CHAPTER 1

Haloalkanes and Haloarenes

INTRODUCTION

- ✦ Haloalkanes and haloarenes are organic compounds in which halogen atom is directly linked with carbon atom.
- ✦ Haloalkanes are also called as alkyl halides.
- ✦ General formula of haloalkanes is $C_nH_{2n+1}X$, (X = F, Br, Cl, I).
- ✦ The carbon that bears functional group (halogen atom) is sp^3 hybridised in alkyl halides.
- ✦ In these compounds, geometry of carbon is tetrahedral.
- ✦ Central carbon atom has a bond angle of 109°28′.
- ✦ On the basis of number of halogen atom(s), haloalkanes are of following types:
  - (i) Monohalides – They possess only one halogen atom; e.g., CH_3Cl, CH_3CH_2Br, etc.
  - (ii) Dihalides – They possess two halogen atoms. These are of following three types: geminal dihalide, vicinal dihalide, and α, ω or terminal dihalide.
  - (iii) Trihalides – They possess three halogen atoms; e.g., $CHCl_3$, CHI_3, etc.
  - (iv) Tetrahalides – They possess four halogen atoms; e.g., CCl_4, etc.
- ✦ Alkyl halide shows chain and position isomerism. If unsymmetrical or chiral carbon is present, then it shows optical isomerism also.
- ✦ Alkyl halides do not show functional isomerism, metamerism, tautomerism, and geometrical isomerism.

PHYSICAL PROPERTIES HALOAIKANES

- Alkyl halides are colourless with sweet smell or pleasant smelling oily liquid. However, CH_3F, CH_3Cl, CH_3Br, CH_3CH_2F, CH_3CH_2Cl are gaseous in nature.
- Although carbon–halogen bond is polar in nature, alkyl halides are partially soluble in H_2O.
- Alkyl halides are completely soluble in organic solvents.
- Boiling point $\propto$ molecular weight

$$\propto \frac{1}{\text{branching (for isomers)}}$$

- Chloroform is colourless and pleasant smelling liquid while iodoform is yellow crystalline solid.
- Chloroform is used as an anaesthetic agent.
- Iodoform is more reactive than chloroform due to large size of iodine atom.

$$CHI_3 + AgNO_3 \rightarrow AgI \text{ (yellow ppt)}$$

$CHCl_3 + AgNO_3 \rightarrow$ No white ppt of AgCl

- Carbon tetrachloride is colourless liquid and used as **FIRE EXTINGUISHER** under the trade name **PYRENE**.
- Chloroform is kept in dark coloured bottles to avoid the following oxidation reaction.

$$CHCl_3 \xrightarrow[\text{air and light}]{[O]} \underset{\text{(Poisonous)}}{COCl_2} \quad \text{(Phosgene)} + HCl$$

- **Test of Chloroform (Before Anaesthetic use):**

Serial Number	Test	Pure $CHCl_3$	$[COCl_2 + HCl]$
(i)	Litmus paper	Blue $\rightarrow$ Blue	Blue $\rightarrow$ Red
(ii)	$AgNO_3$	No ppt	While ppt (AgCl)
(iii)	H_2SO_4	No colouration	Yellow colour

- Polarity order is RF > RCl > RBr > RI
- Reactivity order is RI > RBr > RCl > RF
- For same halide group, the reactivity order is 3° halide > 2° halide > 1° halide
- Fluorides and chlorides are lighter than water whereas bromides and iodides are heavier than H_2O due to more density of bromine than oxygen. CH_2I_2 is heavier liquid after Hg.
- All haloalkanes burn on copper wire with green flame (**BELESTEIN TEST** for halogens)

ALIPHATIC NUCLEOPHILIC SUBSTITUTION

If a substitution reaction is brought about by a nucleophile then it is known as nucleophilic substitution reaction. A general nucleophilic substitution reaction may be represented as:

$$R\text{–}L + \overset{\ominus}{Nu} \longrightarrow R\text{–}Nu + \overset{\ominus}{L}$$

where L is a leaving group and $\overset{\ominus}{Nu}$ is an incoming nucleophile.

In nucleophilic substitution two changes occur:

(i) breaking of the bond with leaving group

(ii) formation of bond with nucleophile

The principal mechanistic variations are associated with changes in the timing of the two processes.

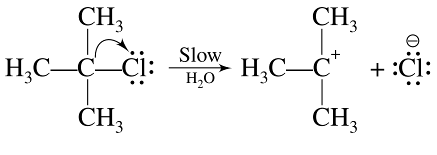
Depending on nucleophiles, substrates, leaving groups and reaction conditions, several mechanisms are possible but the most common are S_N1 and S_N2 mechanisms.

S_N1 Mechanism or S_N1 Reaction

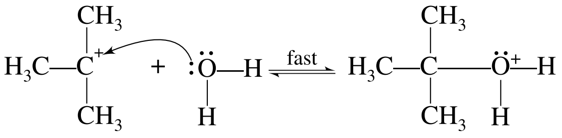
The mechanisms for the reaction of tert-butyl chloride with water are given below:

$(CH_3)_3\,CCl + 2\,H_2O \rightarrow (CH_3)_3\,COH + H_3O^+ + Cl^-$

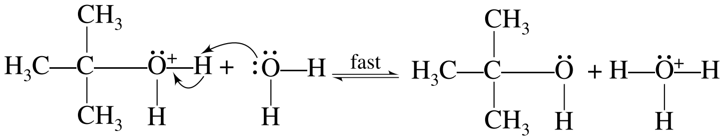
Step 1



Step 2



Step 3



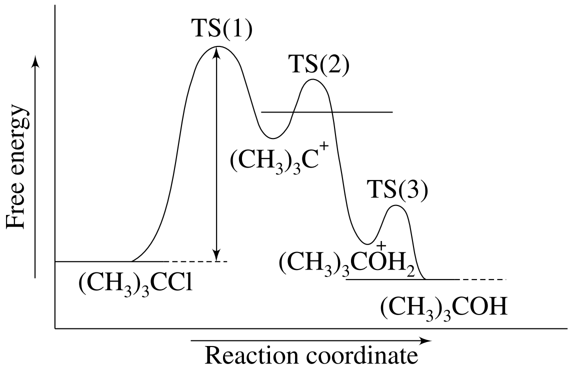
Main characteristics:

(1) The S_N1 mechanism is mostly two-step process.

(2) The first step is a slow ionisation to form carbocation and thus rearrangement into stable carbocation accompanied frequently.

(3) The second step is a fast attack on the carbocation by the nucleophile. The carbocation being a very strong electrophile reacts very fast with both strong and weak nucleophiles.

(4) **Energy profile diagram**



(5) **Kinetics**

The S_N1 reaction is first order reaction which follows the rate law given below:

Rate = K [Substrate]

So that nucleophile plays no role in the mechanism.

(6) **Effect of substrate structure:**

The more stable the carbocation intermediate, the faster the S_N1 mechanism.

The following is the decreasing order of reactivity of some substrates in S_N1 reaction:

$Ar_3CX > Ar_2CHX > R_3CX > ArCH_2X > CH_2 = CH–CH_2–X > R_2CHX > RCH_2X$

(a) S_N1 reactions are highly favoured if there is a heteroatom at the α-carbon because it highly stabilises the carbocation formed.

(b) Substrate containing carbonyl group on β-carbon does not gives S_N1 reaction because carbonyl group has very strong–I effect which destabilises the carbocation reaction intermediate.

(c) The greater the crowding around the carbon having leaving group, the greater is the possibility of S_N1 reaction.

For some tertiary substrates the rate of S_N1 reactions is greatly increased if the β-carbon is highly substituted.

(7) **Effects of solvent:** Polar solvents accelerate the S_N1 reaction because it favours the formation of polar transition state.

(8) **Effect of leaving group:** Weaker bases are good leaving groups and thus favour S_N1 mechanism. Thus the reactivity order among the halide ions is:

$I^- > Br^- > Cl^- > F^-$

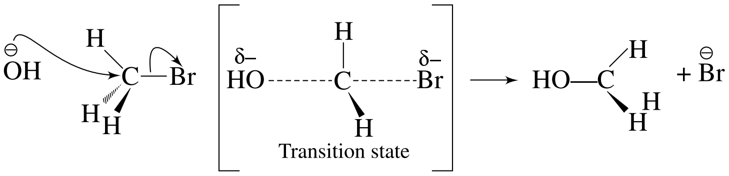
(9) **Effect of attacking nucleophile:** Since the rate determining step of S_N1 reaction does not involve the incoming nucleophile, and neither its nucleophilicity nor its concentration has any effect on the rate of the reaction, so an S_N1 reaction can proceed with weak nucleophiles of low concentration.

