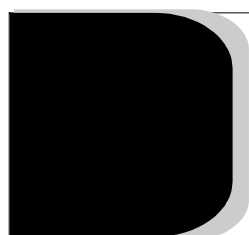




CLASSROOM STUDY
PACKAGE

CHEMISTRY

Haloalkanes and Haloarenes



JEE EXPERT

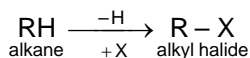
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HALOALKANES AND HALOARENES

1. INTRODUCTION

Alkyl halides or halo alkanes are compounds in which a halogen is bonded to an alkyl group. They have the general formula RX (where R is alkyl group C_nH_{2n+1}) and X is halogen atom.

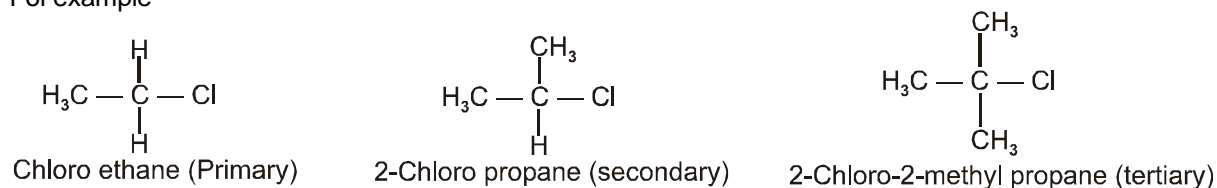


2. CLASSIFICATION

(a) ALKYLHALIDE

Alkyl halides are classified as primary, secondary and tertiary alkyl halides depending on whether the halogen atom is attached to a primary, secondary or tertiary carbon atom respectively.

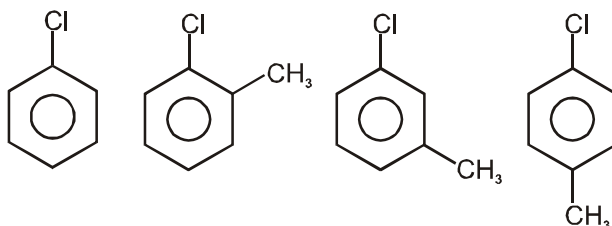
For example



Aromatic halogen compounds or halo arenes are the halogen compounds which contain atleast one aromatic ring. Halogen derivatives of aromatic compounds are of two types.

(b) ARYL HALIDES :

In this type of compounds, the halogen atom is directly linked to the carbon of benzene nucleus e.g.



3. NOMENCLATURE OF ALKYL & ARYL HALIDES :

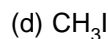
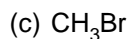
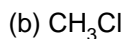
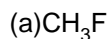
In the common system, aliphatic halogen derivatives are named as alkyl halides. The words n—, sec—, tert—, iso—, neo— are usually used in writing the common names. In IUPAC nomenclature they are named as halo alkanes.

Example :

Formula	Common name	IUPAC name
CH_3Cl	Methyl chloride	Chloro methane
$CH_3CH_2CH_2Cl$	n – propyl chloride	1 – chloro propane
$\begin{array}{c} H_3C \\ \diagdown \\ CHCl \\ \diagup \\ H_3C \end{array}$	Isopropyl chloride	2 – chloro propane
$\begin{array}{c} CH_3 \\ \\ CH_3 - C - Cl \\ \\ CH_3 \end{array}$	ter-Butyl chloride	2 – chloro-2-methyl propane
$\begin{array}{c} CH_3 \\ \\ CH_3 - C - CH_2Cl \\ \\ CH_3 \end{array}$	Neopentylchloride	1-Chloro-2, 2-dimethyl propane

SOLVED EXAMPLES

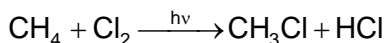
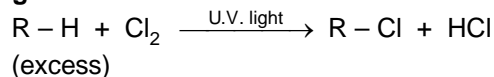
Ex-1. Order of dipole moment



Sol. $\text{CH}_3\text{Cl} > \text{CH}_3\text{Br}$

4. GENERAL METHOD OF PREPARATION OF MONOHALIDES :

(a) Halogenation of alkanes : Alkanes react with halogens in the presence of light to give alkyl halides.

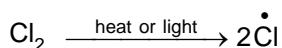


Alkyl halides formed further react with halogen to give di, tri and tetra halogen (CH_3Cl , CH_2Cl_2 , CHCl_3 , CCl_4) compounds.

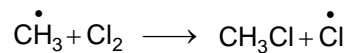
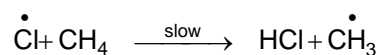
Mechanism of given reaction is free-radical substitution. If Cl_2 is taken in excess amount than CH_3Cl , CH_2Cl_2 , CHCl_3 and CCl_4 also produced.

Mechanism :

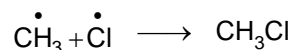
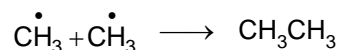
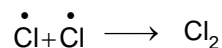
Step-I : Chain initiating step



Step-II : Chain-propagating step



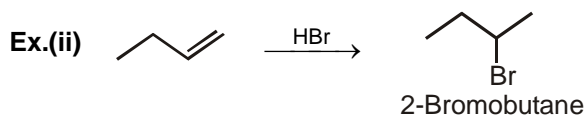
Step-III : Chain-terminating steps

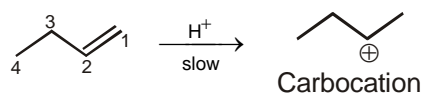
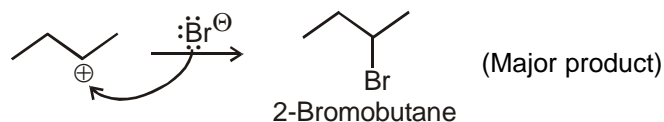


(b) From alkenes: Alkenes add halogen acids to give halides. For example

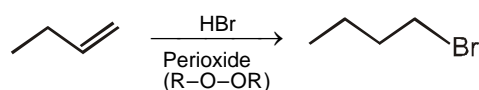
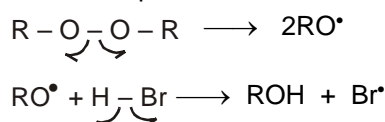
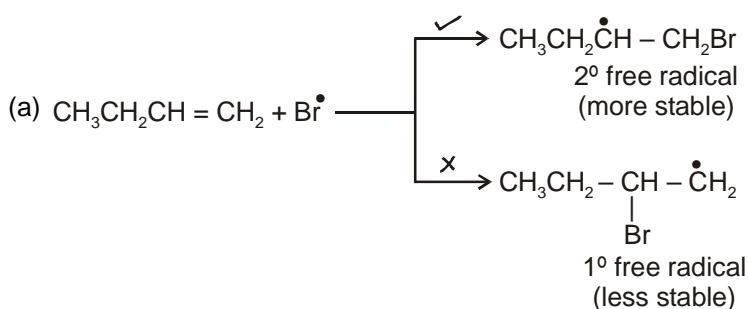
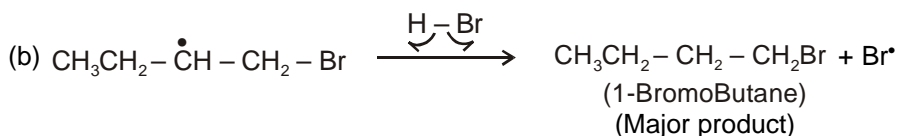
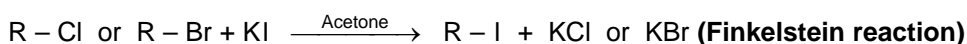


Markonikoff's rule: In the addition reactions of unsymmetrical alkenes the -ve part attaches to the carbon atom having lesser number of H-atoms. E.g.

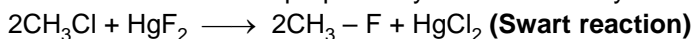


Mechanism :**Step-I :**Approach of H^+ **Step-II :**Approach of Br^\ominus **Carbocation** formed as an intermediate during given reaction.Mechanism of given reaction \Rightarrow electrophilic addition.

In case of HBr if peroxide is added antimarkonikoff's addition takes place which is also called Kharash effect or peroxide effect e.g.

Ex. (iii)**Mechanism :****Step-I :** Chain Initiation step :**Step-II :** Chain propagation step \rightarrow  2° free radical is formed during given reaction**Step-III :** Chain Ending step \rightarrow all free radicals are combined with each other in this step**Note :** Only **HBr** show the **peroxide** effect (Among Halogen acid).**(c) By halide exchange :** Alkyl chlorides and bromides reacts with NaI in acetone to give alkyl iodides. This reactions is possible because NaI is soluble in acetone but NaCl and NaBr are insoluble in acetone.

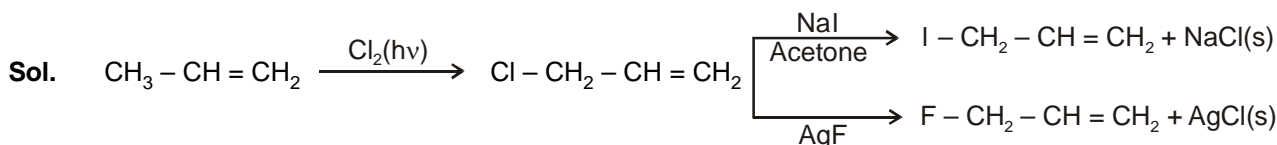
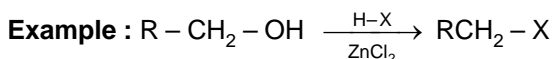
R - I and R - F can be prepared by this method only.



Example.

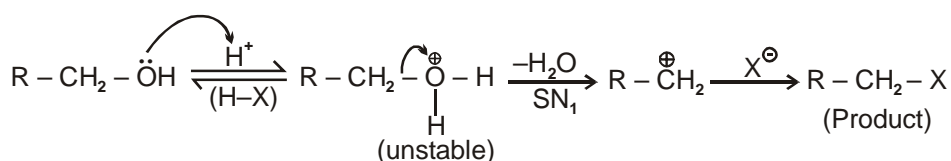
Supply reactions for the preparation from propene of

(a) allyl iodide and (b) allyl fluoride

**(d) From Alcohols :****(i) By the action of hydrogen halides :**

Lucas reagent is 1 conc. HCl + anhydrous ZnCl_2

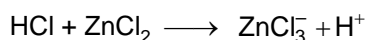
Mechanism :



Given reaction is an example of **SN₁** mechanism.

In this reaction intermediate carbocation is formed so rearrangement (H^- shifting or CH_3^- shifting) can take place.

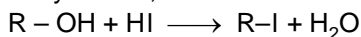
ZnCl_2 act as dehydrating agent and absorbs H_2O from the reaction so good yield of halide is obtained. Also it generates H^+ from HCl.

**Reactivity order for alcohol :**

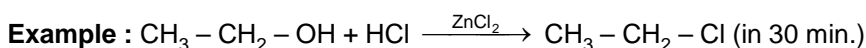
Reactivity \propto stability of intermediate carbocation, so reactivity order : Tert. alcohol > Sec. alcohol > Pri. alcohol,

Reactivity order of $\text{H} - \text{X}$ is : $\text{HI} > \text{HBr} > \text{HCl}$

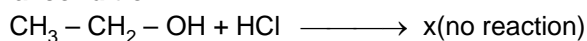
HI is maximum reactive so it reacts readily with 1°, 2° and 3° alcohols.



1° alcohol are less reactive so ZnCl_2 or some amount of H_2SO_4 is needed to increase the reactivity.



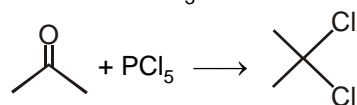
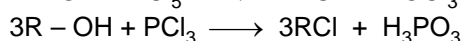
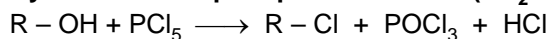
At normal condition :



Note : $\text{HCl} + \text{ZnCl}_2$ is called as lucas reagent, alcohol gives turbidity with lucas reagent.

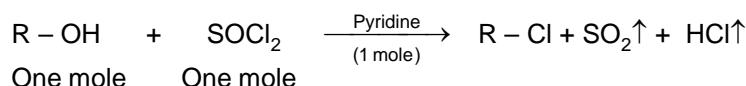
Reactivity towards lucas reagent (difference in 1°, 2° and 3° alcohol).

	1° alcohol	2° alcohol	3° alcohol
Time to give turbidity	in 30 min.	in 5 min.	in 1 min.

(ii) By the action of phosphorus halides (SN₂ mechanism) :

PBr_3 and PI_3 are less stable, thus for bromides and iodides, $(\text{P} + \text{Br}_2)$ Or $(\text{P} + \text{I}_2)$ mixture is used.

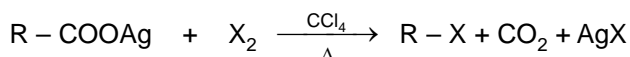
(iii) **By reaction with thionyl chloride** - (Darzen's procedure) :



It's the best method to convert alcohol to chloride because side product are gaseous which are escape out

Note : Due to the less stability of SOBr_2 and SOI_2 , R-Br and RI does not obtained by this method.

(e) **Borodine - Hunsdicker's reaction :**



Silver salt of
a fatty acid (Cl_2 or Br_2)

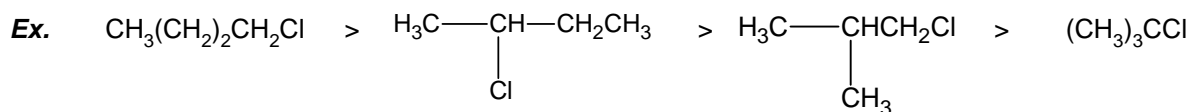
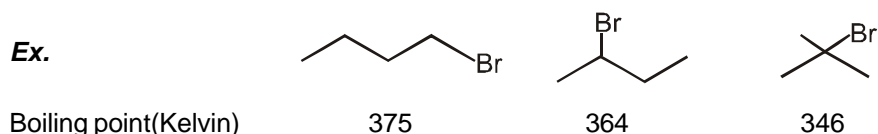
5. PHYSICAL PROPERTIES :

(a) **Boiling Points :**

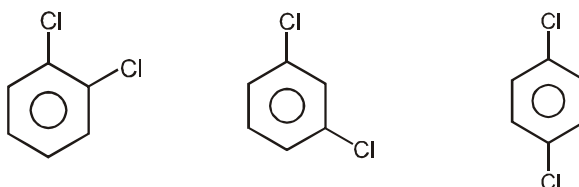
The boiling points of haloalkanes are in the order $\text{RCl} < \text{RBr} < \text{RI}$. It is because with increase in size and mass of halogen atom the magnitude of Vander Waal's forces of attraction increases.

Among isomeric alkyl halides, the boiling point decreases with increase in branching in alkyl group.

e.g the decreasing order of boiling point among the isomers of butane is



- For same halogen, the boiling point increases with increase in molecular mass.
e.g. CH_3Cl has lower boiling point than $\text{CH}_3\text{CH}_2\text{Cl}$
- The boiling points of various halogen compounds increase with increase in number of halogen atoms.
For e.g. boiling point of CCl_4 is more than boiling point of CHCl_3 which is further more than CH_2Cl_2
- The boiling points of mono halogen derivatives of benzene follows the order: Iodo > Bromo > Chloro
The boiling points of isomeric dihalo benzenes are nearly the same. However their melting points are quite different. The melting point of para isomer is generally 70 – 100 degrees more than the melting points of ortho & meta isomers.



Boiling point	453 K	446 K	448 K
Melting point	256 K	249 K	325 K

The higher melting point of p – isomer is due to its symmetry which leads to more close packing of its molecules in the crystal lattice.

(b) The lower members CH_3F , CH_3Cl , CH_3Br , $\text{C}_2\text{H}_5\text{Cl}$ and $\text{C}_2\text{H}_5\text{F}$ are gases at room temp.

CH_3I and members upto C_{18} are colourless sweet smelling liquids.

(c) Higher B.P. than parent alkanes.

Decreasing order of B.P. is : $\text{R} - \text{I} > \text{R} - \text{Br} > \text{R} - \text{Cl} > \text{R} - \text{F}$

among isomeric $\text{R} - \text{X}$ decreasing order of B.P. is : **Primary** > **Secondary** > **tertiary**

(d) $\text{R} - \text{F}$ and $\text{R} - \text{Cl} \longrightarrow$ lighter than water

$\text{R} - \text{Br}$ and $\text{R} - \text{I} \longrightarrow$ heavier than water

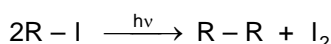
Decreasing order of density is : $\text{R} - \text{I} > \text{R} - \text{Br} > \text{R} - \text{Cl} > \text{R} - \text{F}$

(e) $\text{R} - \text{X}$ are polar co-valent compounds but insoluble in water because they can not form H-bonds. They dissolve in organic solvents.

(f) **Beilstein test** : $\text{R} - \text{X}$ burns with a green flame due to interaction of X with Cu wire.

(g) The stability order is : $\text{R} - \text{F} > \text{R} - \text{Cl} > \text{R} - \text{Br} > \text{R} - \text{I}$

$\text{R} - \text{I}$ is least stable and darkens in light due to photodecomposition.



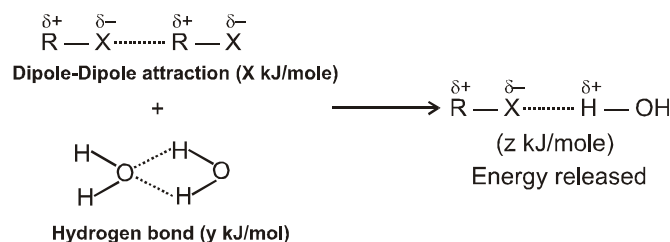
SOLVED EXAMPLES

Ex-2. Although the C-I bond is longer than a C-Cl bond, the C-Cl bond has a larger dipole moment. Explain.

Sol. Dipole moment is the multiplication product of charge & distance between the 2-atoms. It is a vector quantity and direction of dipole moment is always from less electro negative element to high electro negative element.
 $\mu = e \times d$

The multiplication product of charge & distance between the 2-atoms is maximum in C-Cl bond.

(h) **Solubility**



$$(X + Y) > Z$$

◆ The haloalkanes are only very slightly soluble in water. In order for a haloalkane to dissolve in water, energy is required to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules. Less energy is released when new attractions are set up between the haloalkane and the water molecules as these are not as strong as the original hydrogen bonds in water. As a result, the solubility of haloalkanes in water is low.

◆ Haloalkanes tend to dissolve in organic solvents because the new intermolecular attractions between haloalkanes and solvent molecules have much the same strength as the ones being broken in the separate haloalkane and solvent molecules.

6. CHEMICAL PROPERTIES :

The chemical reactions of halo alkanes are of 4 types :

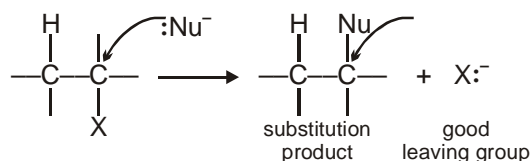
(a) **Nucleophilic substitution reactions**

(b) **Elimination reactions**

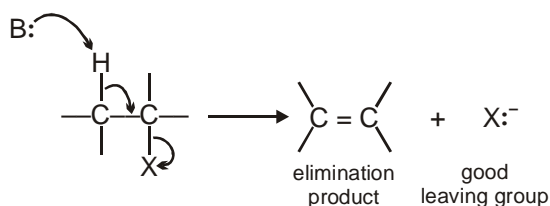
(c) **Reactions with metals**

A COMPARISON BETWEEN NUCLEOPHILIC SUBSTITUTION AND S_N ELIMINATION

Nucleophilic substitution – A nucleophile attacks a carbon atom



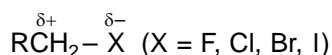
s_N Elimination – A base attacks a proton



Similarities	Differences
<ul style="list-style-type: none"> In both reactions RX acts as an electrophile, reacting with an electron-rich reagent. Both reactions require a good leaving group X^- that can accept the electron density in the C–X bond. 	<ul style="list-style-type: none"> In substitution, a nucleophile attacks a single carbon atom. In elimination, a Bronsted–Lowry base removes a proton to form a π bond, and two carbons are involved in the reaction.

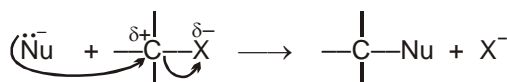
(a) NUCLEOPHILIC SUBSTITUTION

A halogen is more electronegative than carbon. Consequently, the two atoms don't share their bonding electrons equally. Because the more electronegative halogen has a larger share of the electrons, it has a partial negative charge and the carbon to which it is bonded has a partial positive charge.

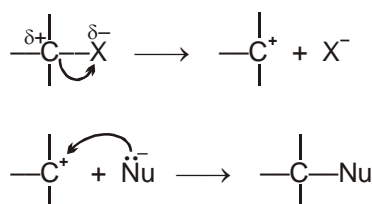


The polar carbon-halogen bond causes alkyl halides to undergo substitution and elimination reactions. There are two important mechanisms for the substitution reaction :

1. A nucleophile is attracted to the partially positively charged carbon. As the nucleophile approaches the carbon, it causes the carbon-halogen bond to break heterolytically (the halogen keeps both of the bonding electrons).



2. The carbon-halogen bond breaks heterolytically without any assistance from the nucleophile, forming a carbocation. The carbocation then reacts with the nucleophile to form the substitution product.



The mechanism that predominates depends on the following :



The structure of the alkyl halide,

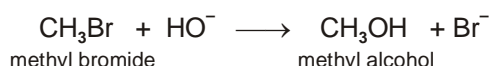
- ◆ The reactivity and structure of the nucleophile,
- ◆ The concentration of the nucleophile,
- ◆ The solvent in which the reaction is carried out.

How is the mechanism of a reaction determined ? We can learn a great deal about the mechanism of a reaction by determining the factors that affect the rate of the reaction. These factors are called the **kinetics** of the reaction.

7. SUBSTITUTION NUCLEOPHILIC BIMOLECULAR (SN₂ REACTION) :

Mechanism of SN₂ :

The rate of a nucleophilic substitution reaction such as the reaction of methyl bromide with hydroxide ion depends on the concentrations of both reagents. If the concentration of methyl bromide in the reaction mixture is doubled, the rate of the nucleophilic substitution reaction doubles. If the concentration of hydroxide ion is doubled, the rate of the reaction also doubles. If the concentrations of both reactants are doubled, the rate of the reaction quadruples.



$$\text{rate} \propto [\text{alkyl halide}] [\text{nucleophile}]$$

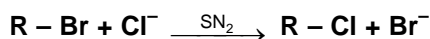
$$\text{rate} = k[\text{alkyl halide}] [\text{nucleophile}]$$

Because the rate of this reaction depends on the concentration of two reactants, it is a second order reaction.

The transition state, therefore, is **bimolecular** because it involves two molecules. The proportionality constant (k) is called the rate constant. The rate constant describes how difficult it is to overcome the energy barrier of the reaction (how hard it is to reach the transition state). The larger the rate constant the easier it is to reach the **transition state**.

The reaction of methyl bromide with hydroxide ion is an example of an SN₂ reaction where **S** stands for substitution, **N** stands for nucleophilic, and **2** stands for bimolecular. In 1937, Edward Hughes and Christopher Ingold proposed a mechanism for an SN₂ reaction.

Salient features of SN₂ reaction :



1. The rate of the reaction depends on the concentration of the alkyl halide and on the concentration of the nucleophile. This means that both reactants are involved in the transition state of the rate-determining step.
2. When the hydrogens of methyl bromide are successively replaced with methyl groups, the rate of the reaction with a given nucleophile becomes progressively slower.
3. The reaction of an alkyl halide in which the halogen is bonded to a chirality center leads to the formation of only one stereoisomer, and its configuration is inverted relative to the configuration of the reacting alkyl halide.

Bromoalkane	Relative rate of SN ₂
CH ₃ Br	1200
CH ₃ CH ₂ Br	40
CH ₃ CH ₂ CH ₂ Br	16
CH ₃ -CH(Br)-CH ₃	1
CH ₃ -C(CH ₃) ₂ -Br	Too slow to measure

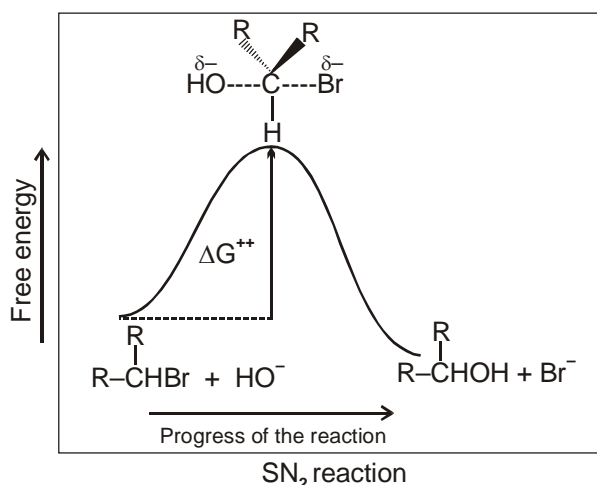
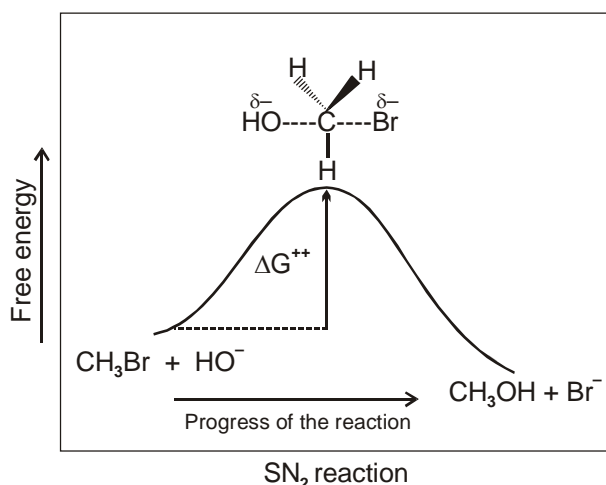
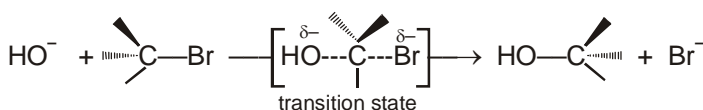
Back side attack occurs because the orbital of the nucleophile that contains its non-bonding electrons interacts with the empty σ^* molecular orbital associated with the C–Br bond. Direct displacement reaction takes place because the nucleophile displaces the leaving group in a single step.

How does this mechanism account for the three observed pieces of experimental evidence? The mechanism shows the alkyl halide and the nucleophile coming together in the transition state of the one-step reaction. Therefore, increasing the concentration of either of them makes their coming together more probable. Thus, the reaction will follow second-order kinetics, exactly as observed.

Because the nucleophile attacks the back side of the carbon that is bonded to the halogen, bulky substituents attached to this carbon will make it harder for the nucleophile to get to the back side and, therefore, will decrease the rate of the reaction. This explains why substituting methyl groups for the hydrogens in methyl bromide progressively slow the rate of the substitution reaction.

Relative reactivities of alkyl halides in an S_N2 reaction

methyl halide > 1° alkyl halide > 2° alkyl halide > 3° alkyl halide

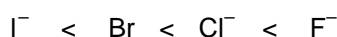


One way to visualize movement of the groups bonded to the carbon at which substitution occurs is to picture an umbrella that turns inside out. This is called **inversion of configuration**. The carbon at which substitution occurs has inverted its configuration during the course of the reaction just as an umbrella has a tendency to invert in a windstorm. The inversion is known as a Walden inversion, since Paul Walden was the first to discover that compounds could invert their configurations as a result of substitution reactions.

If an alkyl iodide, an alkyl bromide, an alkyl chloride, and an alkyl fluoride (all with the same alkyl group) were allowed to react with the same nucleophile under the same conditions, we would find that the alkyl iodide is the most reactive and the alkyl fluoride is the least reactive.

Relative rates of reaction		
$\text{HO}^- + \text{RCH}_2\text{I} \longrightarrow \text{RCH}_2\text{OH} + \text{I}^-$		30,000
$\text{HO}^- + \text{RCH}_2\text{Br} \longrightarrow \text{RCH}_2\text{OH} + \text{Br}^-$		10,000
$\text{HO}^- + \text{RCH}_2\text{Cl} \longrightarrow \text{RCH}_2\text{OH} + \text{Cl}^-$		200
$\text{HO}^- + \text{RCH}_2\text{F} \longrightarrow \text{RCH}_2\text{OH} + \text{F}^-$		1

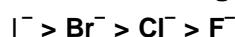
Relative basicities of the halide ions :



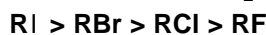
increasing basicity

Furthermore, because weaker bases are better leaving groups, the halide ions have the following relative leaving abilities.

Relative leaving abilities of the halide ions :



As a consequence of the relative leaving abilities of the halide ions, alkyl halides have the following relative reactivities in an $\text{S}_{\text{N}}2$ reaction.



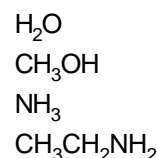
A base shares its nonbonding electrons with a proton. **Basicity** is a measure of how well the base shares those electrons with a proton. The stronger the base, the better it shares its electrons. Basicity is measured by an equilibrium constant (the acid dissociation constant, K_{a}) that indicates the tendency of the conjugate acid of the base to lose a proton.

Nucleophilicity is a measure of how readily the nucleophile is able to attack such an atom. It is measured by a rate constant (k). In the case of an $\text{S}_{\text{N}}2$ reaction, nucleophilicity is a measure of how readily the nucleophile attacks an sp^3 hybridized carbon bonded to a leaving group. Thus, a base forms a new bond with a proton, whereas a nucleophile forms a new bond with an atom other than a proton.

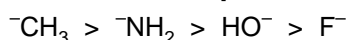
Stronger base, better nucleophile



Weaker base, poorer nucleophile

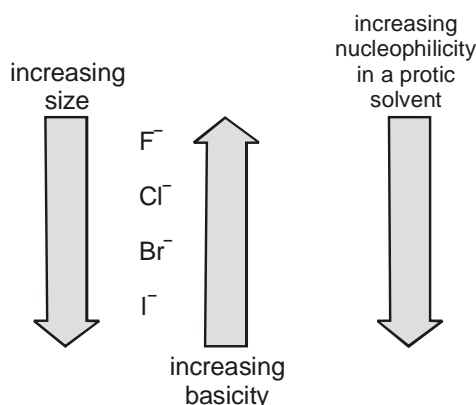


Relative base strengths and relative nucleophilicities :



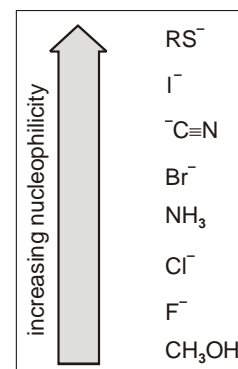
When comparing molecules with attacking atoms that are very different in size, the direct relationship between basicity and nucleophilicity is maintained if the reaction occurs in the gas phase. If, however, the reaction occurs in a solvent-as most organic reactions do-the relationship between basicity and nucleophilicity depends on the solvent.

A protic solvent contains a hydrogen bonded to an oxygen or a nitrogen; it is a hydrogen bond donor.



The effect of solvent on nucleophilicity :

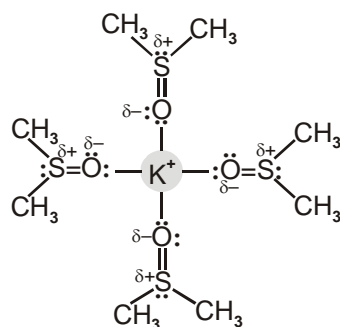
The interaction between the ion and the dipole of the protic solvent is called an ion dipole interaction. At least one of the ion-dipole interactions must be broken before the nucleophile can participate in an $\text{S}_{\text{N}}2$ reaction. Weak bases interact weakly with protic solvent, when strong bases interact more strongly because they are better at sharing their electrons.



strong nucleophiles	$(\text{CH}_3\text{CH}_2)_3\text{P:}$	moderate nucleophiles	$:\ddot{\text{Br}}:^-$
	$^-\ddot{\text{S}}-\text{H}$		$:\text{NH}_3$
	$:\ddot{\text{I}}:^-$		$\text{CH}_3-\ddot{\text{S}}-\text{CH}_3$
	$(\text{CH}_3\text{CH}_2)_2\ddot{\text{N}}\text{H}$	weak nucleophiles	$:\ddot{\text{Cl}}:^-$
	$^-\text{C}\equiv\text{N}$		$\text{CH}_3\text{C}(=\text{O})-\ddot{\text{O}}:^-$
	$(\text{CH}_3\text{CH}_2)_3\text{N:}$		$:\ddot{\text{F}}:^-$
	$\text{H}-\ddot{\text{O}}:^-$		$\text{H}-\ddot{\text{O}}-\text{H}$
	$\text{CH}_3-\ddot{\text{O}}:^-$		$\text{CH}_3-\ddot{\text{O}}-\text{H}$

◆ **The effect of the solvent on the rate of an $\text{S}_\text{N}2$ reaction :**

If a reactant in the rate-limiting step is charged, increasing the polarity of the solvent will decrease the rate of the reaction. If none of the reactants in the rate-limiting step is charged, increasing the polarity of the solvent will increase the rate of the reaction.

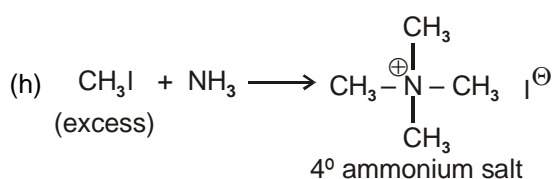
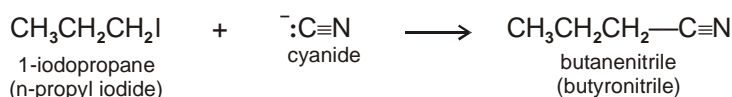
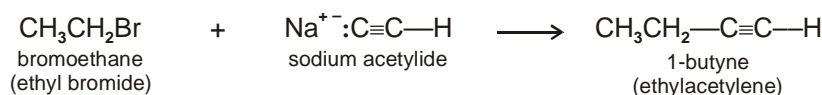
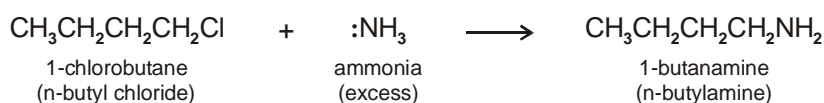
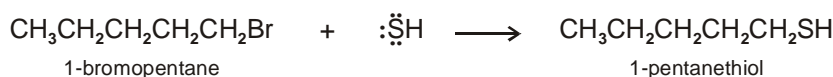
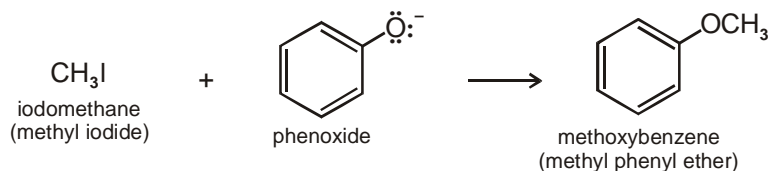
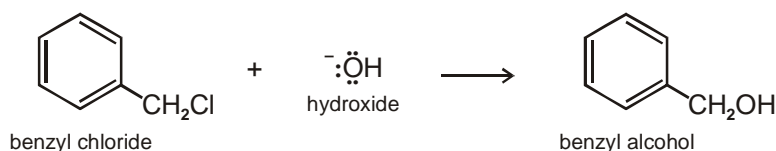


DMSO can solvate a cation better than it can solvate an anion

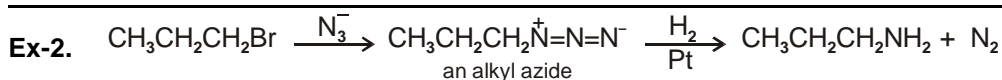
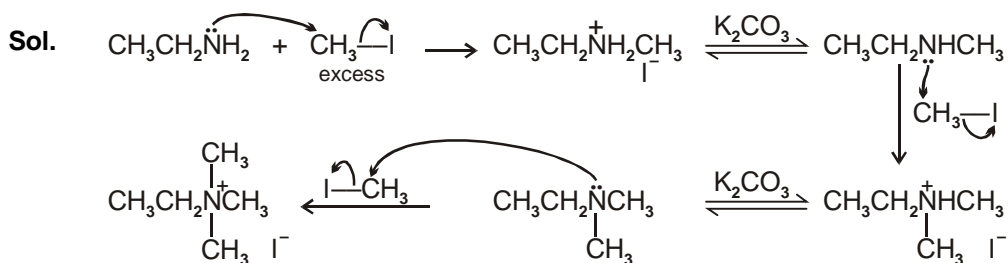
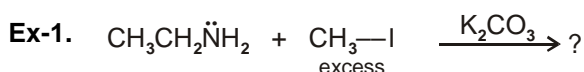
EXAMPLES OF $\text{S}_\text{N}2$ REACTION :

Nucleophile	Product	Class of Product
$\text{R}-\text{X} + ^-\ddot{\text{I}}:$	$\rightarrow \text{R}-\ddot{\text{I}}:$	alkyl halide
$\text{R}-\text{X} + ^-\ddot{\text{O}}\text{H}$	$\rightarrow \text{R}-\ddot{\text{O}}\text{H}$	alcohol
$\text{R}-\text{X} + ^-\ddot{\text{O}}\text{R}'$	$\rightarrow \text{R}-\ddot{\text{O}}\text{R}'$	ether
$\text{R}-\text{X} + ^-\ddot{\text{S}}\text{H}$	$\rightarrow \text{R}-\ddot{\text{S}}\text{H}$	thiol (mercaptan)
$\text{R}-\text{X} + ^-\ddot{\text{S}}\text{R}'$	$\rightarrow \text{R}-\ddot{\text{S}}\text{R}'$	thioether (sulfide)
$\text{R}-\text{X} + ^-\ddot{\text{N}}\text{H}_3$	$\rightarrow \text{R}-\ddot{\text{N}}\text{H}_3^+ \text{X}^-$	amine
$\text{R}-\text{X} + ^-\ddot{\text{N}}=\ddot{\text{N}}=\ddot{\text{N}}:^-$	$\rightarrow \text{R}-\ddot{\text{N}}=\ddot{\text{N}}=\ddot{\text{N}}:^-$	azide
$\text{R}-\text{X} + ^-\text{C}\equiv\text{C}-\text{R}'$	$\rightarrow \text{R}-\text{C}\equiv\text{C}-\text{R}'$	alkyne
$\text{R}-\text{X} + ^-\text{C}\equiv\text{N:}$	$\rightarrow \text{R}-\text{C}\equiv\text{N:}$	nitrile
$\text{R}-\text{X} + ^-\text{R}'-\text{CO}\ddot{\text{O}}:^-$	$\rightarrow \text{R}'-\text{COO}-\text{R}$	ester
$\text{R}-\text{X} + :\text{P}(\text{Ph})_3$	$\rightarrow [\text{R}-\ddot{\text{P}}\text{Ph}_3]^+ \text{X}^-$	phosphonium salt

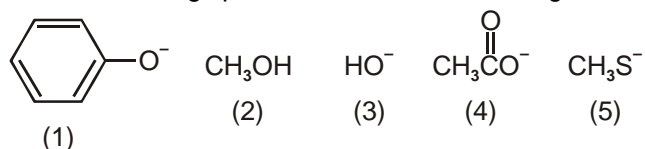
Examples :



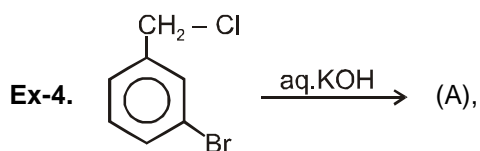
SOLVED EXAMPLES



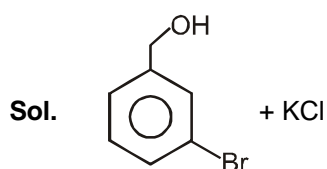
Ex-3. List the following species in order of decreasing nucleophilicity in an aqueous solution :



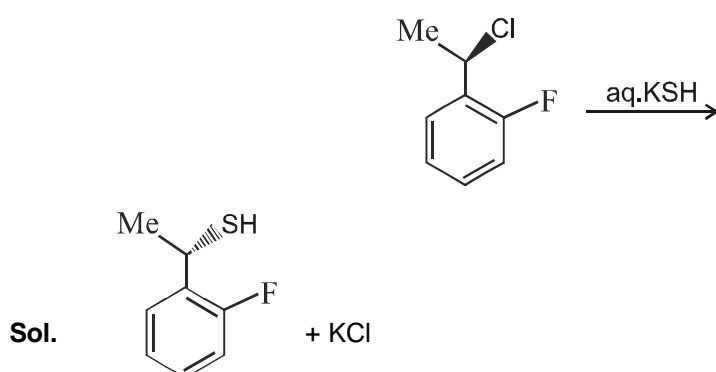
Sol. $5 > 3 > 1 > 4 > 2$



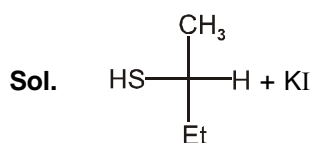
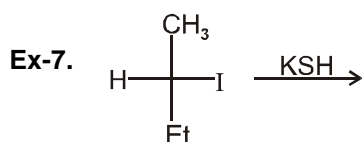
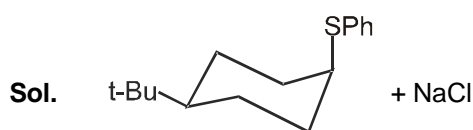
Structure of product (A) is :



Ex-5. The major product of the following reaction is



Major-product (A) is



Ex-8. Arrange the compounds of each set in order of reactivity towards S_N2 displacement :

(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

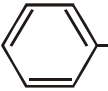
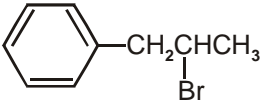
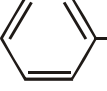
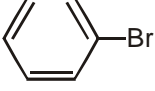
- (ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 3-Bromo-2-methylbutane
 (iii) 1-Bromobutane, 1-Bromo-2, 2-dimethylpropane, 1-Bromo-2-methylbutane,
 1-Bromo-3-methylbutane.

