequence bottom, top, bottom, top gives the mirror image (RSSR). The products

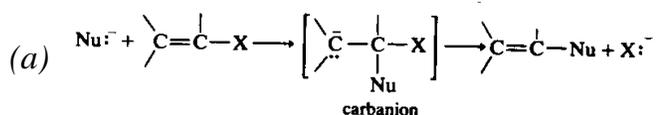
are a *meso* and a racemate. The products from *cis*-2-butene are a *meso* (*RRSS*) and a racemate (*RRRR*) and (*SSSS*).



### Example 8

- (a) Outline a plausible mechanism for a nucleophilic displacement on a vinyl halide by the two step addition elimination mechanism.
- (b) What structural features must be vinyl compound have to make this mechanism viable? Give an example.

### Solution



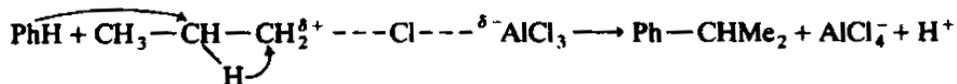
- (b) This reaction cannot take place unless the carbanion is stabilized by having electron-withdrawing groups on the  $\text{C}^-$ . For example,  $\text{F}_2\text{C}=\text{CHBr}$  could react by this route because of the electron-withdrawing F's.

### Example 9

- (a) Compare the products of the reaction of benzene with *i*-PrCl and *n*-PrCl in  $\text{AlCl}_3$ .
- (b) Account for the products mechanistically.

### Solution

- (a) The expected  $\text{Ph}-\text{CHMe}_2$  is isolated from the reaction with *i*-PrCl. With *n*-PrCl, both  $\text{Ph}-\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{Ph}-\text{CHMe}_2$  form.
- (b)  $1^\circ$  RX's are less reactive than  $2^\circ$  and  $3^\circ$  halides. At the higher temperatures required for  $1^\circ$  RX, some rearrangement always occurs. A possible pathway is for benzene to displace on the  $2^\circ\text{C}$  while a  $\text{H}$  shifts to the  $1^\circ$  carbon.



Formation of a "free"  $1^\circ$  carbocation is unlikely. Rearrangement limits the scope of this reaction.

### Example 10

Provide the products of the reactions of the following substrates with  $\text{NaNO}_2$  in  $\text{EtOH}$ :

- (i) *n*-BuCl and (ii)  $\text{ClCH}_2\text{OCH}_2\text{CH}_3$

### Solution

(i)  $n\text{-Bu-NP}_2$  and (ii)  $\text{ONO-CH}_2\text{OCH}_2\text{CH}_3 + \text{EtO-CH}_2\text{OCH}_2\text{CH}_3$   
The less the positive charge on the attacked carbon, the more likely it will bond to the less electronegative nucleophilic site of the ambident ion (N). This happens in the  $\text{S}_{\text{N}}2$  reaction in (i) where a C – N bond forms. The greater the positive charge on the attacked carbon, the more likely it will bond to the more electronegative nucleophilic site of the ambident ion (O). This happens in the  $\text{S}_{\text{N}}1$  reaction in (ii), where a C – O bond forms. Since the  $\text{R}^+$  in (ii) is so stable, it has a long enough half-life to react with any added nucleophile as well as nucleophilic solvent.

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### Exercise - I

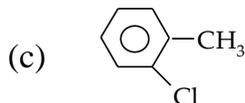
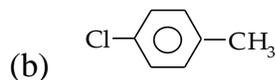
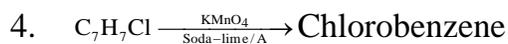
#### OBJECTIVE TYPE QUESTIONS