(10) **Stereochemistry:** The S_N1 reaction on a chiral starting material ends up with the racemisation of the product (enantiomers) because the carbocation formed in the first step of an S_N1 reaction has a trigonal planar structure, when it react with nucleophile, it may do so form either front side or back side.

S_N2 Mechanism or S_N2 Reaction:

A typical example of this process is the hydrolysis of methyl bromide in the presence of NaOH.

$$CH_3\text{–}Br + NaOH \longrightarrow CH_3\text{–}OH + NaBr$$



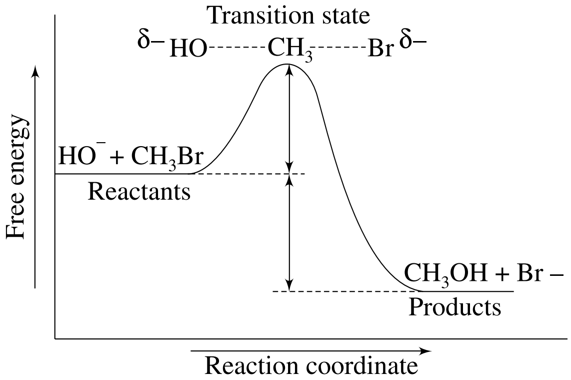
Main characteristics:

(1) S_N2 mechanism is a one-step (concerted) process.

(2) There is no intermediate, only transition state is formed.

(3) The conversion of reactants to transition state is the rate determining step.

(4) **Energy profile diagram**



(5) **Kinetics:** The S_N2 reaction is a second order reaction that follows the rate law given below:

Rate = K [Substrate] [Nucleophile]

(6) **Effect of substrate structure:** The rate of reaction depends on the steric bulk of the alkyl group. Kinetic studies have shown that the methyl halides are the most reactive in S_N2 reactions. The increase in the length of chain of alkyl group decreases the rate of reaction. Alkyl branching next to the leaving group decreases the rate drastically. The reactivity order for S_N2 reactions follows the following order.

$CH_3 > 1° > 2° >> \text{neopentyl} > 3°$

(7) **Effects of solvent:** Aprotic solvents increase the rate of S_N2 reactions.

(8) **Effect of leaving group:** Weaker bases are good leaving groups and thus favour S_N2 mechanism. Thus the reactivity order among the halide ions is:

$I^- > Br^- > Cl^- > F^-$

(9) **Effect of attacking nucleophile:** Since the single step S_N2 reaction involves the substrate and the nucleophile, the rate of the reaction depends on largely on the concentration of nucleophile and its nucleophilicity. Strong nucleophiles increases the rate of the S_N2 reaction while weak nucleophiles decrease it.

(10) **Stereochemistry:** S_N2 reaction involves the inversion of stereochemistry around carbon atom of the substrate. This inversion is known as Walden inversion because in this reaction the nucleophile attaches the substrate from the just opposite (back) side (at 180°) to the leaving group.

Summary of structural variations and nucleophilic substitution:

We are now in position to summarise structural variation for S_N1 and S_N2 reaction in ordinary condition:

Substrate		S_N1 reaction	S_N2 reaction
1.	$CH_3–X$	no	very good
2.	$R–CH_2–X$	no	good
3.	$R_2CH–X$	yes	yes
4.	$R_3C–X$	very good	no
5.	$CH_2=CH–CH_2–X$	yes	good
6.	$Ar–CH_2–X$	yes	good
7.	$R–CO–CH_2–X$	no	excellent
8.	$R–O–CH_2–X$	excellent	good
9.	$R_2N–CH_2–X$	excellent	good
10	$CH_2=CH-X/Ar–X$	no	no

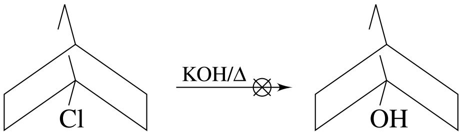
No substitutions at bridgehead carbons:

S_N1 reactions proceed through carbocation which must be planar. Because of rigid like structures of the substrate, bridgehead carbon atoms cannot assume planarity. Hence, heterolysis leading to the formation of carbocation is also prevented.

S_N2 reaction proceed through backside attack by the nucleophile, inversion of configuration and coplanarity of the nonreacting groups in the TS all of which are prevented at the bridgehead carbons due to rigid cage like structures of the compounds containing the bridgehead carbons.

Thus bridgehead carbons are resistant towards substitution by the SN1 and SN2 mechanism.

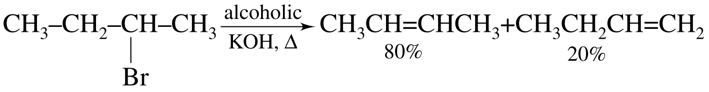
For example:



(No reaction)

Elimination Reaction:

In the presence of alcoholic KOH and heating, elimination reaction occurs resulting into a double bond. If more than one product is possible, the major product is of more substituted alkene (Saytzeff rule).



$$CH_3–CH_2–\underset{\underset{Br}{|}}{CH}–CH_3 \xrightarrow[KOH,\ \Delta]{alcoholic} \underset{80\%}{CH_3CH=CHCH_3} + \underset{20\%}{CH_3CH_2CH=CH_2}$$

Competition between Substitution and Elimination Reactions:

The relative proportion of products depends on mainly three factors, namely, basicity of the nucleophile, hindrance in the haloalkane, and steric bulk around the nucleophilic atom.

Factor 1: Weak bases (H_2O, ROH, halides, RS^-, N_3^-, NC^-, $RCOO^-$) lead to more substitution.

Strong bases (HO^-, RO^-, H_2N^-, R_2N^-) lead to more elimination.

Factor 2: Steric hindrance around the reacting carbon.

Sterically unhindered (primary) haloalkanes lead to more substitution.

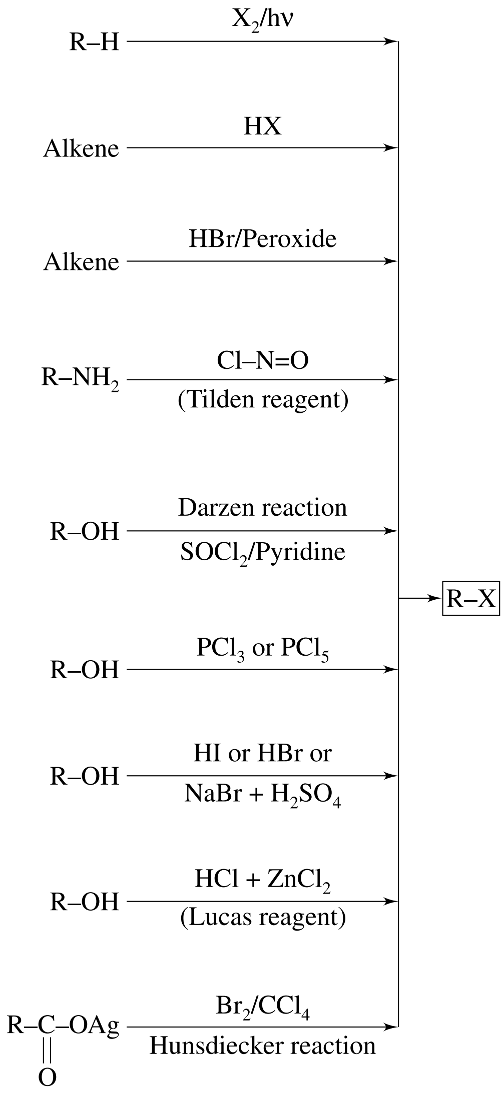
Sterically hindered (branched primary, secondary, tertiary) haloalkanes lead to more elimination.

Factor 3: Steric hindrance in the nucleophile.