Sol. In S_N2 displacement the order of reactivity of various types of alkyl halides is $1^\circ > 2^\circ > 3^\circ$. For alkyl halides of the same class the one which is sterically less hindered is more reactive.

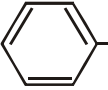
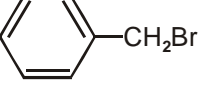
- (i) $1\text{-Bromo-pentane} > 2\text{-Bromo-pentane} > 2\text{-Bromo-2-methylbutane}$
 $(1^\circ) \quad (2^\circ) \quad (3^\circ)$
- (ii) $1\text{-Bromo-3-methylbutane} > 2\text{-Bromo-3-methylbutane} > 2\text{-Bromo-2-methylbutane}$
 $(1^\circ) \quad (2^\circ) \quad (3^\circ)$
- (iii) 1-Bromobutane > 1-Bromo-3-methylbutane > 1-Bromo-2-methylbutane > 1-Bromo-2, 2-dimethylpropane.

All these halides are 1° . The halide which has less steric hindrance about the carbon to which halogen atom is attached, is more reactive towards S_N2 displacement.

Ex-9. Which alkyl halide would you expect to be more reactive in an S_N2 reaction with a given nucleophile ?

- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ or $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ or $\text{CH}_3\text{OCH}_2\text{Cl}$
- (c) $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{Br}$ or $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{Br}$ (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{Br}$ or $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Br}$
- (e)  or  (f)  or 
- (g) $\text{CH}_3\text{CH}=\text{C}(\text{Br})\text{CH}_3$ or $\text{CH}_3\text{CH}=\text{CHCH}(\text{Br})\text{CH}_3$

Sol. Rate of S_N2 will mainly depend on 2 factors

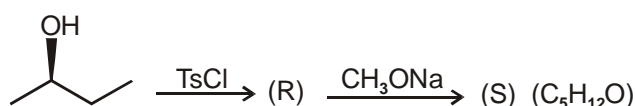
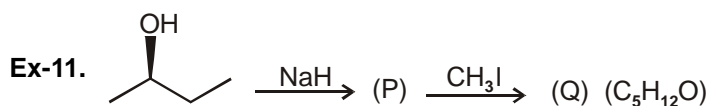
- (1) Steric hindrance (2) Stability of transition state
- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ (b) $\text{CH}_3\text{OCH}_2\text{Cl}$
- (c) $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{Br}$ (d) $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Br}$
- (e)  (f) 
- (g) $\text{CH}_3\text{CH}=\text{CHCH}(\text{Br})\text{CH}_3$

Ex-10. Which reaction in each of the following pairs will take place more rapidly ?

- (a) $\text{CH}_3\text{Br} + \text{HO}^- \longrightarrow \text{CH}_3\text{OH} + \text{Br}^-$
 $\text{CH}_3\text{Br} + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{OH} + \text{HBr}$
- (b) $\text{CH}_3\text{I} + \text{HO}^- \longrightarrow \text{CH}_3\text{OH} + \text{I}^-$
 $\text{CH}_3\text{Cl} + \text{HO}^- \longrightarrow \text{CH}_3\text{OH} + \text{Cl}^-$
- (c) $\text{CH}_3\text{Br} + \text{NH}_3 \longrightarrow \text{CH}_3\text{NH}_3^+ + \text{Br}^-$
 $\text{CH}_3\text{Br} + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{OH} + \text{HBr}$
- (d) $\text{CH}_3\text{Br} + \text{HO}^- \xrightarrow{\text{DMSO}} \text{CH}_3\text{OH} + \text{Br}^-$
 $\text{CH}_3\text{Br} + \text{HO}^- \xrightarrow{\text{EtOH}} \text{CH}_3\text{OH} + \text{Br}^-$
- (e) $\text{CH}_3\text{Br} + \text{NH}_3 \xrightarrow{\text{Et}_2\text{O}} \text{CH}_3\text{NH}_3^+ + \text{Br}^-$
 $\text{CH}_3\text{Br} + \text{NH}_3 \xrightarrow{\text{EtOH}} \text{CH}_3\text{NH}_3^+ + \text{Br}^-$

Sol. Strong nucleophile and polar aprotic solvent always favour the S_N2 mechanism.

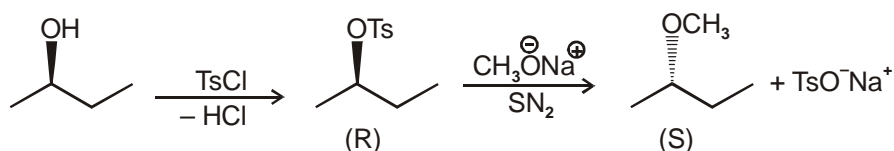
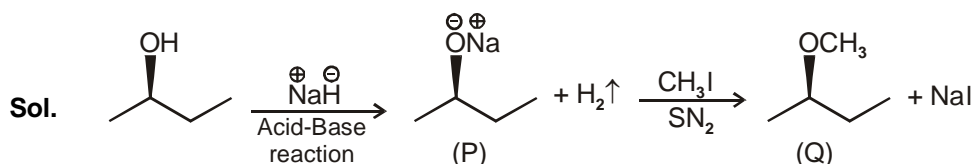
- (a) $\text{CH}_3\text{Br} + \text{HO}^- \longrightarrow \text{CH}_3\text{OH} + \text{HBr}$
 (b) $\text{CH}_3\text{I} + \text{HO}^- \longrightarrow \text{CH}_3\text{OH} + \text{I}^-$
 (c) $\text{CH}_3\text{Br} + \text{NH}_3 \longrightarrow \text{CH}_3\text{NH}_3^+ + \text{Br}^-$
 (d) $\text{CH}_3\text{Br} + \text{HO}^- \xrightarrow{\text{DMSO}} \text{CH}_3\text{OH} + \text{Br}^-$
 (e) $\text{CH}_3\text{Br} + \text{NH}_3 \xrightarrow{\text{Et}_2\text{O}} \text{CH}_3\text{NH}_3^+ + \text{Br}^-$



Correct relation ship between (Q) and (S) is

- (A) Diastereomer (B) Enantiomer (C) Structural Isomer (D) Identical

Ans. (B)



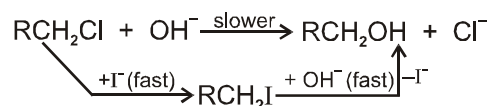
(Q) and (S) are mirror image, non-superimposeable on each other that's why they are enantiomers of each other.

Ex-12. ROH does not react with NaBr, but adding H_2SO_4 forms RBr. Explain.

Sol. Br^- , an extremely weak Bronsted base, cannot displace the strong base OH^- . In acid, ROH_2^+ is first formed. Now, Br^- displaces H_2O , which is a very weak base and a good leaving group.

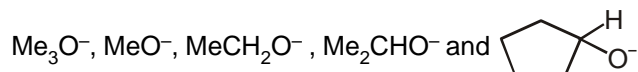
Ex-13. Account for the observation that catalytic amounts of KI enhance the rate of reaction of RCH_2Cl with OH^- to give the alcohol RCH_2OH .

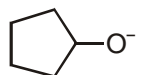
Sol. Since I^- is a better nucleophile than OH^- , it reacts rapidly with RCH_2Cl . Only a catalytic amount of I^- is needed, because the regenerated I^- is recycled in the reaction.



Ex-14. Racemic cis-4-iodoethylcyclohexane + OH⁻ → Racemic trans-4-ethyl cyclohexanol

Ex-15. List the following alkoxide nucleophiles in order of SN² reactivity.



Sol. MeO⁻ > MeCH₂O⁻ >  > Me₂CHO⁻ > Me₃CO⁻

SUBSTITUTION NUCLEOPHILIC UNIMOLECULAR (SN₁ REACTION)

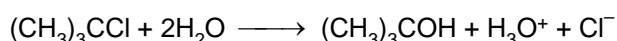
A Mechanism of the SN₁ reaction :

The reaction between tert-butyl bromide and water is an **SN₁** reaction, where "S" stands for substitution, "N" stands for nucleophilic, and "1" stands for unimolecular. **Unimolecular** means that only one molecule is involved in the rate-determining step.

Note : Hydrolysis → Cleavage of bond by the help of H₂O

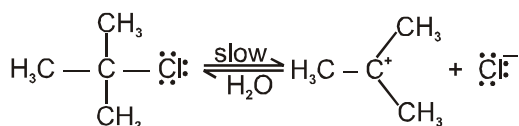
The mechanism of SN₁ reaction based on the following experimental evidence :

1. The rate law shows that the rate of the reaction depends only on the concentration of the alkyl halide. This means that we must be observing a reaction whose rate-determining step involves only the alkyl halide.
2. When the methyl groups of tert-butyl bromide are successively replaced by hydrogens, the rate of the SN₁ reaction decreases progressively. This is opposite to the order of reactivity exhibited by alkyl halides in SN₂ reactions.
3. The reaction of an alkyl halide in which the halogen is bonded to an asymmetric carbon forms two stereoisomers: one with the same relative configuration at the asymmetric carbon as the reacting alkyl halide, the other with the inverted configuration.



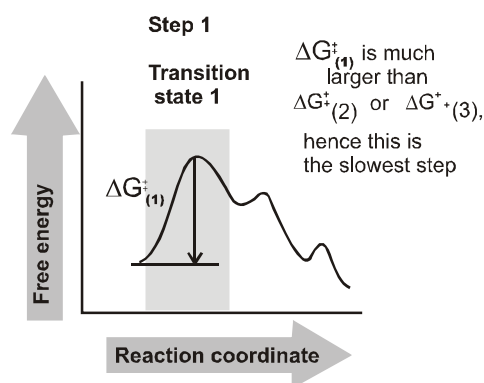
Mechanism :

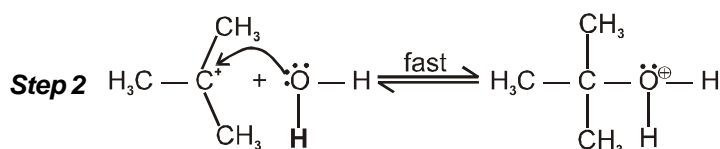
Step 1



Aided by the polar solvent a chlorine departs with the electron pair that bonded it to the carbon.

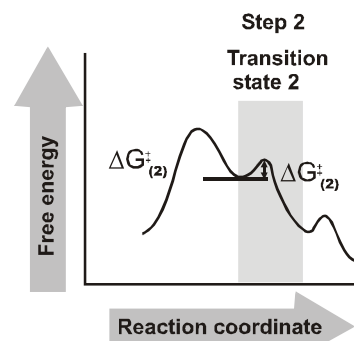
This slow step produces the relatively stable 3° carbocation and a chloride ion. Although not shown here, the ions are solvated (and stabilized) by water molecules.



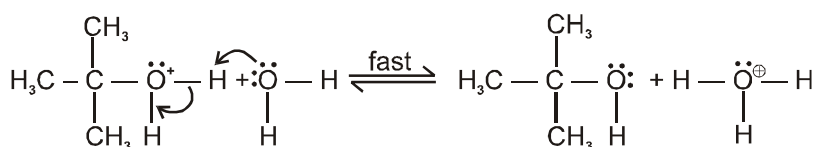


A water molecule acting as a Lewis base donates an electron pair to the carbocation (a Lewis acid). This gives the cationic carbon eight electrons.

The product is a tert-butyloxonium ion (or protonated tert-butyl alcohol).

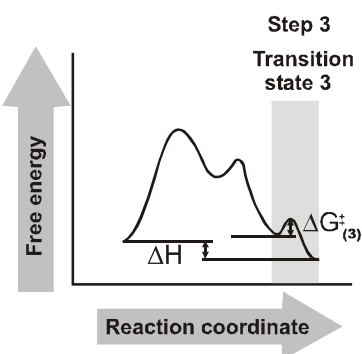


Step 3

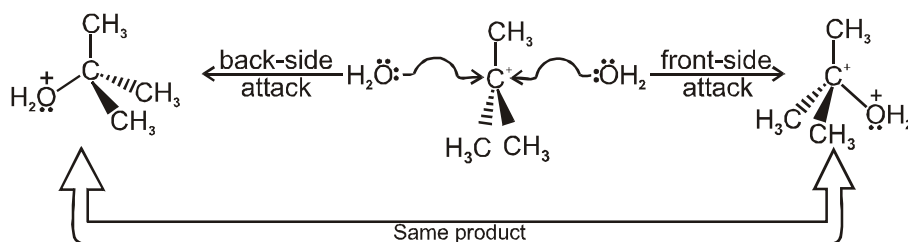


A water molecule acting as a Bronsted base accepts a proton from the tert-butyloxonium ion.

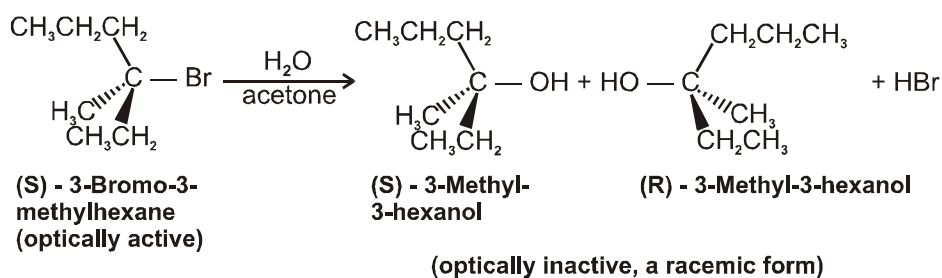
The products are tert-butyl alcohol and a hydronium ion.



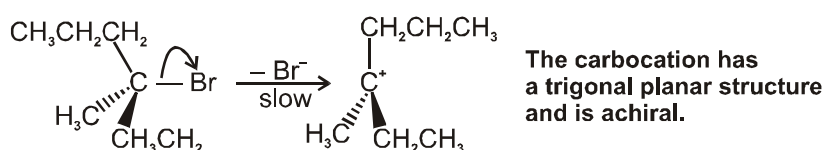
Stereochemistry of S_N1 Reaction

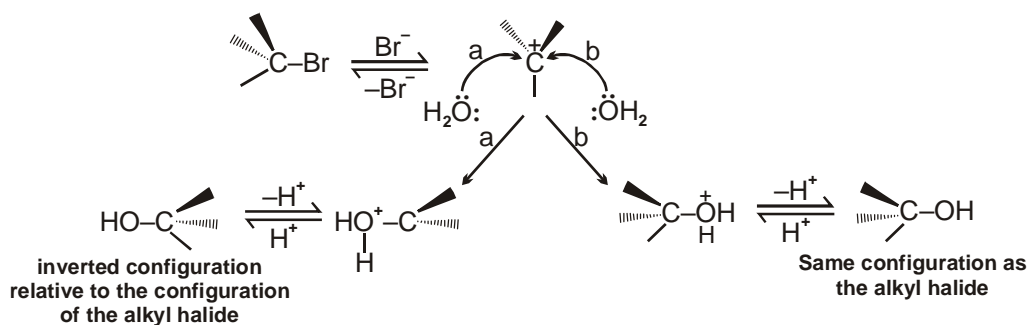
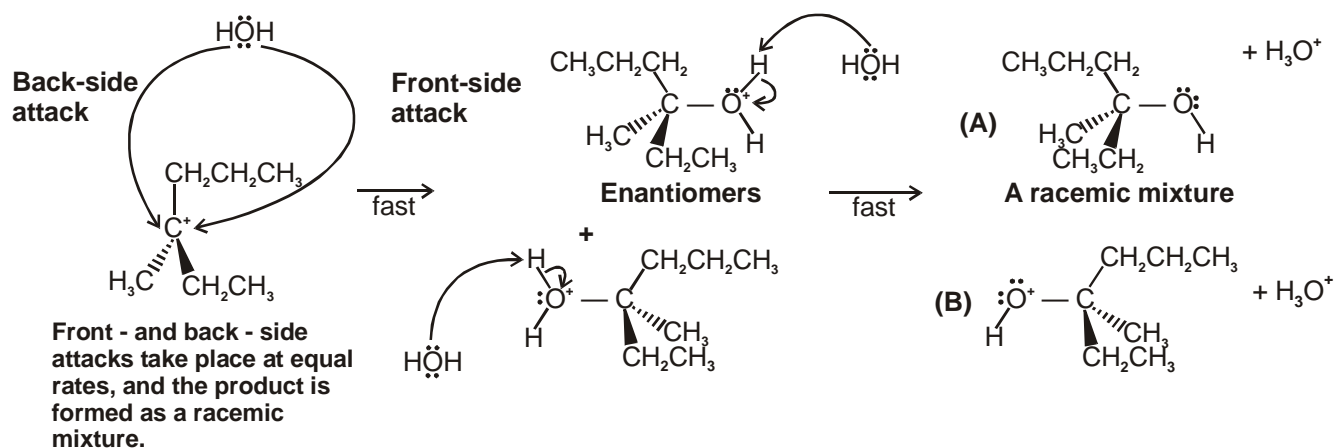


Reaction that involve Racemization :

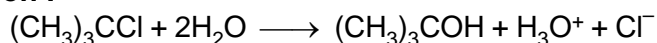


The stereochemistry of an S_N1 reaction :





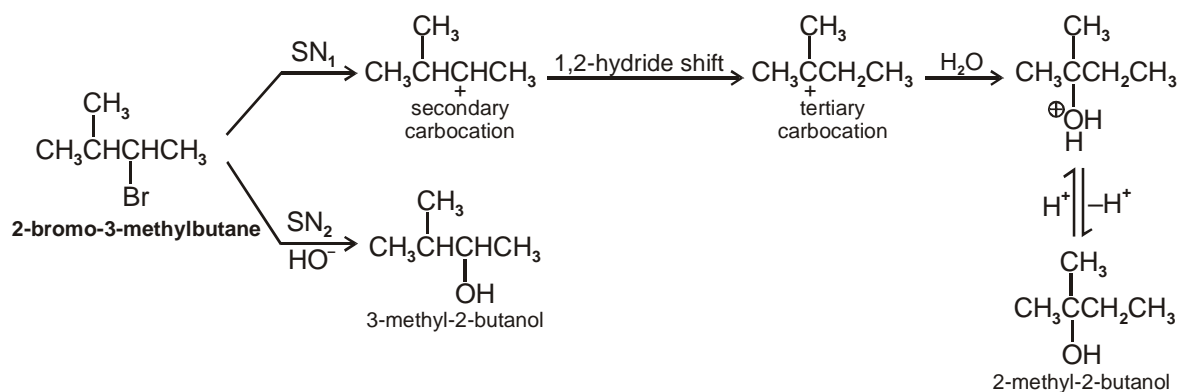
Reaction :

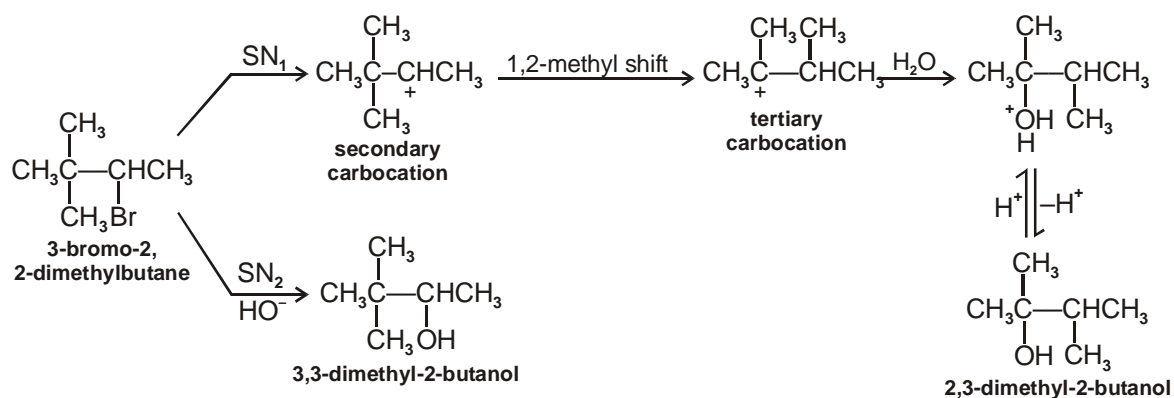


Reactive rates of $\text{S}_\text{N}1$ reactions for several alkyl bromides (Solvent is H_2O , nucleophile is H_2O).

Alkyl bromide	Class	Relative rate
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{C}-\text{Br} \\ \\ \text{CH}_3 \end{array}$	3°	1,200,000
$\begin{array}{c} \text{CH}_3\text{CH}-\text{Br} \\ \\ \text{CH}_3 \end{array}$	2°	11.6
$\text{CH}_3\text{CH}_2-\text{Br}$	1°	1

Carbocation Rearrangements



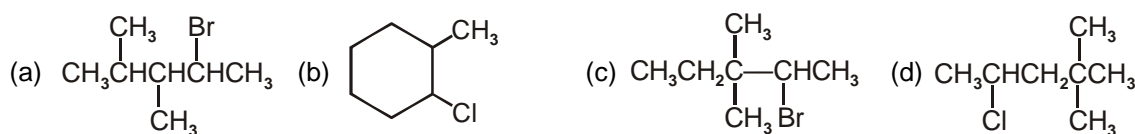


SOLVED EXAMPLES

Ex-16. Arrange the following alkyl halides in order of decreasing reactivity in an SN₁ reaction :
2-bromopentane, 2-chloropentane, 1-chloropentane, 3-bromo-3-methylpentane.

Sol. $d > a > b > c$

Ex-17. Which of the following alkyl halides form a substitution product from an SN₁ reaction that is different from the substitution product formed from an SN₂ reaction ?

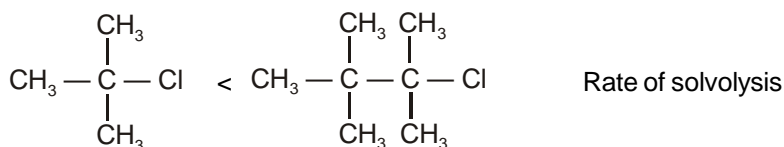


Sol. a, b, c

Ex-18. Account for the following observations

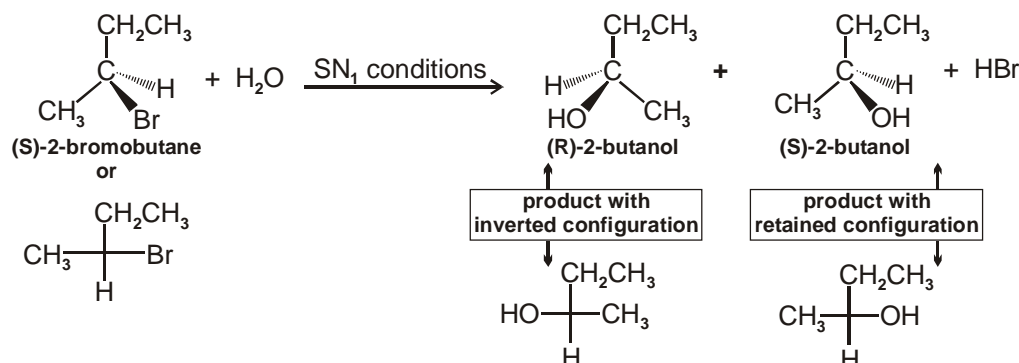
- (a) t-BuCl is solvolysed more slowly than 2-chloro-2,3,3-trimethyl butane
(b) t-BuCl is solvolysed more slowly in 90% D₂O – 10% dioxane
then in 90% H₂O – 10% dioxane solution

Sol. (a) Formation of $\text{Me}_3\text{C}-\text{C}^+(\text{Me})_2$ relieves some of the steric crowding. This is an example of **steric acceleration**.



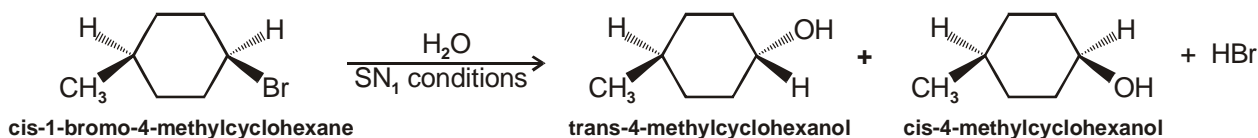
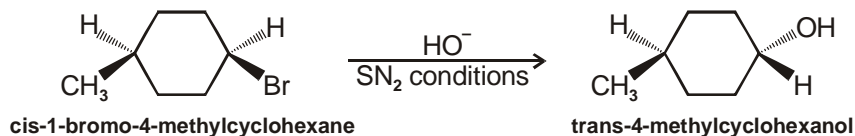
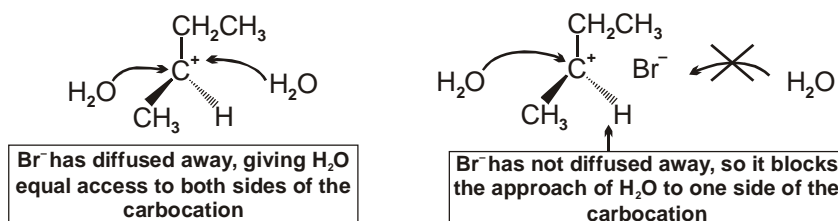
(b) D-bonds are not as stabilising as H-bonds.

The Stereochemistry of SN₁ reaction



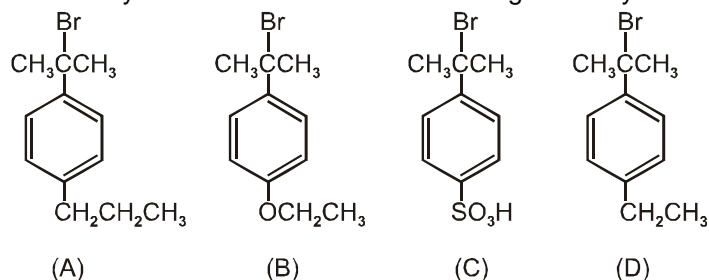
Typically, 50-70% of the product of an SN₁ reaction is the inverted product. If the reaction leads to equal amounts of the two stereoisomers, the reaction is said to take place with **complete racemization**. When more of the inverted product is formed, the reaction is said to take place with **partial racemization**.

Saul Winstein was the first to explain why extra inverted product generally is formed in an SN₁ reaction. He postulated that dissociation of the alkyl halide initially results in the formation of an **intimate ion pair**. In an intimate ion pair, the bond between the carbon and the leaving group has broken but the cation and anion remain next to each other. This species then forms an ion pair in which one or more solvent molecules have come between the cation and the anion. This is called a **solvent separated ion pair**. Further separation between the two results in dissociated ions.



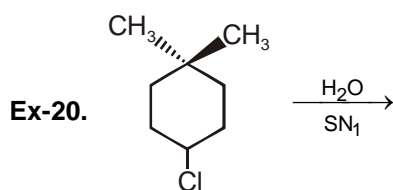
SOLVED EXAMPLES

Ex-19. The following tertiary alkyl bromides undergo an $\text{S}_{\text{N}}1$ reaction in aqueous acetone to form the corresponding tertiary alcohols. List the alkyl bromides in order of decreasing reactivity.



Ans. $\text{B} > \text{A} > \text{D} > \text{C}$

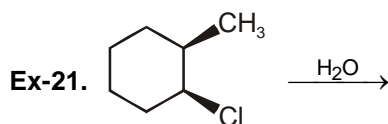
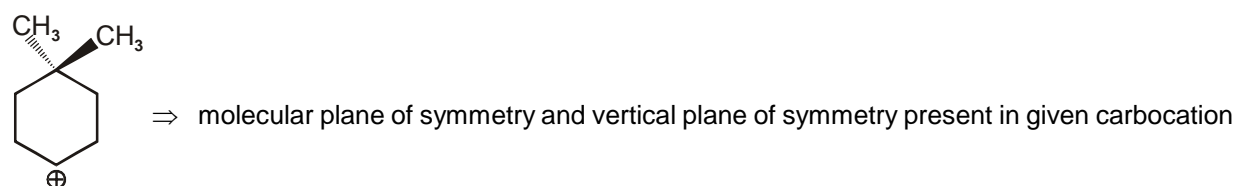
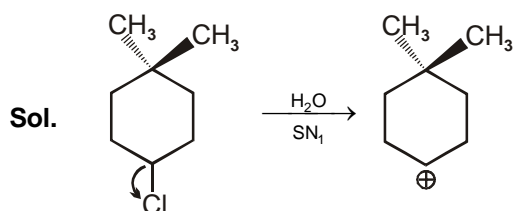
Sol. Rate of $\text{S}_{\text{N}}1$ mainly depend on stability of carbocation
More stable carbocation and more is the rate of $\text{S}_{\text{N}}1$



Total number of plane of symmetry present in carbocation formed (of given compound) in rate determining step will be ?

- (A) 1 (B) 2 (C) 3 (D) 4

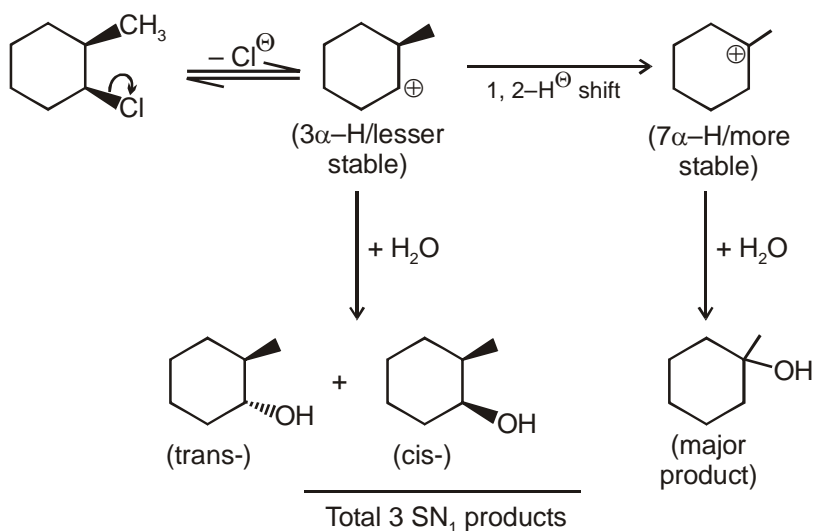
Ans. (B)



Total number of $\text{S}_{\text{N}}1$ products (including stereoisomer) possible for given compound is (x) ?
so the value of (x) is

Ans. 3 or 5

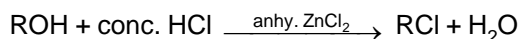
Sol. Step-1 :



Ex-22. Which of the following alcohol will give immediate turbidity of alkyl chloride at room temperature when reacts with Lucas reagent ?



Sol. (D)

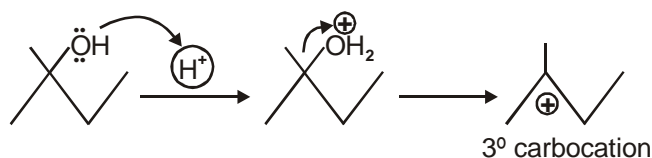


Intermediate carbocation is produced when alcohol reacts with Lucas reagent.

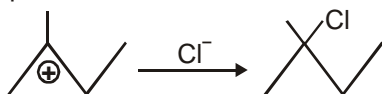
Stability of carbocation \propto Rate of reaction with Lucas reagent.

Mech.

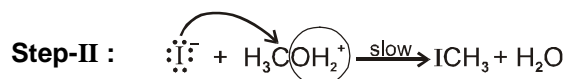
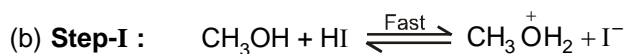
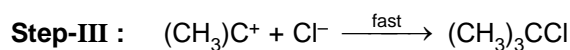
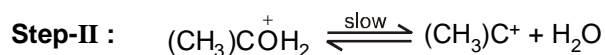
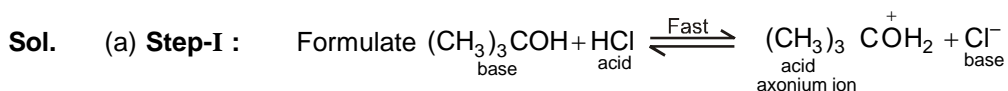
... I : Approach of H^+



Step-II : Approach of Cl^-



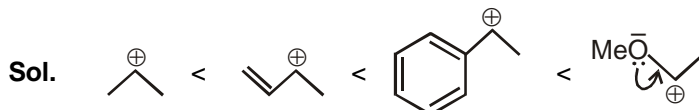
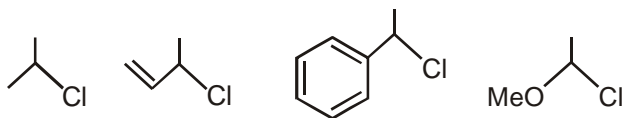
Ex-23. (a) Formulate $(CH_3)_3COH + HCl \rightarrow (CH_3)_3CCl + H_2O$ as an S_N1 reaction. (b) Formulate the reaction $CH_3OH + HI \rightarrow CH_3I + H_2O$ as an S_N2 reaction.



Ex-24. $\text{H}_2\text{C}=\text{CHCH}_2\text{Cl}$ is solvolyzed faster than $(\text{CH}_3)_2\text{CHCl}$. Explain.

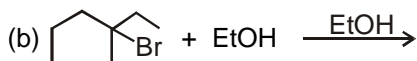
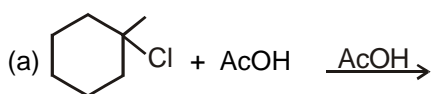
Sol. Solvolyses go by an $\text{S}_{\text{N}}1$ mechanism. Relative rates of different reactants in $\text{S}_{\text{N}}1$ reactions depend on the stabilities of intermediate carbocations. $\text{H}_2\text{C}=\text{CHCH}_2\text{Cl}$ is more reactive because $[\text{H}_2\text{C}^+=\text{CH}-\text{CH}_2]^+$ is more stable than $(\text{CH}_3)_2\text{CH}^+$.

Ex.25 Rate of $\text{S}_{\text{N}}1$:



Stability of C^+

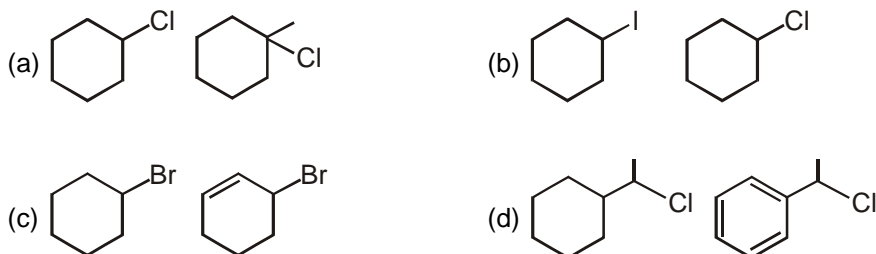
Ex.26 Give products



Sol. Above 2 are solvolytic substitution reactions.



Ex.27 Which of each pair of haloalkanes is more reactive in an $\text{S}_{\text{N}}1$ reaction.