##### Multiple choice questions with ONE option correct

- In the reaction of p-chlorotoluene with  $\text{KNH}_2$  in liquid  $\text{NH}_3$ , the major product is  
(a) o-toluidine      (b) m-toluidine      (c) p-toluidine      (d) p-chloroaniline
- A compound (a) of formula  $\text{C}_3\text{H}_6\text{Cl}_2$  on reaction with alkali can give compound (b) of formula  $\text{C}_3\text{H}_6\text{O}$  or compound (c) of formula  $\text{C}_3\text{H}_4$  depending upon the conditions employed. Compound (b) on oxidation gave a compound of the formula  $\text{C}_3\text{H}_6\text{O}_2$ . Compound (c) with dilute  $\text{H}_2\text{SO}_4$  containing  $\text{Hg}^{2+}$  ion gave compound (d) of formula  $\text{C}_3\text{H}_6\text{O}$ , which on reaction with bromine and  $\text{NaOH}$  gave the sodium salt of  $\text{C}_2\text{H}_4\text{O}_2$ . The most probable structure of compound (a) would be  
(a)  $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl}$       (b)  $\text{CH}_3\text{CCl}_2\text{CH}_3$   
(c)  $\text{CH}_3\text{CH}_2\text{CHCl}_2$       (d)  $\text{CH}_3\text{CHClCH}_2\text{Cl}$
- Rank the following species in order of decreasing nucleophilicity in a polar protic solvent.  
(a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$       (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{S}^-$       (c)  $\text{CH}_3\text{CH}_2\text{-}\overset{\text{O}}{\parallel}{\text{C}}\text{-O}^-$   
(a) (c) > (a-) > (b)      (b) (b) > (c) > (a)      (c) (a) > (c) > (b)      (d) (b) > (a) > (c)

4. Which of the following statement is true?
- $\text{CH}_3\text{CH}_2\text{S}^-$  is both a stronger base and more nucleophilic than  $\text{CH}_3\text{CH}_2\text{O}^-$ .
  - $\text{CH}_3\text{CH}_2\text{S}^-$  is a stronger base but is less nucleophilic than  $\text{CH}_3\text{CH}_2\text{O}^-$ .
  - $\text{CH}_3\text{CH}_2\text{S}^-$  is a weaker base but is more nucleophilic than  $\text{CH}_3\text{CH}_2\text{O}^-$ .
  - $\text{CH}_3\text{CH}_2\text{S}^-$  is both a weaker base and less nucleophilic than  $\text{CH}_3\text{CH}_2\text{O}^-$ .
5. Which of the following is correct order of reactivity.
- Vinyl chloride > Altyl chloride > Propyl chloride
  - Propyl chloride > Vinyl chloride > Allyl chloride
  - Allyl chloride > Propyl chloride > vinyl chloride
  - None of these
6. The reaction condition leading to the best yield of  $\text{C}_2\text{H}_5\text{Cl}$  are
- $\text{C}_2\text{H}_6(\text{excess}) + \text{Cl}_2 \xrightarrow{\text{UV light}}$
  - $\text{C}_2\text{H}_6 + \text{Cl}_2 \xrightarrow[\text{room temperature}]{\text{Dark}}$
  - $\text{C}_2\text{H}_6 + \text{Cl}_2(\text{excess}) \xrightarrow{\text{UV light}}$
  - $\text{C}_2\text{H}_6 + \text{Cl}_2 \xrightarrow{\text{UV light}}$
7. The intermediate during the addition of HCl to propene in presence of peroxide is
- $\text{CH}_3\dot{\text{C}}\text{HCH}_2\text{Cl}$
  - $\text{CH}_3\overset{+}{\text{C}}\text{HCH}_3$
  - $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{H}_2$
  - $\text{CH}_3\text{CH}_2\overset{\cdot}{\text{C}}\text{H}_2$
8. During debromination of meso-dibromobutane, the major compound formed is
- n-butane
  - 1-butene
  - cis-2-butene
  - trans-2-butene
9. The reaction of propene with HOCl proceeds through the addition of
- $\text{H}^+$  in the first step
  - $\text{Cl}^+$  in the first step
  - $\text{OH}^-$  in the first step
  - $\text{Cl}^+$  and  $\text{OH}^-$  in a single step
10. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markovnikov's addition to alkenes because
- both are highly ionic
  - one is oxidising and the other is reducing
  - one of the steps is endothermic in both the cases
  - all the steps are exothermic in both the reactions
11. Identify the set of reagents/reaction conditons 'X' and 'Y' in the following set of transformations.





(d) None of these



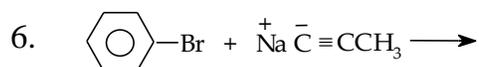
In the above sequence A can be

(a) Pentan-2-one

(b) Acetophenone

(c) 4-Ketopentanoic acid

(d) Hexane-2,5-dione



In this reaction the major product (s) formed is (are) ;

(a) Propyne

(b) Cyclohexane

(c) 3-Cyclohexylpropyne

(d) 2-Cyclohexylpropane

7. Which of the following reagents/tests cannot be used to distinguish allyl bromide from n-propyl bromide

(a)  $Br_2/CCl_4$

(b) KOH followed by acidifying with  $HNO_3$  and adding  $AgNO_3$  (aq)