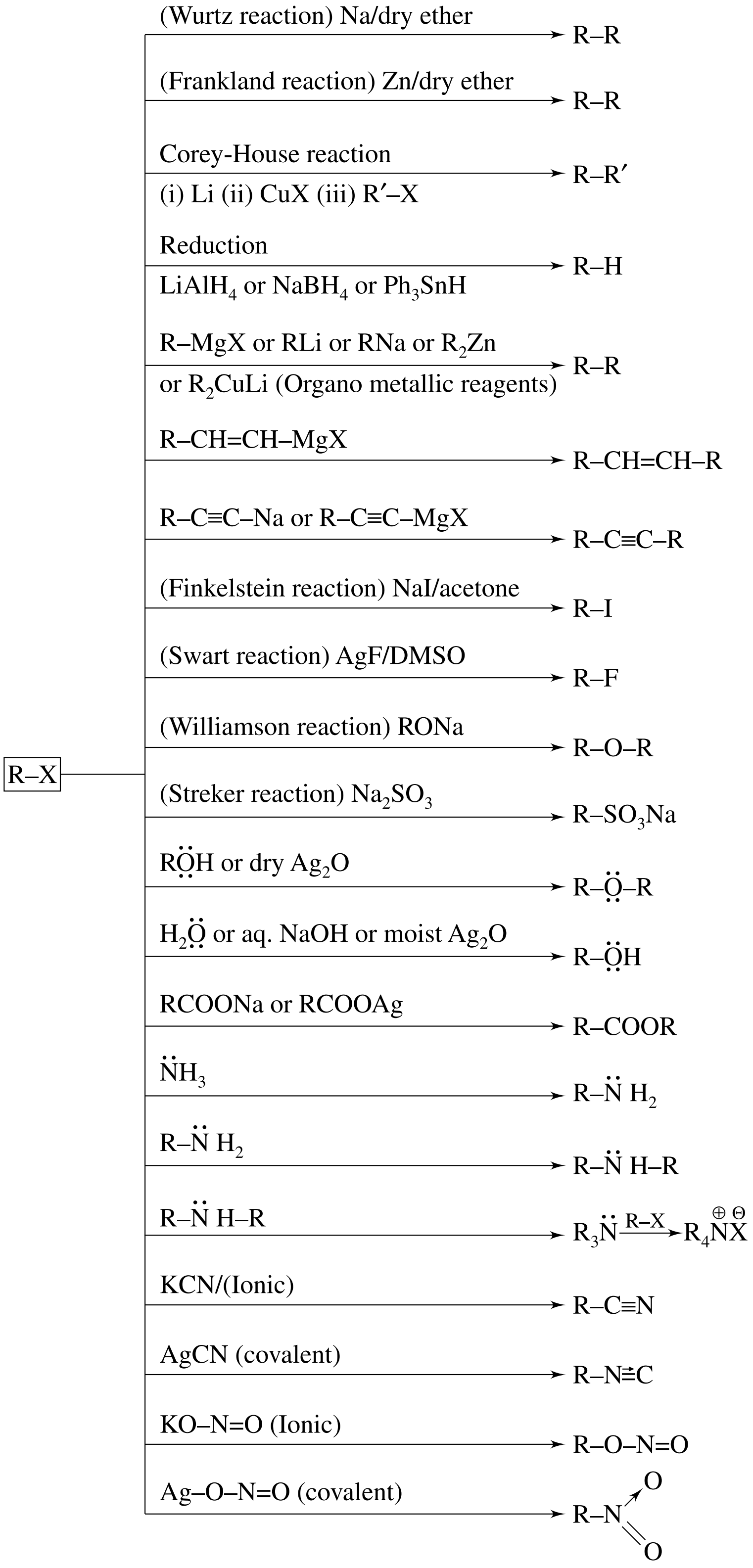
Sterically unhindered (HO^-, CH_3O^-, $CH_3CH_2O^-$, H_2N^-) nucleophile lead to more substitution.

Sterically hindered $(CH_3)_3CO^-$, $[(CH_3)_2CH_2NH^-]$ nucleophiles lead to more elimination.

Methods of Preparation of Haloalkanes:



Chemical Properties of Haloalkane:



Formation and reaction of Grignard Reagent

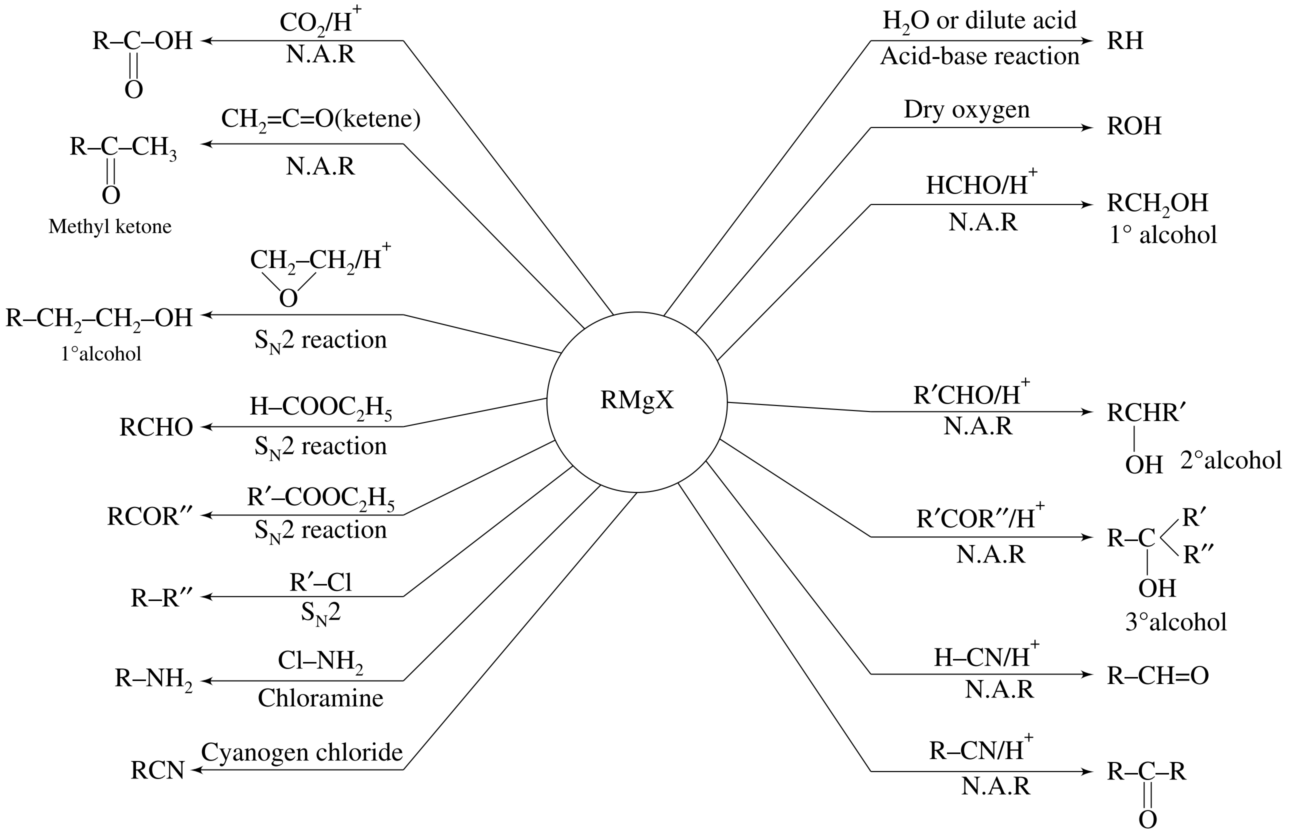
Haloalkanes react with magnesium metal (turnings) in dry ether to form alkyl magnesium halide, known as Grignard reagent.

$$\left.\begin{array}{l} RX+Mg \xrightarrow{\text{Dry ether}} RMgX \\[2ex] ArX+Mg \xrightarrow{\text{Dry ether}} ArMgX \end{array}\right\}\begin{array}{l}\text{Grignard}\\ \text{reagents}\end{array}$$

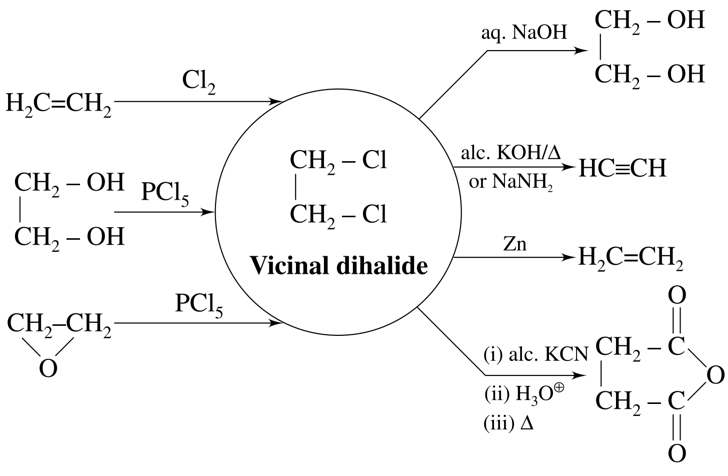
The order of reactivity of halides with magnesium is RI > RBr > RCl.