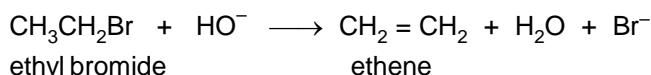
Sol. (a) ii (b) i (c) ii (d) ii

Comparison of the $\text{S}_{\text{N}}2$ and $\text{S}_{\text{N}}1$ reactions :

	$\text{S}_{\text{N}}2$ mechanism	$\text{S}_{\text{N}}1$ mechanism
[1] Mechanism	One step	Two steps
[2] Alkyl halide	Order of reactivity: $\text{CH}_3\text{X} > \text{RCH}_2\text{X} > \text{R}_2\text{CHX} > \text{R}_3\text{CX}$	Order of reactivity : $\text{R}_3\text{CX} > \text{R}_2\text{CHX} > \text{RCH}_2\text{X} > \text{CH}_3\text{X}$
[3] Rate equation	Rate = $k[\text{RX}][\text{Nu}^-]$ Second-order kinetics	Rate = $k[\text{RX}]$ First-order kinetics
[4] Stereochemistry	Backside attack of the nucleophile Inversion of configuration at a stereogenic center	Trigonal planar carbocation intermediate Racemization at a single stereogenic center
[5] Nucleophile	Favoured by stronger nucleophiles	Favoured by weaker nucleophiles
[6] Leaving group	Better leaving group \longrightarrow faster reaction	Better leaving group \longrightarrow faster reaction
[7] Solvent	Favoured by polar aprotic solvents	Favoured by polar protic solvents.

Summary of the reactivity of alkyl halides in nucleophilic substitution reactions :

methyl and 1° alkyl halides	→ SN ₂ only	vinyl and aryl halides	→ neither SN ₁ nor SN ₂
2° alkyl halides	→ SN ₁ and SN ₂	1° and 2° benzylic and 1° and 2° allylic halides	→ SN ₁ and SN ₂
3° alkyl halides	→ SN ₁ only	3° benzylic and 3° allylic halides	→ SN ₁ only

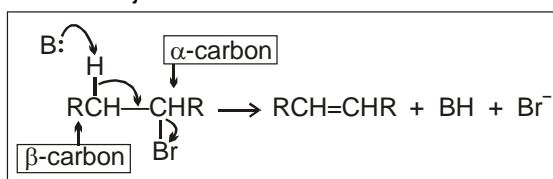
(b) ELIMINATION REACTION :**Eimination bimolecular (E₂ reaction) :**

$$\text{rate} = k[\text{alkyl halide}][\text{base}]$$

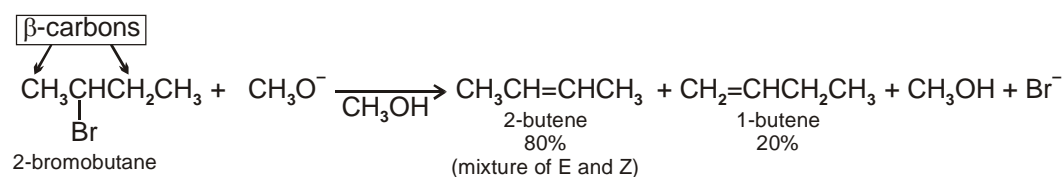
Mechanism of the E₂ reaction :

In an E₂ reaction of an alkyl halide, a base removes a proton from a carbon adjacent to the carbon bonded to the halogen. As the proton is removed, the electrons that the hydrogen shared with carbon move toward the carbon bonded to the halogen. As these electrons move toward the carbon, the halogen leaves, taking its bonding electrons with it. The electrons that were bonded to the hydrogen in the reactant have formed the π bond of the double bond in the product. Removal of a proton and a halide ion is called **dehydrohalogenation**.

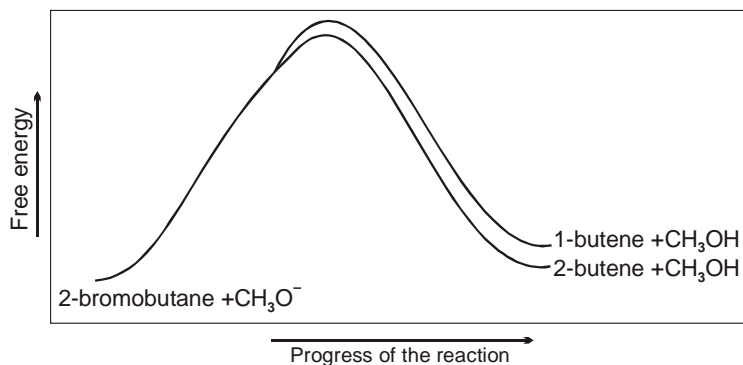
The carbon to which the halogen is attached is called the α -carbon. A carbon adjacent to an α -carbon is called a β -carbon. Because the elimination reaction is initiated by removing a proton from a β -carbon, an E₂ reaction is sometimes called a β -elimination reaction. It is also called a **1,2-elimination reaction** because the atoms being removed are on adjacent carbons.



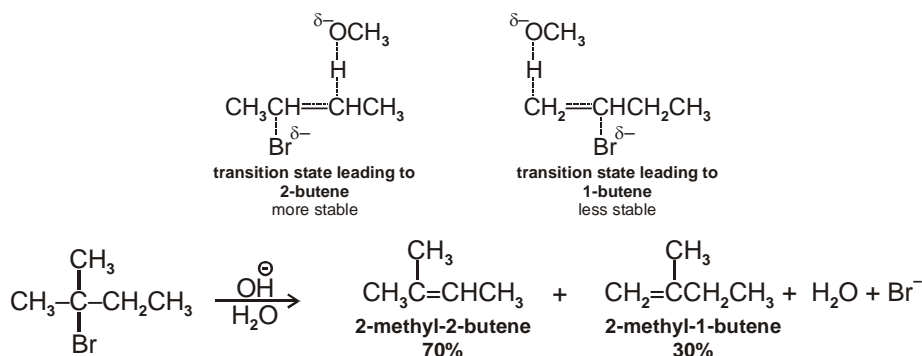
2-Bromobutane has two structurally different β -carbons from which a proton can be removed. So when 2-bromobutane reacts with a base, two elimination products are formed, 2-butene and 1-butene.



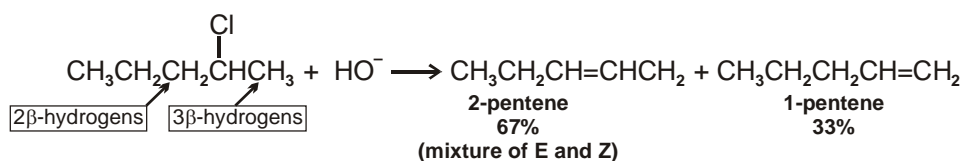
How do you know which of the two elimination products will be formed in greater yield? To answer this question, you must determine which of the alkenes is formed more easily - that is, which is formed faster. The reaction coordinate diagram for the reaction is shown in figure.



You know that alkene stability depends on the number of alkyl substituents bonded to the sp^2 carbons - the greater that number, the more stable the alkene. For example, 2-butene, with a total of two methyl substituents bonded to its sp^2 carbons, is more stable than 1-butene, with one ethyl substituent.

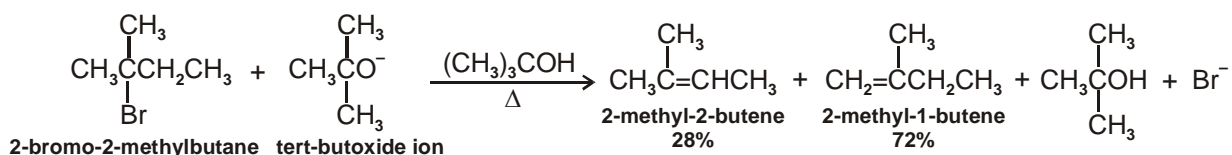
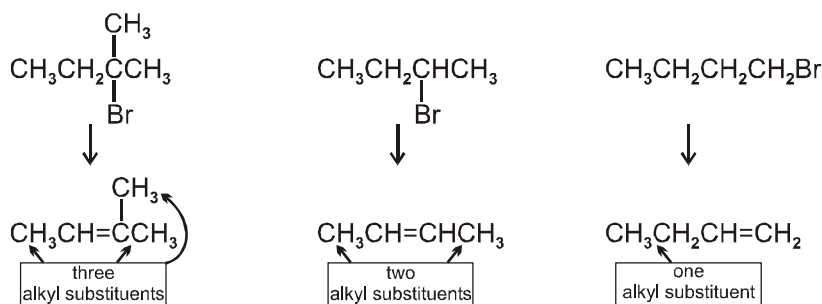


ZAITSEV'S/SAYTZEFF'S RULE :

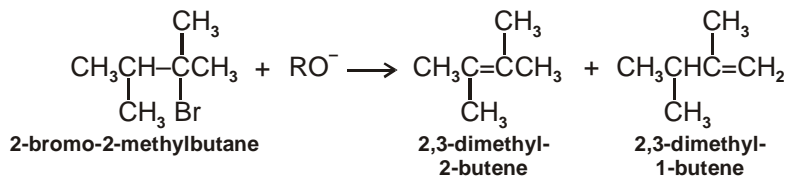


Relative reactivities of alkyl halides in an E_2 reaction

3° alkyl halide > 2° alkyl halide > 1° alkyl halide

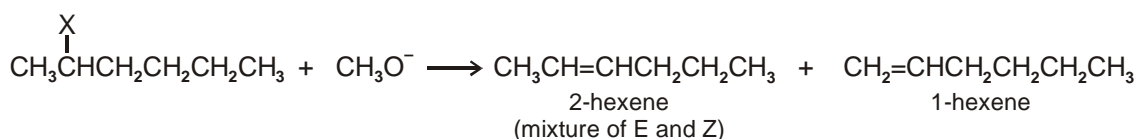


Effect of the steric properties of the base on the distribution of products in an E_2 reaction :

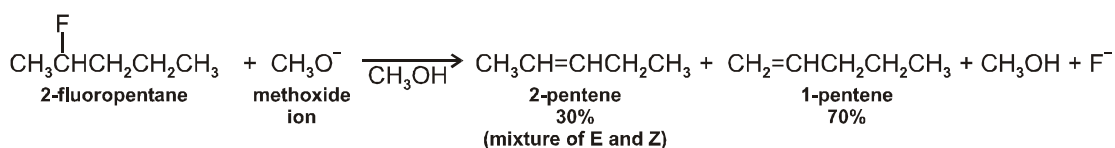


Base	More substituted product	Less substituted product
$\text{CH}_3\text{CH}_2\text{O}^-$	79%	21%
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CO}^- \\ \\ \text{CH}_3 \end{array}$	27%	73%

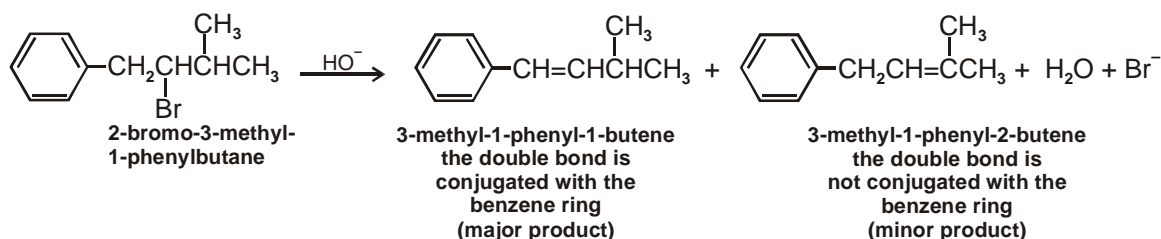
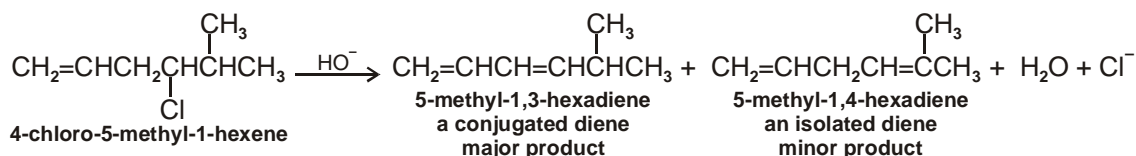
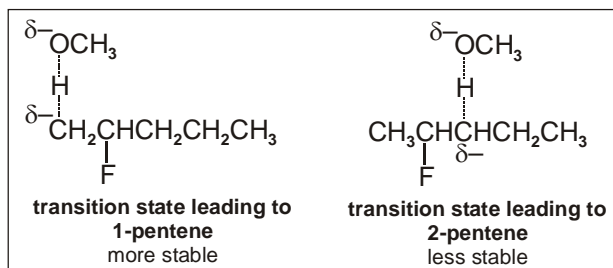
Although the major product of the E_2 dehydrohalogenation of alkyl chlorides, alkyl bromides, and alkyl iodides is normally the more substituted alkene, the major product of the E_2 dehydrohalogenation of alkyl fluorides is the less substituted alkene.

Table : Products obtained from the E₂ reaction of CH₃O[−] and 2-Halohekanes**More substituted product****Less substituted product**

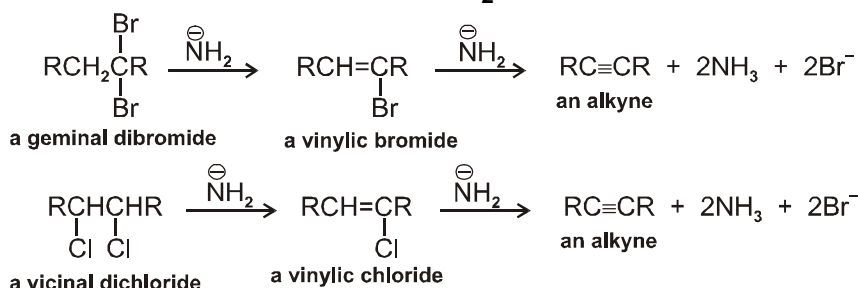
Leaving group	Conjugate acid	pKa		
X = I	HI	−10	81%	19%
X = Br	HBr	−9	72%	28%
X = Cl	HCl	−7	67%	33%
X = F	HF	3.2	30%	70%



So when a base begins to remove a proton from an alkyl fluoride, the fluoride ion has less tendency to leave than the other halide ions. As a result, negative charge develops on the carbon that is losing the proton, causing the transition state to resemble a carbanion rather than an alkene. To determine which of the carbanion-like transition states is more stable, we must determine which carbanion would be more stable.



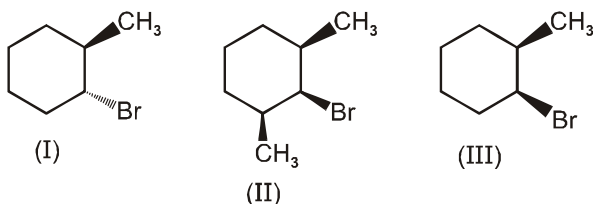
CONSECUTIVE E₂ ELIMINATION REACTIONS :



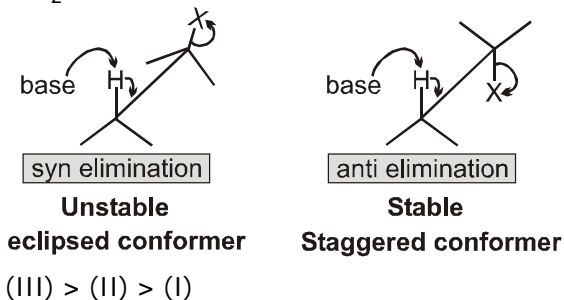
Note : In E₂ reaction NaNH₂(sodamide) prefer over than alc.KOH because NH₂[−] is stronger base than OH[−]

SOLVED EXAMPLES

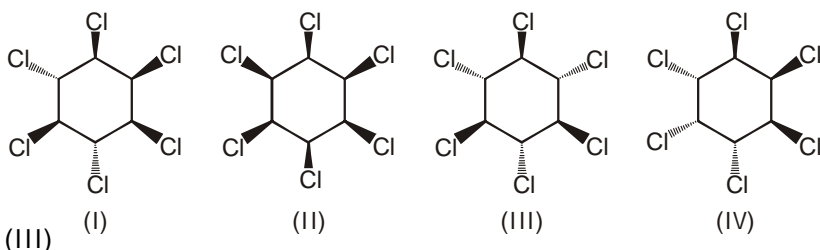
Ex-28. Rank the following compounds in order of decreasing rate in an E_2 reaction with alc. KOH.



Sol. In E_2 -reaction H and Br must be anti to each other (an staggered conformer)

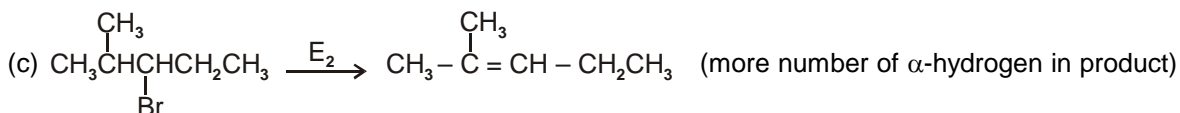
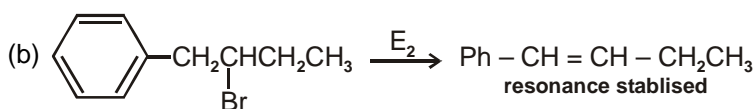
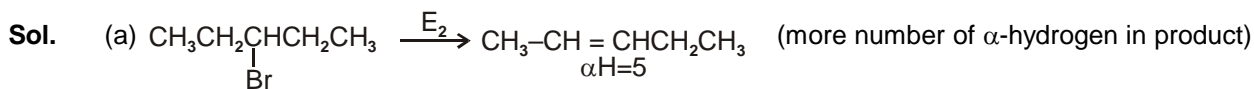
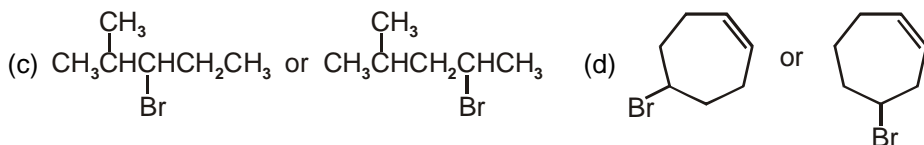
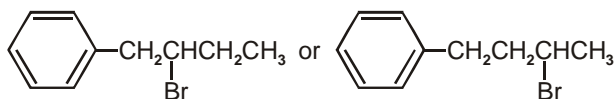
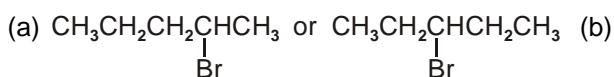


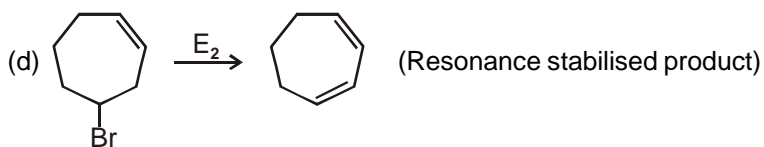
Ex-29. Which of the following hexachlorocyclohexanes is the least reactive in an E_2 reaction ?



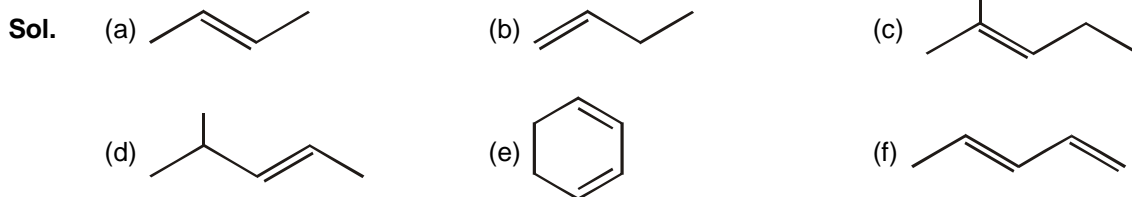
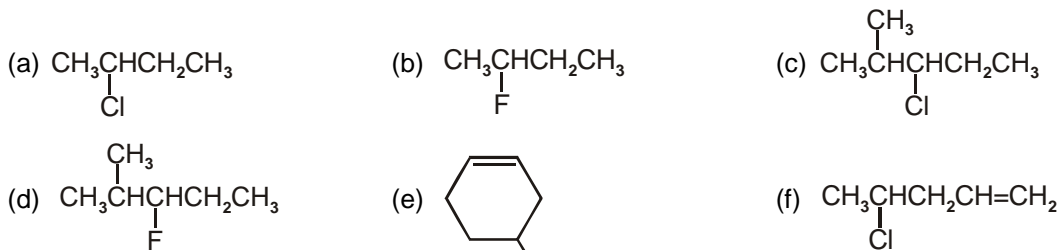
Sol.

Ex-30. Which alkyl halide would you expect to be more reactive in an E_2 reaction ?

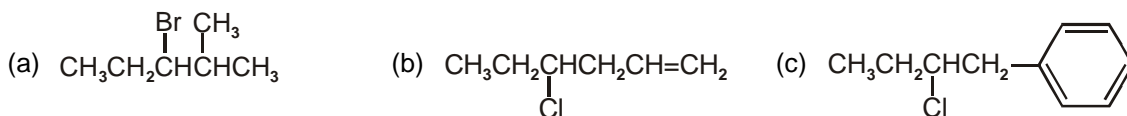




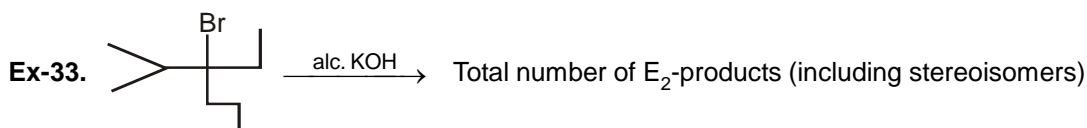
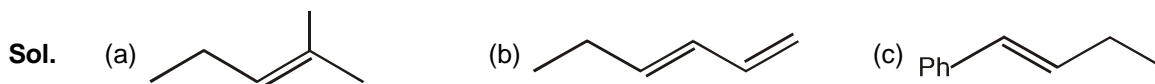
Ex-31. Give the major elimination product obtained from an E_2 reaction of each of the following alkyl halides with hydroxide ion :



Ex-32. (a) Determine the major product that would be obtained from an E_2 reaction of each of the following alkyl halides. In each case, indicate the configuration of the product :

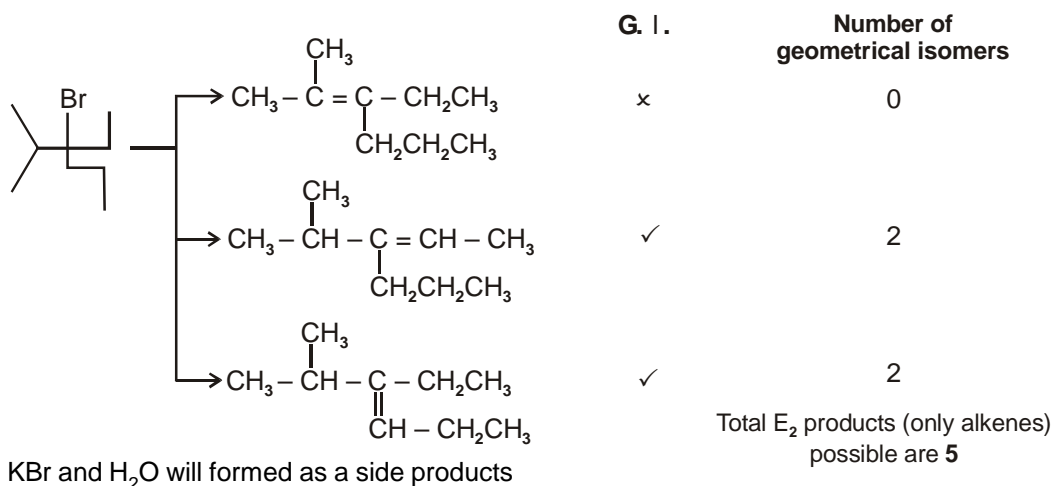


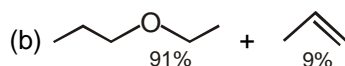
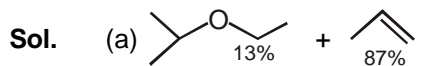
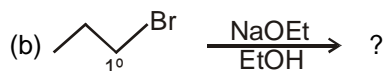
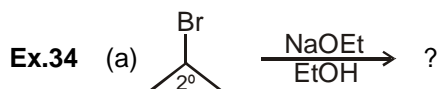
(b) Does the product obtained depend on whether you started with the R or S enantiomer of the reactant ?



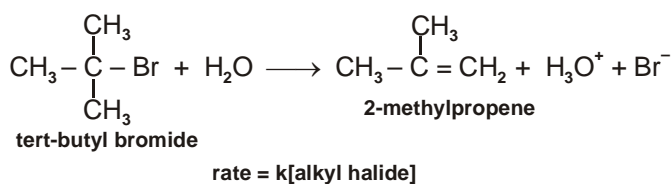
Ans. 5 or 7

Sol. Elimination of β -hydrogen takes place during E_2 reaction

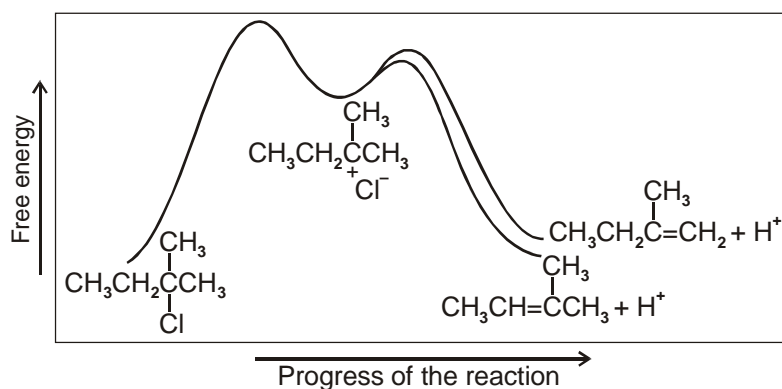
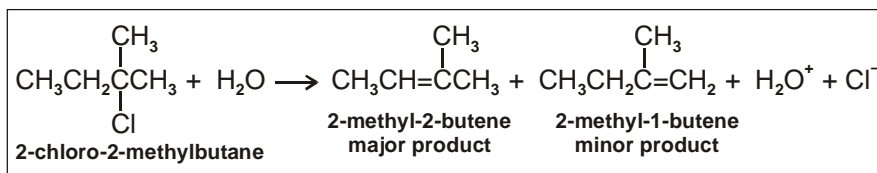
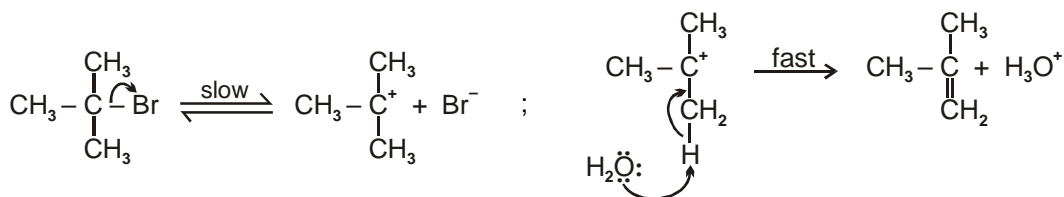




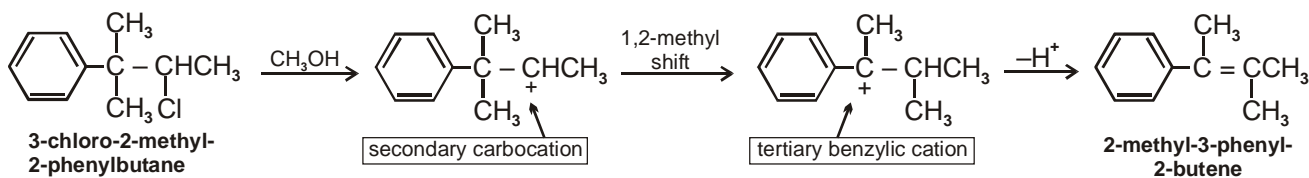
ELIMINATION UNIMOLECULAR (E₁ REACTION) :



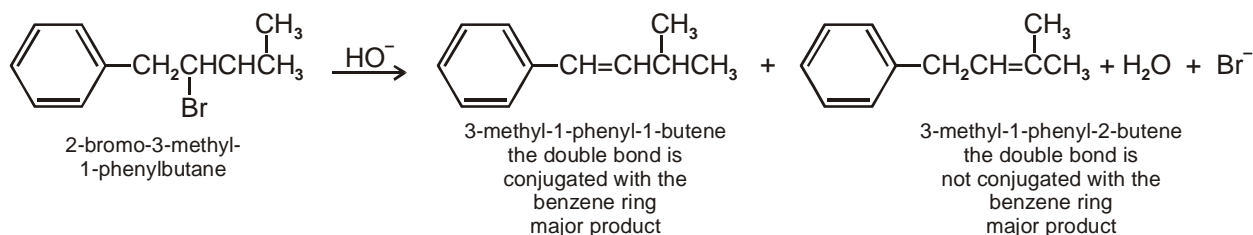
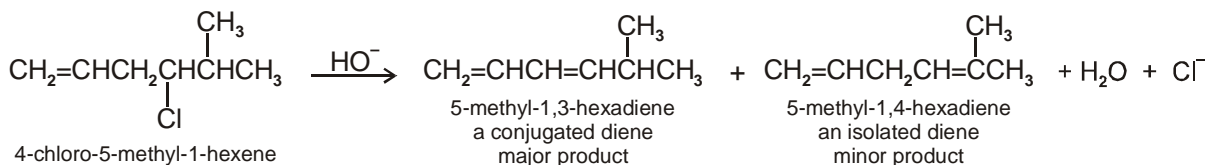
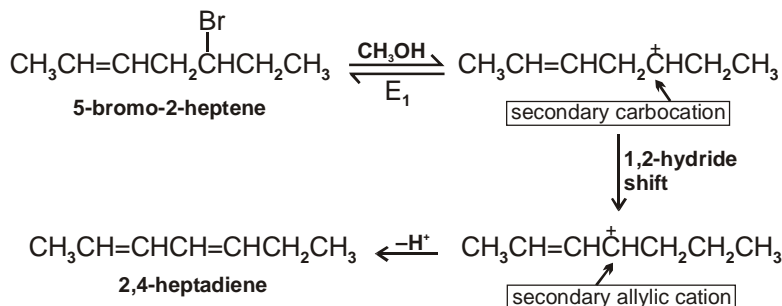
Mechanism of the E₁ reaction :



E₁ reaction involves the formation of a carbocation intermediate, rearrangement of the carbon skeleton can occur before the proton is lost. For example, the secondary carbocation that is formed when a chloride ion dissociated from 3-chloro-2-methyl-2-phenylbutane undergoes a 1,2-methyl shift to form a more stable tertiary benzylic cation.

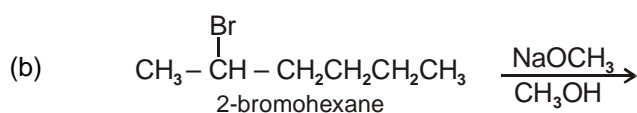
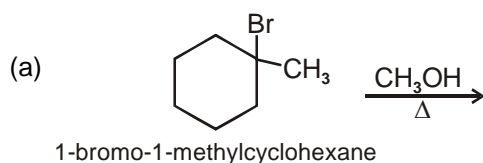


In the following example, the secondary carbocation undergoes a 1,2-hydride shift to form a more stable secondary allylic cation.

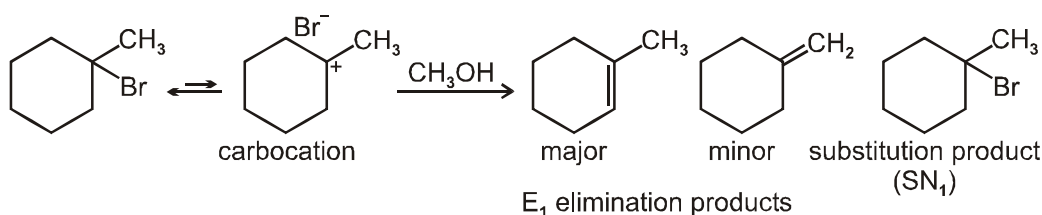


SOLVED EXAMPLES

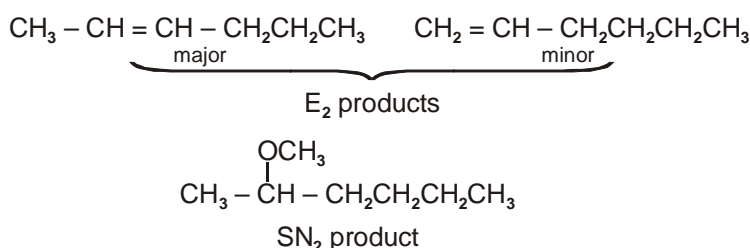
Ex-35. Predict the mechanisms and products of the following reactions.



Sol. (a) There is no strong base or nucleophile present, so this reaction must first occur, with an ionization of the alkyl halide as the slow step. Deprotonation of the carbocation gives either of two elimination products, and nucleophilic attack gives a substitution product.



(b) This reaction takes place with a strong base, so it is second order. This secondary halide can undergo both S_N2 substitution and E₂ elimination. Both products will be formed, with the relative proportions of substitution and elimination depending on the reaction conditions.



E1 and E2 Mechanisms Comparison :

	E2 mechanism	E1 mechanism
Mechanism	One step	Two steps
Alkyl halide	Rate: R ₃ CX > R ₂ CHX > RCH ₂ X	Rate : R ₃ CX > R ₂ CHX > RCH ₂ X
Rate equation	Rate = k[RX][B:]	Rate = k[RX]
	Second-order kinetics	First-order kinetics
Stereochemistry	Anti periplanar arrangement of H and X	Trigonal planar carbocation intermediate
Base	Favored by strong bases	Favoured by weak bases
Leaving group	Better leaving group → faster reaction	Better leaving group → faster reaction
Solvent	Favoured by polar aprotic solvents	Favoured by polar protic solvents
Product	More substituted alkene favored	More substituted alkene favored

Summary Chart on the Four Mechanisms : S_N1, S_N2, E1 or E2

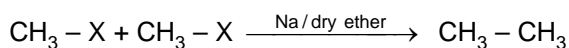
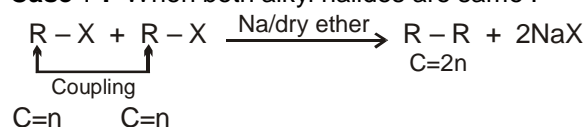
Alkyl halide type	Conditions	Mechanism
1° RCH ₂ X	strong nucleophile	→ S _N 2
	strong bulky base	→ E2
2° R ₂ CHX	strong base and nucleophile	→ S _N 2 + E2
	strong bulky base	→ E2
	weak base and nucleophile	→ S _N 1 + E1
3° R ₃ CX	weak base and nucleophile	→ S _N 1 + E1
	strong base	→ E2

REACTION WITH METAL

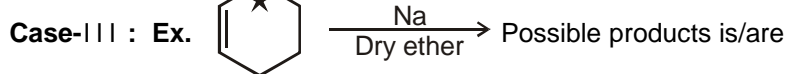
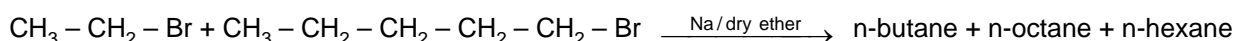
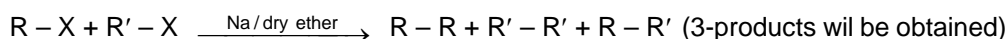
WURTZ REACTION :

This reaction involves the condensation of two molecules of alkyl halides in the presence of sodium and dry ether.

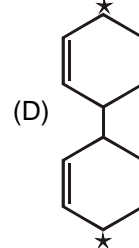
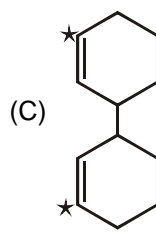
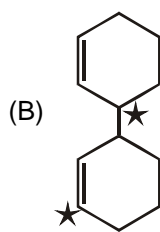
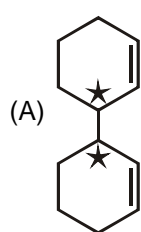
Case-I : When both alkyl halides are same :



Case-II : When both alkyl halides are different :

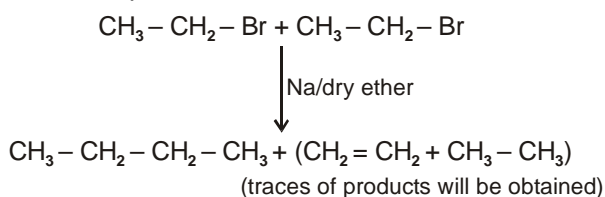


★ = C-14 Isotope



Ans. (A, B, C)

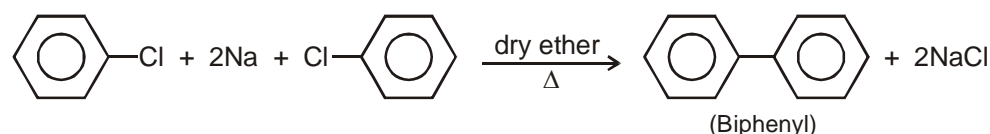
- Note :**
- Methane cannot be prepared by this method.
 - Tertiary alkyl halides do not give this reaction.
 - Best result is obtained when both alkyl halides are same, i.e., this method is suitable for preparation of alkanes having even number of carbons.
 - Disproportionation takes place which leads the formation of alkene and alkane as the by products.



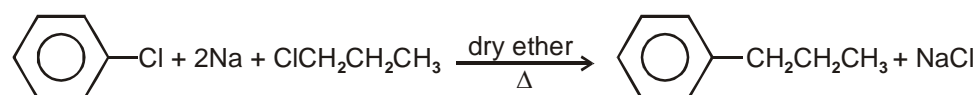
- (e) Reaction is used for ascending the series.