(c) Lassaigne's test (d) Alkaline  $KMnO_4$

8. Dipole moment is shown by

(a) Benzoyl chloride

(b) cis-1, 2-Dichloroethene

(c) trans-1, 2-Dichloroethene

(d) trans-1, 2-Dichloro-2-pentene

9. Which of the following will give yellow precipitate with  $I_2/NaOH$ ?

(a)  $ICH_2COCH_2CH_3$

(b)  $CH_3COOCOCH_3$

(c)  $CH_3CONH_2$

(d)  $CH_3CH(OH)CH_2CH_3$

10. Toluene when treated with  $Br_2/Fe$ , gives p-bromotoluene as the major product because the methyl group

(a) is para directing

(b) is m-directing

(c) activates the ring by hyperconjugation (d) deactivates the ring

\*\*\*\*\*

## Exercise - II

### ASSERTION & REASON , COMPREHENSION & MATCHING TYPE

#### Assertion and Reason

In each of the following questions two statements are given one labeled as the Assertion (A) and the other labeled as the reason (R). Examine these statements carefully and mark the correct choice as per following instructions.

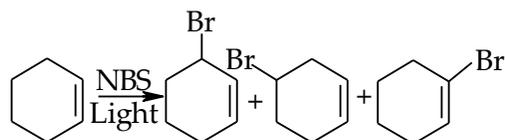
- Both A and R are true and R is the correct explanation of A
  - Both A and R are true but R is not a correct explanation
  - A is false but R is true
  - Both A and R are false
- A.: The reaction of vinyl chloride and hydro-iodic acid produces 1-chloro-1-iodoethane.  
R.: HI adds on vinyl chloride against Markownikoff's rule
  - A.: Chloroform is generally stored in brown bottles which are filled to brims.  
R.: Chloroform reacts with glass in the presence of sunlight.
  - A.: Chlorobenzene is easily hydrolysed as compared to chloroethane  
R.: Carbon-chlorine bond in chlorobenzene is relatively shorter than in chloroethane.
  - A.: Carbon tetrachloride is used as fire extinguisher.  
R.: Carbon tetrachloride is a non polar substance.
  - A.:  $C_2H_5Br$  and alcoholic silver nitrite react to give nitroethane as a major product  
R.:  $NO_2^-$  is an ambident nucleophile.
  - A.: Methyl chloride can give methane as well as ethane separately.  
R.: Wurtz reaction proceeds through free radical mechanism.
  - A.: Ethylidene chloride on treatment with aqueous KOH yield ethanal.  
R.: Ethylene dichloride is a Gemdihalide.
  - A.: ROH does not react with NaBr.  
R.:  $Br^-$  is an extremely weak Bronsted base and cannot displace strong base  $OH^-$ .
  - A.: RCl is hydrolysed to ROH slowly but reaction is rapid if catalytic amounts of KI are added to the reaction mixture  
R.:  $I^-$  is a powerful nucleophile which reacts rapidly with RCl to form RI.  $I^-$  is a better leaving group than  $Cl^-$  and RI is hydrolysed rapidly to ROH.
  - A.: 1, 4-dichlorobenzene has higher melting point than that of 1, 2-dichlorobenzene.  
R.: 1,4-Dichlorobenzene is more symmetrical than 1, 2-dichlorobenzene.

## Passage based question

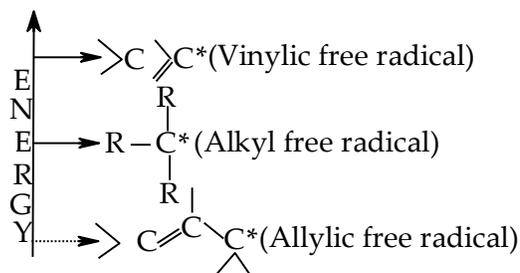
### Passage – 1

Karl Ziegler reported that alkenes react with-N-bromosuccinimide (NBS) in presence of light to give products resulting from substitution of hydrogen by bromine at the allylic position, i.e., the position next to the double bond.

Let us consider the halogenation of cyclohexene

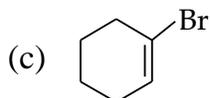
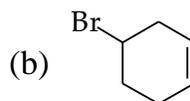
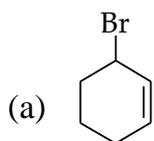


Energy level diagram for allylic, vinylic and alkylic free radicals is given below:



### Answer the following questions:

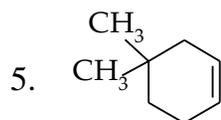
1. In the treatment of cyclohexene with NBS; which of the following product will be least stable?