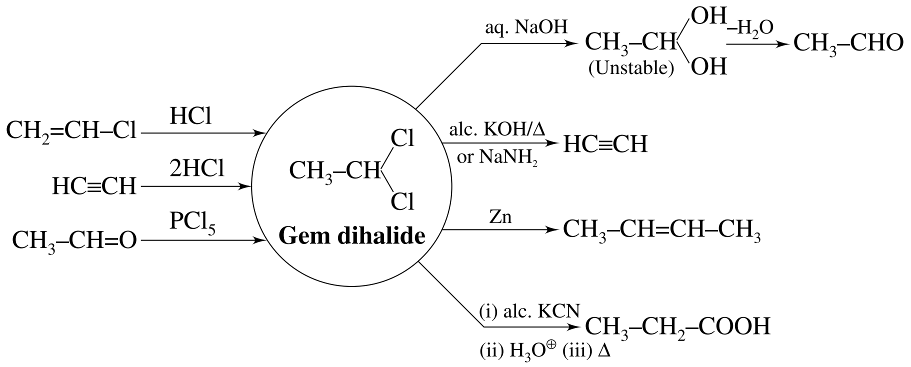
Reaction of Grignard reagent:

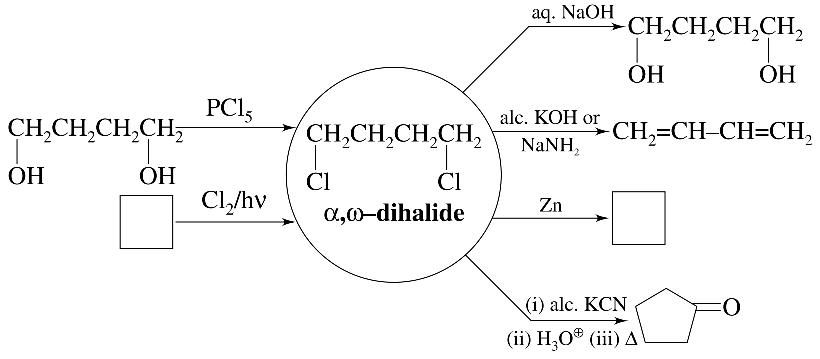
Grignard reagent is most versatile compound as it can be used in the preparation of many different types of compounds.



Chemical Properties and Methods of Preparation of Dihalides:



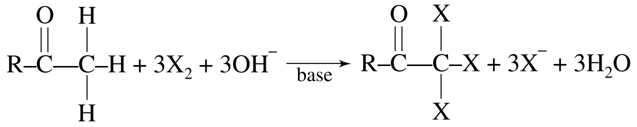




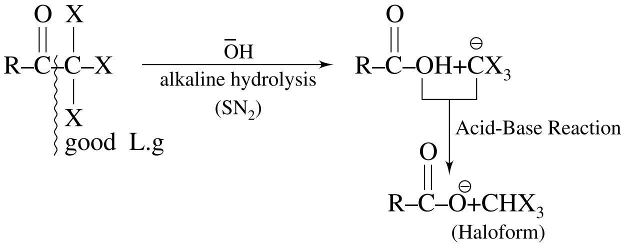
Trihalides

Haloform Reaction

When methyl ketones react with halogens in the presence of base multiple halogenations always occur at the carbon of the methyl group. Multiple halogenations occur because introduction of the first halogen (owing to its electronegativity) makes the remaining α hydrogens on the methyl carbon more acidic.



$$R-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{H}{C}}-H + 3X_2 + 3OH^- \xrightarrow[\text{base}]{} R-\overset{O}{\overset{\|}{C}}-\underset{X}{\overset{X}{C}}-X + 3X^- + 3H_2O$$



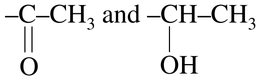
$$R-\overset{O}{\overset{\|}{C}}-\underset{X}{\overset{X}{C}}-X \xrightarrow[\text{alkaline hydrolysis (S}_N2)]{\bar{O}H} R-\overset{O}{\overset{\|}{C}}-OH+\overset{\ominus}{C}X_3 \xrightarrow{\text{Acid-Base Reaction}} R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}+CHX_3$$

good L.g

(Haloform)

The Iodoform Test

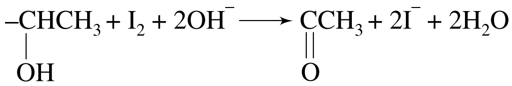
The haloform reaction using iodine and aqueous sodium hydroxide is called the iodoform test. The iodoform test was once frequently used in structure determinations because it allows identification of the following two groups:



$$-\underset{O}{\underset{\|}{C}}-CH_3 \text{ and } -\underset{OH}{\underset{|}{CH}}-CH_3$$

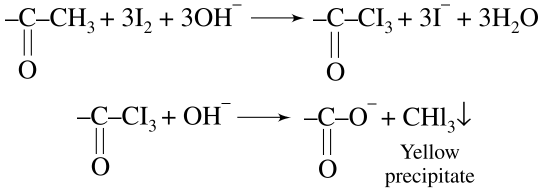
Compounds containing either of these groups react with iodine in sodium hydroxide to give a bright yellow precipitate of iodoform (CHI_3, mp 119°).

Compounds containing the $-CHOHCH_3$ group give a positive iodoform test because they are first oxidized to methyl ketones:



$$-\underset{OH}{\underset{|}{C}}HCH_3 + I_2 + 2OH^- \longrightarrow \underset{O}{\underset{\|}{C}}CH_3 + 2I^- + 2H_2O$$

Methyl ketones then react with iodine and hydroxide ion produce iodoform:

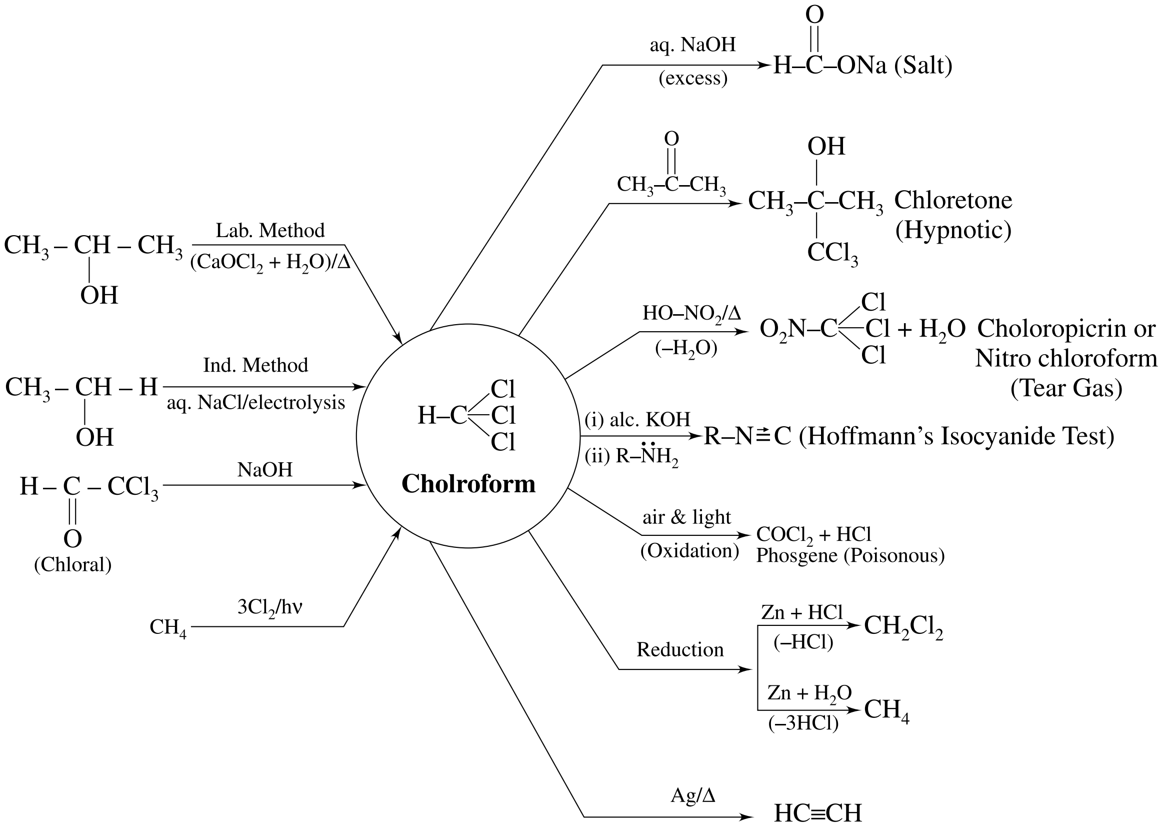


$$\underset{\overset{\|}{O}}{-C}-CH_3 + 3I_2 + 3OH^- \longrightarrow \underset{\overset{\|}{O}}{-C}-CI_3 + 3I^- + 3H_2O$$