SOME REACTIONS OF HALOBENZENE :

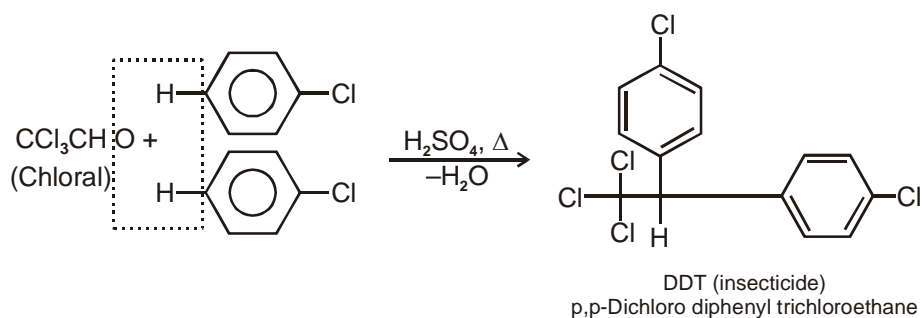
Fitting reaction :



Wurtz fitting reaction :



DDT formation :



GRIGNARD REAGENT

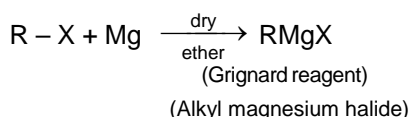
1. Introduction :

Most organic chlorides, bromides and iodides react with certain metals to give compounds having carbon-metal bonds. Such compounds are known as **organo-metallic compounds**.

An important class of organo-metallic compounds discovered by **Victor Grignard** in 1900 is alkyl magnesium halide, RMgX , referred as **Grignard Reagents**.

2. General Method of Preparation :

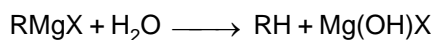
Grignard reagents are prepared in the laboratory by the action of alkyl halides on magnesium metal in the presence of dry ether.



The ease of formation of Grignard reagent is in the order $\text{RI} > \text{RBr} > \text{RCl}$.

Ether is used to dissolve the Grignard reagent by coordination.

Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons. Even water, alcohols, amines are sufficiently acidic to convert them to corresponding hydrocarbons.



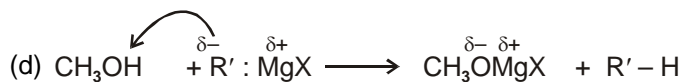
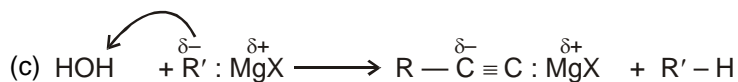
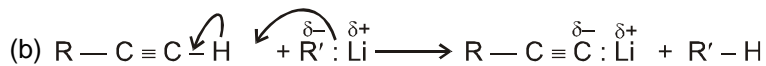
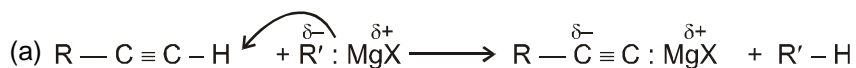
It is therefore necessary to avoid even traces of moisture from a Grignard reagent. On the other hand, this could be considered as one of the methods for converting halides to hydrocarbons.

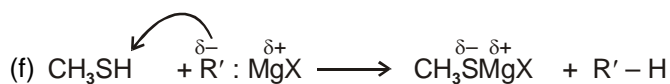
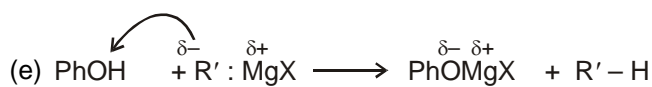
3. Chemical Reactions :

Grignard reagent basically gives 2-types of reactions

- (i) Reactions in which it behaves like as an **base**
- (ii) Reactions in which it behaves like as an **nucleophile**

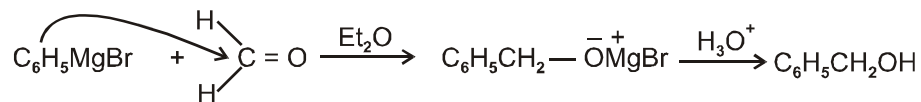
1. Reactions in which it behaves like as an base :



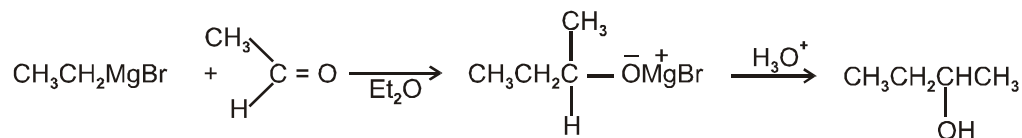


2. Reactions in which it behave like as an nucleophile :

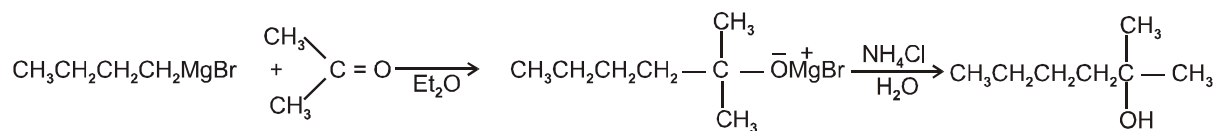
(a) Reaction with formaldehyde :



(b) Reaction with a Higher Aldehyde :



(c) Reaction with Ketone :

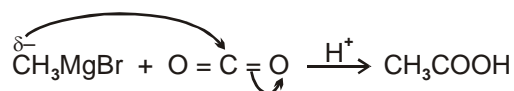


Mechanism of (a), (b), (c) reaction is nucleophilic addition.

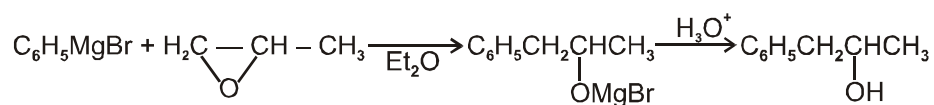
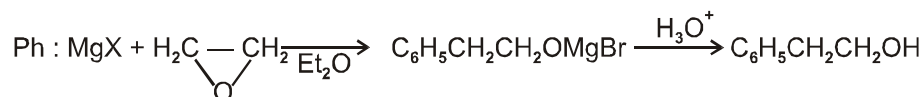
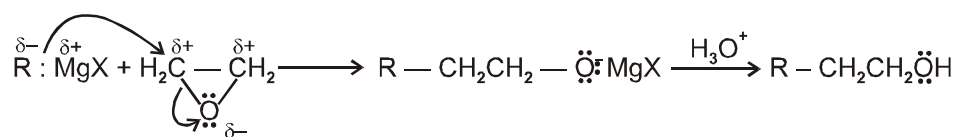
Order of rate of reaction is (a) > (b) > (c).

Aldehyde is more reactive than ketone towards **nucleophilic addition due to less steric hindrance**

..... 2 :

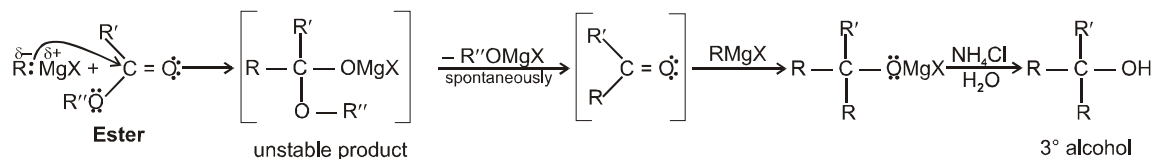


(e) Reaction with cyclic ether :

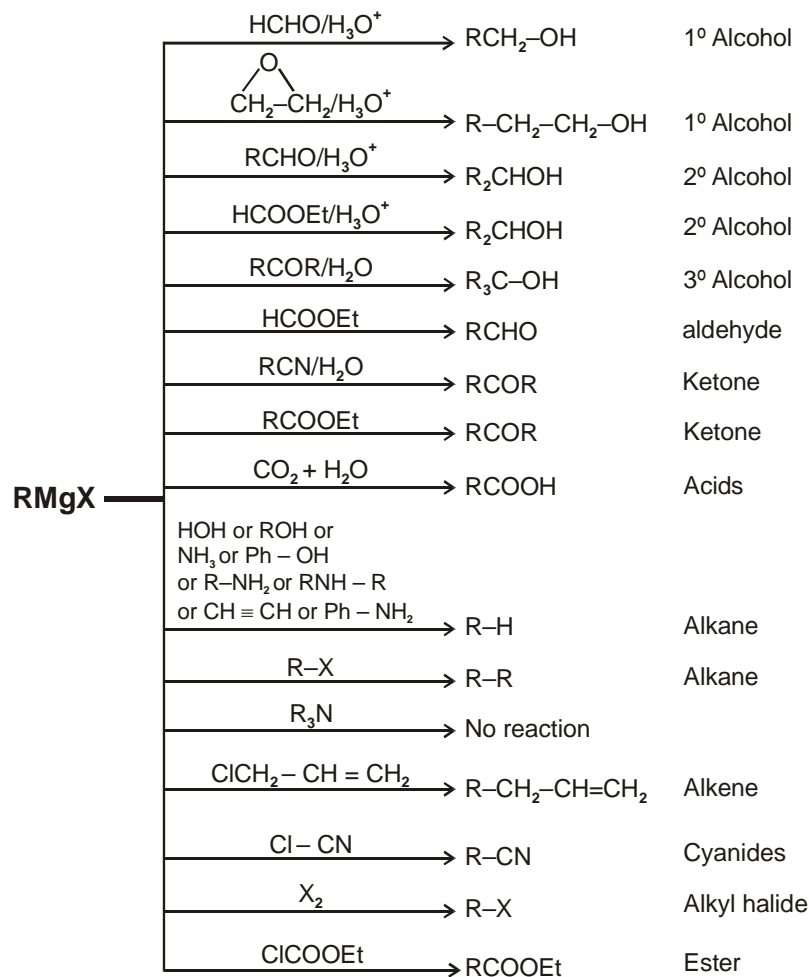


(f) Reaction with ester :

mechanism of this reaction is **SNAE**

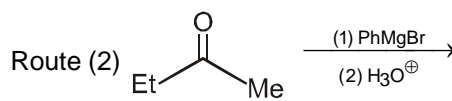
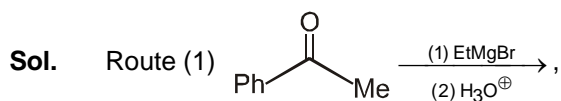
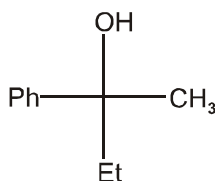


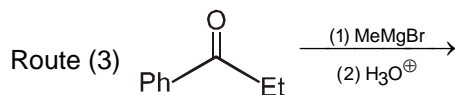
Road map of reactions of grignard reagent :



SOLVED EXAMPLES

Ex-36. Propose the 3 routes to synthesize given compound by the help of grignard reagent (RMgX)





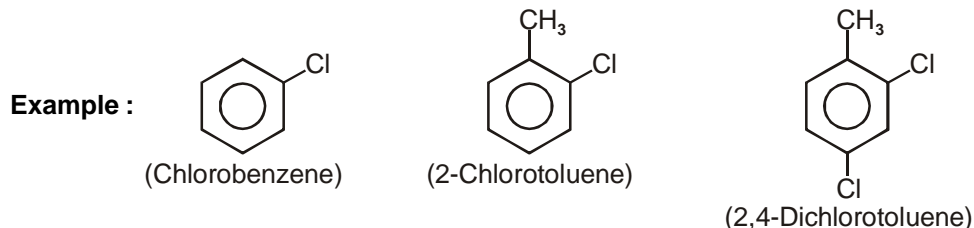
Ex-37. Reactivity towards grignard reagent ($R-CHO$, $R-COR$) ?

Sol. $R-\overset{\overset{O}{\parallel}}{C}-H > R-\overset{\overset{O}{\parallel}}{C}-R$ (Aldehyde is more reactive because of less steric hindrance and less + I effect.)

HALOARENES / ARYL HALIDE

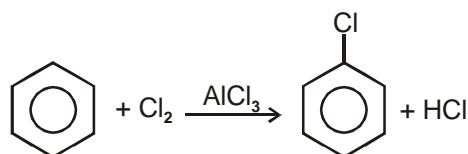
1. Introduction :

If halogen atom is directly attached to the benzene ring, then compound is called as Haloarene or arylhalide.

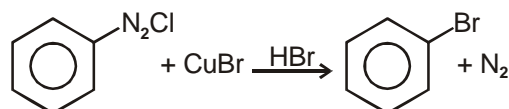
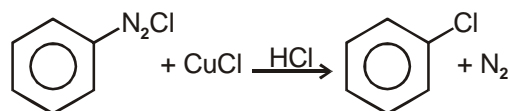


2. General Methods of Preparation :

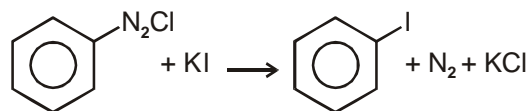
(a) Halogenation of Benzene :



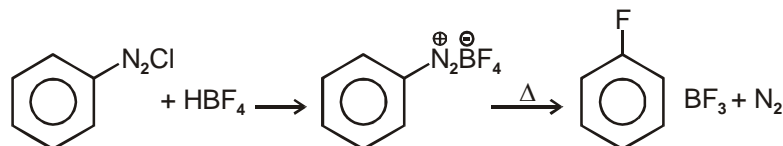
(b) Sandmeyer's reaction :



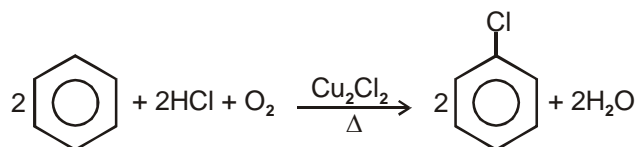
(c) Reaction with KI :



(d) Balz-schiemann's reaction :



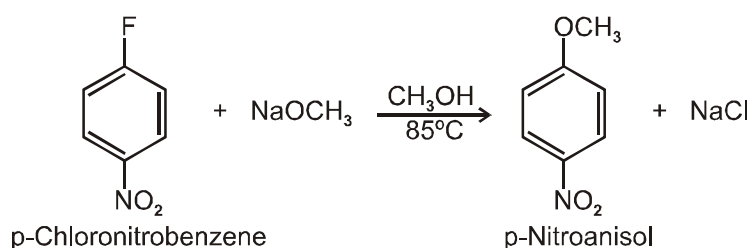
(e) Raschig Process :



3. Chemical Properties :

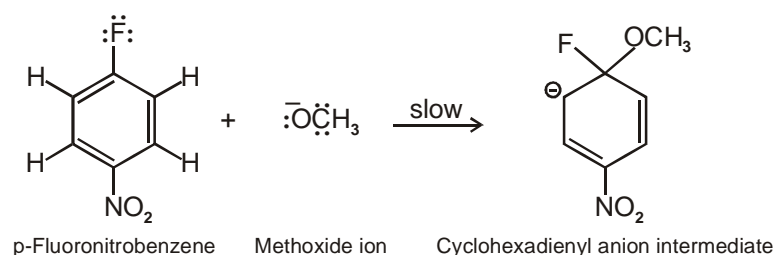
- (i) Aryl halides are **extremely less reactive** towards **nucleophilic substitution** reactions due to the following reasons
- | | |
|----------------------------------|---|
| (a) Resonance effect | (b) Difference in hybridisation of C – X bond |
| (c) Instability of phenyl cation | (d) Because of the possible repulsion |
- (ii) Aryl halide are very less reactive than alkyl halides in nucleophilic substitution reactions.
- (iii) The optimal transition state geometry required for $\text{S}_{\text{N}}2$ process cannot be achieved.
- (iv) Nucleophilic attack from the side opposite the carbon-halogen bond is blocked by the aromatic ring.

Nucleophilic Aromatic Substitution (addition Elimination Mechanism) S_NAr or S_{NAE} :

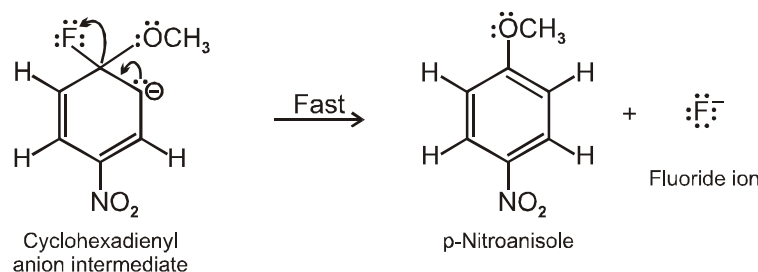


Mechanism :

Step-I : Addition stage : The nucleophile, in this case is methoxide ion, which adds to the carbon atom that bears the leaving group to give a cyclohexadienyl anion intermediate.



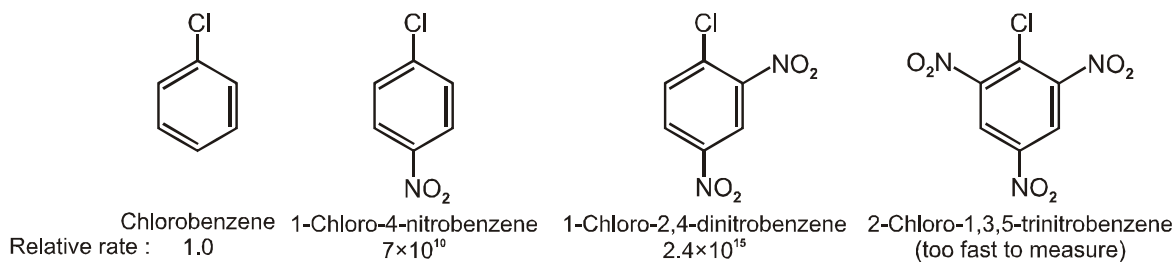
Step-II : Elimination stage : Loss of halide from the cyclohexadienyl intermediate restores the aromaticity of the ring and gives the product of nucleophilic aromatic substitution.



Salient features of Reactions :

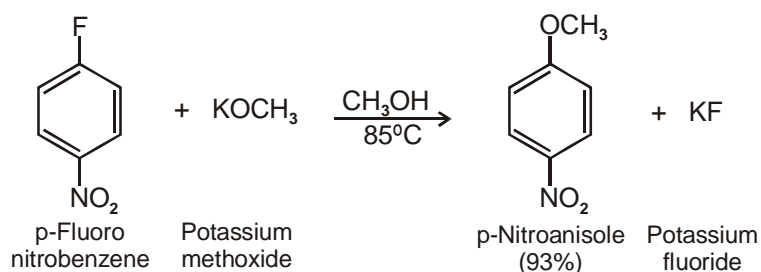
- (i) An ortho - nitro group exerts a comparable rate-enhancing effect, m-chloronitrobenzene while much more reactive than chlorobenzene itself, is thousand of times less reactive than either o-or p-chloronitrobenzene.

- (ii) The effect of o- & p-nitro substituents is cumulative, as the rate data for substitution with methoxide ion in a series of nitro-substituted chlorobenzene derivative demonstrate increasing rate of reaction as:

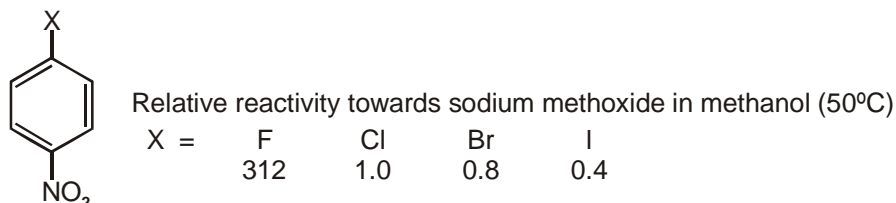


– M effect of Nitro group \propto rate of $\text{S}_{\text{N}}\text{Ar}$.

- (iii) In contrast to nucleophilic substitution in alkyl halides, where alkyl fluorides are exceedingly unreactive, aryl fluorides undergo nucleophilic substitution readily when the ring bears an ortho or a para-nitro group.



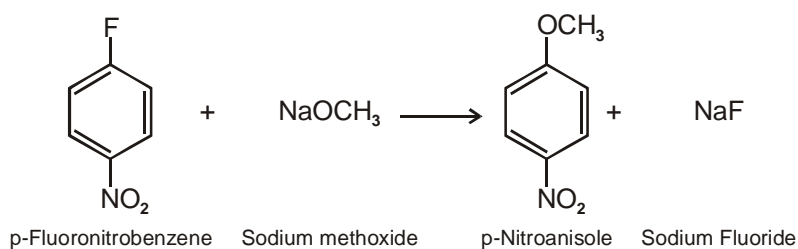
- (iv) Indeed, the order of leaving group reactivity in nucleophilic aromatic substitution is the opposite of that seen in aliphatic substitution.
- (v) Fluoride is the best reactive leaving group in nucleophilic aromatic substitution, iodide the least reactive.



- (vi) Kinetic studies of many of the reactions described in the section have demonstrated that they follow a second-order rate law.

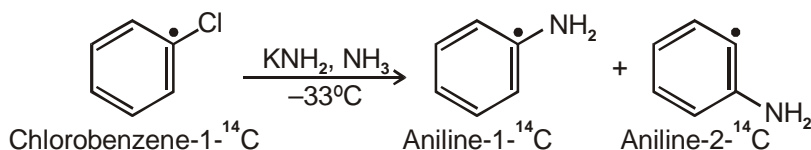
$$\text{Rate} = k[\text{aryl halide}][\text{nucleophile}]$$

- (vii) Second order kinetics is usually interpreted in terms of a bimolecular rate determining step.



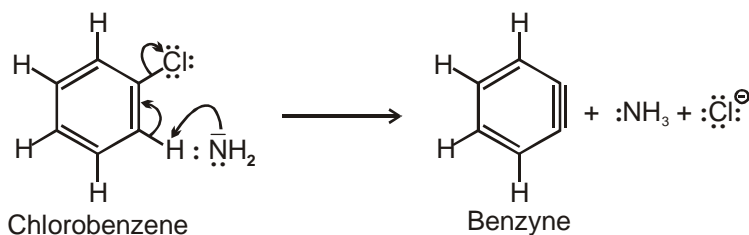
Elimination-Addition Mechanism of Nucleophilic Aromatic Substitution (Benzyne):

- (i) Very strong base such as sodium or potassium amide react with aryl halide, even those without electron withdrawing substituents to give products corresponding to nucleophilic substitution of halide by the base

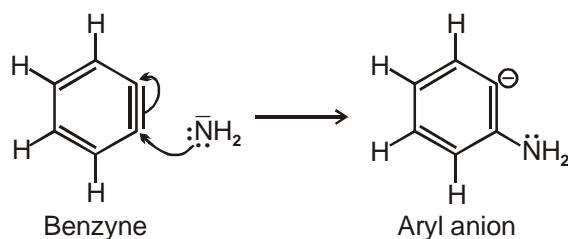


Mechanism :

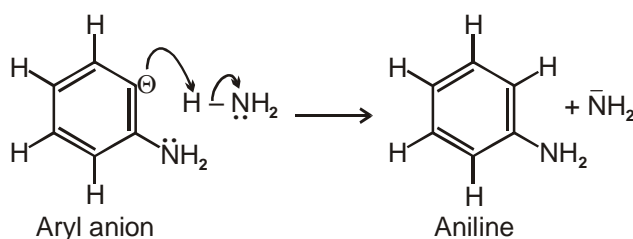
Step-I : Elimination stage ; Amide ion is a very strong base and brings about the dehydrohalogenation of chlorobenzene by abstracting a proton from the carbon adjacent to the one that bears the leaving group. The product of this step is an unstable intermediate called benzyne.



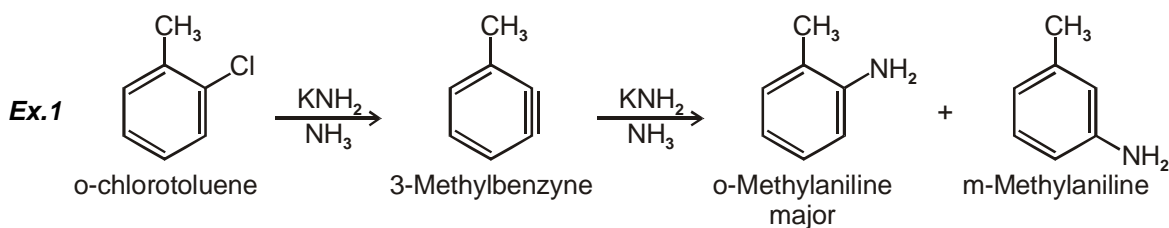
Step-II : Beginning of addition phase ; Amide ion acts as a nucleophile and adds to one of the carbons of the triple bond. The product of this step is a carbanion.



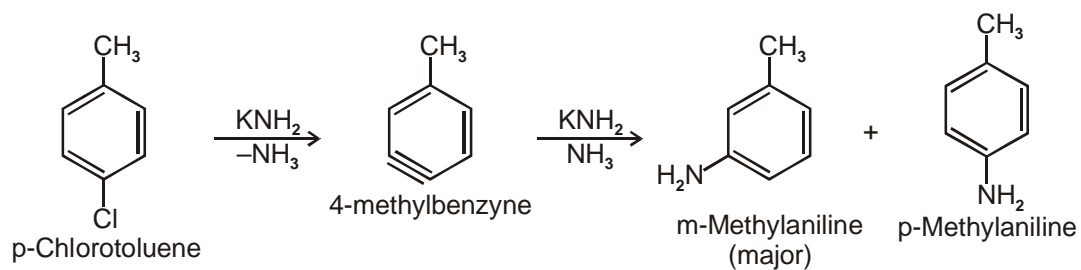
Step-III : Completion of addition phase ; The aryl anion abstracts a proton from the ammonia used as the solvent in the reaction.



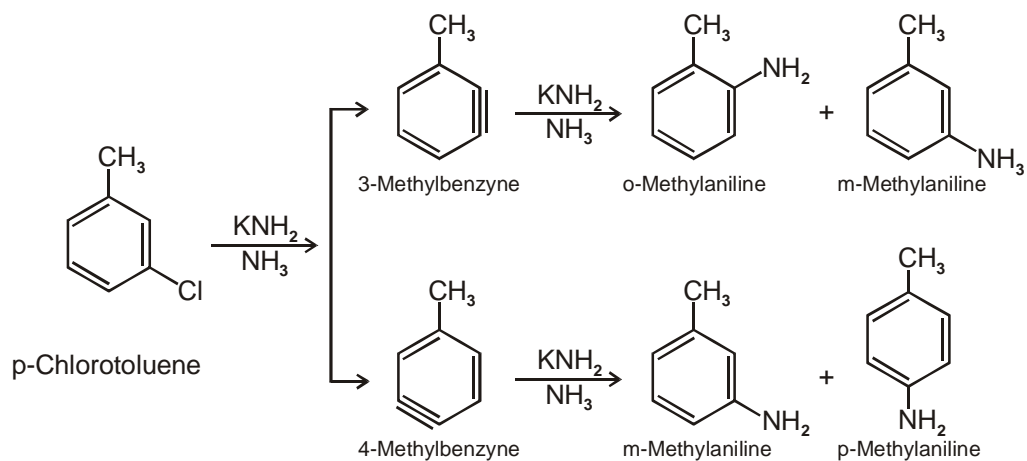
NOTE : The sp^2 orbital in the plane of the ring in benzyne are not properly aligned for good overlap thus π bonding is weaker than alkyne.



Ex.2



Ex.3

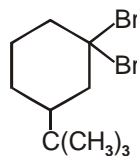


EXERCISE-I

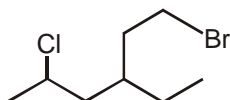
Single Choice Questions :

1. What is the IUPAC name of the following compound ?

- (A) 3-tert-butyl-1,1-dibromocyclohexane
(B) 1,1-dibromo-3-tert-butylcyclohexane
(C) 1,1-dibromo-3-isopropylcyclohexane
(D) 3,3-dibromo-1-tert-butylcyclohexane



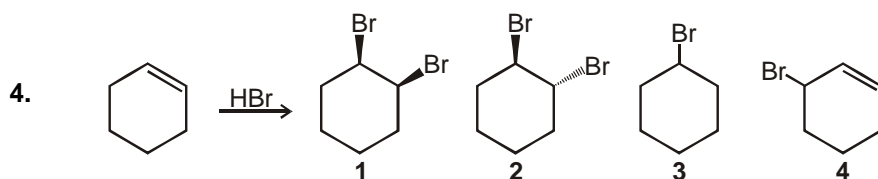
2. What is the IUPAC name of the following compound ?



- (A) 1-bromo-3-(2-chloropropyl)pentane
(B) 6-bromo-2-chloro-4-ethylhexane
(C) 2-chloro-4-ethyl-6-bromohexane
(D) 1-bromo-5-chloro-3-ethylhexane

3. Which of the following has the greatest dipole moment ?

- (A) Methyl chloride (B) Methyl bromide (C) Methyl iodide (D) Methyl fluoride

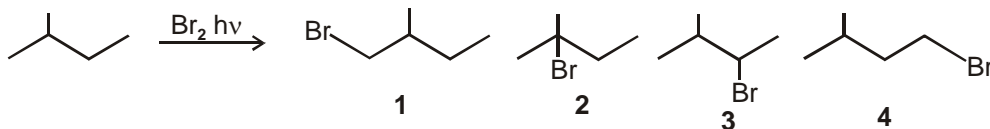


- (A) 2 (B) 1 (C) 4 (D) 3

5. Which of the following is a termination step in the radical chain chlorination of methane ?

1. $\cdot\ddot{\text{Cl}} - \ddot{\text{Cl}}\cdot \longrightarrow \cdot\ddot{\text{Cl}}\cdot + \cdot\ddot{\text{Cl}}\cdot$ 2. $\cdot\ddot{\text{Cl}}\cdot + \cdot\text{CH}_3 \longrightarrow \cdot\ddot{\text{Cl}} - \text{CH}_3$
3. $\cdot\ddot{\text{Cl}}\cdot + \text{CH}_3 - \text{H} \longrightarrow \cdot\ddot{\text{Cl}} - \text{H} + \cdot\text{CH}_3$ 4. $\text{H}_3\text{C}\cdot + \cdot\ddot{\text{Cl}} - \ddot{\text{Cl}}\cdot \longrightarrow \text{H}_3\text{C} - \ddot{\text{Cl}}\cdot + \ddot{\text{Cl}}\cdot$
(A) 2 (B) 1 (C) 3 (D) 4

6. What is the major organic product obtained from the following reaction ?

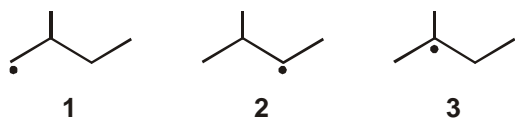


- (A) 1 (B) 4 (C) 3 (D) 2

7. Which of the following statements is not true regarding the halogenation of alkanes upon treatment with halogen and light ?

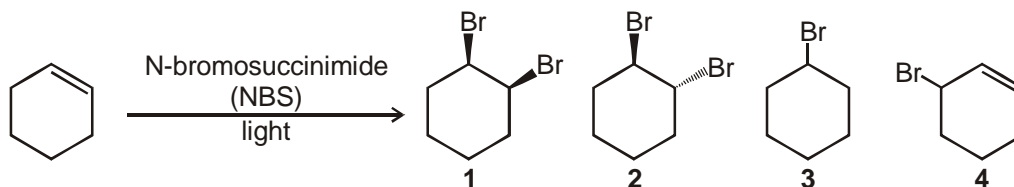
- (A) The reaction proceeds via a radical intermediate
(B) Bromination is more selective for 3° positions than chlorination.
(C) Bromine is more reactive than chlorine towards halogenation of alkane
(D) This is a useful process for the formation of fluorides, chlorides, bromides and iodides

8. What is the correct order of stability of the following radicals (more stable >; less stable) ?



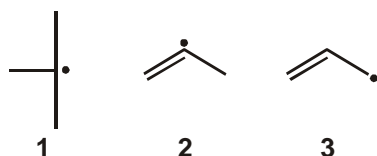
- (A) 3 >; 1 >; 2 (B) 3 >; 2 >; 1 (C) 1 >; 3 >; 2 (D) 1 >; 2 >; 3

9. What is the major organic product obtained from the following reaction ?



- (A) 2 (B) 3 (C) 4 (D) 1

10. What is the correct order of stability of the following radicals (more stable >; less stable) ?

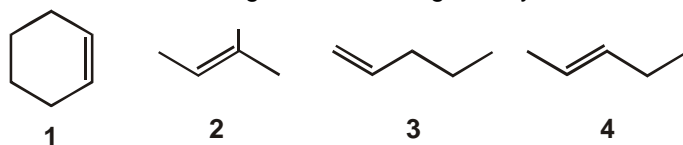


- (A) 2 >; 1 >; 3 (B) 2 >; 3 >; 1 (C) 3 >; 1 >; 2 (D) 1 >; 2 >; 3

11. What type of reactive intermediate is formed in the reaction of propene with N-bromosuccinimide (NBS) to give 3-bromo-1-propene ?

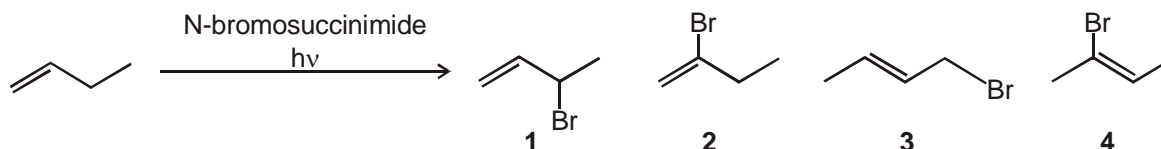
- (A) Allylic radical (B) Allylic carbanion (C) Cyclic bromonium ion (D) Allylic carbocation

12. Which of the following alkenes undergoes allylic bromination to form a single monobrominated product ?



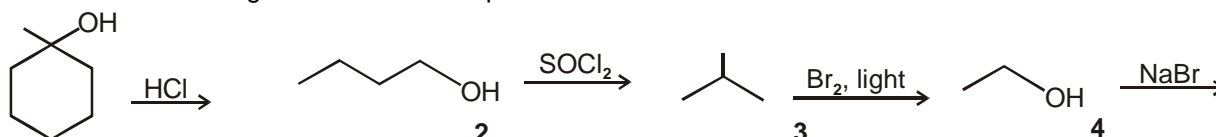
- (A) 2 (B) 3 (C) 1 (D) 4

13. What are the major organic products obtained from the following reaction ?



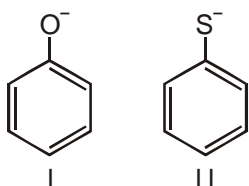
- (A) 2 and 4 (B) 3 and 4 (C) 1 and 2 (D) 1 and 3

14. Which of the following reactions does not proceed to form a haloalkane ?

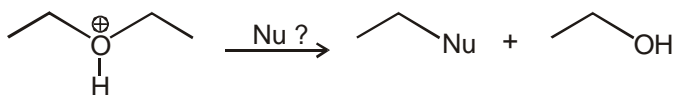


- (A) 2 (B) 4 (C) 3 (D) 1

15. Which of the following statements is not true regarding Grignard reagents ?
 (A) Phenylmagnesium chloride reacts with water to give benzene.
 (B) Grignard reagents can be prepared from fluoroalkanes, chloroalkanes, bromoalkanes and iodoalkanes.
 (C) Diethyl ether is a suitable solvent for the reaction between bromobenzene and magnesium to give phenylmagnesium bromide.
 (D) The carbon atom of methylmagnesium iodide is nucleophilic.
16. Consider the following two anionic molecules. Which of the following statements is TRUE ?

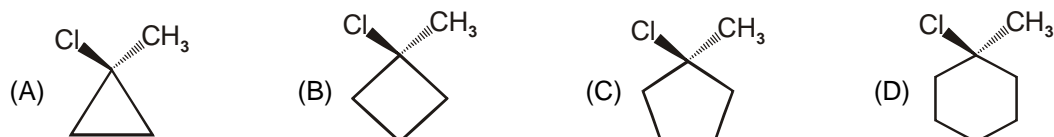
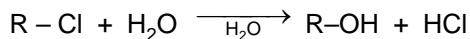


- (A) I is more basic and more nucleophilic than II.
 (B) I is less basic and less nucleophilic than II.
 (C) I is more basic but less nucleophilic than II.
 (D) I is less basic but more nucleophilic than II.
17. Consider ammonia (I) and water (II). Which of the following statements is TRUE ?
- H₃N : H₂O :
 I II
- (A) I is more basic and more nucleophilic than II.
 (B) I is less basic and less nucleophilic than II.
 (C) I is more basic but less nucleophilic than II.
 (D) I is less basic but more nucleophilic than II.
18. Which halide ion is the best nucleophile in dimethyl sulfoxide solution ?
 (A) Fluoride (B) Chloride (C) Bromide (D) Iodide
19. Which is the best leaving group in a substitution reaction of an alkyl halide ?
 (A) Cl⁻ (B) Br⁻ (C) I⁻ (D) F⁻
20. Which statement is TRUE with respect to an S_N2 reaction ?
 (A) A good leaving group is a strong base.
 (B) A good leaving group is a weak base.
 (C) A leaving group must be negatively charged.
 (D) A leaving group must be a halide.
21. Which of the following nucleophiles is going to promote an S_N2 reaction ?

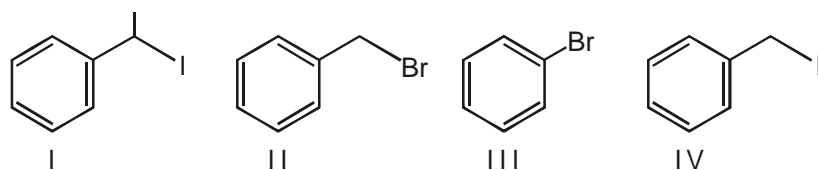


- (A) NaI (B) Water (C) NH₄Cl (D) MeONa
22. Which of the following is an S_N1 reaction ?
- (A) (B)
- (C) (D)

23. The reaction of 3-chloro-2,2-dimethylbutane and sodium iodide yields
 (A) 3-iodo-2,2-dimethylbutane. (B) 2-iodo-3,3-dimethylbutane.
 (C) 3-iodo-2,3-dimethylbutane. (D) 2-iodo-2,3-dimethylbutane.
24. Which substrate will react most readily in the following reaction ?



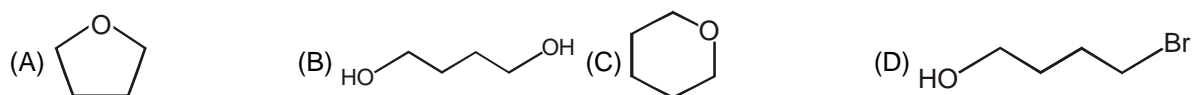
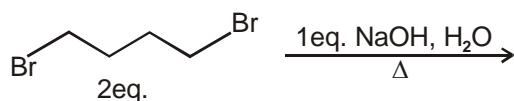
25. Rank the following in order of decreasing reactivity with methanol.