(d) cannot be predicted

2. Which of the following sequences is correct about C—H bond energy?

- (a) (C—H) Vinylic > (C—H)Alkylic > (C—H)Allylic
- (b) (C—H) Vinylic < (C—H)Alkylic < (C—H)Allylic
- (c) (C—H) Vinylic < (C—H)Alkylic < (C—H)Allylic
- (d) (C—H) Vinylic = (C—H)Alkylic = (C—H)Allylic

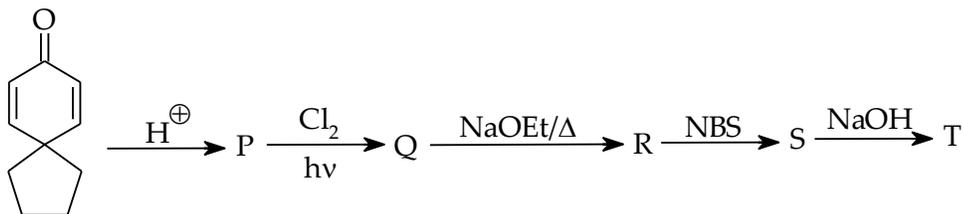


(4,4-Dimethyl cyclohexene)

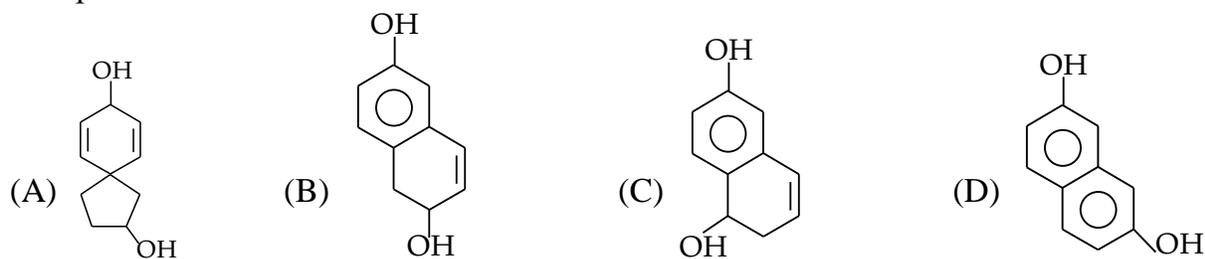
Above compound on treatment with NBS gives allylic bromides. How many product(s) will be obtained in this reaction?

- (a) One                      (b) Two                      (c) Three                      (d) Four