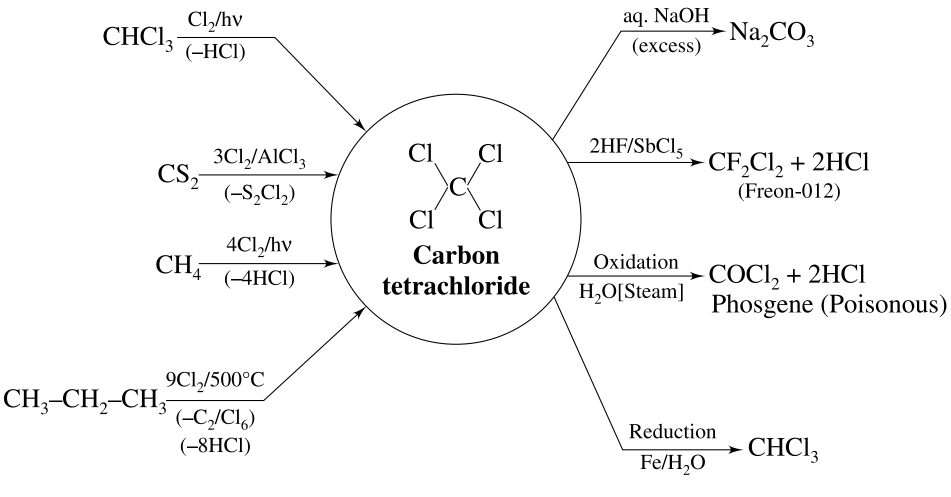
$$\underset{\overset{\|}{O}}{-C}-CI_3 + OH^- \longrightarrow \underset{\overset{\|}{O}}{-C}-O^- + \underset{\text{Yellow precipitate}}{CHI_3\downarrow}$$

The group to which the $-COCH_3$ or $-CHOHCH_3$ function is attached can be aryl, alkyl, or hydrogen. Thus, even ethanol and acetaldehyde give positive iodoform test.

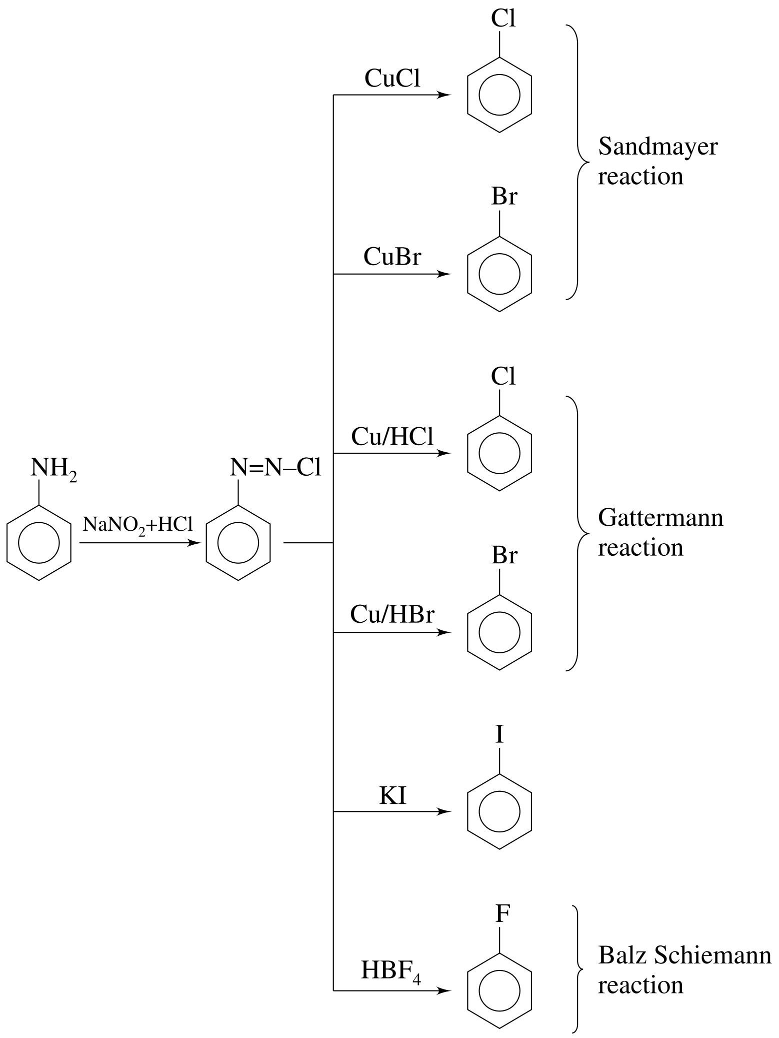
Chemical Properties and Methods of Preparation of Chloroform:

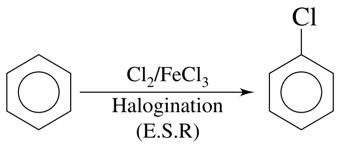


Chemical Properties and Methods of Preparation of Carbon Tetrachloride:



Methods of Preparation of Aryl Halides:

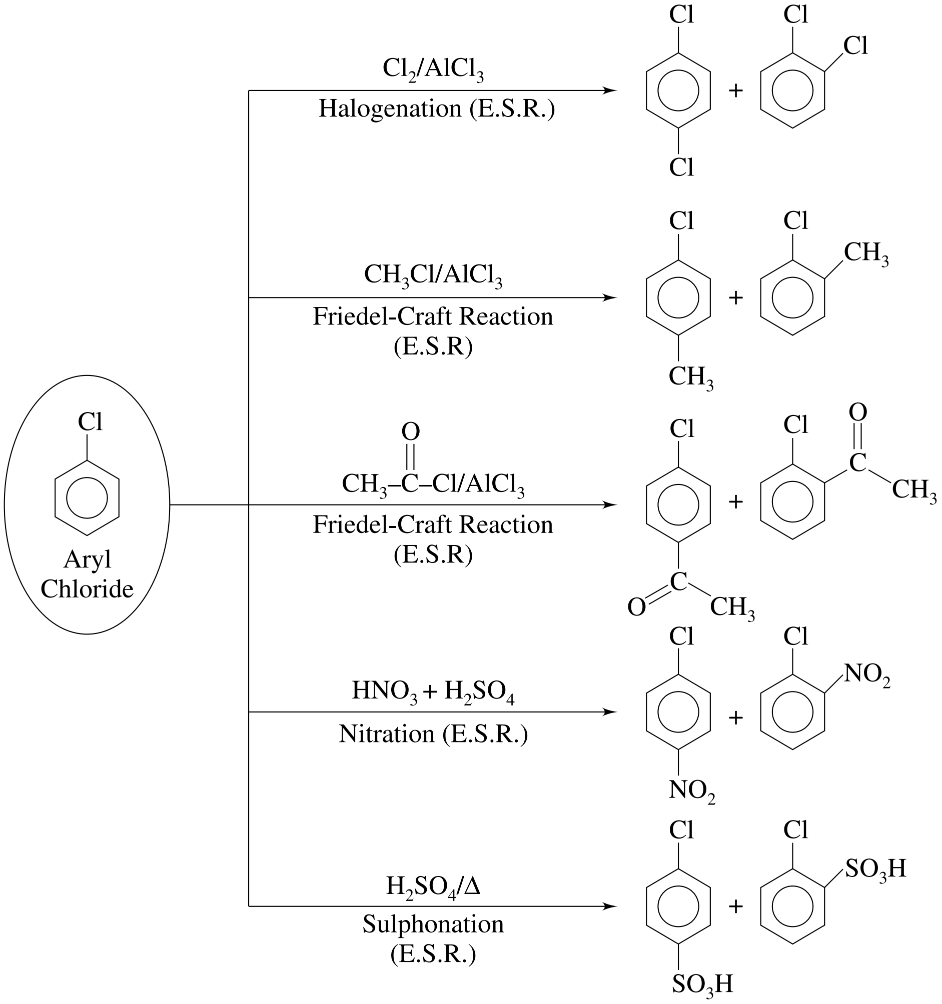




Chemical Properties of Aryl Halides:

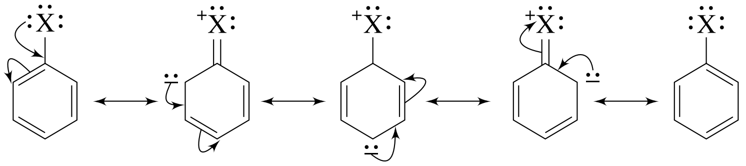
(1) Electophilic Aromatic Substitution Reaction (Ar-S_E)

The halo groups are the only ortho-para directors even that are deactivating group. It is due to the fact that electron withdrawing inductive effect influences reactivity and their electron donating resonace effect governs orientation.