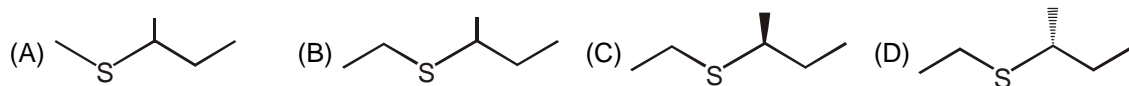
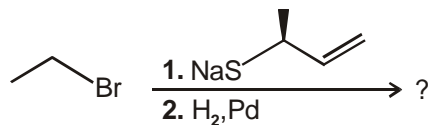
- (A) III > II > IV > I (B) IV > I > II > III (C) I > IV > II > III (D) I > IV > III > II

26. Which compound RX reacts most rapidly in an S_N2 reaction ?
 (A) 2-Bromohexane (B) 1-Bromo-3-methylhexane
 (C) 2-Bromo-2-methylhexane (D) 3-Bromohexane

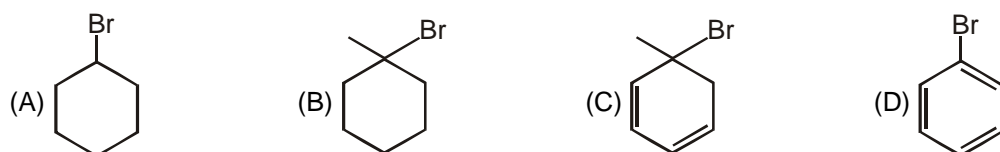
27. What is the major product of the following synthesis ?



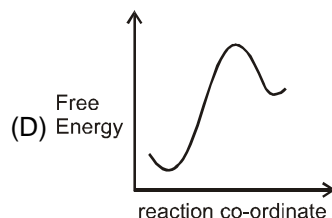
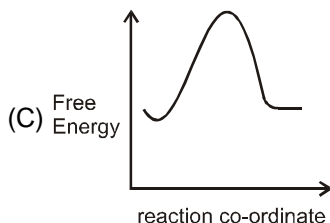
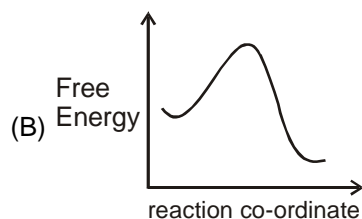
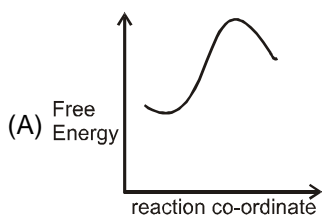
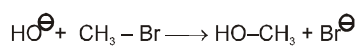
28. What is the major product of the following synthesis ?



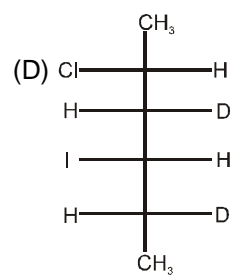
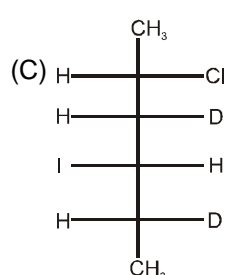
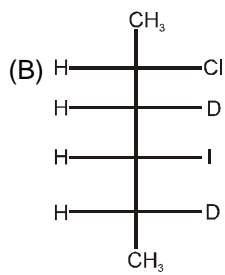
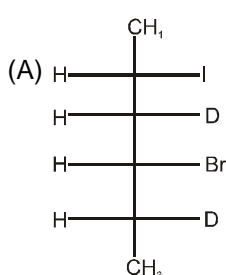
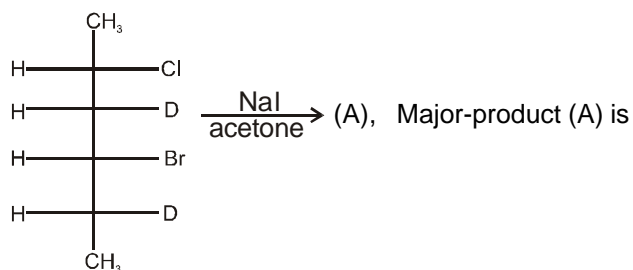
29. Which of the following can not be made in good yield from $\text{CH}_3\text{CH}_2\text{Cl}$ using an S_N2 reaction ?
 (A) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ (B) $\text{CH}_3\text{CH}_2\text{OC(CH}_3)_3$ (C) $\text{CH}_3\text{CH}_2\text{OH}$ (D) $\text{CH}_3\text{CH}_2\text{SH}$
30. What is the MOST reactive alkyl halide for the following reaction ?
 $\text{RX} + \text{H}_2\text{O} \longrightarrow \text{R-OH} + \text{X}^-$



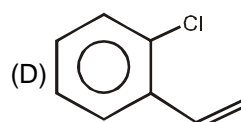
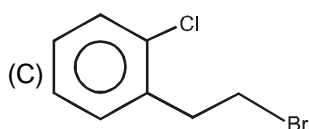
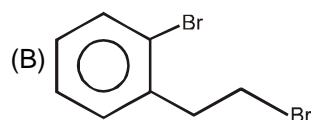
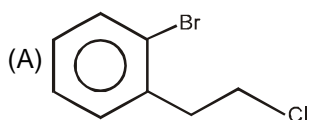
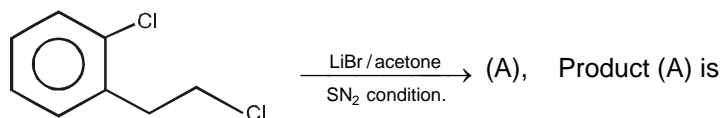
31. Free energy profile for given reaction is



32.

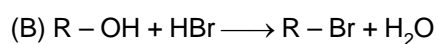
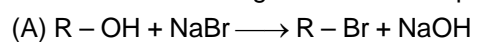


33.



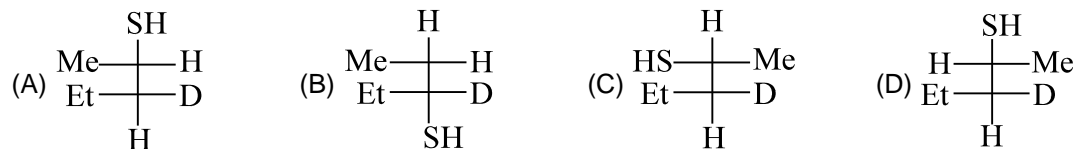
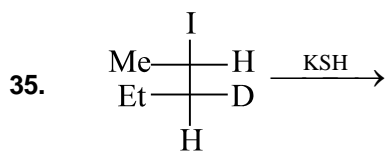
34.

Which of the following reactions is not possible?

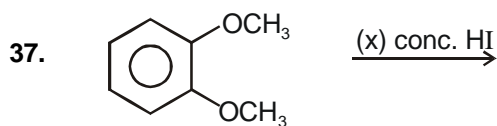
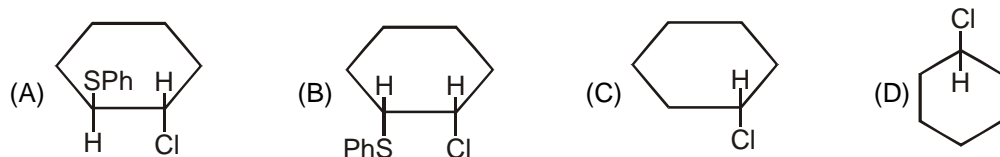


(C) both reactions are possible

(D) both reactions are not possible

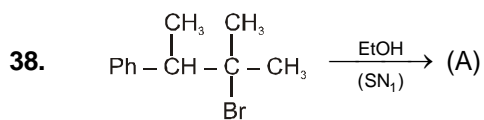


36. Which of following compounds will show NGP ?

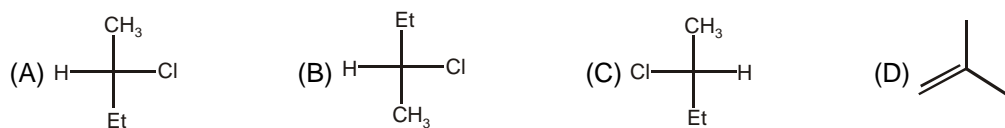
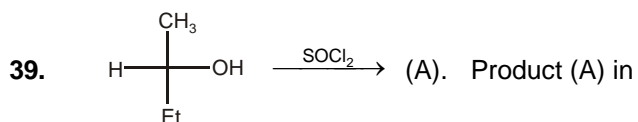
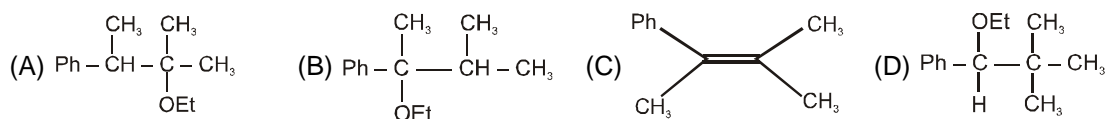


Value of x in above reaction is

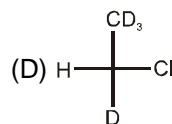
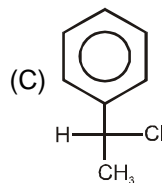
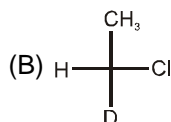
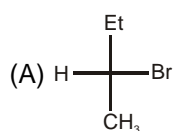
- (A) 2 (B) 3 (C) 4 (D) 5



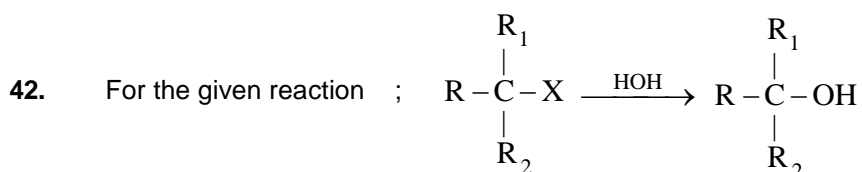
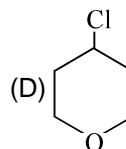
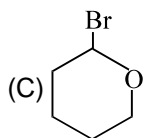
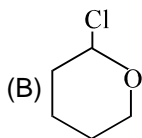
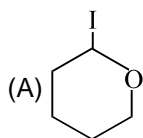
Major- product (A) is



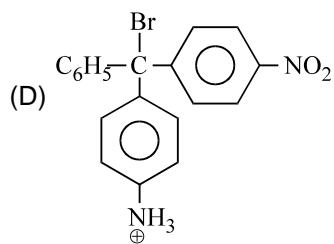
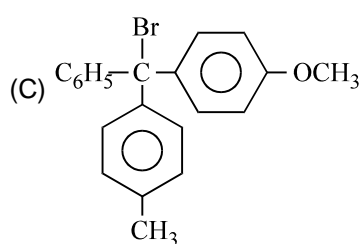
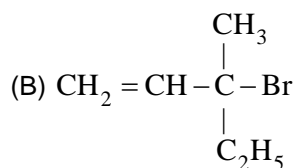
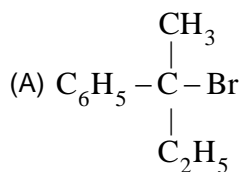
40. Under identical conditions, solvolysis of which of the following substrates would lead to maximum racemization?



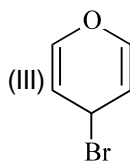
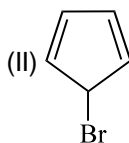
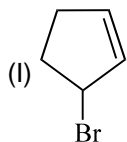
41. Which one of the following compounds will be most reactive for S_N1 & S_N2 reactions:



Which substrate will give maximum racemisation ?



43. Among the bromides I–III given below, the order of reactivity is S_N1 reaction is:

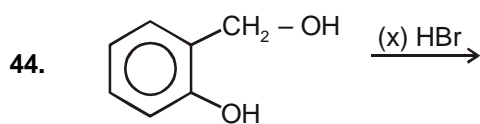


(A) III > I > II

(B) III > II > I

(C) II > III > I

(D) II > I > III



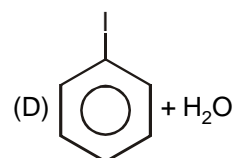
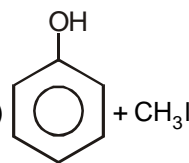
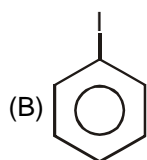
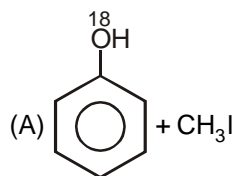
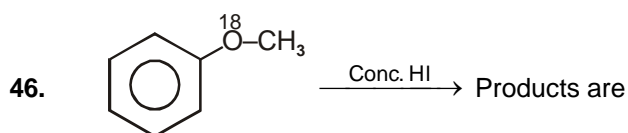
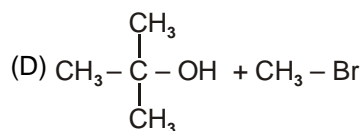
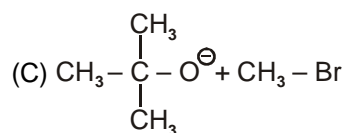
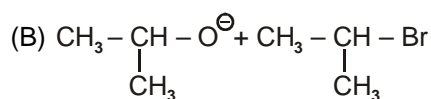
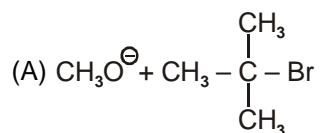
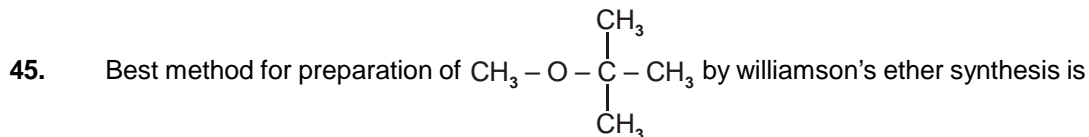
Value of (x) is

(A) 1

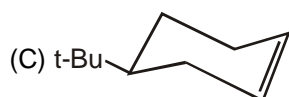
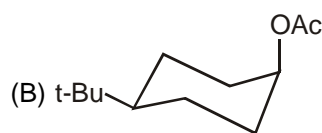
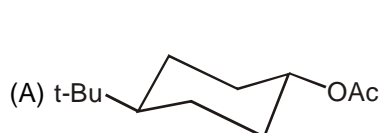
(B) 2

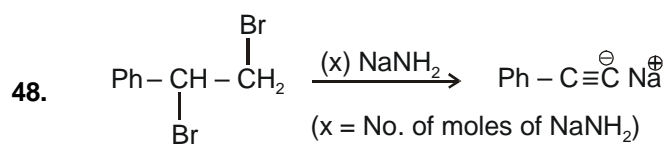
(C) 3

(D) 4



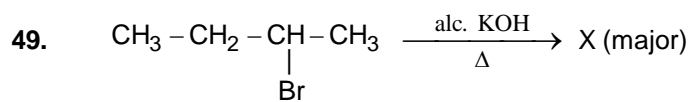
Major-product (A) is



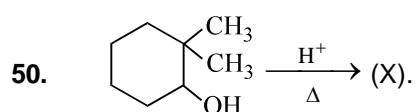


Value of x is

- (A) 1 (B) 2 (C) 3 (D) 4

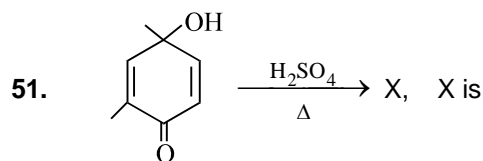


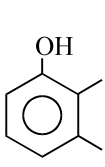
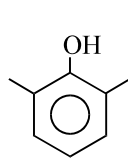
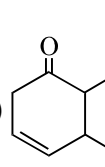
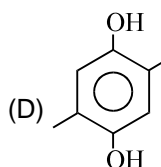
- (A)  (B)  (C)  (D) None of these

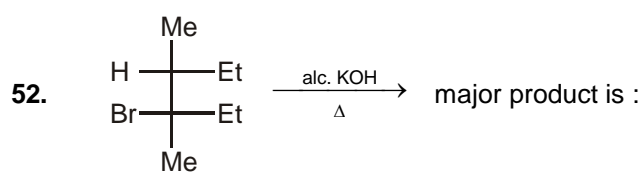


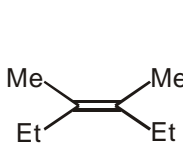
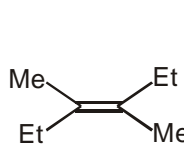
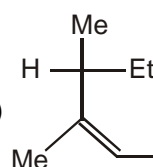
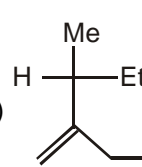
Major product (X) is

- (A)  (B)  (C)  (D) 

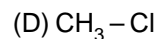
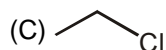
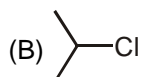
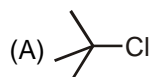


- (A)  (B)  (C)  (D) 



- (A)  (B)  (C)  (D) 

Comprehension (Q.53 to Q.56)

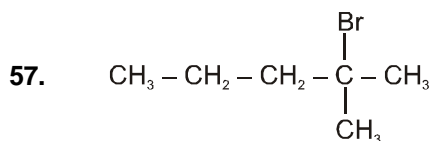


53. Most reactive towards $\text{S}_\text{N}1$ reaction

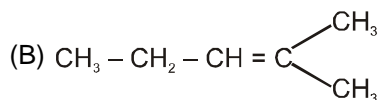
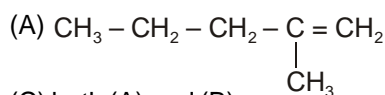
54. Most reactive towards $\text{S}_\text{N}2$ reaction ?

55. Most reactive towards E_2 reaction ?

56. Most reactive towards E_1 reaction ?

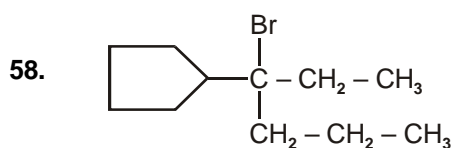


Identify all possible product obtained by E_2 reaction ?



(C) both (A) and (B)

(D) none of these



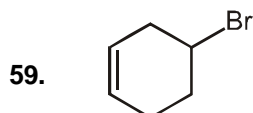
Total number of products obtained when this substrate is subjected to E_2 reaction will be (including stereoisomer).

(A) 3

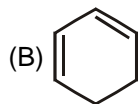
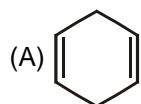
(B) 4

(C) 5

(D) 6

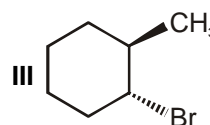
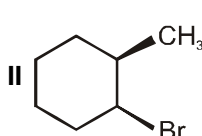
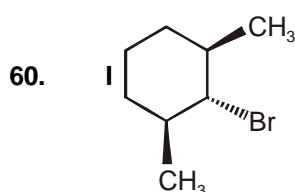


The major products obtained when this substrate is subjected to E_2 reaction will be



(C) both (A) and (B)

(D) none of these



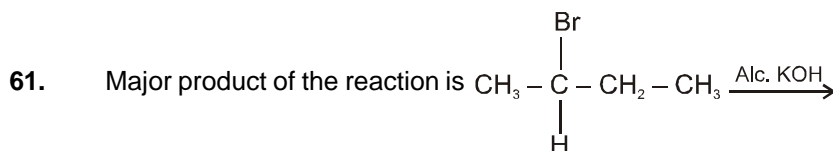
Ease of β -dehydrobromination among these substrates under the treatment of strong base will be in the order as

(A) I > II > III

(B) III > II > I

(C) II > I > III

(D) II > III > I



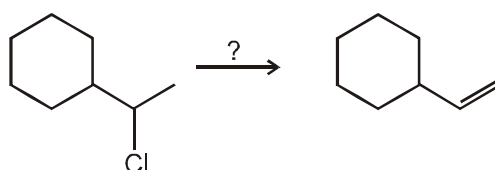
(A) Butene-1

(B) Trans-2-butene

(C) cis-2-butene

(D) Butyne-1

62. In order to accomplish the following conversion, what reagent and conditions would be required?

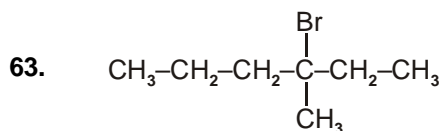


(A) Cold sodium hydroxide

(B) Hot conc. sodium hydroxide

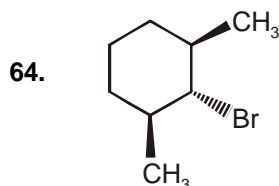
(C) Potassium t-butoxide and heat

(D) Hot water

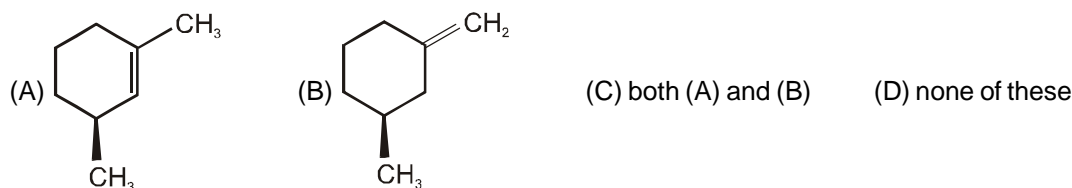


Total number of $\text{S}_{\text{N}}1 + \text{E}_1$ products obtained will be -

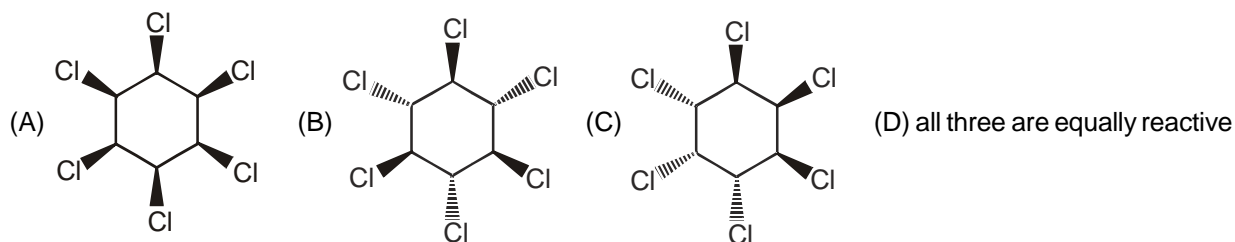
- (A) 5 (B) 6 (C) 7 (D) 8



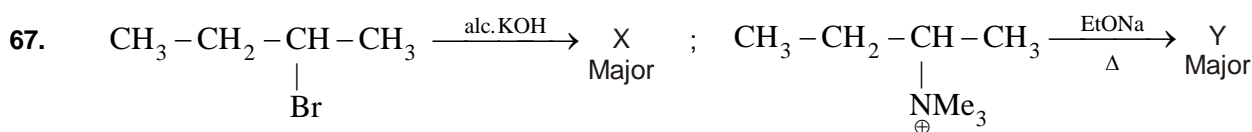
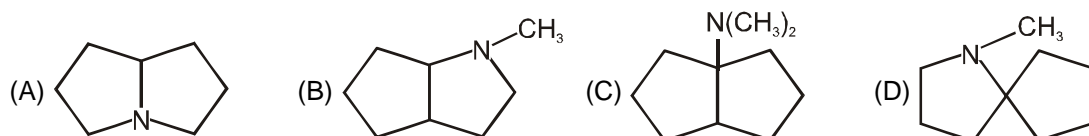
The major product obtained when this substrate is subjected to E_2 reaction will be



65. Which of the following isomeric hexachlorocyclohexanes is least reactive in β -dehydrochlorination on treatment with strong base ?

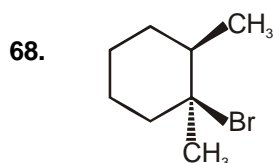


66. The nitrogen atom in each of the following tertiary amines may be removed as trimethyl amine by repeated Hofmann eliminations (exhaustive methylation followed by heating with AgOH). Which of the amines requires the greater number of Hofmann sequences to accomplish this ?

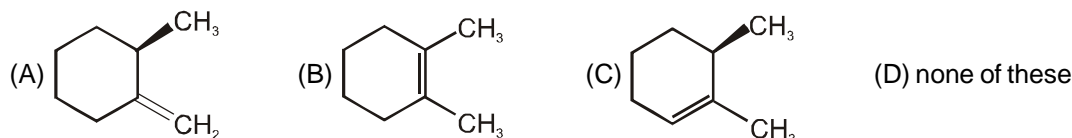


Product (X) & (Y) respectively is

- (A) 1-butene, trans-2-butene (B) 1-butene, cis-2-butene
(C) cis-2-butene, 1-butene (D) trans-2-butene, 1-butene



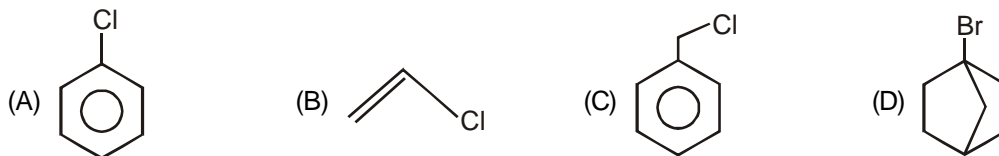
The major product obtained when this substrate is subjected to E_1 reaction will be



EXERCISE-II

Choose the correct option. One or more than one are correct :

1. Which of the following compound will not undergo Nucleophilic substitution reaction.



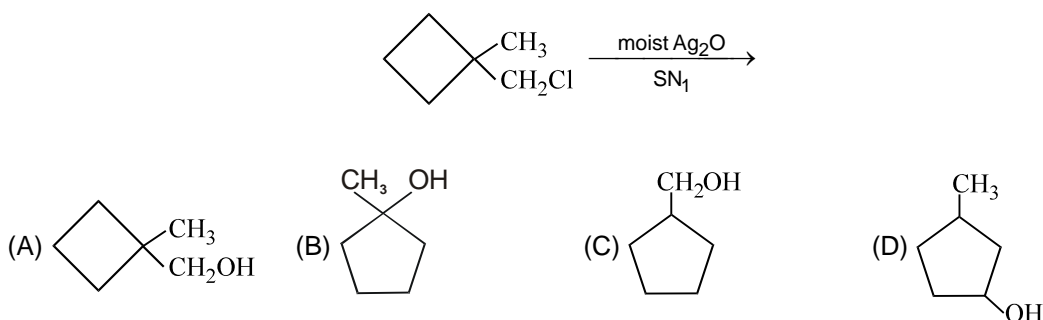
2. Consider the given reaction :
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}-\text{C}-\text{OTs} \\ | \\ \text{C}_2\text{H}_5 \end{array} (\text{S}) \xrightarrow{\text{NaCN}} \begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}-\text{CN} \\ | \\ \text{CH}_3 \end{array}$$

Which of following statements are correct for above reaction.

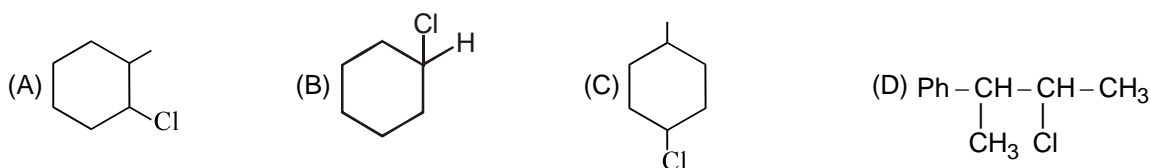
- (A) Product formation takes place due to the breaking of O-Ts
 (B) The reaction is $\text{S}_{\text{N}}2$
 (C) The reaction is $\text{S}_{\text{N}}1$
 (D) Configuration of product is (R)
3. Rate of $\text{S}_{\text{N}}2$ will be negligible in



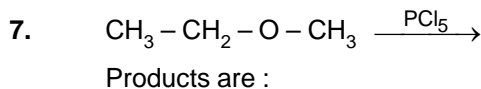
4. Which are possible products in following




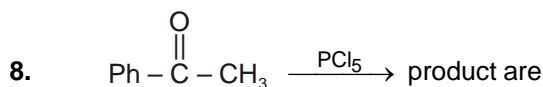
5. $\text{S}_{\text{N}}1$ & $\text{S}_{\text{N}}2$ product are same in (excluding stereoisomer)



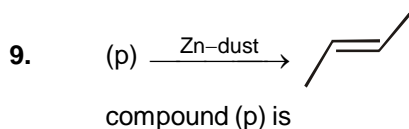
6. Statement 1: On moving 1° to 3° alkyl halide rate of E_2 increases while rate of S_N2 decreases
 Statement 2: E_2 reaction give elemental effect with respect to halogen.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.

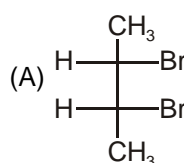
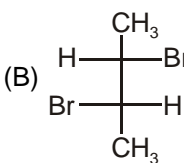
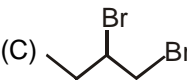



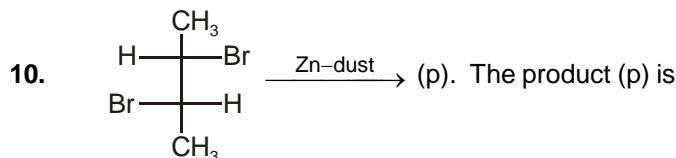
- (A) $\text{CH}_3 - \text{Cl}$ (B) $\text{Et} - \text{Cl}$ (C)  (D) 



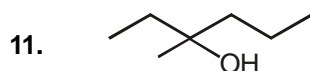
- (A) $\text{Ph} - \overset{\text{Cl}}{\underset{\text{Cl}}{\text{C}}} - \text{CH}_3$ (B) $\text{Ph} - \underset{\text{Cl}}{\text{CH}} - \underset{\text{Cl}}{\text{CH}_2}$ (C) $\text{Ph} - \text{CH}_2 - \underset{\text{Cl}}{\underset{\text{Cl}}{\text{CH}}}$ (D) $\text{Ph} - \text{CH}_2 - \text{CH}_2$



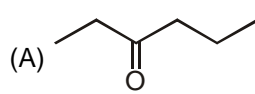
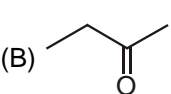
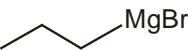
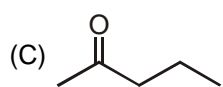
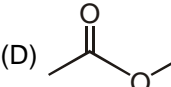
- (A)  (B)  (C)  (D) 

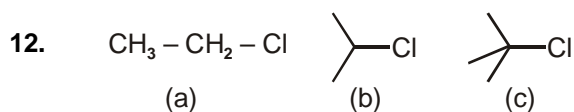


- (A)  (B)  (C)  (D) 



What are the possible combinations to prepare given alcohol

- (A)  + CH_3MgBr (B)  + 
 (C)  + EtMgBr (D)  + EtMgBr



correct order regarding given compound is/are :

- (A) rate of SN_1 ($c > b > a$) (B) rate of SN_2 ($a > b > c$)
 (C) rate of E_1 ($c > b > a$) (D) rate of E_2 ($c > b > a$)

EXERCISE-III

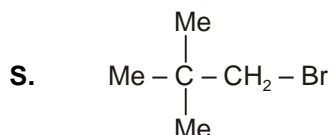
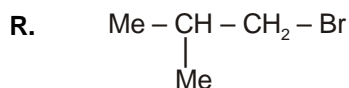
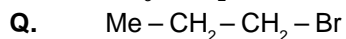
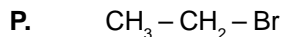
Matching List Type

This section contains **12 multiple choice questions**. Each question has matching list. The codes for the lists have choices (A), (B), (C) and (D) out of which **ONLY ONE** is correct.

1.

List-I

Primary alkyl bromide



List - II

$\text{S}_\text{N}2$ relative rate

1. 10^{-5}

2. 10^{-2}

3. 0.8

4. 1

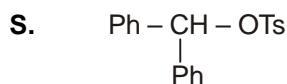
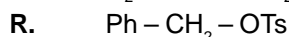
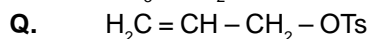
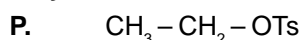
Codes :

	P	Q	R	S
(A)	3	2	1	4
(B)	3	4	2	1
(C)	4	3	2	1
(D)	3	4	1	2

2.

List-I

Alkyl-P-toluene sulfonate



List - II

Ethanolysis relative rate (50°C)

1. 10^{10}

2. 10^5

3. 400

4. 35

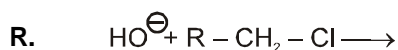
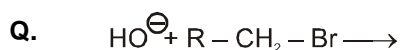
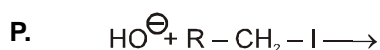
Codes :

	P	Q	R	S
(A)	4	3	2	1
(B)	3	4	2	1
(C)	4	2	3	1
(D)	3	4	1	2

3.

List-I

Reaction



List - II

Relative rate of reaction

1. 1

2. 200

3. 10,000

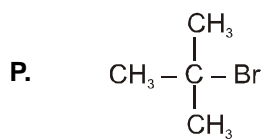
4. 30,000

Codes :

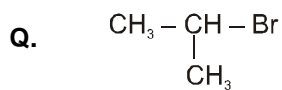
	P	Q	R	S
(A)	2	3	1	4
(B)	1	2	3	4
(C)	3	4	1	2
(D)	4	3	2	1

List - II

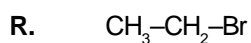
Relative rate of SN¹



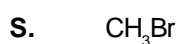
1. .01



2. 1



3. 11.6

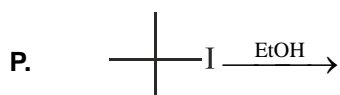


4. 1,200,000

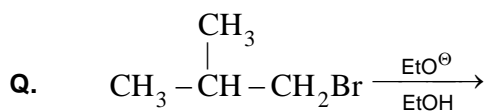
Codes :

	P	Q	R	S
(A)	2	3	1	4
(B)	1	2	3	4
(C)	4	3	2	1
(D)	4	2	3	1

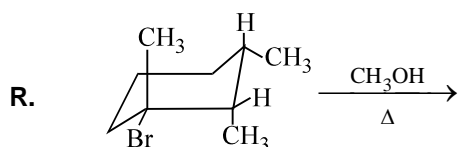
List - II



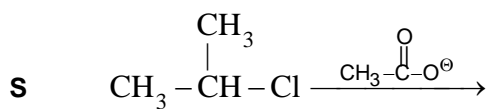
1. S_N2 reaction



2. E_1 reaction



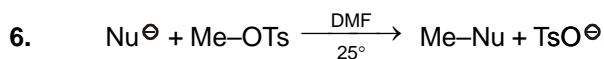
3. E₂ reaction



4. S_N1 reaction

Codes :

	P	Q	R	S
(A)	4	3	2	1
(B)	3	1	2	4
(C)	4	2	3	1
(D)	4	2	1	3



This is a $\text{S}_\text{N}2$ reaction where nucleophile attack Me-OTs in the rate determining step to give the product. Rate of this reaction increases with concentration as well as nucleophilicity of the nucleophile. Match the column I with column II for the above reaction

List-I

(Nucleophile)

P. F^\ominus

Q. Cl^\ominus

R. Br^\ominus

S. I^\ominus

List - II

(Relative rate)

1. 3.25

2. 6.25

3. 1.0

4. 7.75

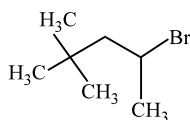
Codes :

	P	Q	R	S
(A)	4	3	2	1
(B)	4	2	1	3
(C)	4	2	3	1
(D)	4	1	2	3

7. Match List-I with List-II (no. of structural isomers produced in $\beta\text{-E}_2$ elimination) and select the correct answer.

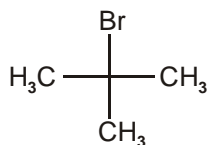
List-I

P.



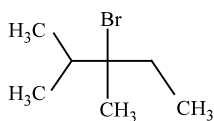
1. Three

Q.



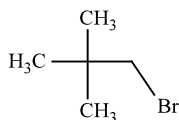
2. Zero

R.



3. One

S.

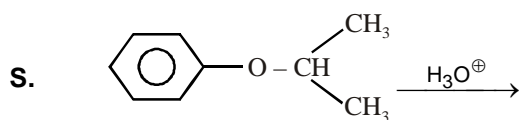
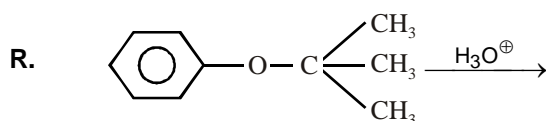
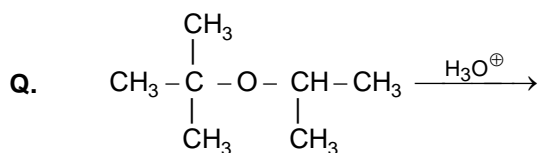
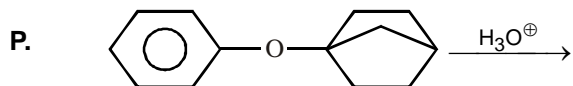


4. Two

Codes :

	P	Q	R	S
(A)	1	2	4	3
(B)	4	3	1	2
(C)	4	3	2	1
(D)	1	3	4	2

8. List-I



Codes :

	P	Q	R	S
(A)	4	1	2	3
(B)	3	4	1	3
(C)	2	4	1	3
(D)	1	4	2	3

9. List-I

P. Best leaving group

Q. Best nucleophile in polar protic solvent

R. Best nucleophile in polar aprotic solvent

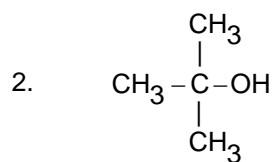
S. Weakest base

Codes :

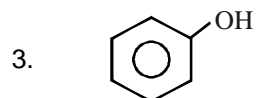
	P	Q	R	S
(A)	4	1	2	3
(B)	3	4	1	3
(C)	4	4	1	3
(D)	1	4	2	3

List - II

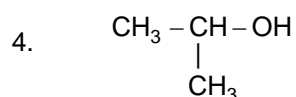
1. No-reaction



is one of the product of the reaction



is one of the product of the reaction



is one of the product of the reaction

List - II

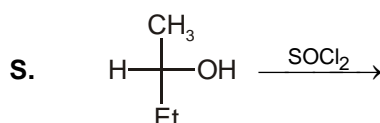
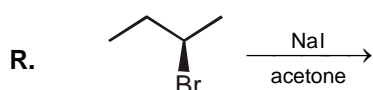
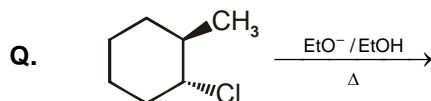
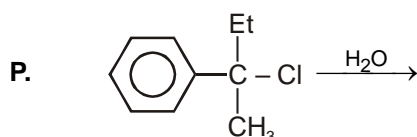
1. F^\ominus

2. Cl^\ominus

3. Br^\ominus

4. I^\ominus

10. List-I



List - II

1. SO_2 gas is side product
2. Racemic mixture will be formed
3. Only inverted product will obtain
4. Elimination reaction

Codes :

	P	Q	R	S
(A)	2	4	3	1
(B)	4	2	3	1
(C)	3	1	3	2
(D)	2	3	1	4

11.	Substrate	E_2 elimination	$\text{S}_\text{N}2$ -substitution
(A)	$\text{CH}_3 - \text{CH}_2 - \text{Br}$	(P) 1	(W) ≈ 0
(B)	$(\text{CH}_3)_2\text{CH} - \text{Br}$	(Q) 80	(X) 20
(C)	$(\text{CH}_3)_3\text{CBr}$	(R) 100	(Y) 90

12. Substitution Logistics :

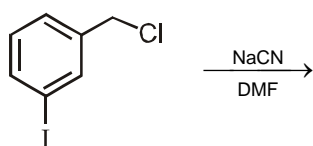
You were asked to run a series of reactions in the lab with different experimental conditions. Based on the experimental observations you gathered (listed below), indicate which mechanism this evidence supports. (Check the appropriate box to correspond to your answer.)