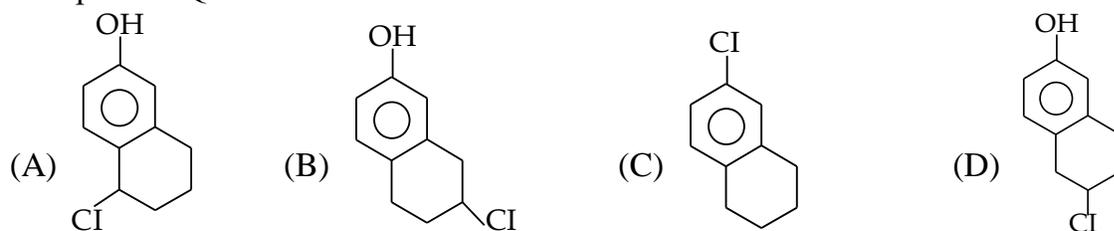
**Passage – 2**



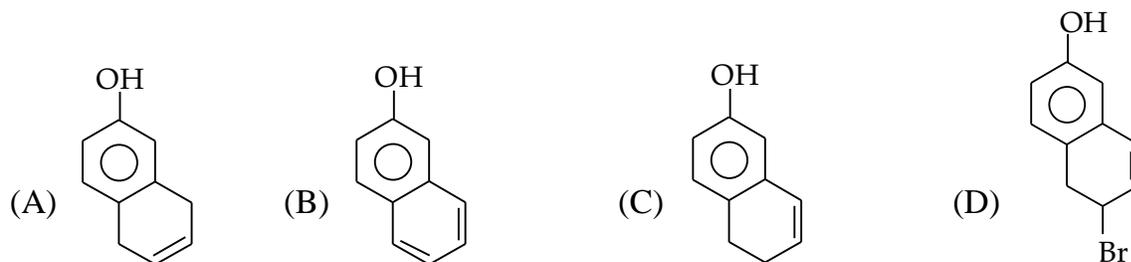
1. Compound 'T' is



2. Compound 'Q' is



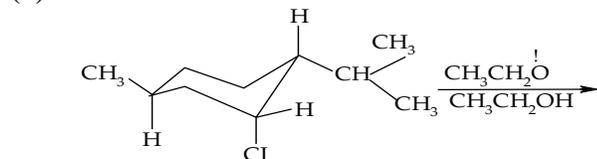
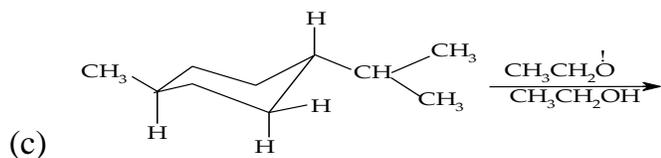
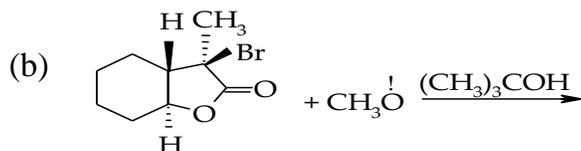
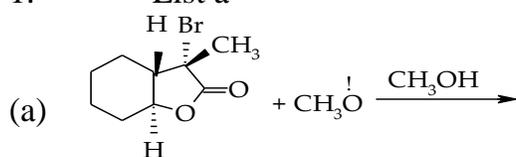
3. When treating 'S' with strong base, product obtained is



## Matching Type Questions

1.

List a

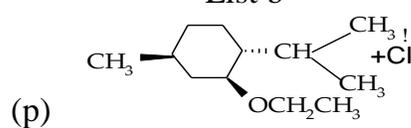


(d)

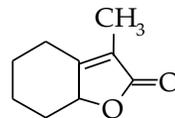
(a) (a-q), (b-s), (c-p), (d-r)

(c) (a-q), (b-r), (c-s), (d-p)

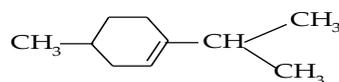
List b



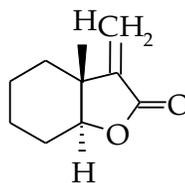
(q)



(r)



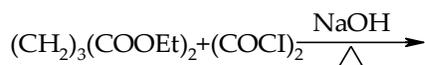
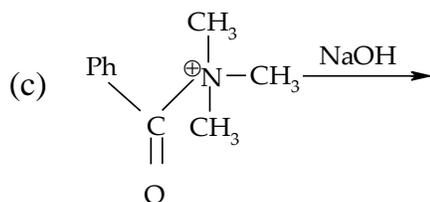
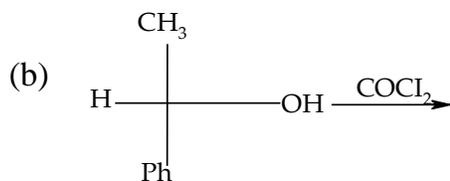
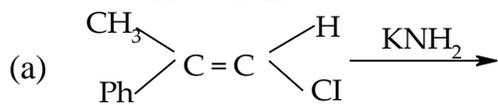
(s)



(b)(a-s), (b-p), (c-r), (d-q)

(d)(a-r), (b-p), (c-q), (d-s)

## 2. Column-(I) Reactions



## Column-(II) Reactions

(p)  $S_{N_2}TH$

(q)  $S_{N_2}$

(r)  $\alpha$ -elimination

SN<sub>i</sub>

(d)

(s)

(a) (a-q), (b-s), (c-p), (d-r)

(b)(a-r), (b-s), (c-q), (d-p)

(c) (a-q), (b-r), (c-s), (d-p)

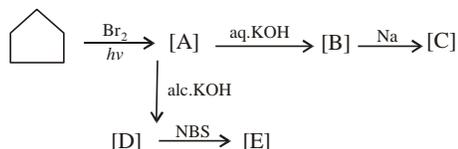
(d)(a-r), (b-p), (c-q), (d-s)

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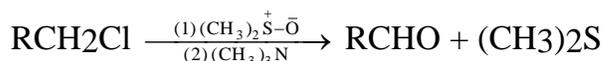
Exercise - III