(2) Nucleophilic Aromatic Substitution Reaction (Ar-SN)

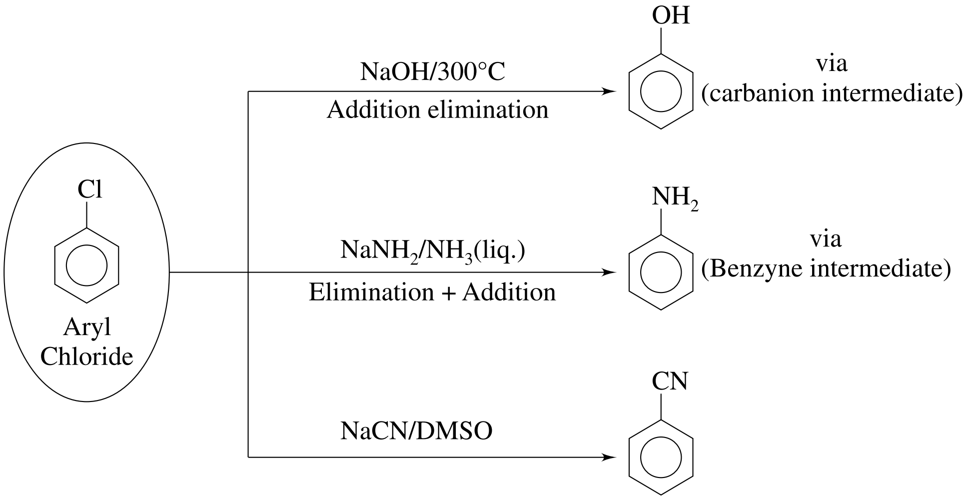
In general, aryl halides are less reactive than alkyl halides towards nucleophilic substitution reactions. This is due to the resonance effect in which lone pair of electron on halogen atom is delocalised to benzene ring imparting a partial double bond character to C–X bond.



In alkyl halide, the C–X bond involves sp^3(C) whereas in aryl halide, sp^2(C) is involved. Since the sp^2(C) is more electronegative than the sp^3(C), the C–X bond in aryl halide is shorter than in alkyl halides. This makes C–X bond more strong in aryl halides.

Under normal conditions, halobenzenes are inert to nucleophiles. However, Chlorobenzene can be made to react if the experimental conditions are:

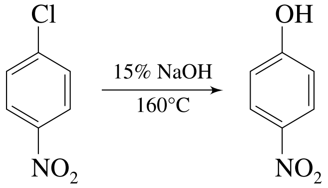
1. At high temperature and high pressure.
2. In presence of strong electron-withdrawing substituent at ortho and/or para positions.

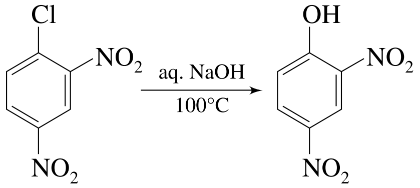


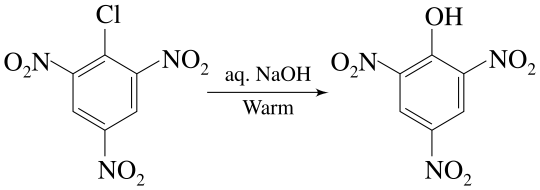
(A) Addition Elimination reaction

The presence of electron-withdrawing substituent at ortho and/or para positions is a favourable factor for the nucleophilic substitution reaction.

More such substituents, the faster the reaction.





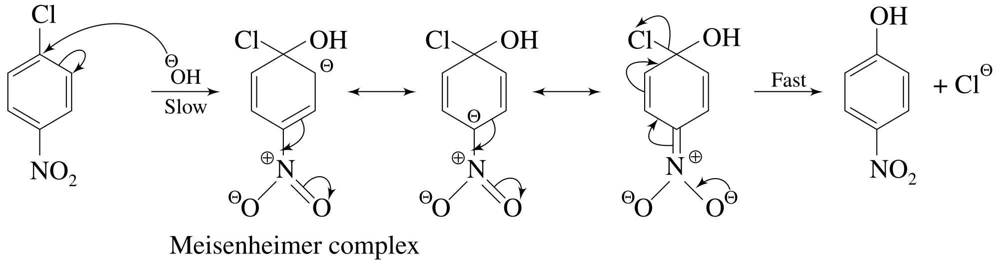


Mechanism

S_N Ar reaction takes place by a two steps reaction,

In the first step nucleophile attacks on the carbon bearing the leaving group.

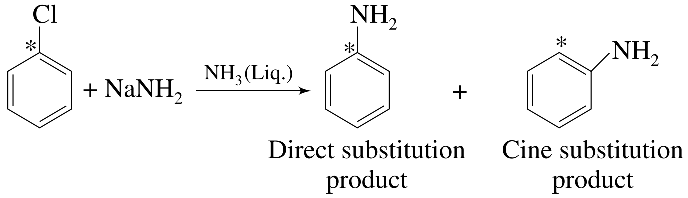
In the second step leaving group departs, re-estabilishing the aromaticity of the ring.



The carbanion is stabilised by electron-withdrawing groups in the positions ortho and para to the halogen atom.

(B) Elimination Addition Reaction (Benzyne)

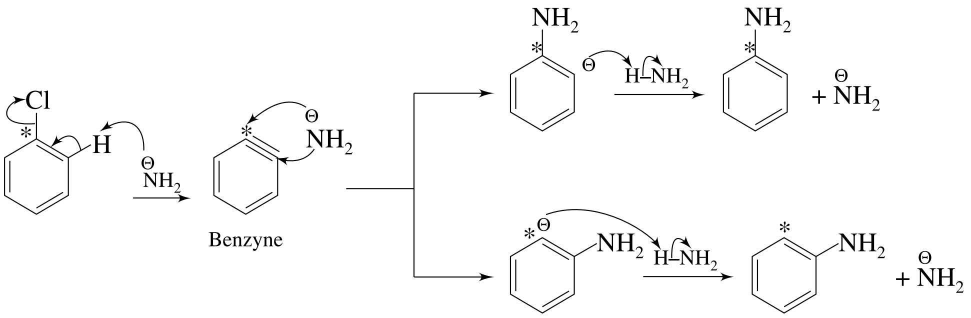
An aromatic halide such as chlorobenzene can undergo nucleophilic substitution in presence of very strong base such as $NaNH_2$ or KNH_2



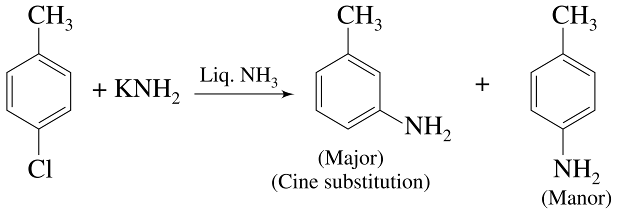
Substitution at the carbon that was attached to the leaving group is called direct substitution. Substitution at the adjacent carbon is called cine substitution.

Mechanism

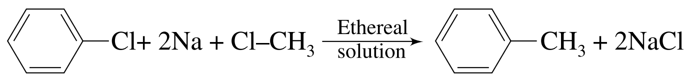
The mechanism of reaction proceed through benzyne intermediate.



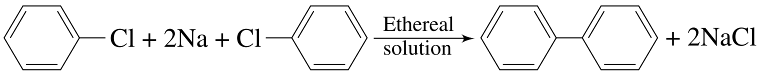
The substituted halobenzene give different products through benzyne formation. The major product formation can be predicted on the basis of inductive electronic effect of the stability of the intermediate carbanion.



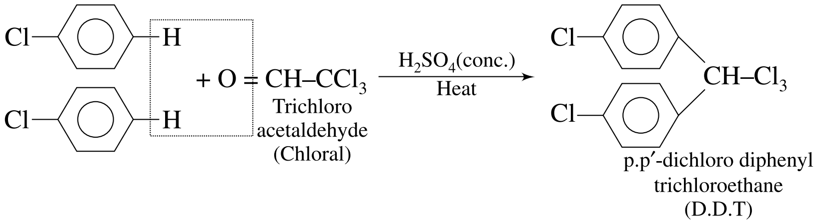
(3) Wurtz-Fittig Reaction



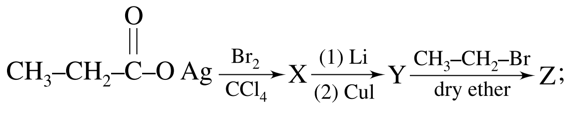
(4) Fittig Reaction



(5) Chlorobenzene to D.D.T



SOLVED EXAMPLE

1. 