S.No.	Observation	$\text{S}_\text{N}1$	$\text{S}_\text{N}2$	Both
1	The rate of the reaction decreased when the concentration of the Nu is decreased.			
2	The rate of the reaction increased when the concentration of the RX was increased.			
3	The rate increased when the X was changed from Cl to I.			
4	The products showed a skeletal rearrangement.			
5	The product showed inversion of configuration.			
6	The Nu was changed from methoxide to isopropoxide and the rate decreased.			
7	The RX was changed from 2° alkyl halide to a 2° allyl halide and the rate increased.			
8	The solvent was switched from ethanol to acetone and the rate decreased.			

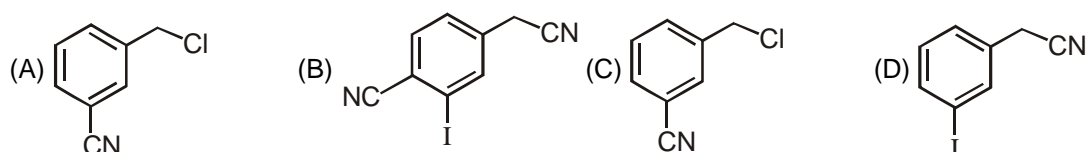
EXERCISE-IV (A)


PREVIOUS YEAR AIEEE QUESTIONS

1. The reaction : $(\text{CH}_3)_3\text{C} - \text{Br} \xrightarrow{\text{H}_2\text{O}} (\text{CH}_3)_3\text{C} - \text{OH}$ [AIEEE-2002]
(A) elimination reaction (B) substitution reaction
(C) free radical reaction (D) displacement reaction
2. The compound formed on heating chlorobenzene with chloral in the presence concentrated sulphuric acid is [AIEEE-2004]
(A) gammexene (B) hexachloroethane
(C) Freon (D) DDT
3. The correct order of the thermal stability of hydrogen halides ($\text{H} - \text{X}$) is [AIEEE-2005]
(A) $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$ (B) $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$
(C) $\text{HCl} < \text{HF} > \text{HBr} < \text{HI}$ (D) $\text{HI} > \text{HCl} < \text{HF} < \text{HBr}$
4. Tertiary alkyl halides are practically inert to substitution by S_N^2 mechanism because of [AIEEE-2005]
(A) insolubility (B) instability (C) inductive effect (D) steric hindrance
5. Elimination of bromine from 2-bromobutane results in the formation of- [AIEEE-2005]
(A) equimolar mixture of 1 and 2-butene (B) predominantly 2-butene
(C) predominantly 1-butene (D) predominantly 2-butyne
6. $\text{CH}_3\text{Br} + \text{Nu}^- \longrightarrow \text{CH}_3 - \text{Nu} + \text{Br}^-$ [AIEEE-2006]
The decreasing order of the rate of the above reaction with nucleophiles (Nu^-) A to D is
[$\text{Nu}^- = (\text{A}) \text{PhO}^-$, (B) AcO^- , (C) HO^- , (D) CH_3O^-]
(A) $\text{D} > \text{C} > \text{A} > \text{B}$ (B) $\text{D} > \text{C} > \text{B} > \text{A}$
(C) $\text{A} > \text{B} > \text{C} > \text{D}$ (D) $\text{B} > \text{D} > \text{C} > \text{A}$
7. The structure of the major product formed in the following reaction [AIEEE-2006]

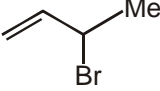


is

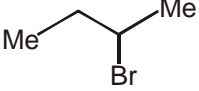


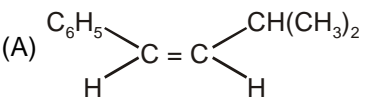
8. Reaction of trans-2-phenyl-1-bromocyclopentane on reaction with alcoholic KOH produces [AIEEE-2006]
 (A) 4-phenylcyclopentene (B) 2-phenylcyclopentene
 (C) 1-phenylcyclopentene (D) 3-phenylcyclopentene
9. Which of the following is the correct order of decreasing S_N2 reactivity? [AIEEE-2007]
 (A) $RCH_2X > R_3CX > R_2CHX$ (B) $RCH_2X > R_2CHX > R_3CX$
 (C) $R_3CX > R_2CHX > RCH_2X$ (D) $R_2CHX > R_3CX > RCH_2X$
10. The organic chloro compound, which shows complete stereochemical inversion during a S_N2 reaction, is [AIEEE-2008]
 (A) $(C_2H_5)_2CHCl$ (B) $(CH_3)_3CCl$ (C) $(CH_3)_2CHCl$ (D) CH_3Cl
11. Which of the following on heating with aqueous KOH, produces acetaldehyde? [AIEEE-2009]
 (A) CH_2ClCH_2Cl (B) CH_3CHCl_2 (C) CH_3COCl (D) CH_3CH_2Cl
12. From amongst the following alcohols the one that would react fastest with conc. HCl and anhydrous $ZnCl_2$, is [AIEEE-2010]
 (A) 2-Methylpropanol (B) 1-Butanol (C) 2-Butanol (D) 2-Methylpropan-2-ol
13. Consider the following bromides : [AIEEE-2010]
- 

(A)

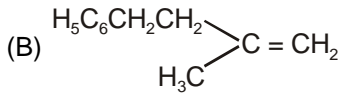


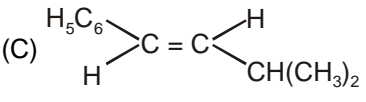
(B)



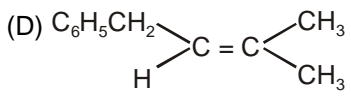
(C)
- The correct order of S_N1 reactivity is
 (A) $C > B > A$ (B) $A > B > C$ (C) $B > C > A$ (D) $B > A > C$
14. The main product of the following reaction is [AIEEE-2010]
 $C_6H_5CH_2CH(OH)CH(CH_3)_2 \xrightarrow[\Delta]{conc. H_2SO_4} ?$
- 

(A)



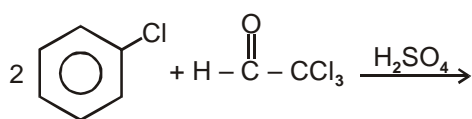
(B)
- 

(C)



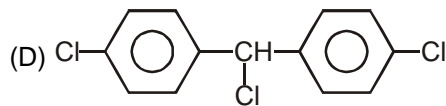
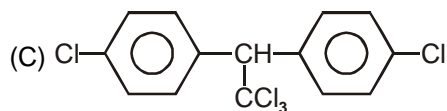
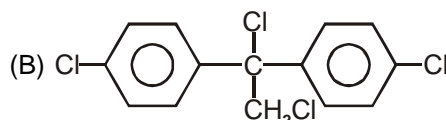
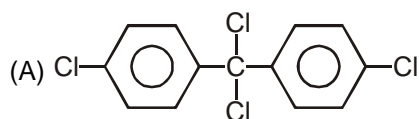
(D)
15. An unknown alcohol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism : [JEE-Mains-2013]
 (A) tertiary alcohol by S_N2 (B) secondary alcohol by S_N1
 (C) tertiary alcohol by S_N1 (D) secondary alcohol by S_N2
16. A solution of (–) – 1 – chloro – 1 – phenylethane in toluene racemises slowly in the presence of a small amount of $SbCl_5$, due to the formation of : [JEE-Mains-2013]
 (A) free radical (B) carbanion (C) carbene (D) carbocation

17. For the compounds CH_3Cl , CH_3Br , CH_3I and CH_3F , the correct order of increasing C-halogen bond length is : **[JEE-Main-Online-2014]**
 (A) $\text{CH}_3\text{F} < \text{CH}_3\text{Cl} < \text{CH}_3\text{Br} < \text{CH}_3\text{I}$ (B) $\text{CH}_3\text{F} < \text{CH}_3\text{Br} < \text{CH}_3\text{Cl} < \text{CH}_3\text{I}$
 (C) $\text{CH}_3\text{F} < \text{CH}_3\text{I} < \text{CH}_3\text{Br} < \text{CH}_3\text{Cl}$ (D) $\text{CH}_3\text{Cl} < \text{CH}_3\text{Br} < \text{CH}_3\text{F} < \text{CH}_3\text{I}$
18. Alkyl phenyl ether can be prepared by heating : **[JEE-Main-Online-2014]**
 (A) $\text{C}_6\text{H}_5\text{Br} + \text{CH}_2 = \text{CH} - \text{CH}_2 - \text{ONa}$ (B) $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{Br} + \text{C}_6\text{H}_5\text{ONa}$
 (C) $\text{C}_6\text{H}_5 - \text{CH} = \text{CH} - \text{Br} + \text{CH}_3 - \text{ONa}$ (D) $\text{CH}_2 = \text{CH} - \text{Br} + \text{C}_6\text{H}_5 - \text{CH}_2 - \text{ONa}$
19. In a nucleophilic substitution reaction : **[JEE-Main-Online-2014]**
 $\text{R} - \text{Br} + \text{Cl}^- \xrightarrow{\text{DMF}} \text{R} - \text{Cl} + \text{Br}^-$
 Which one of the following undergoes complete inversion of configuration ?
 (A) $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5\text{Br}$ (B) $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ (C) $\text{C}_6\text{H}_5\text{CHCH}_3\text{Br}$ (D) $\text{C}_6\text{H}_5\text{CCH}_3\text{C}_6\text{H}_5\text{Br}$
20. Chlorobenzene reacts with trichloro acetaldehyde in the presence of H_2SO_4



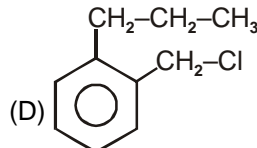
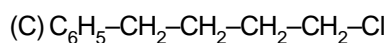
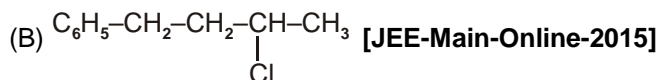
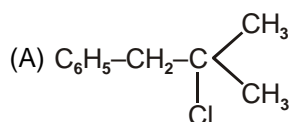
The major product formed is :

[JEE-Main-Online-2014]

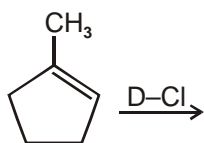


21. The major product obtained in the photo catalysed bromination of 2-methylbutane is : **[JEE-Main-Online-2014]**
 (A) 1-bromo-2-methylbutane (B) 1-bromo-3-methylbutane
 (C) 2-bromo-3-methylbutane (D) 2-bromo-2-methylbutane
22. The major product formed when 1,1,1-trichloro-propane is treated with aqueous potassium hydroxide is : **[JEE-Main-Online-2014]**
 (A) Propyne (B) 1-Propanol (C) 2-Propanol (D) Propionic acid
23. Williamson synthesis of ether is an example of : **[JEE-Main-Online-2014]**
 (A) Nucleophilic addition (B) Electrophilic addition
 (C) Electrophilic substitution (D) Nucleophilic substitution
24. In the reaction, $\text{CH}_3\text{COOH} \xrightarrow{\text{LiAlH}_4} \text{A} \xrightarrow{\text{PCl}_5} \text{B} \xrightarrow{\text{alc. KOH}} \text{C}$, the product C is **[JEE-Main-2014]**
 (A) Acetylene (B) Ethylene (C) Acetyl chloride (D) Acetaldehyde

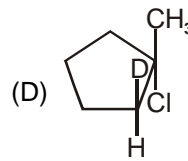
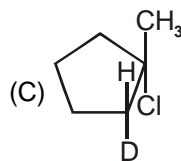
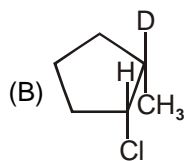
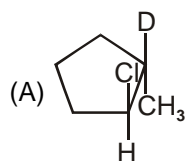
25. The major organic compound formed by the reaction of 1, 1, 1-trichloroethane with silver powder is [JEE-Main-2014]
 (A) Ethene (B) 2-Butyne (C) 2-Butene (D) Acetylene
26. In S_N2 reactions, the correct order of reactivity for the following compounds : [JEE-Main-2014]
 CH_3Cl , $\text{CH}_3\text{CH}_2\text{Cl}$, $(\text{CH}_3)_2\text{CHCl}$ and $(\text{CH}_3)_3\text{CCl}$ is
 (A) $\text{CH}_3\text{Cl} > \text{CH}_3\text{CH}_2\text{Cl} > (\text{CH}_3)_2\text{CHCl} > (\text{CH}_3)_3\text{CCl}$
 (B) $\text{CH}_3\text{CH}_2\text{Cl} > \text{CH}_3\text{Cl} > (\text{CH}_3)_2\text{CHCl} > (\text{CH}_3)_3\text{CCl}$
 (C) $(\text{CH}_3)_2\text{CHCl} > \text{CH}_3\text{CH}_2\text{Cl} > \text{CH}_3\text{Cl} > (\text{CH}_3)_3\text{CCl}$
 (D) $\text{CH}_3\text{Cl} > (\text{CH}_3)_2\text{CHCl} > \text{CH}_3\text{CH}_2\text{Cl} > (\text{CH}_3)_3\text{CCl}$
27. 1.4g of an organic compound was digested according to Kjeldahl's method and the ammonia evolved was absorbed in 60 mL of M/10 H_2SO_4 solution. The excess sulphuric acid required 20 mL of M/10 NaOH solution for neutralization. The percentage of nitrogen in the compound is [JEE-Main-Online-2015]
 (A) 3 (B) 5 (C) 10 (D) 24
28. A compound A with molecular formula $\text{C}_{10}\text{H}_{13}\text{Cl}$ gives a white precipitate on adding silver nitrate solution. A on reacting with alcoholic KOH gives compound B as the main product. B on ozonolysis gives C and D. C gives Cannizzaro reaction but not aldol and D gives aldol but not Cannizzaro reaction. A is



29. What is the major product expected from the following reaction? [JEE-Main-Online-2015]



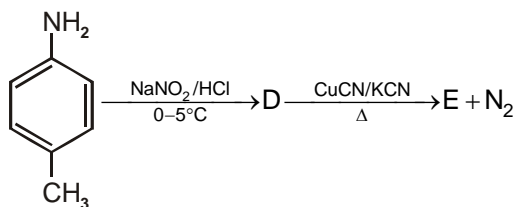
Where D is an isotope of hydrogen



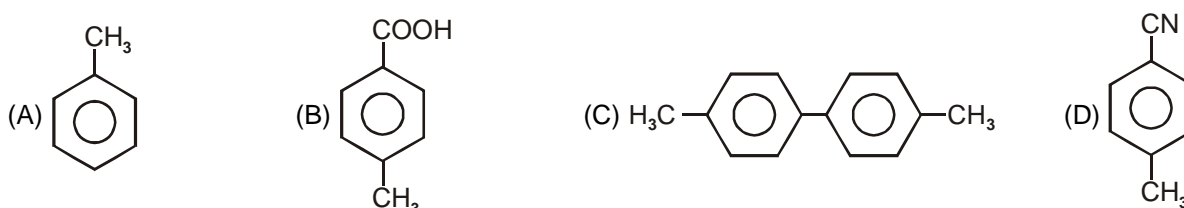
30. In Carius method of estimation of halogens, 250 mg of an organic compound gave 141 mg of AgBr. The percentage of bromine in the compound is (at. mass Ag = 108 ; Br = 80) [JEE-Main-2015]
 (A) 60 (B) 24 (C) 36 (D) 48

31. The synthesis of alkyl fluorides is best accomplished by [JEE-Main-2015]
 (A) Swarts reaction (B) Free radical fluorination
 (C) Sandmeyer's reaction (D) Finkelstein reaction

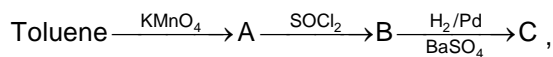
32. In the reaction [JEE-Main-2015]



the product E is



33. In the following sequence of reaction [JEE-Main-2015]

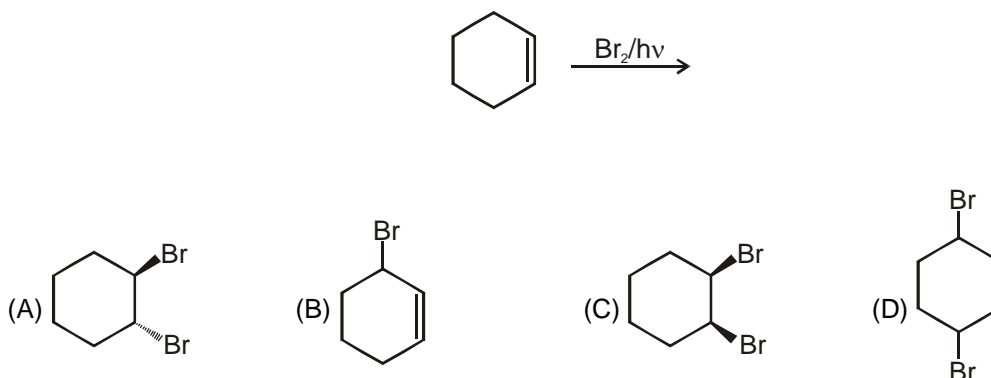


the product C is

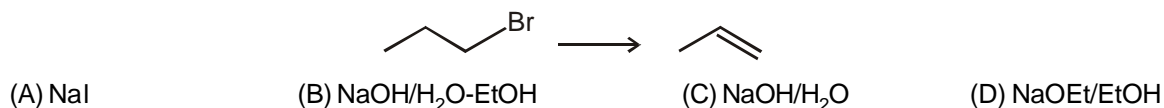
- (A) $\text{C}_6\text{H}_5\text{CHO}$
 (B) $\text{C}_6\text{H}_5\text{COOH}$
 (C) $\text{C}_6\text{H}_5\text{CH}_3$
 (D) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$

34. The gas evolved on heating CH_3MgBr in methanol is [JEE-Main Online -2016]
 (A) Methane (B) Ethane (C) Propene (D) HBr

35. Bromination of cyclohexene under conditions given below yields : [JEE-Main Online -2016]

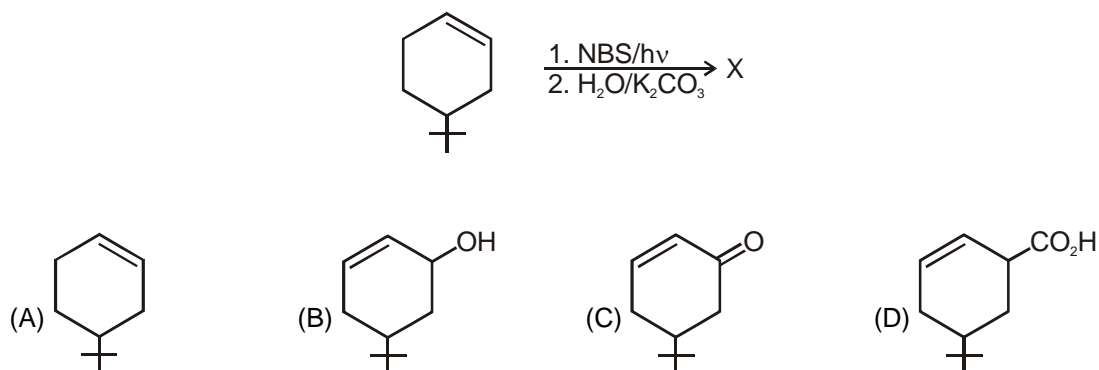


36. Which one of the following reagents is not suitable for the elimination reaction ? [JEE-Main Online -2016]

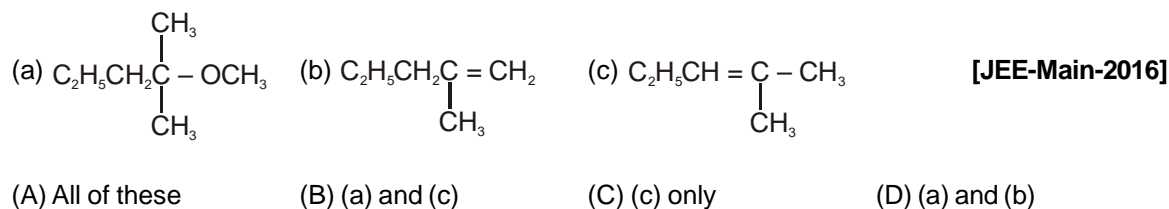


37. Fluorination of an aromatic ring is easily accomplished by treating a diazonium salt with HBF_4 . Which of the following conditions is correct about this reaction ? [JEE-Main Online -2016]
 (A) Only heat (B) NaNO_2/Cu (C) $\text{Cu}_2\text{O}/\text{H}_2\text{O}$ (D) NaF/Cu

38. The product of the reaction given below is : [JEE-Main-2016]



39. 2-chloro-2methylpentane on reaction with sodium methoxide in methanol yields :



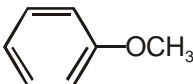
40. The reaction of propene with HOCl ($\text{Cl}_2 + \text{H}_2\text{O}$) proceeds through the intermediate : [JEE-Main-2016]
 (A) $\text{CH}_3-\text{CH}^+-\text{CH}_2-\text{OH}$ (B) $\text{CH}_3-\text{CH}^+-\text{CH}_2-\text{Cl}$
 (C) $\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_2^+$ (D) $\text{CH}_3-\text{CHCl}-\text{CH}_2^+$

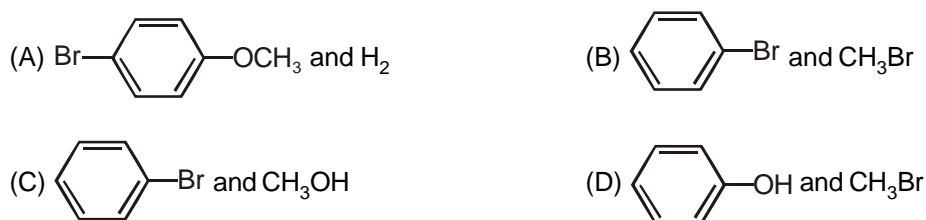
EXERCISE-IV (B)

PREVIOUS YEAR IIT QUESTIONS

SCQ :

1. Ethyl alcohol is heated with conc. H_2SO_4 . The product formed is [IIT 1980]
 (A) $\text{H}_3\text{C}-\overset{\text{O}}{\underset{\text{O}}{\parallel}}-\text{OC}_2\text{H}_5$ (B) C_2H_2 (C) C_2H_4 (D) C_2H_6
2. The compound which reacts fastest with Lucas reagent at room temperature is [IIT 1981]
 (A) butan-2-ol (B) butan-1-ol
 (C) 2-methyl propan-1-ol (D) 2-methyl propan-2-ol
3. Diethyl ether on heating with conc. HI gives two moles of [IIT 1983]
 (A) ethanol (B) iodoform (C) ethyl iodide (D) methyl iodide
4. When propyne is treated with aqueous H_2SO_4 in presence of HgSO_4 , the major product is [IIT 1983]
 (A) propanal (B) propyl hydrogen sulphate
 (C) acetone (D) propanol
5. Beayer's reagent is [IIT 1984]
 (A) alkaline permanganate solution (B) acidified permanganate solution
 (C) neutral permanganate solution (D) aqueous bromine solution
6. HBr reacts fastest with [IIT 1986]
 (A) 2-methyl propan-2-ol (B) propan-1-ol (C) propan-2-ol (D) 2-methyl propan-1-ol
7. The reaction of $\text{CH}_3\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{OH}$ with HBr gives [IIT 1998]
 (A) $\text{CH}_3\text{CHBrCH}_2-\text{C}_6\text{H}_4-\text{OH}$ (B) $\text{CH}_3\text{CH}_2\text{CHBr}-\text{C}_6\text{H}_4-\text{OH}$
 (C) $\text{CH}_3\text{CHBrCH}_2-\text{C}_6\text{H}_4-\text{Br}$ (D) $\text{CH}_3\text{CH}_2\text{CHBr}-\text{C}_6\text{H}_4-\text{Br}$
8. Alcoholic solution of KOH is a specific reagent for [IIT 1990]
 (A) Dehydration (B) Dehydrogenation
 (C) Dehydro halogenation (D) Dehalogenation
9. 1-Chlorobutane on reaction with alcoholic potash gives: [IIT 1991]
 (A) 1-butene (B) 1-butanol (C) 2-butene (D) 2-butanol
10. The products of reaction of alcoholic AgNO_2 with ethyl bromide are [IIT 1991]
 (A) Ethane (B) Ethyl nitrite (C) Nitroethane (D) Ethyl alcohol
11. **Statement-1** 1-butene on reaction with HBr in the presence of a peroxide produces 1-bromobutane.
Statement-2 It involves the formation of a primary radical. [IIT 2000]
 (A) Statement-1 is true, Statement-2 is true and Statement-2 is correct explanation for Statement-1
 (B) Statement-1 is true, Statement-2 is true and Statement-2 is **NOT** the correct explanation for Statement-1
 (C) Statement-1 is true, Statement-2 is false
 (D) Statement-1 is false, Statement-2 is true

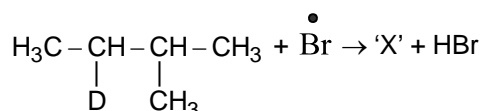
12. In the reaction  $\xrightarrow{\text{HBr}}$ the products are [IIT 2000]



13. The order of reactivity of the following alkyl halides for a $\text{S}_{\text{N}}2$ reaction is: [IIT 2000]
- (A) $\text{RF} > \text{RCI} > \text{R-Br} > \text{R-I}$ (B) $\text{R-F} > \text{R-Br} > \text{R-Cl} > \text{R-I}$
- (C) $\text{R-Cl} > \text{R-Br} > \text{RF} > \text{RI}$ (D) $\text{R-I} > \text{RBr} > \text{R-Cl} > \text{R-F}$

14. **Statement-1** Addition of bromine to trans-2-butene yields meso-2, 3-dibromo butane.
Statement-2 Bromine addition to an alkene is an electrophilic addition. [IIT 2001]
- (A) Statement-1 is true, Statement-2 is true and Statement-2 is correct explanation for Statement-1
 (B) Statement-1 is true, Statement-2 is true and Statement-2 is **NOT** the correct explanation for Statement-1
 (C) Statement-1 is true, Statement-2 is false
 (D) Statement-1 is false, Statement-2 is true

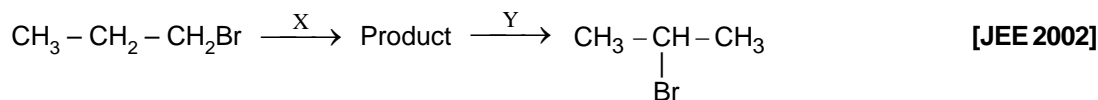
15. Consider the following reactions – [IIT '2002]



Identify the structure of the major product 'X'

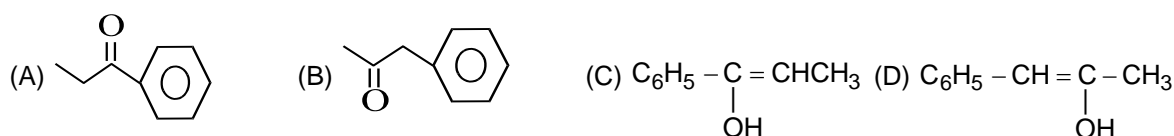


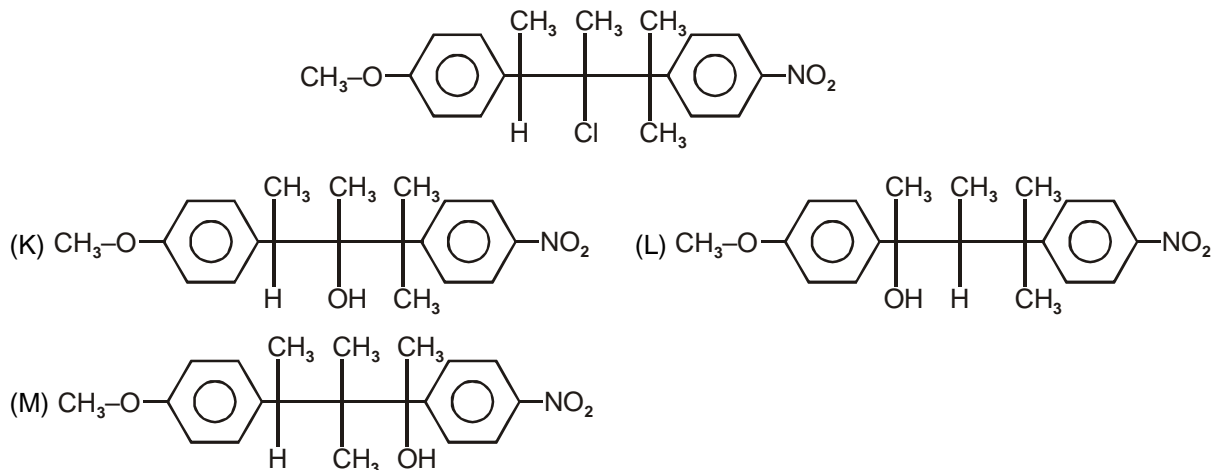
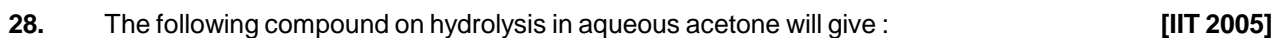
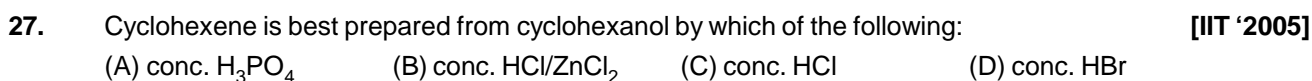
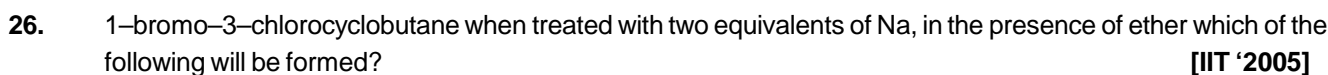
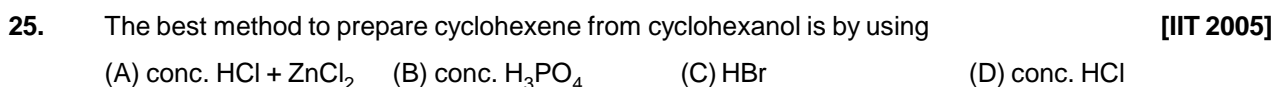
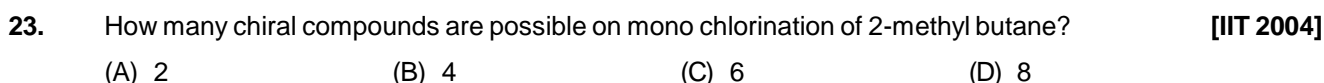
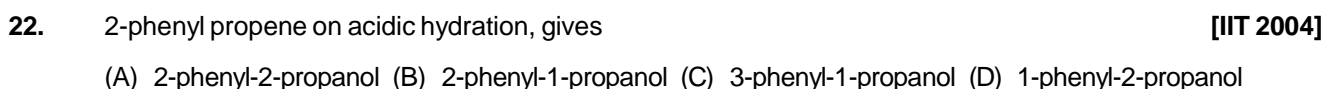
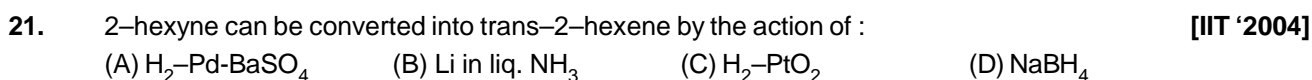
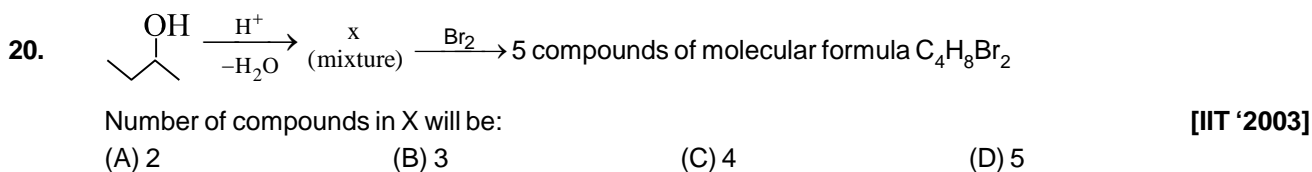
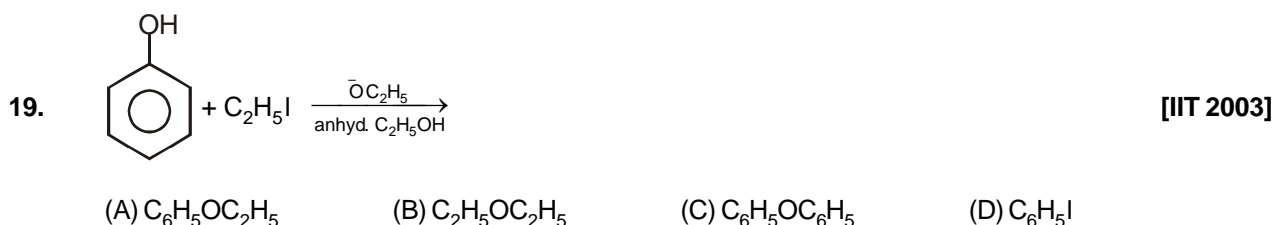
16. Identify a reagent from the following list which can easily distinguish between 1-butyne and 2-butyne- [IIT '2002]
- (A) bromine, CCl_4 (B) H_2 , Lindlar catalyst
 (C) dilute H_2SO_4 , HgSO_4 (D) ammonical Cu_2Cl_2 solution
17. Identify the set of reagents / reaction conditions 'X' and 'Y' in the following set of transformation:



- (A) X = dilute aqueous NaOH, 20°C ; Y = HBr / acetic acid, 20°C
 (B) X = concentrated alcoholic NaOH, 80°C ; Y = HBr / acetic acid 20°C
 (C) X = dilute aqueous NaOH, 20°C ; Y = Br_2 / CHCl_3 , 0°C
 (D) X = concentrated alcoholic NaOH, 80°C ; Y = $\text{Br}_2/\text{CHCl}_3$, 0°C

18. $\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\text{CH}_3 \xrightarrow[\text{H}_2\text{SO}_4]{\text{HgSO}_4} \text{A}$ [IIT '2003]

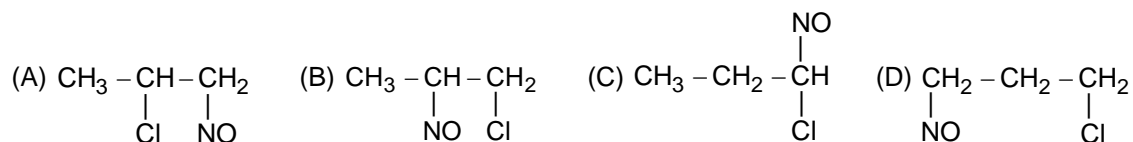




- (A) mixture of (K) and (L) (B) mixture of (K) and (M)
(C) only (M) (D) only (K)

29. $\text{CH}_3\text{--CH=CH}_2 + \text{NOCl} \rightarrow \text{P}$
Identify the adduct.

[IIT 2006]



30. $\text{H}_3\text{C--CH(CH}_3\text{)--CH}_2\text{--CH}_3 \xrightarrow{\text{Cl}_2, h\nu} \text{N(isomeric products) C}_5\text{H}_{11}\text{Cl} \xrightarrow{\text{fractional distillation}} \text{M(isomeric products)}$

What are N and M?