**SUBJECTIVE TYPE**

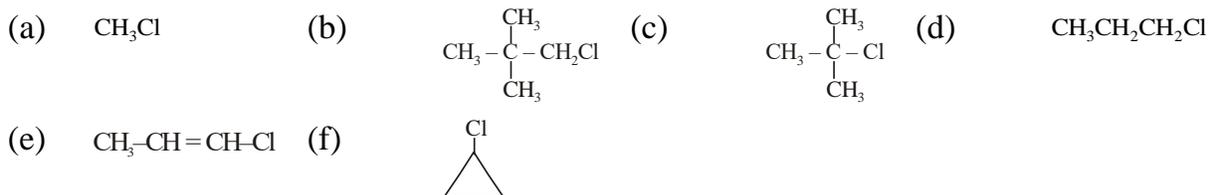
1. Identify A, B, C, D and E in the following series of reactions:



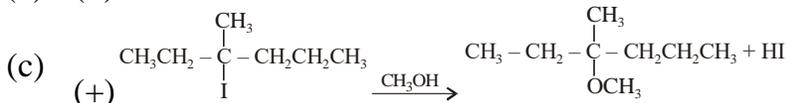
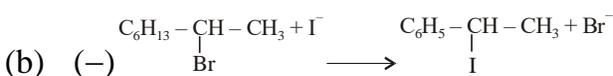
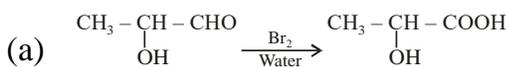
2. Give the structures of the major organic products from 3-ethylpent-2-ene under each of the following reaction conditions :
- HBr in the presence of peroxide
  - Br<sub>2</sub>/H<sub>2</sub>O.
3. Primary halides can be oxidised to aldehydes in good yields using dimethyl sulphoxide, (CH<sub>3</sub>)<sub>2</sub>SO.



4. Arrange the following compounds in order of increasing activity towards the bromide under S<sub>N</sub><sup>2</sup> conditions.



5. Which of the following reactions occur with retention of configuration, inversion of configuration or racemization ?



6. An organic compound (A) contains 52.18% carbon, 3.727% hydrogen and 44.11% Cl. On shaking (A) and refluxing (A) with Ca(OH)<sub>2</sub>, a liquid (B) is formed which forms 2,4-DNP but does not reduce Fehling's solution. With conc.NaOH, (B) gives a neutral compound (C) and (D). (D) on heating with soda-lime, gives benzene. What is A ?
7. Hydrolysis of compound (A) of molecular formula C<sub>9</sub>H<sub>10</sub>Cl Br yields (B) of molecular formula C<sub>9</sub>H<sub>10</sub>O. (B) gives the haloform reaction. Strong oxidation of (B) yields a dibasic acid which forms only one mononitro derivative. What is A ?

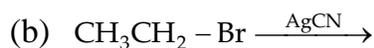
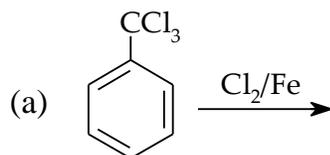
8. When Bromobenzene is monochlorinated two isomeric compounds (A) and (B) are obtained. Monobromination of (A) gives several products of molecular formula  $C_6H_3ClBr_2$ , while monobromination of (B) yields only two isomers (C) and (D). Compound (C) is identical with one of the compounds obtained from the bromination of (A). Give the structures of (A), (B), (C) and (D) and also structures of four isomeric monobrominated products of (A). Support your answer with reasoning.
9. 0.450 g of an aromatic organic compound (A) on ignition gives 0.905 g of  $CO_2$  and 0.185 g of  $H_2O$ . 0.350 g of (A) on boiling with  $HNO_3$  and on adding  $AgNO_3$  solution gives 0.574 g of  $AgCl$ . The vapour density of (A) is 87.5. (A) on hydrolysis with  $Ca(OH)_2$  yields (B) which on mild oxidation produced along with (D). With  $HCl$ , (D) gives a solid which is markedly more soluble in hot water than in cold. Identify (A) to (D) with proper explanation.
10. Two isomeric compounds (A) and (B), have same formula  $C_{11}H_{13}OCl$ . Both are unsaturated, and yield the same compound (C) on catalytic hydrogenation and produce 4-Chloro-3-ethoxybenzoic acid on vigorous oxidation. (A) exists in geometrical isomers (D) and (E), but not (B). Give structures of (A) to (E) with proper reasoning.