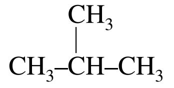
$$CH_3–CH_2–\overset{\overset{O}{||}}{C}–O\,Ag \xrightarrow[CCl_4]{Br_2} X \xrightarrow[(2)\ CuI]{(1)\ Li} Y \xrightarrow[\text{dry ether}]{CH_3–CH_2–Br} Z;$$

Z is:

(1) $CH_3–CH_3$

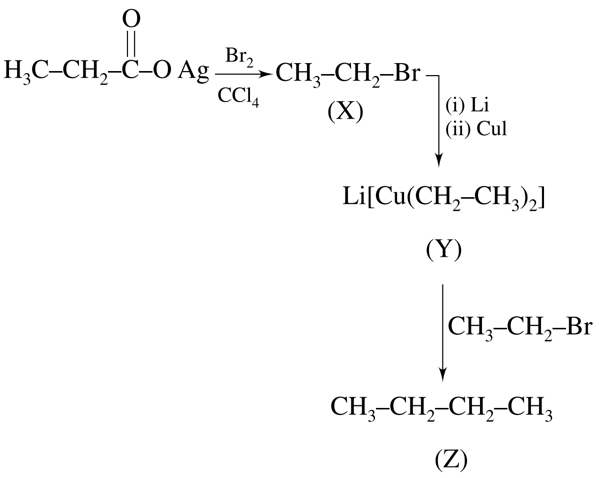
(2) $CH_3–CH_2–CH_3$

(3) $CH_3–CH_2–CH_2–CH_3$

(4) 

$$CH_3–\overset{\overset{CH_3}{|}}{C}H–CH_3$$

Sol. **[3]**



2. An S_N1 reaction at the asymmetric carbon of an enantiomerically pure chiral alkyl halide gives a product:

(1) with retention of configuration

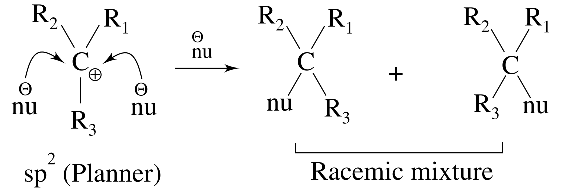
(2) with inversion of configuration

(3) with racemisation

(4) with partial racemisation

Sol. **[3]**

Since intermediate is carbocation thus nucleophile attack from both front as well back side.



3. 1, 1-Dichloropropane on hydrolysis gives:

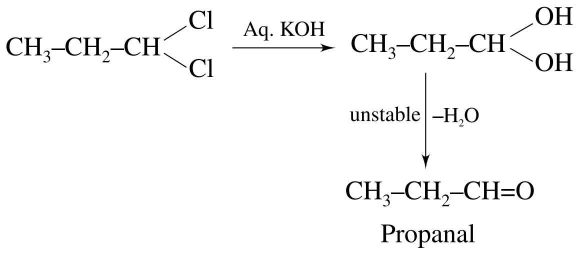
(1) propanone

(2) propanal

(3) ethanal

(4) 1, 1-Propanediol

Sol. **[2]**



4. Which of the following reagents may not be used to convert alkyl chlorides and alkyl bromides into alkyl fluorides?

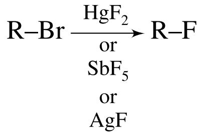
(1) Hg_2F_2

(2) SbF_5

(3) AgF

(4) CaF_2

Sol. **[4]**



Swart reaction

5. Which of the following statements is incorrect for ethylene dichloride and ethylidene chloride?

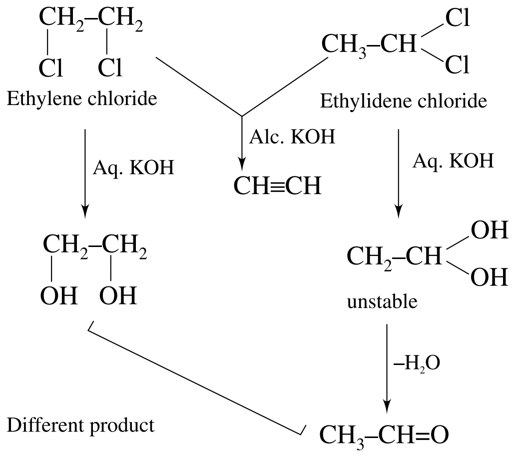
(1) These are structural isomers

(2) Both of these yield same product on reaction with alcoholic KOH solution

(3) Both of these yield same product on treatment with aqueous KOH solution

(4) Both of these yield same product on reduction

Sol. **[3]**

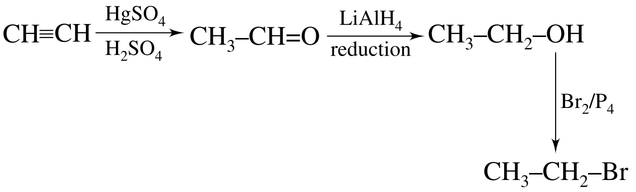


6. $CH\equiv CH \xrightarrow[H_2SO_4]{HgSO_4} (X) \xrightarrow{LiAlH_4} (Y) \xrightarrow{P_4/Br_2} (Z)$

In this sequence of reaction, (Z) is:

(1) Ethylene bromide (2) Ethanol
(3) Ethyl bromide (4) Ethylidene bromide

Sol. **[3]**



$$CH\equiv CH \xrightarrow[H_2SO_4]{HgSO_4} CH_3-CH=O \xrightarrow[reduction]{LiAlH_4} CH_3-CH_2-OH \xrightarrow{Br_2/P_4} CH_3-CH_2-Br$$

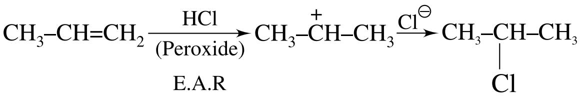
Ethyl bromide

7. When HCl gas is passed through propene in the presence of benzoyl peroxide it gives

(1) n-propyl chloride (2) 2-chloropropane
(3) allyl chloride (4) no reaction

Sol. **[2]**

HCl is not affected by peroxide so major product formed by E.A.R.



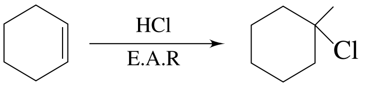
$$CH_3-CH=CH_2 \xrightarrow[(Peroxide)]{HCl} CH_3-\overset{+}{C}H-CH_3 \xrightarrow{Cl^{\ominus}} CH_3-\underset{\underset{Cl}{|}}{C}H-CH_3$$

E.A.R

8. 1-Methylcyclohexene on addition of HCl produces

(1) 1-chloro-1methylcyclohexane
(2) (±)-trans-2-chloro-1-methylcyclohexane
(3) (±) cis-2-chloro-1-methylcyclohexane
(4) 1-chloro-2-methylcyclohexane

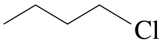
Sol. **[1]**

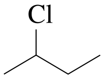


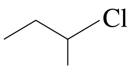
Markowrikaff addition No chiral C

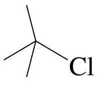
l-chloro-lmethylcyclohexane

9. Which of the following compounds has the highest boiling point?

(1) 

(2) 

(3) 

(4) 

Sol. **[1]**

Boiling point ∝ Molecular weight

$$\propto \frac{1}{\text{Branching (for isomer)}}$$

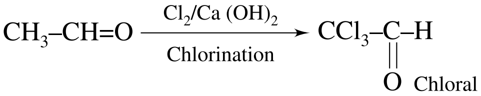
10. Ethyl alcohol is heated with bleaching powder and water. The final product formed is:

(1) Cl_3CCHO (2) CH_3CH_2Cl
(3) Cl_3CCO_2H (4) $CHCl_3$

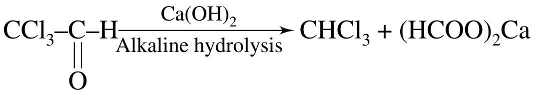
Sol. **[4]**

$$Ca(OCl)Cl + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

$$CH_3-CH_2-OH \xrightarrow[Oxidataion]{Cl_2} CH_3-CH=O$$

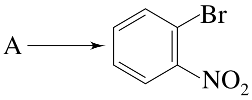


$$CH_3-CH=O \xrightarrow[Chlorination]{Cl_2/Ca\ (OH)_2} CCl_3-\underset{\underset{O}{\|}}{C}-H \quad \text{Chloral}$$



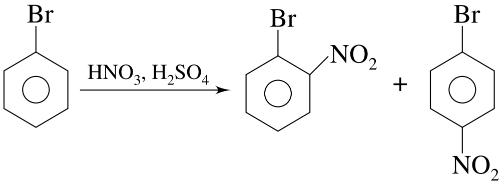
$$CCl_3-\underset{\underset{O}{\|}}{C}-H \xrightarrow[Alkaline\ hydrolysis]{Ca(OH)_2} CHCl_3 + (HCOO)_2Ca$$

11. For the given reaction, A is:

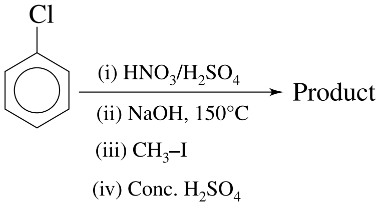


(1) $C_6H_5Br + HNO_3, H_2SO_4$
(2) $C_6H_5NO_2 + Br_2, FeBr_3$
(3) $C_6H_5Br + H_2SO_4$, heat
(4) $C_6H_5NO_2 + HBr$

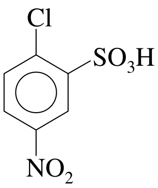
Sol. **[1]**

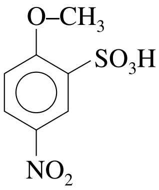


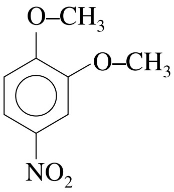
Br → o/p directive

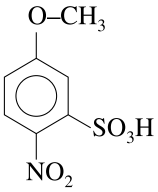
12. 