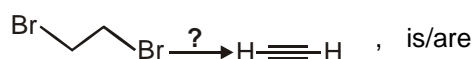
[IIT 2006]

- (A) 6, 6 (B) 6, 4 (C) 4, 4 (D) 3, 3

31. The number of stereoisomers obtained by bromination of trans-2-butene is
(A) 1 (B) 2 (C) 3 (D) 4

[IIT 2007]

32. The reagent(s) for the following conversion,

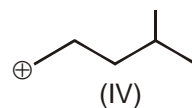
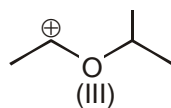
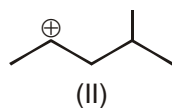
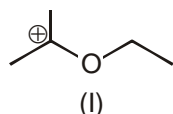


[IIT 2007]

- (A) alcoholic KOH (B) alcoholic KOH followed by NaNH_2
(C) aqueous KOH followed by NaNH_2 (D) $\text{Zn} / \text{CH}_3\text{OH}$

33. The correct stability order for the following species is

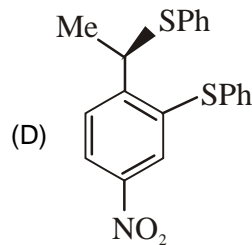
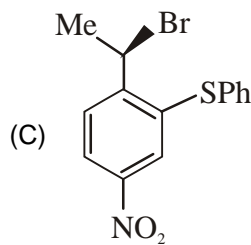
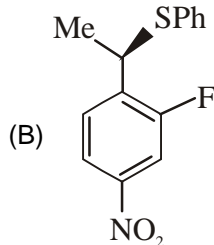
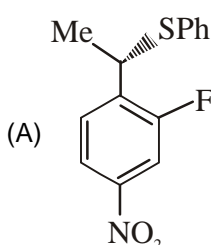
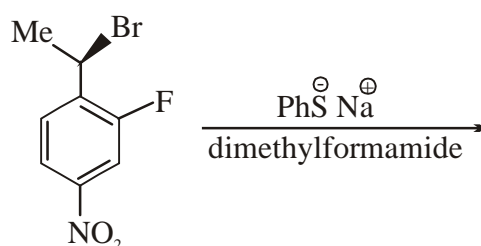
[JEE 2008]



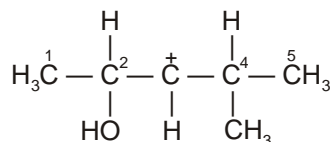
- (A) II > IV > I > III (B) I > II > III > IV (C) II > I > IV > III (D) I > III > II > IV

34. The major product of the following reaction is

[IIT 2008]



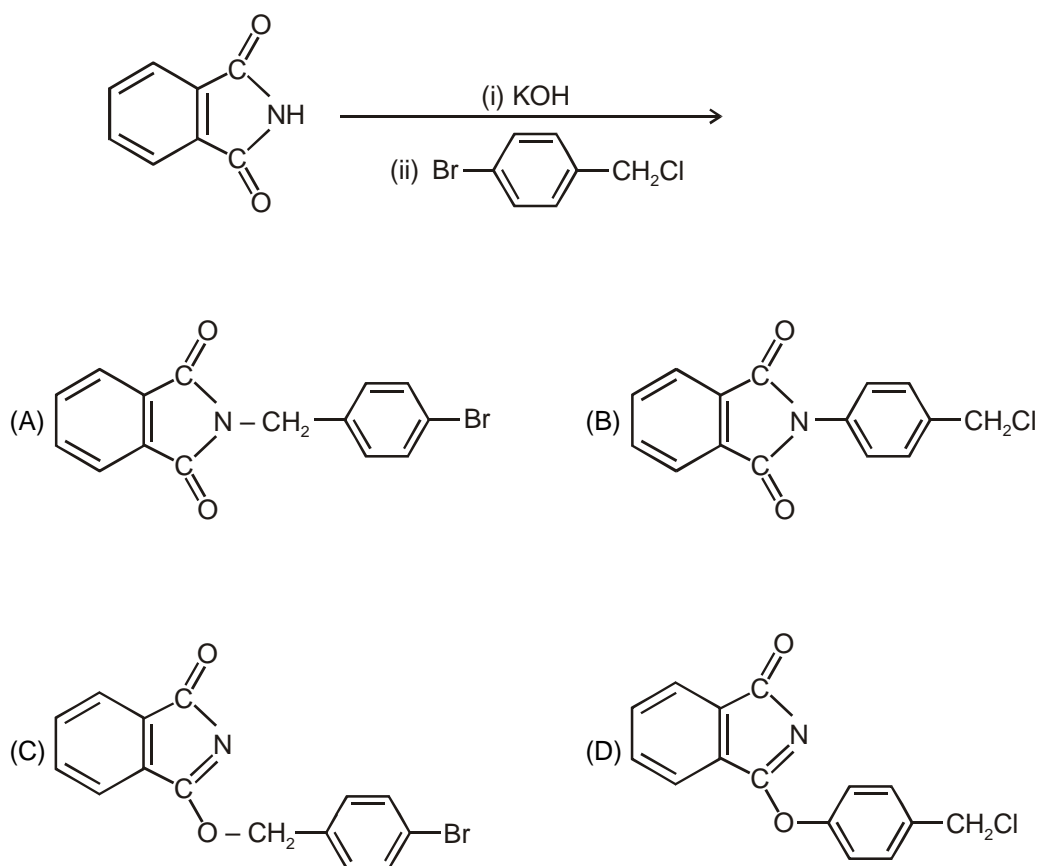
35. In the following carbocation, H/ CH_3 that is most likely to migrate to the positively charged carbon is



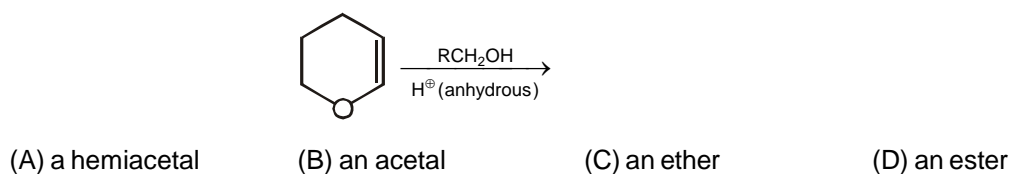
[JEE 2009]

- (A) CH_3 at C-4 (B) H at C-4 (C) CH_3 at C-2 (D) H at C-2

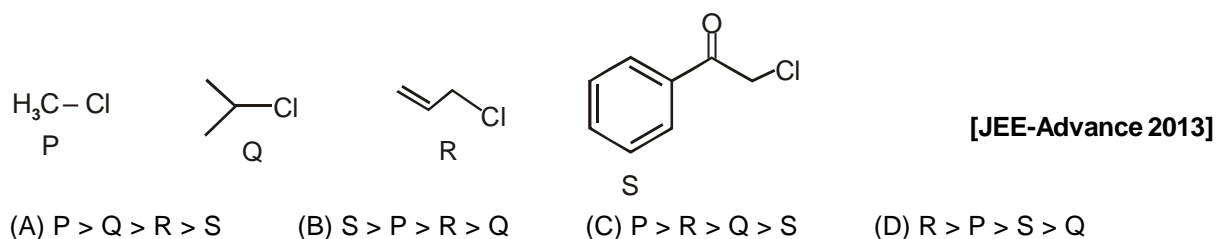
36. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are – [IIT 2010]
- (A) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$ (B) $\text{BrCH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$
 (C) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{C}\equiv\text{CH}$ (D) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$
37. The bond energy (in kcal mol^{-1}) of a C–C single bond is approximately [JEE 2010]
- (A) 1 (B) 10 (C) 100 (D) 1000
38. The major product of the following reaction is : [IIT 2011]



39. The major product of the following reaction is [JEE 2011]



40. KI in acetone, undergoes $\text{S}_{\text{N}}2$ reaction with each of P, Q, R and S. The rates of the reaction vary as

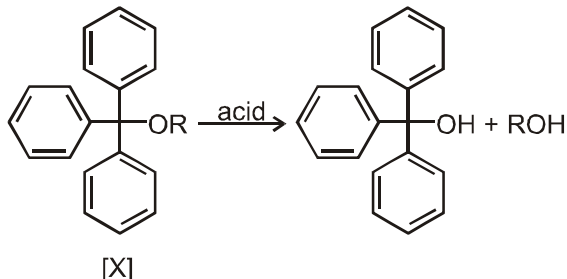


41. The hyperconjugative stabilities of tert-butyl cation and 2-butene, respectively, are due to
 (A) $\sigma \rightarrow p$ (empty) and $\sigma \rightarrow \pi^*$ electron delocalisations.
 (B) $\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \pi$ electron delocalisations.
 (C) $\sigma \rightarrow p$ (filled) and $\sigma \rightarrow \pi$ electron delocalisations.
 (D) p (filled) $\rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ electron delocalisations.

[JEE-Advance 2013]

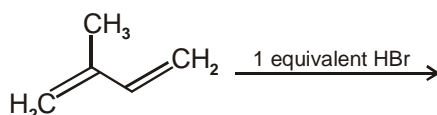
42. The acidic hydrolysis of ether (X) shown below is fastest when

[IIT Advance - 2014]



- (A) one phenyl group is replaced by a methyl group.
 (B) one phenyl group is replaced by a para-methoxyphenyl group.
 (C) two phenyl groups are replaced by two para-methoxyphenyl groups.
 (D) No structural change is made to X.
43. In the following reaction, the major product is

[IIT Advance - 2015]



- (A) (B) (C) (D)

MCQ :

44. The ether when treated with HI produces

[IIT 1999]

- (A) (B) (C) (D)

Matrix :

45. Match the following:

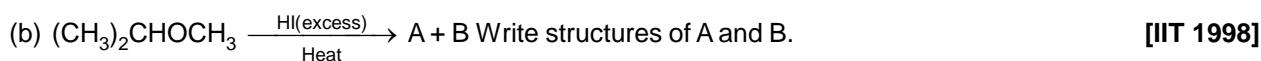
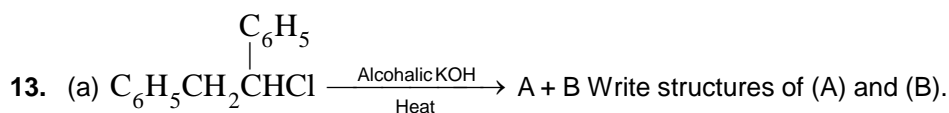
[IIT 2006]

- | Column I | Column II |
|---|--------------------------|
| (A) $\text{CH}_3\text{-CHBr-CD}_3$ on treatment with alc. KOH gives $\text{CH}_2=\text{CH-CD}_3$ as a major product. | (P) E1 reaction |
| (B) Ph-CHBr-CH_3 reacts faster than Ph-CHBr-CD_3 . | (Q) E2 reaction |
| (C) $\text{Ph-CH}_2\text{-CH}_2\text{Br}$ on treatment with $\text{C}_2\text{H}_5\text{OD/C}_2\text{H}_5\text{O}^-$ gives Ph-CD=CH_2 as the product. | (R) E1cb reaction |
| (D) $\text{PhCH}_2\text{CH}_2\text{Br}$ and $\text{PhCD}_2\text{CH}_2\text{Br}$ react with same rate. | (S) First order reaction |

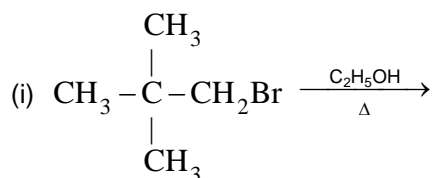
EXERCISE-IV (C)

PREVIOUS YEAR IIT SUBJECTIVE QUESTIONS

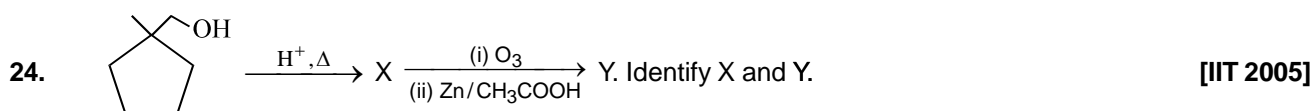
1. Suggest a reason for the large difference between the boiling points of butanol and butanal, although they have almost the same solubility in water. [IIT 1985]
2. Write the structure of the major organic product expected from each of the following reaction :
(i) $\text{CH}_3\text{CH}_2\text{CHCl}_2 \xrightarrow[\text{alkali}]{\text{Boil(aq)}} \quad$ [IIT 1992]
3. Fill in the blanks:
(a) Butane nitrile can be prepared by heating _____ with alcoholic KCN. [IIT 1992]
(b) Amongst three isomers of nitrophenol, the one that is least soluble in water is ____ [IIT 1992]
4.
$$\begin{array}{c} \text{Cl} \\ | \\ (\text{CH}_3)_2\text{C}-\text{CH}_2\text{CH}_3 \end{array} \xrightarrow{\text{alc.KOH}} ?$$
 [IIT 1992]
5. Aryl halides are less reactive than alkyl halides towards nucleophilic reagents. Give reason. [IIT 1994]
6. Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain briefly. [IIT 1995]
7. An alkyl halide X of formula $\text{C}_6\text{H}_{13}\text{Cl}$ on treatment with potassium tertiary butoxide gives two isomeric alkenes Y and Z (C_6H_{12}). Both alkenes on hydrogenation give 2,3-dimethylbutane. Predict the structures of X, Y and Z. [IIT 1996]
8. 3, 3-dimethylbutan-2-ol loses a molecule of water in the presence of concentrated sulphuric acid to give tetramethylethylene as a major product. Suggest a suitable mechanism. [IIT 1996]
9. An alkyl halide, (X) of formula $\text{C}_6\text{H}_{13}\text{Cl}$ on treatment with potassium tertiary butoxide gives two isomeric alkenes (Y) and (Z) (C_6H_{12}). Both alkenes on hydrogenation give 2, 3-dimethylbutane. Predict the structures of (X), (Y) and (Z) [IIT 1996]
10. 2, 2-dimethyloxirane can be cleaved by dil. acid. Write mechanism. [IIT 1997]
11. Which of the following is the correct method for synthesising methyl-t-butyl ether and why ?
(i) $(\text{CH}_3)_3\text{CBr} + \text{Na}^+\text{OMe}^- \longrightarrow$ (ii) $\text{CH}_3\text{Br} + \text{t-BuO}^-\text{Na}^+ \longrightarrow$ [IIT 1997]
12. Give reasons for the following in one or two sentences. "Acid catalysed dehydration of t-butanol is faster than that of n-butanol. [IIT 1998]



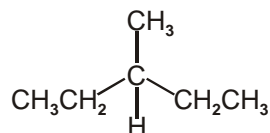
14. What would be the major product in each of the following reactions? [IIT 2000]



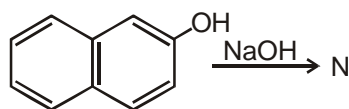
15. is most acidic. (Ethane, Ethene, Ethyne) [IIT 1981]
16. Give reasons for the following in one or two sentences :
 (i) Methane does not react with chlorine in the dark.
 (ii) Propene reacts with HBr to give isopropyl bromide but does not give n-propyl bromide. [IIT 1983]
17. The terminal carbon atom in 2-butene is hybridised. [IIT 1985]
18. Write the balanced chemical equation for the following "Ethylene glycol is obtained by the reaction of ethylene with potassium permanganate." [IIT 1991]
19. Write down the structures of the stereoisomers formed when cis-2-butene is reacted with bromine. [IIT 1995]
20. An organic compound E(C₅H₈) on hydrogenation gives compound F(C₅H₁₂). Compound E on ozonolysis gives formaldehyde and 2-ketopropanal. Deduce the structure of compound E. [IIT 1995]
21. One mole of the compound A (molecular formula C₈H₁₂), incapable of showing stereoisomerism, reacts with only one mole of H₂ on hydrogenation over Pd. A undergoes ozonolysis to give a symmetrical diketone B (C₈H₁₂O₂). What are the structure of A and B? [IIT 1997]
22. The central carbon-carbon bond in 1, 3-butadiene is shorter than that of n-butane. Why? [IIT 1998]
23. CH₂=CH⁻ is more basic than HC≡C⁻ [IIT 2000]



25. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is : [IIT 2011]
26. The maximum number of isomers (including stereoisomers) that are possible on monochlorination of the following compound is [IIT 2011]



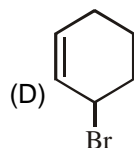
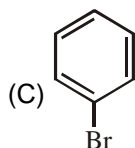
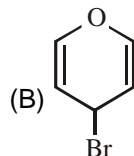
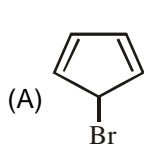
27. The number of resonance structures for N is [IIT Advanced 2015]

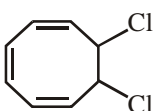


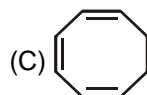
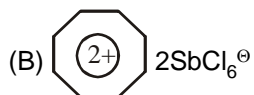
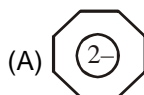
ARYL HALIDE

EXERCISE-V

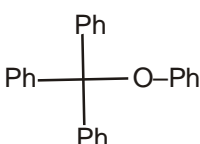
1. Ease of ionization to produce carbocation and bromide ion under the treatment of Ag^+ will be maximum in ?

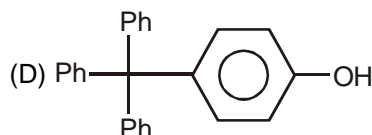
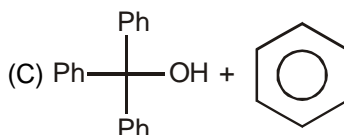
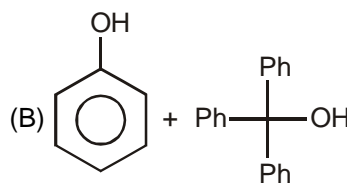
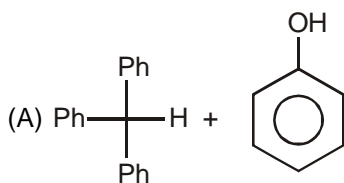


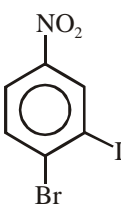
2.  $\xrightarrow{2\text{SbCl}_5}$ P ; P will be

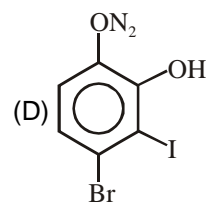
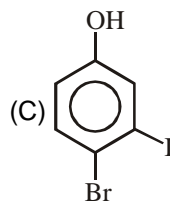
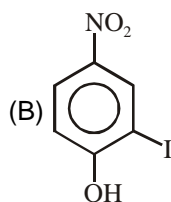
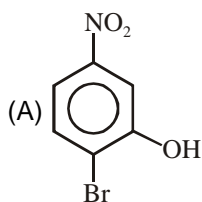


(D) mixture of (A) and (B)

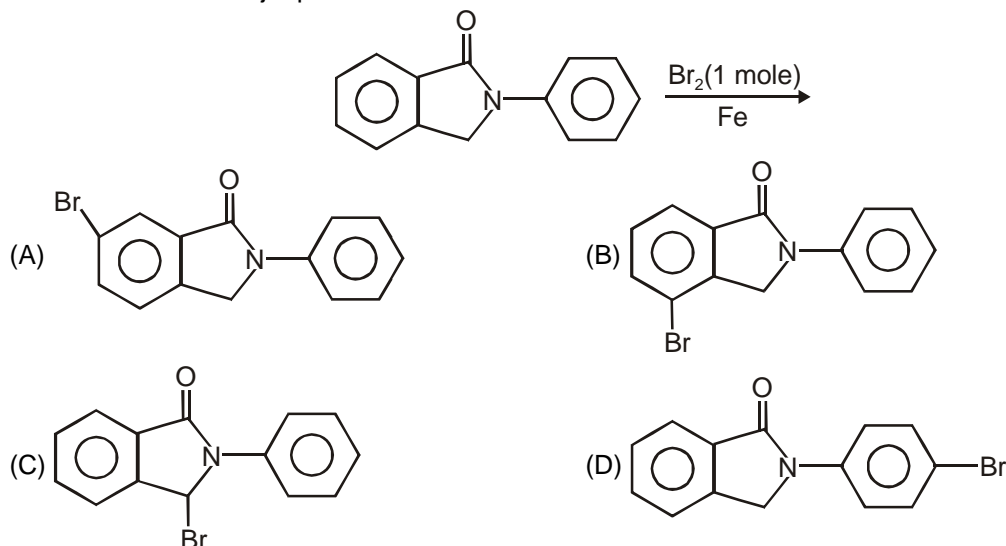
3.  $\xrightarrow{\text{HBF}_4}$ Product of this reaction is :



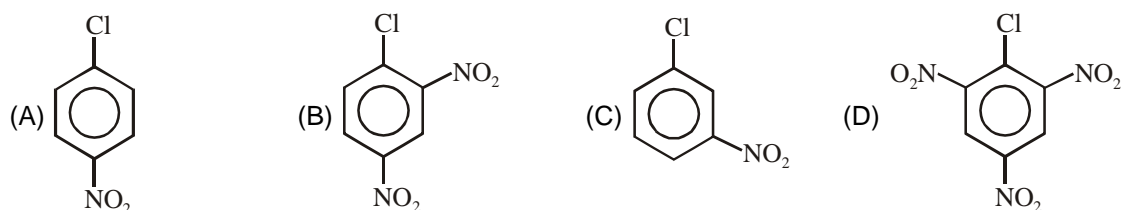
4.  $\xrightarrow[(2) \text{H}_3\text{O}^+]{(1) \text{NaOH}, \Delta}$ (A) , Product (A) is



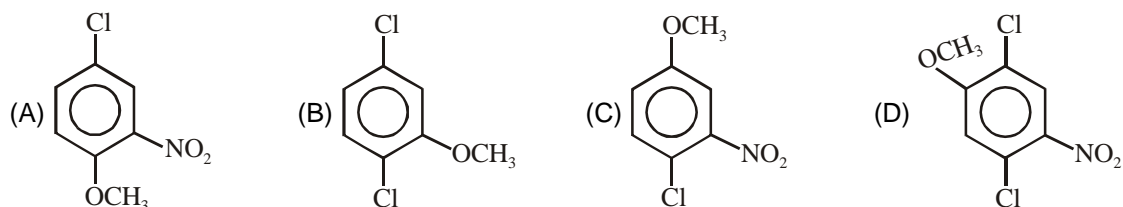
5. In the reaction the major product formed is :



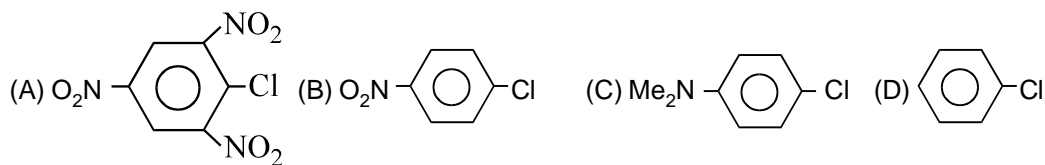
6. Which of the following is most reactive toward $\text{S}_{\text{N}}\text{Ar}$.



7. $\xrightarrow[\Delta]{\text{HNO}_3}$ (A) $\xrightarrow[\Delta]{\text{CH}_3\text{ONa}}$ (B) (Major) , Product (B) is



8. Which chloroderivative of benzene among the following would undergo-hydrolysis most readily with aq. NaOH to furnish the corresponding hydroxy derivative.

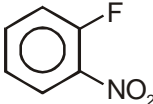


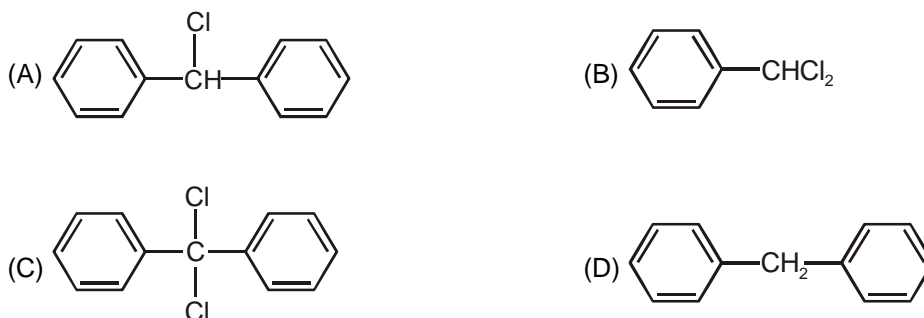
9. Chloral + $\xrightarrow{\text{Conc. H}_2\text{SO}_4}$ product. The product is:



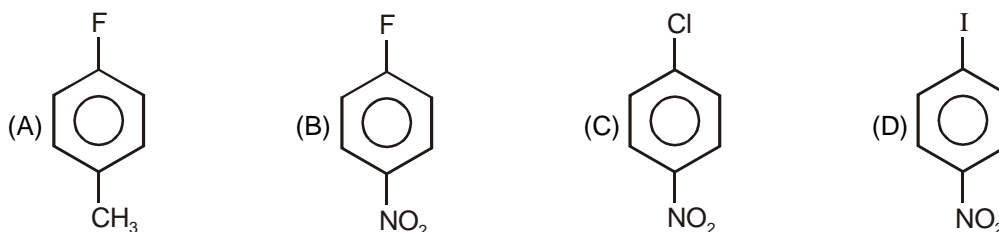
10. + $\text{H}_2 \xrightarrow[\text{high pressure}]{\text{Ni, high temp.}}$ (A). Which of the following can be isolated as the product of this reaction.

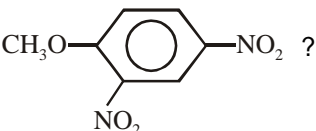


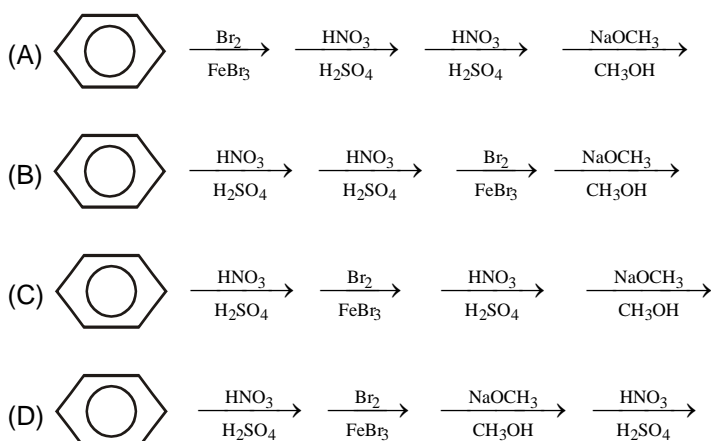
11.  Above compound undergoes
- (A) SN_1 (B) SN_2 (C) Elimination (D) Nucleophilic aromatic substitution
12. In a reaction of $\text{C}_6\text{H}_5\text{Y}$, the major product (>60%) is m-isomer, so the group Y is:
- (A) $-\text{COOH}$ (B) $-\text{Cl}$ (C) $-\text{OH}$ (D) $-\text{NH}_2$
13. Which of the following structures correspond to the product expected, when excess of C_6H_6 reacts with CH_2Cl_2 in presence of anhydrous AlCl_3 ?



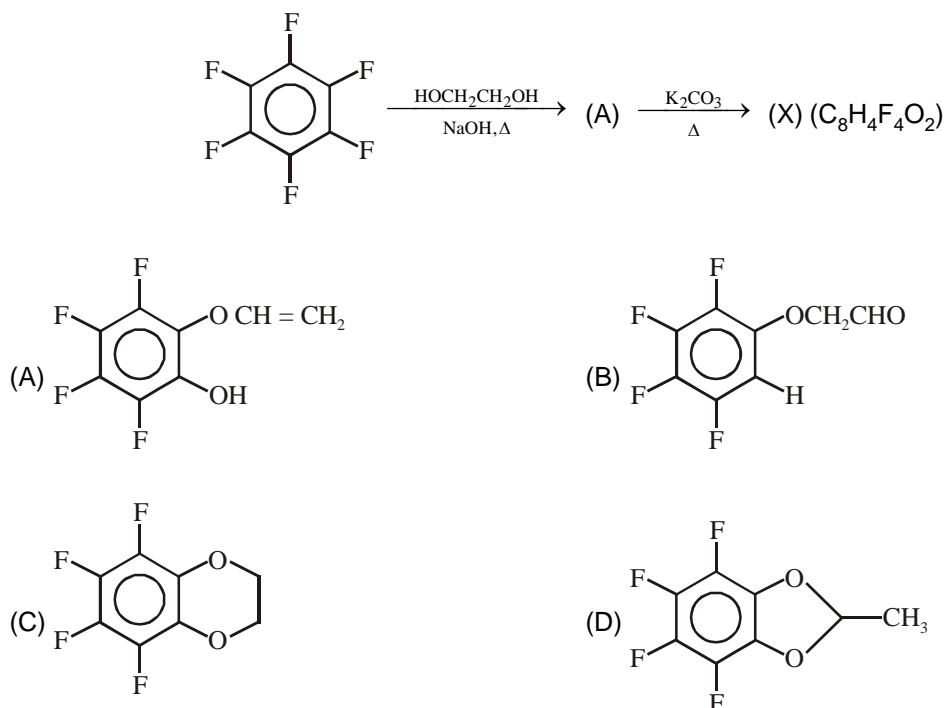
14. Which of most reactive towards nucleophilic aromatic substitution.



15. Which is the best synthesis of  ?



16. The cumulative effect of their fluorine activate the rings of penta and hexa fluorobenzene toward nucleophilic aromatic substitution. What is compound X in the following synthesis ?



17. **Statement-1** : Nitro benzene reacts with $\text{Me}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$, AlCl_3 to produce m-nitroacetophenone. .

Statement-2 : NO_2 group attached to the ring is a meta directing during S_{E} .

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.

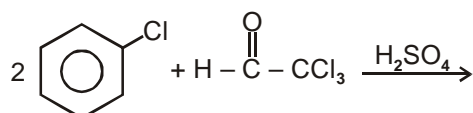
18. The reaction of toluene with Cl_2 in presence of FeCl_3 gives predominantly
 (A) benzoyl chloride (B) benzyl chloride
 (C) o- and p-chlorotoluene (D) m-chlorotoluene

[AIEEE-2007]

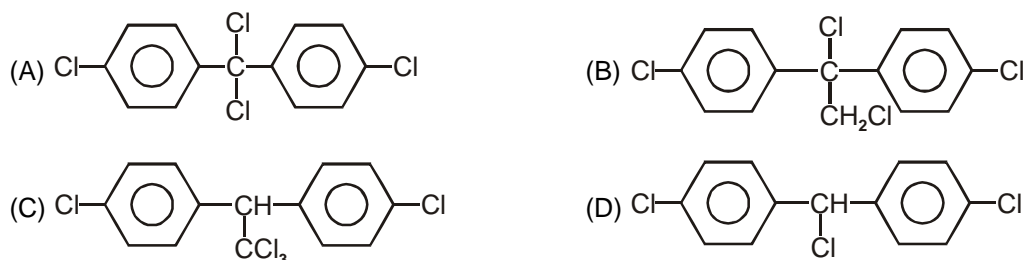
19. Presence of a nitro group in a benzene ring
 (A) activates the ring towards electrophilic substitution
 (B) renders the ring basic
 (C) deactivates the ring towards nucleophilic substitution
 (D) deactivates the ring towards electrophilic substitution

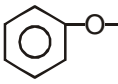
[AIEEE-2007]

20. Chlorobenzene reacts with trichloro acetaldehyde in the presence of H_2SO_4 [IIT-JEE Mains (Online)2014]



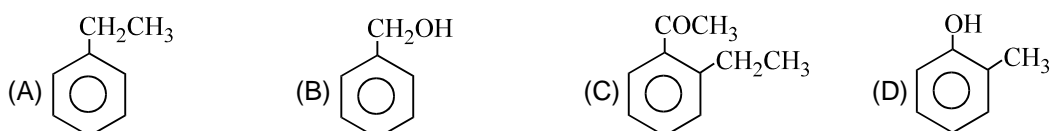
The major product formed is :




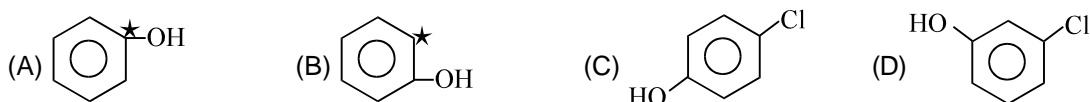
21. Which one of the following substituents at para-position is most effective in stabilizing the phenoxide ion ? 
- [IIT-JEE Mains (Online)2014]**
- (A) $-\text{CH}_3$ (B) $-\text{OCH}_3$ (C) $-\text{COCH}_3$ (D) $-\text{CH}_2\text{OH}$

22. Which one of the following compounds will not be soluble in sodium bicarbonate ?
- (A) 2,4,6- Trinitrophenol (B) Benzoic acid **[IIT-JEE Mains (Online)2014]**
(C) o-Nitrophenol (D) Benzene sulphonic acid

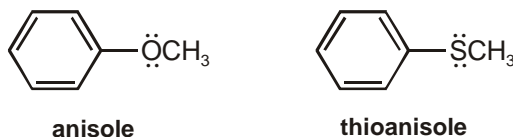
23. Benzoic acid may be prepared by the oxidation of:



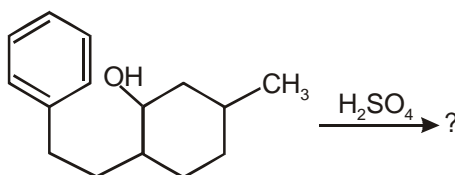
24.  $\xrightarrow[395^\circ\text{C}]{\text{NaOH } \text{H}_2\text{O}}$ Product is:



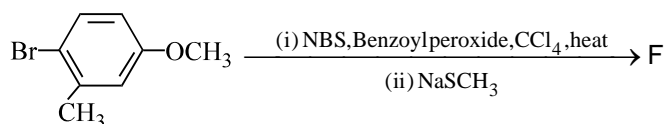
25. Explain why the nitration of anisole is much faster than the nitration of thioanisole under the same conditions.

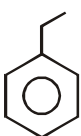


26. When the following compound is treated with H_2SO_4 , the product of the resulting reaction has the formula $\text{C}_{15}\text{H}_{20}$ and does not decolorize Br_2 in CCl_4 . Suggest a structure for this product and give a curved-arrow mechanism for its formation.



27. Write the principal organic product in each of the following reactions:

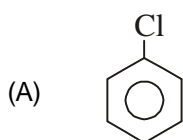


28.  $\xrightarrow{\text{Cl}_2 / \text{AlCl}_3}$ (A)
 $\xrightarrow{\text{Cl}_2 / h\nu}$ (B) Product (A) and (B) is

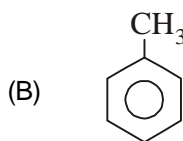
29.

Column I

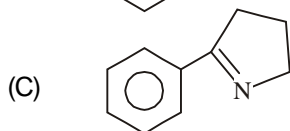
Column II



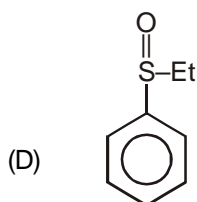
(P) Group attached to benzene ring is a +M group here.



(Q) Group attached to benzene ring is a -M group here.

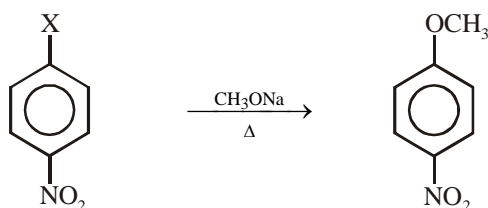


(R) Electrophile would attack on ortho or para position.



(S) Rate of electrophilic substitution is less than that of benzene.

30. Match the column :



X = halogen

relative reactivity toward (S_NAr).

(A) - F

(P) 312

(B) - Cl

(Q) 1

(C) - Br

(R) 0.8

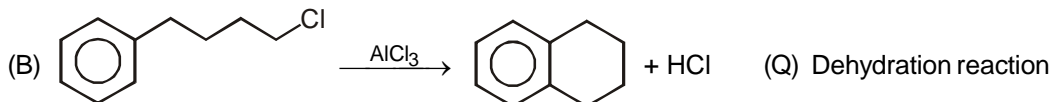
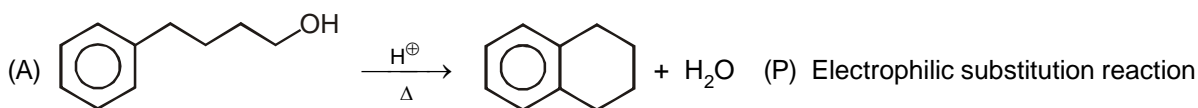
(D) - I

(S) -1

31.

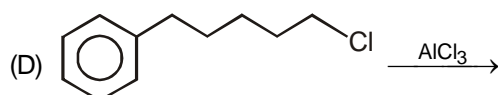
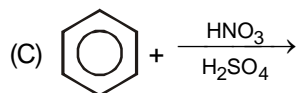
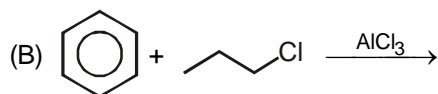
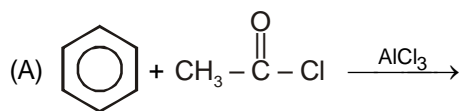
Column-I

Column-II



(T) Elimination reaction

32. Column-I



Column-II

(P) Electrophilic aromatic substitution

(Q) Carbocation intermediate

(R) Rearrangement takes place

(S) Carbanion intermediate

33. Among the following, the compound that can be most readily sulphonated is [JEE 1982]

- (A) Benzene (B) Nitrobenzene (C) Toluene (D) Chlorobenzene

34. Arrange in order of decreasing trend towards S_E reactions: [JEE 1995]

- (I) Chlorobenzene (II) Benzene (III) Anilinium chloride (IV) Toluene
 (A) II > I > III > IV (B) III > I > II > IV (C) IV > II > I > III (D) I > II > III > IV

35. **Statement-1** : p-Hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid.

Statement-2 : o-Hydroxybenzoic acid has intramolecular hydrogen bonding.

- (A) STATEMENT-1 is True, STATEMENT-2 is True ; STATEMENT-2 is a correct explanation for STATEMENT-1
 (B) STATEMENT-1 is True, STATEMENT-2 is True ; STATEMENT-2 is NOT a correct explanation for STATEMENT-1

(C) STATEMENT-1 is True, STATEMENT-2 is False

(D) STATEMENT-1 is False, STATEMENT-2 is True

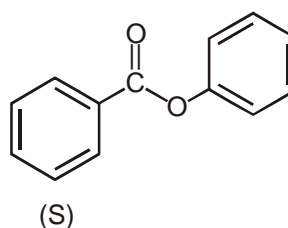
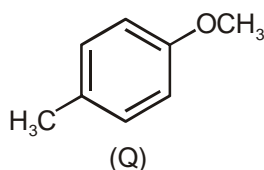
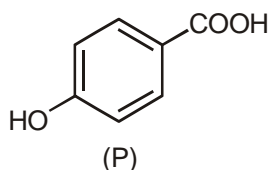
[JEE 2007]

36. **Statement-1** : Bromobenzene upon reaction with Br_2 / Fe gives 1, 4-dibromobenzene as the major product.