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Exercise - IV

**NEET PROBLEMS**

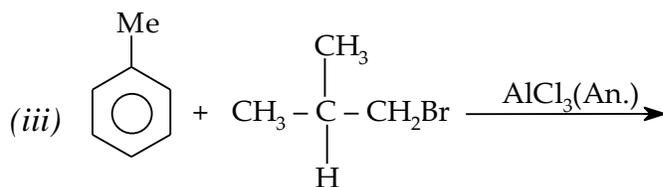
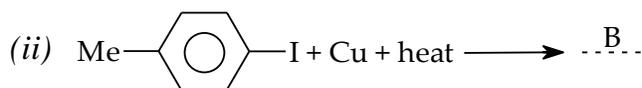
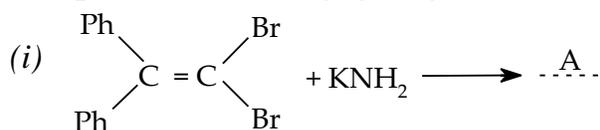
- Give reasons in one or two sentences for the following:  
Iodoform is obtained by the reaction of acetone with hypiodite but not with iodide ion.
- Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity.
- Give the name of the major organic products from 3-ethylpent-2-ene under each of the following conditions.
  - HBr in presence of peroxide
  - Br<sub>2</sub>/H<sub>2</sub>O
- Predict the major product in each of the following reactions:



- Write down the structures of A and B.

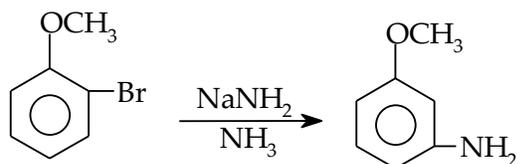


- Complete the following, giving the structures of the principal organic products.

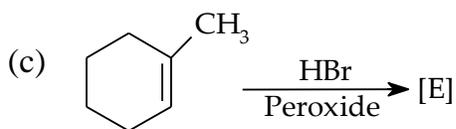
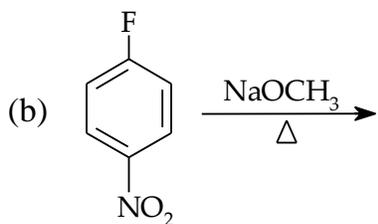
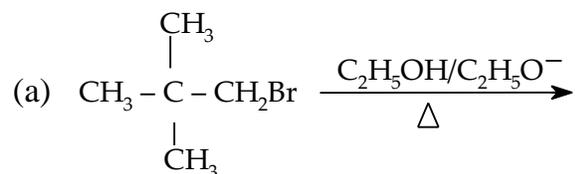


- The following reaction gives two products. C6H5CH2CHClC6H5>>[alcoholic KOH, heat].  
Write the structures of the products.

8. Explain briefly the formation of the product giving the structure of the intermediate.



9. What would be the major products in the following reactions?



\*\*\*\*\*

## ANSWERS

### Exercise - I

#### Only One Option is correct

- |         |         |         |         |         |
|---------|---------|---------|---------|---------|
| 1. (b)  | 2. (c)  | 3. (b)  | 4. (c)  | 5. (c)  |
| 6. (a)  | 7. (b)  | 8. (d)  | 9. (b)  | 10. (c) |
| 11. (b) | 12. (b) | 13. (a) | 14. (a) | 15. (c) |

#### More Than One Choice Correct

- |           |           |              |           |            |
|-----------|-----------|--------------|-----------|------------|
| 1. (a, c) | 2. (c, d) | 3. (a, c, d) | 4. (b, c) | 5. (c, d)  |
| 6. (a, b) | 7. (b, c) | 8. (a, b, d) | 9. (a, d) | 10. (a, c) |

### Exercise – II

#### Assertion and Reason

- |        |        |        |        |         |
|--------|--------|--------|--------|---------|
| 1. (a) | 2. (c) | 3. (d) | 4. (b) | 5. (b)  |
| 6. (b) | 7. (c) | 8. (a) | 9. (a) | 10. (a) |

#### Passage – 1

- |        |        |          |        |
|--------|--------|----------|--------|
| 1. (c) | 2. (a) | 3. (a,c) | 4. (c) |
|--------|--------|----------|--------|

#### Passage – 2

- |        |        |        |
|--------|--------|--------|
| 1. (a) | 2. (a) | 3. (b) |
|--------|--------|--------|

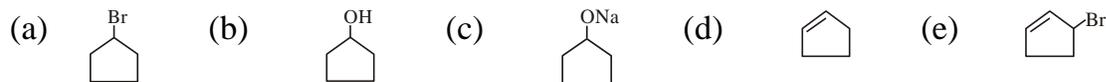
#### Matching Type Questions

- |        |        |
|--------|--------|
| 1. (a) | 2. (b) |
|--------|--------|

### Exercise - III

#### Subjective Type

1.

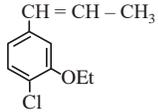
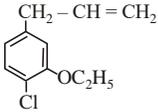
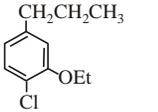


2. (a) 2-Bromo-3-ethyl pentane (b) 2,3-dibromo-3-ethyl-pentane

4.  $C < D < F < B < E < A$

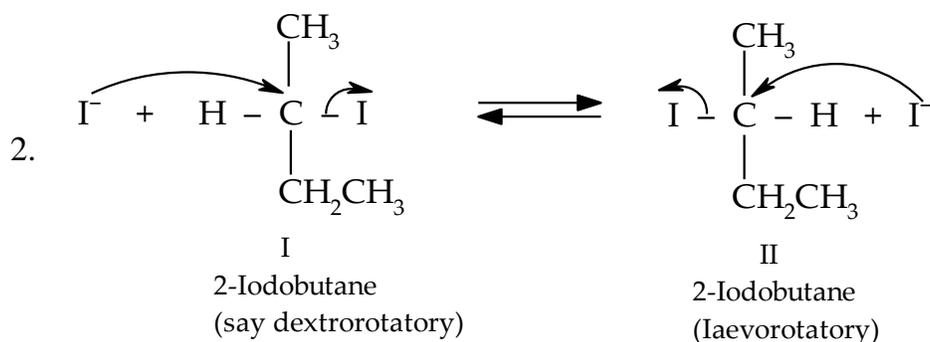
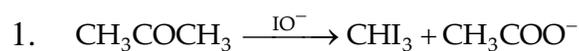
5. (a) R (b) I (c) RA

6. (A) = Benzyl chloride (B) = Benzaldehyde (C) = Benzyl alcohol (D) = Sodium Benzoate

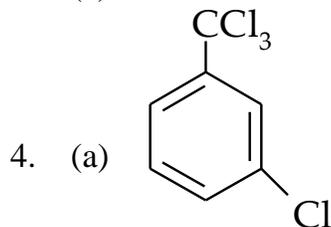
7. (A) = 1-Bromo-1-chloro-1-(4-Methyl phenyl) ethane (B) = 1-(4-Methyl phenyl) ethanone
8. (A) = 2-chloro-1-bromobenzene (B) = 4-chloro-1-bromobenzene  
(C) = 4-chloro-1,2-dibromobenzene (D) = 4-chloro-1,3-dibromobenzene
9. (A) =  $\text{CH}_3\text{C}(\text{Cl})_2\text{Ph}$  (B) = Acetophenone (C) = 1-Phenyl ethanol (D) = Sodium benzoate
10. (a) =  (b) =  (c) = 

### Exercise - IV

#### NEET Level Problem

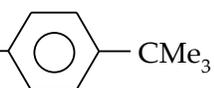


3. (a) 2-Bromo-3-ethylpentan-3-ol (b) 2-Bromo-3-ethylpentan-3-ol

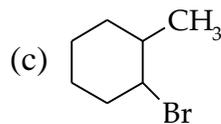
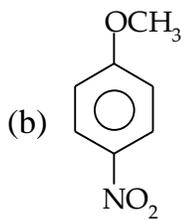
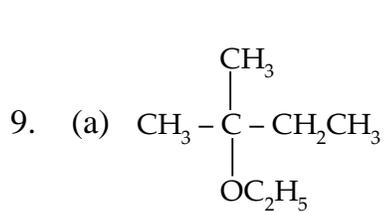
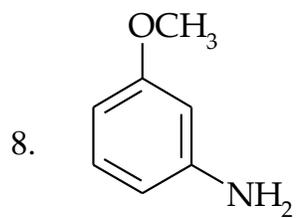


(b)  $\text{AgCN}$  reacts with ethyl bromide to give ethyl isocyanide as the major product.

5. A = 1-Phenylprop-1-yne B = trans-1-Phenylprop-1-ene

6. (i)  $\text{Ph} - \text{C} \equiv \text{C} - \text{Ph}$  (ii) 4, 4'-Dimethyldiphenyl (iii) 

7. trans-1, 2-Diphenylethene (Major product) and cis-1, 2-Diphenylethene (minor product)



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