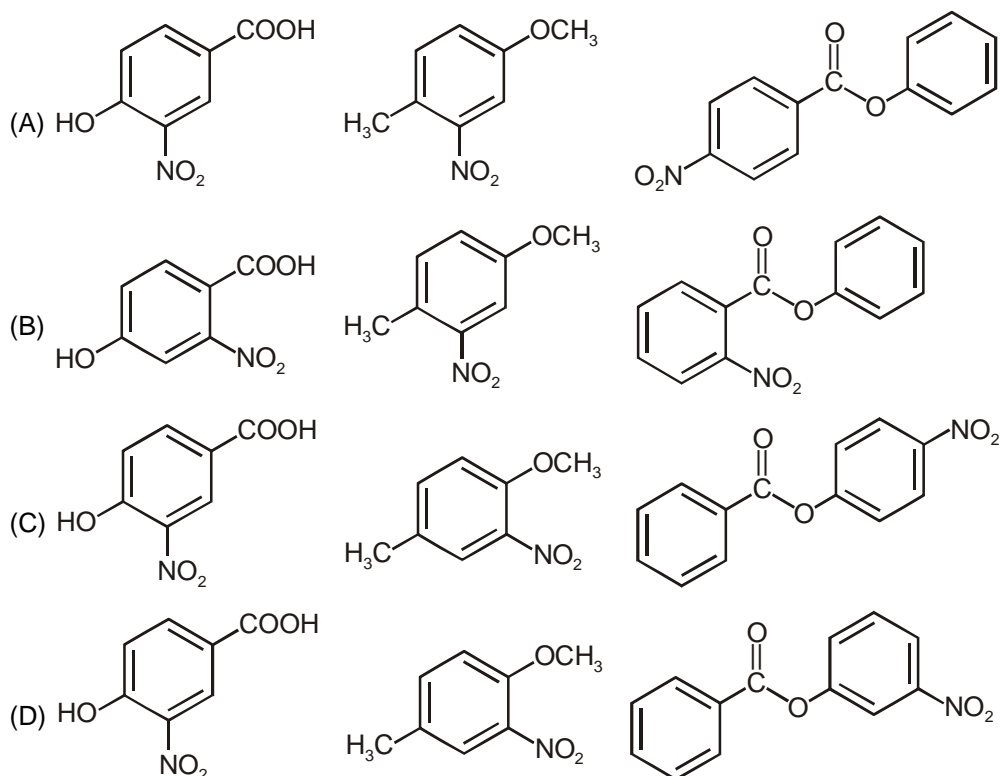
Statement-2 : In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile.

- (A) Statement-1 is true, Statement-2 is true and Statement-2 is correct explanation for Statement-1
 (B) Statement-1 is true, Statement-2 is true and Statement-2 is **NOT** the correct explanation for Statement-1
 (C) Statement-1 is true, Statement-2 is false
 (D) Statement-1 is false, Statement-2 is true

37. The compounds P, Q and S [JEE 2010]



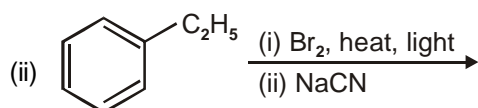
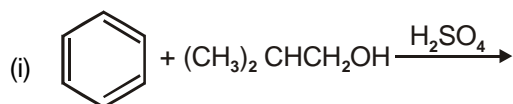
were separately subjected to nitration using $\text{HNO}_3 / \text{H}_2\text{SO}_4$ mixture. The major product formed in each case respectively, is



38. Write down the reaction involved in the preparation of following using the reagents indicated against in parenthesis. "Ethyl benzene from benzene." $[C_2H_5OH, PCl_5, \text{anhyd. } AlCl_3]$ [JEE 1984]

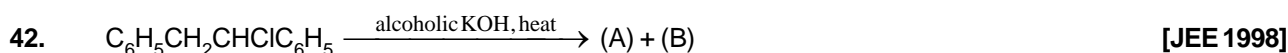


40. Predict the major product in the following reactions [JEE 1994]



41. Show the steps to carry out the following transformations: [JEE 1998]

- (a) Ethylbenzene \longrightarrow benzene
(b) Ethylbenzene \longrightarrow 2-phenylpropionic acid



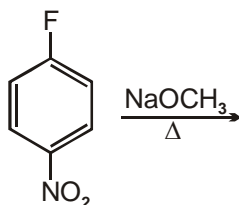
43. Give reasons for the following in one or two sentences [JEE 1998]

"Nitrobenzene does not undergo Friedel-Crafts alkylation."

44. Explain, why o-hydroxy benzaldehyde is a liquid at room temperature while p-hydroxy benzaldehyde is a high melting solid ? [JEE 1999]

45. What would be the major product in the following reaction ?

[JEE 2000]



46. Give reasons for the following :

- tert-butylbenzene does not give benzoic acid on treatment with acidic KMnO_4 .
- Normally, benzene gives electrophilic substitution reaction rather than electrophilic addition reaction although it has double bond.

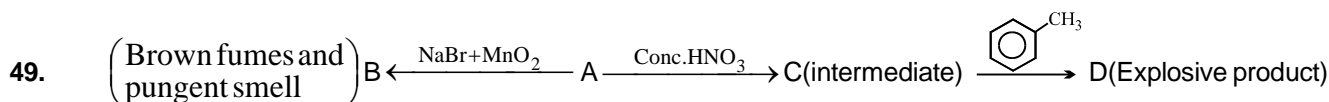
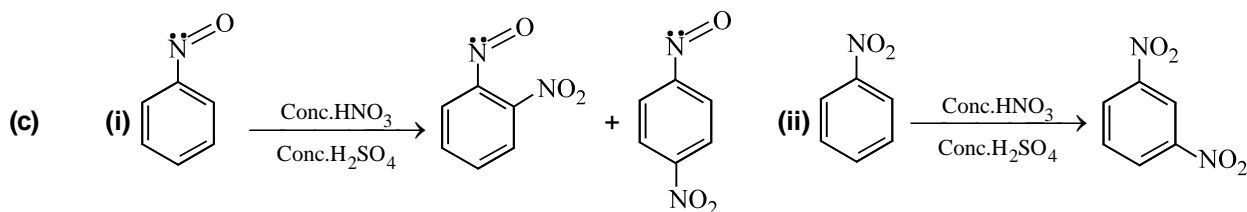
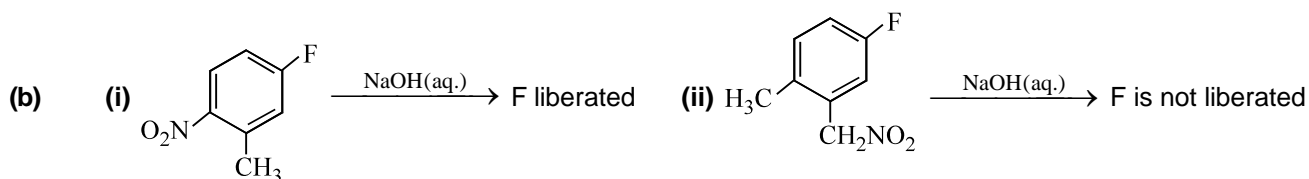
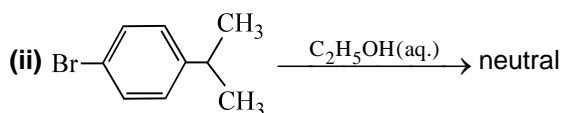
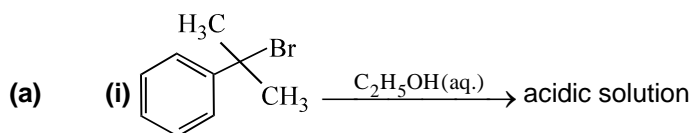
[JEE 2000]

47. A compound $\text{C}_9\text{H}_7\text{O}_2\text{Cl}$ exists in keto form A and enolic form B. Enolic form B predominates at equilibrium. On oxidation with KMnO_4 gives m-chlorobenzoic acid gives structures of A and B.

[JEE 2003]

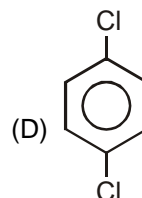
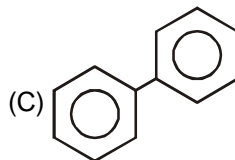
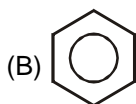
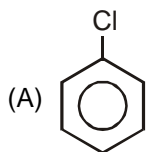
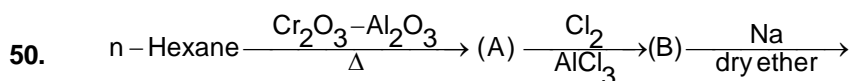
48. Give reasons:

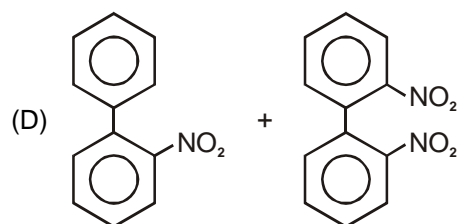
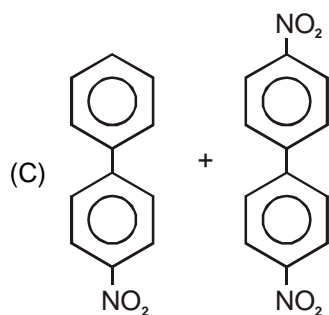
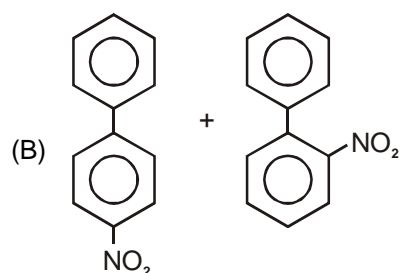
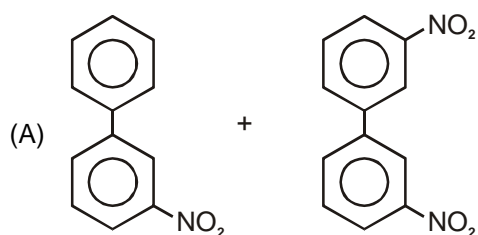
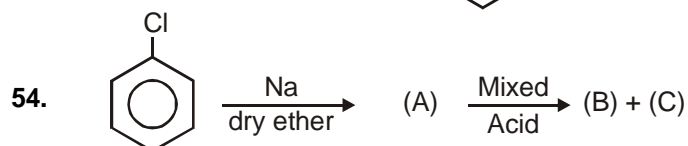
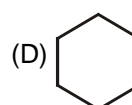
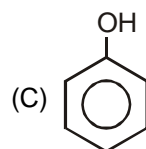
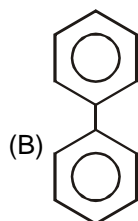
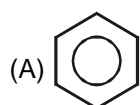
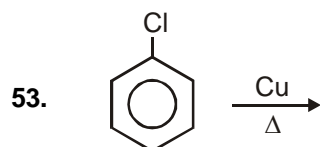
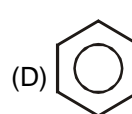
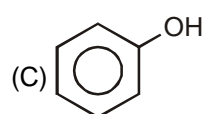
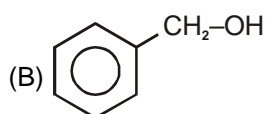
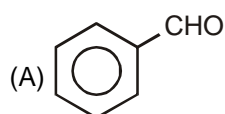
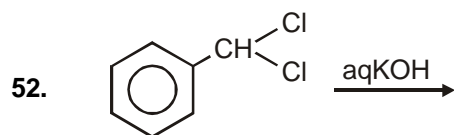
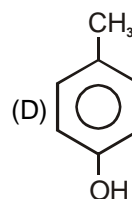
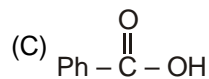
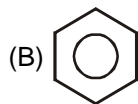
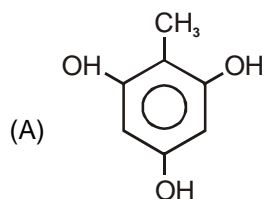
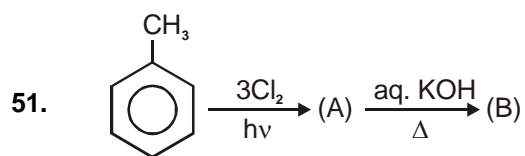
[JEE 2005]

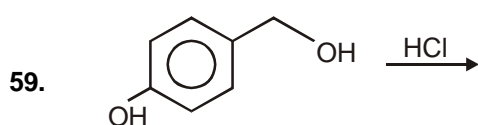
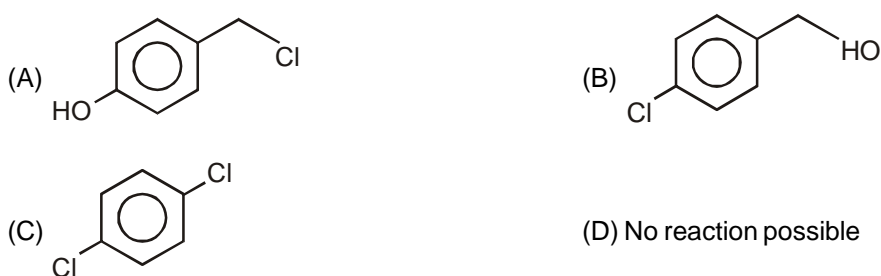
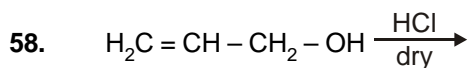
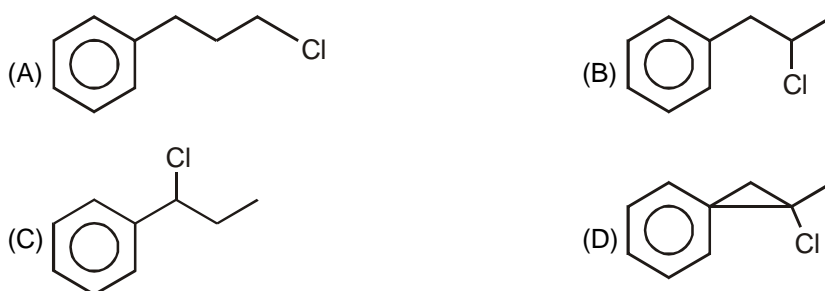
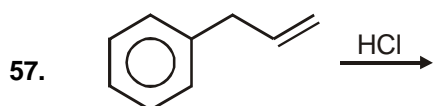
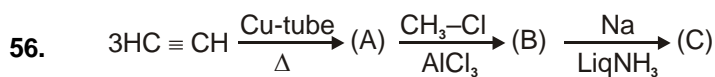
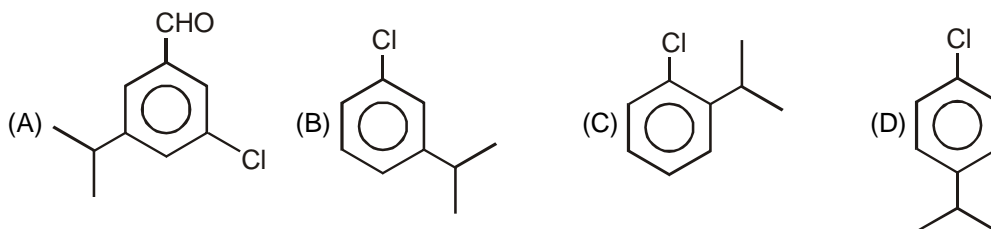
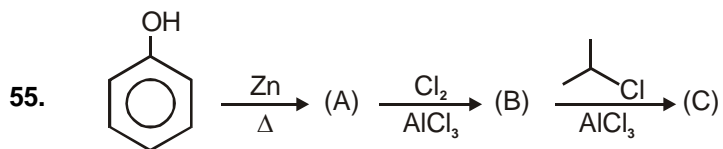


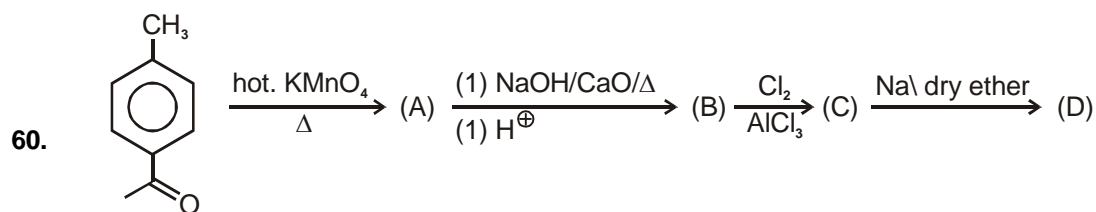
Find A, B, C and D. Also write equations A to B and A to C.

[JEE 2005]

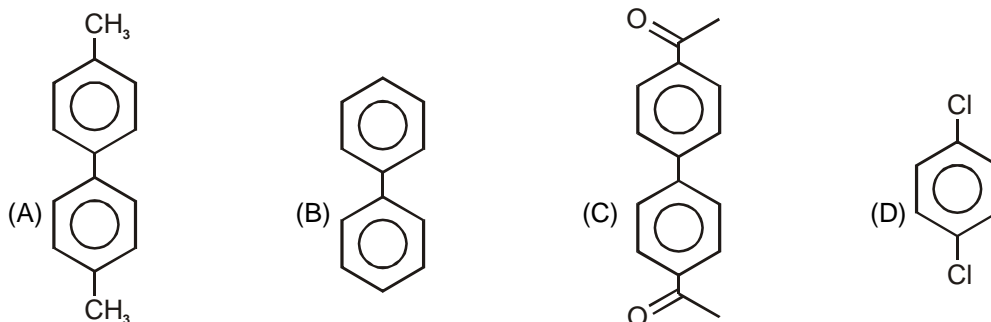








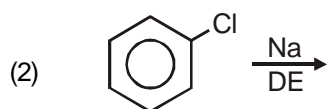
Major product (D) is



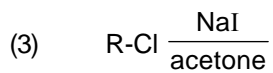
Match the Column



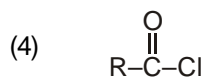
(P) Rosenmund reduction



(Q) Swart reaction



(R) Finkelstein reaction



(S) Fittig reaction

ANSWER KEY

EXERCISE-I

- | | | | | | | |
|-------|-------|-------|-------|-------|-------|-------|
| 1. B | 2. D | 3. A | 4. D | 5. A | 6. D | 7. C |
| 8. B | 9. C | 10. C | 11. A | 12. C | 13. D | 14. B |
| 15. B | 16. C | 17. A | 18. D | 19. C | 20. B | 21. A |
| 22. D | 23. A | 24. D | 25. C | 26. B | 27. A | 28. C |
| 29. B | 30. C | 31. B | 32. C | 33. C | 34. A | 35. D |
| 36. A | 37. A | 38. B | 39. A | 40. C | 41. A | 42. C |
| 43. A | 44. A | 45. C | 46. A | 47. B | 48. C | 49. A |
| 50. A | 51. D | 52. B | 53. A | 54. D | 55. A | 56. A |
| 57. C | 58. C | 59. B | 60. D | 61. B | 62. C | 63. C |
| 64. D | 65. B | 66. A | 67. D | 68. B | | |

EXERCISE-II

- | | | | | | | |
|------------|---------|------------|-------------|----------------|------|---------|
| 1. A, B, D | 2. B, D | 3. A, B, C | 4. A, B | 5. B, C | 6. B | 7. A, B |
| 8. A | 9. A | 10. B | 11. A, B, C | 12. A, B, C, D | | |

EXERCISE-III

Matching List Type

- | | | | | | |
|------|------|------|-------|--|------|
| 1. C | 2. A | 3. D | 4. C | 5. A | 6. B |
| 7. B | 8. D | 9. C | 10. A | 11. $A \rightarrow P, Y ; B \rightarrow Q, X ; C \rightarrow R, W$ | |

12.

S.No.	SN1	SN2	Both
1		✓	
2			✓
3			✓
4	✓		
5		✓	
6		✓	
7			✓
8	✓		

EXERCISE-IV (A)

PREVIOUS YEAR AIEEE QUESTIONS

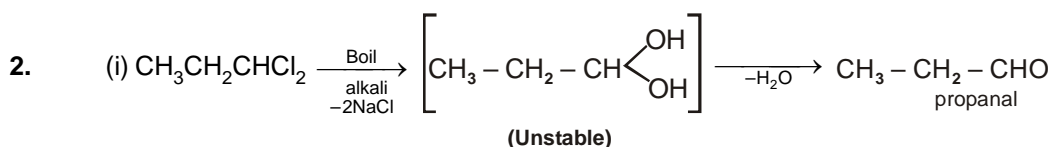
- | | | | | | | |
|-------|-------|-------|-------|-------|-------|-------|
| 1. B | 2. D | 3. B | 4. D | 5. B | 6. A | 7. D |
| 8. D | 9. B | 10. D | 11. B | 12. D | 13. C | 14. C |
| 15. C | 16. D | 17. A | 18. B | 19. B | 20. C | 21. D |
| 22. D | 23. D | 24. B | 25. B | 26. A | 27. C | 28. A |
| 29. C | 30. B | 31. A | 32. D | 33. A | 34. A | 35. B |
| 36. A | 37. A | 38. B | 39. C | 40. B | | |

EXERCISE-IV (B)

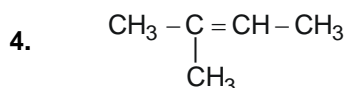
- | | | | | | | |
|-------|--------|---|-------|-------|-------|-------|
| 1. C | 2. D | 3. C | 4. C | 5. A | 6. A | 7. B |
| 8. C | 9. A | 10. C | 11. C | 12. D | 13. D | 14. B |
| 15. B | 16. D | 17. B | 18. A | 19. A | 20. B | 21. B |
| 22. A | 23. B | 24. B | 25. B | 26. D | 27. A | 28. A |
| 29. A | 30. B | 31. A | 32. B | 33. D | 34. A | 35. D |
| 36. D | 37. C | 38. A | 39. B | 40. B | 41. A | 42. C |
| 43. D | 44. AD | 45. A – Q ; B – Q ; C – R, S ; D – P, S | | | | |

EXERCISE-IV (C)

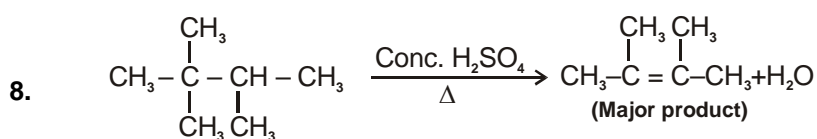
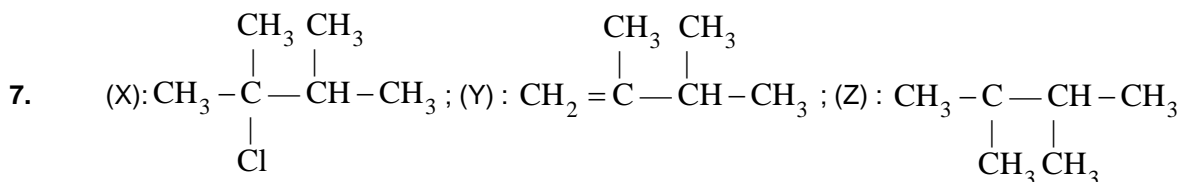
1. Butanol has capacity for inter molecular hydrogen bonding.



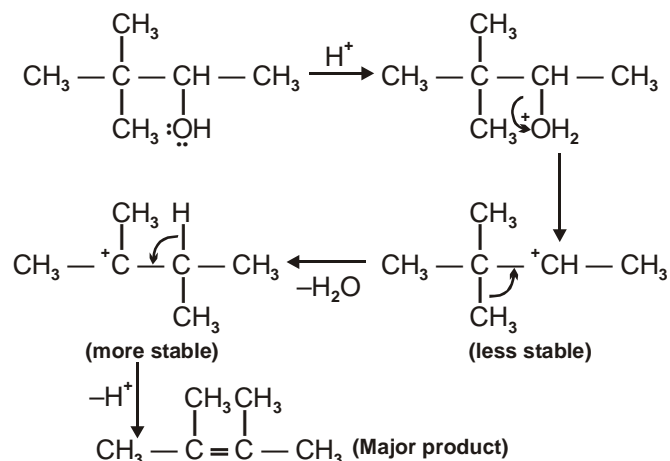
3. (a) propyl chloride, (b) ortho

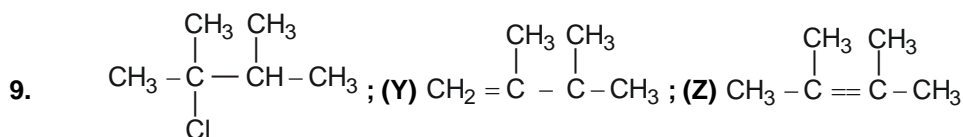


5. Due to the presence of resonance in alkyl halide carbon halogen bond acquires the character of partial double bond and halogen is directly attached to sp^2 hybridised carbon so the halogen is not capable to leave as an leaving group.
6. The product obtained after the reaction contain equal amount of both d and l -isomers of 2-iodobutane and this racemic mixture does not show optical activity due to external compensation.

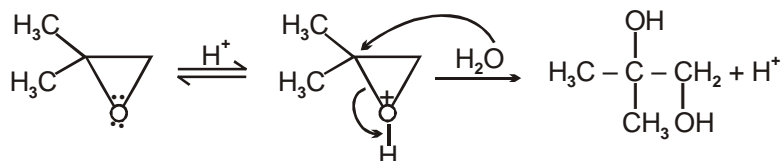


Mechanism of above reaction is represented as follows :

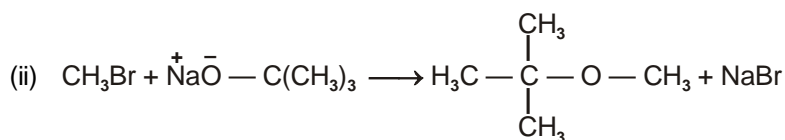
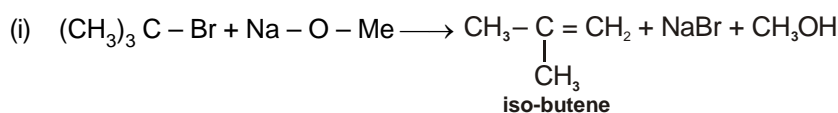




10. The oxirane ring is cleaved by the following mechanism :

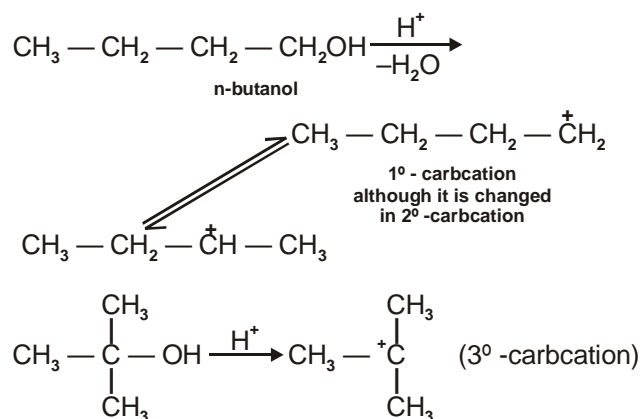


11. In these two methods, method (ii) is the correct method for the formation of ether because in method (i), alkene is formed in place of ether.

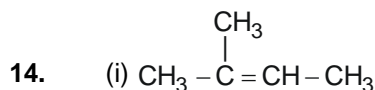


This reaction is called as Williamson's synthesis and it is based upon $\text{S}_{\text{N}}2$ -reaction mechanism.

12. Due to formation of more stable 3° -carbonium ion with t-butanol that 1° -carbonium ion in n-butanol.



13. (a) Cis and trans forms of stilbene $\text{C}_6\text{H}_5\text{CH}=\text{CHC}_6\text{H}_5$; (b) $\text{CH}_3 \text{---} \text{C} \text{---} \text{CH}_3 \longrightarrow \text{CHI} + \text{CH}_3\text{I}$

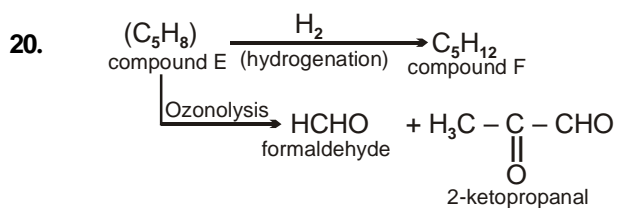
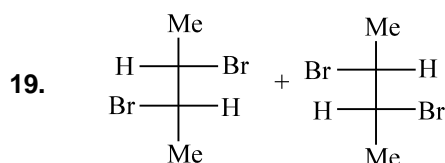
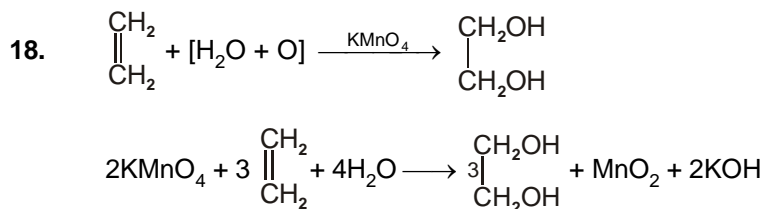


15. Ethyne

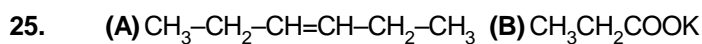
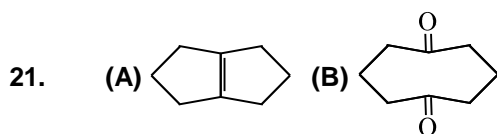
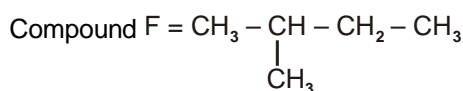
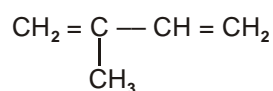
16. (i) Methane does not react with chlorine in the dark because chlorine atoms are required for this reaction and chlorine atoms are obtained only in the presence of light.

(ii) It is in accordance with Markownikoff's rule which predicts the stability of secondary carbonium ion over primary carbonium ion.

17. sp^3

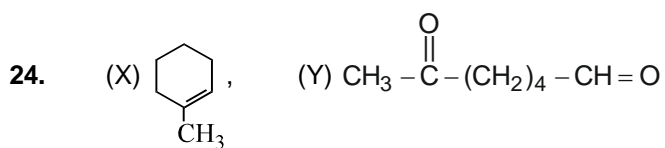


Hence, compound E must be diene.



22. Resonance is present in 1, 3-butadiene that's why every bond acquire the character of partial double bond.

23. higher electronegativity of sp carbon



25. 5

26. 8

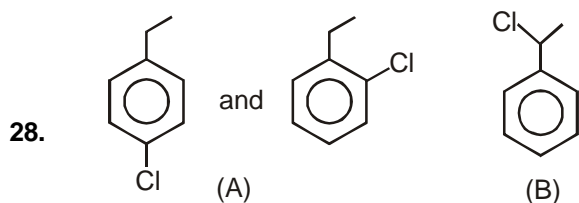
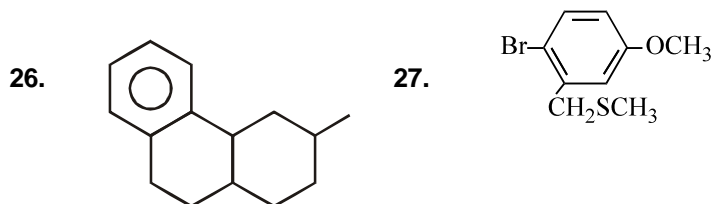
27. 9

ARYL HALIDE

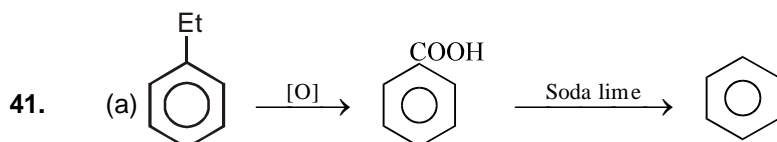
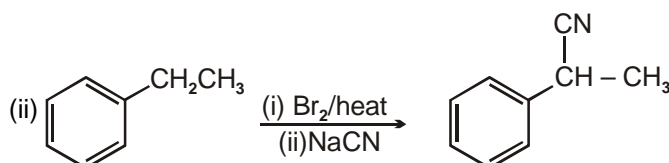
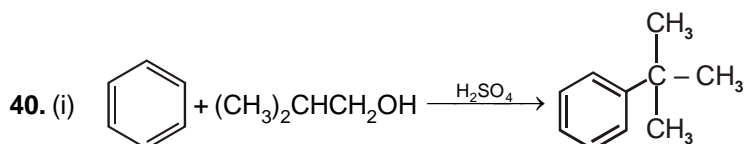
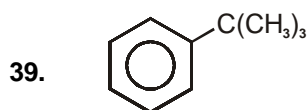
EXERCISE-V

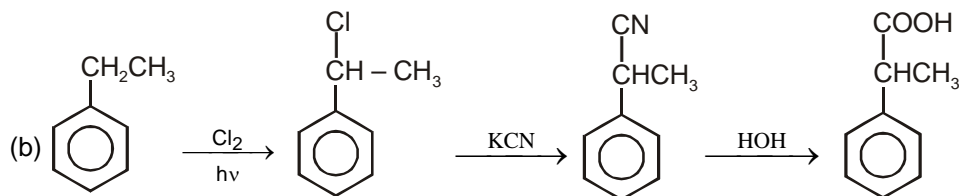
1. B 2. B 3. D 4. B 5. D 6. D 7. A 8. A 9. B 10. A
 11. D 12. A 13. D 14. B 15. A 16. C 17. D 18. C 19. D 20. C
 21. C 22. C 23. A,B 24. A,B

25. Due to effective delocalization of 2p-2p in comparison to 2p-3p, that's why anisole is more reactive towards nitration.



29. $A \rightarrow P, R, S$; $B \rightarrow P, R$; $C \rightarrow Q, S$; $D \rightarrow Q, R, S$
 30. $A \rightarrow P$; $B \rightarrow Q$; $C \rightarrow R$; $D \rightarrow S$
 31. $A - P, Q$; $B - P, R$; $C - S, R$; $D - P$
 32. $A - P, Q$; $B - P, Q, R$; $C - P, Q$; $D - P, Q, R$
 33. C 34. C 35. D 36. C 37. C
 38. $CH_3CH_2OH + PCl_5 \rightarrow POCl_3 + HCl + CH_3CH_2Cl$
 $C_6H_6 + CH_3CH_2Cl \xrightarrow{AlCl_3} C_6H_5-CH_2CH_3$
 Friedel-Crafts reaction

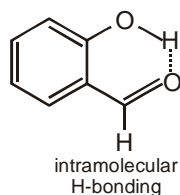




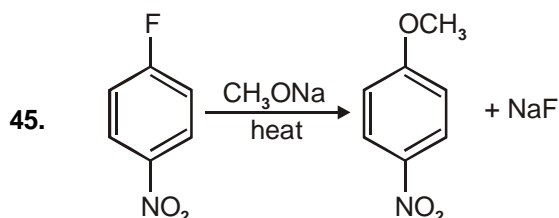
42. $\text{C}_6\text{H}_5\text{CH}=\text{CHC}_6\text{H}_5$
(Cis and trans forms)

43. Nitro group is a very strong deactivating group, the very slow Friedel-Crafts reaction does not take place in presence of nitro group.

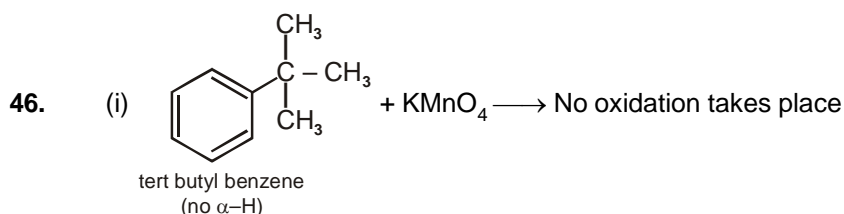
44. Intramolecular H-bonding in ortho hydroxy benzaldehyde is responsible for decrease in melting and boiling points.



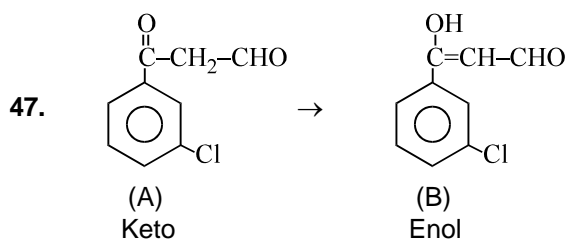
p-hydroxy benzaldehyde molecules are associated by intermolecular H-bonds, has higher melting and boiling points.



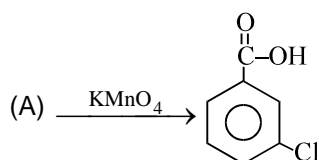
Nucleophilic aromatic substitution occurs which is assisted by electron withdrawing $-\text{NO}_2$ group from para position.

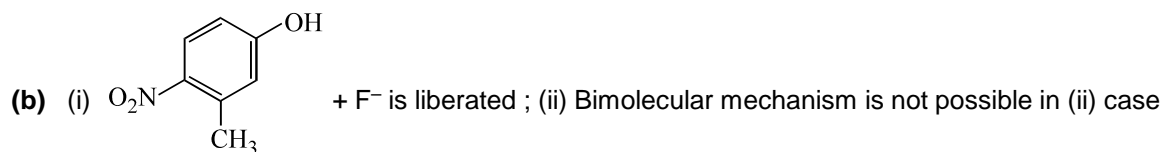
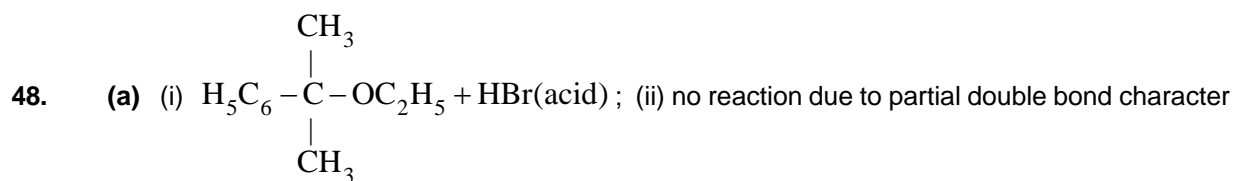


(ii) π -electrons of double bonds are involved in aromatic delocalisation (aromaticity) hence, electrophilic addition does not occur as it would destroy aromatic stability. However, electrophilic substitution does not destroy aromaticity.

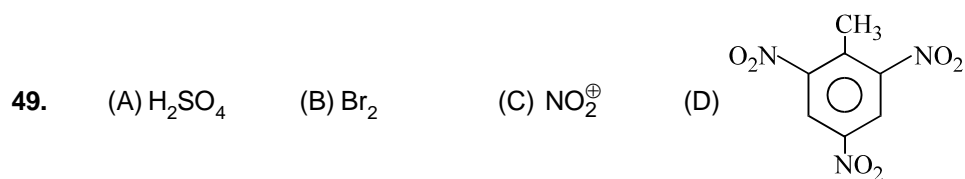


Enol form is more stable due to extended conjugation





- (c) (i) due to presence of lone pair of nitrogen atom NO group is electron denating and ortho, para directing
(ii) NO_2 group is electron withdrawing and meta directing



50. C 51. C 52. A 53. B 54. B 55. D 56. A
57. C 58. A 59. D 60. B 61. (1-Q) (2-S) (3-R) (4-P)