Product is:

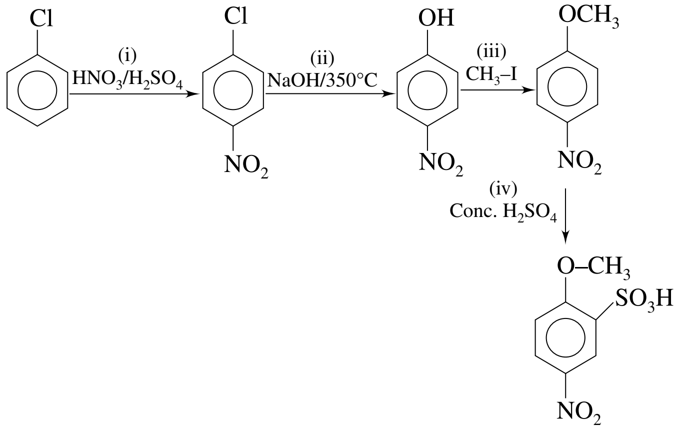
(1) 

(2) 

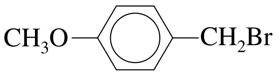
(3) 

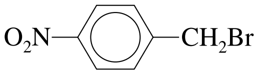
(4) 

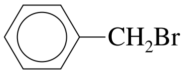
Sol. **[2]**

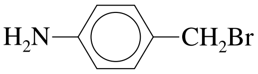


13. Which one of the following compounds undergoes predominantly S_N2 reaction with aqueous NaOH in a polar aprotic solvent?

(1) 

(2) 

(3) 

(4) 

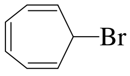
Sol. **[2]**

In primary halide

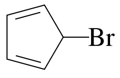
$$\text{Rate of } S_N2 \propto \text{EWG} \propto \frac{1}{\text{ERG}}$$

$-O-CH_3$(ERG), $-NO_2$(EWG), $-NH_2$(ERG)

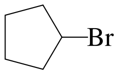
14. Among the compounds



I



II



III

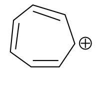
The order of decreasing S_N1 reactivity is

(1) I > II > III (2) I > III > II

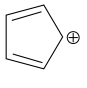
(3) II > III > I (4) III > I > II

Sol. **[2]**

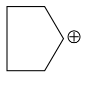
Rate of SN_1 reaction $\propto$ stability of carbocation



Aromatic
(I)



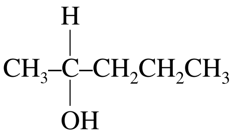
Anti Aromatic
(II)



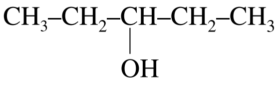
Non Aromatic
(III)

(I) > (III) > (II)

15. Which of the following alcohols will give the positive iodoform test?

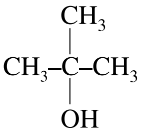
(1) 

$CH_3-\underset{OH}{\overset{H}{C}}-CH_2CH_2CH_3$

(2) 

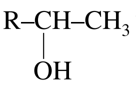
$CH_3-CH_2-\underset{OH}{CH}-CH_2-CH_3$

(3) $C_6H_5-CH_2-CH_2OH$

(4) 

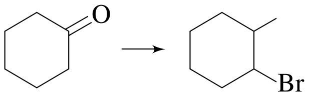
$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3$

Sol. **[1]**



Substance like $R-\underset{OH}{CH}-CH_3$ will give positive iodoform test.

16. Which combination of reagents will bring about the following conversion?



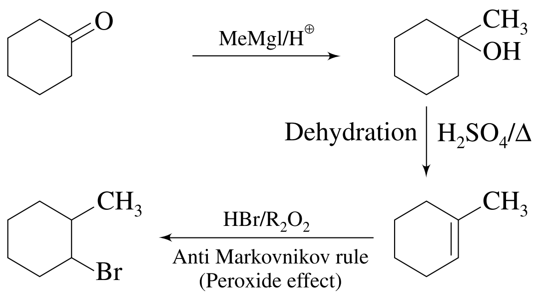
(1) (i) MeMgl/H^+, (ii) H_2SO_4/Δ, (iii) HBr/R_2O_2

(2) (i) MeMgl/H^+, (ii) H_2SO_4/Δ, (iii) HBr

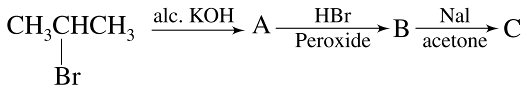
(3) (i) MeMgl/H^+, (ii) HBr

(4) (i) MeMgl/H^+ (ii) H_2SO_4/Δ, (iii) $Br_2/h\nu$

Sol. **[1]**



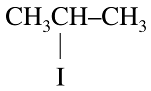
17. In the reaction



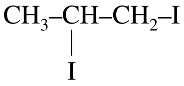
$\underset{\displaystyle Br}{CH_3\underset{|}{C}HCH_3} \xrightarrow{\text{alc. KOH}} A \xrightarrow[\text{Peroxide}]{HBr} B \xrightarrow[\text{acetone}]{NaI} C$

C is–

(1) $CH_3CH_2CH_2–I$

(2) 

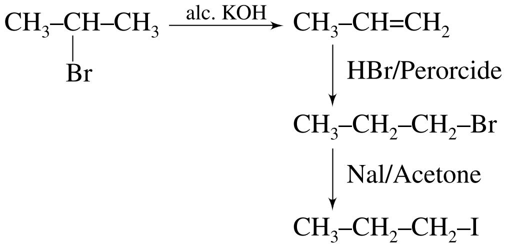
$CH_3\underset{\underset{\displaystyle I}{|}}{C}H–CH_3$

(3) 

$CH_3–\underset{\underset{\displaystyle I}{|}}{C}H–CH_2–I$

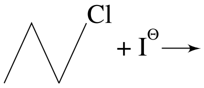
(4) $CH_3CH=CHI$

Sol. **[1]**

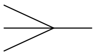


$CH_3–\underset{\underset{\displaystyle Br}{|}}{C}H–CH_3 \xrightarrow{\text{alc. KOH}} CH_3–CH=CH_2 \xrightarrow{\text{HBr/Perorcide}} CH_3–CH_2–CH_2–Br \xrightarrow{\text{Nal/Acetone}} CH_3–CH_2–CH_2–I$

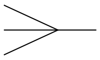
18. Which of the following is an S_N2 reaction?

(1) 

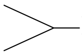
$+ I^{\ominus} \longrightarrow$

(2) 

$Br + {}^{\ominus}CN \longrightarrow$

(3) 

$Br + \overset{\ominus}{O}H(aq.) \longrightarrow$

(4) 

$Br + \overset{\ominus}{O}H(alc.) \longrightarrow$

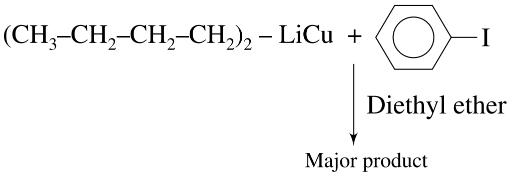
Sol. **[1]**

→ 3° halide gives β-elimination

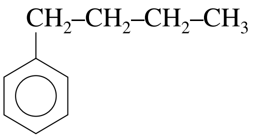
→ 2° halide also gives β-elimination with alcohalic $\overset{\ominus}{O}H$

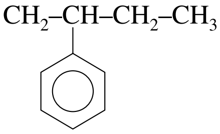
→ 1° halide give SN_2 reaction predominantly.

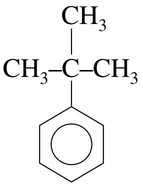
19. Major product of given chemical reaction is



$(CH_3–CH_2–CH_2–CH_2)_2 – LiCu$ + C₆H₅–I $\xrightarrow{\text{Diethyl ether}}$ Major product

(1) 

(2) 

(3) 

(4) No reaction takes place

Sol. **[1]**

S_N2 reaction takes place in presence of diethyl ether (Polar aprotic solvent) and $CH_3–CH_2–CH_2–\bar{C}H_2(Nu^-)$

20. These given number of factor influences relative rate of SN_1 reaction except

(1) The structure of substrate

(2) The concentration and reactivity of nucleophile

(3) The effect of solvent

(4) The nature of leaving group

Sol. **[2]**

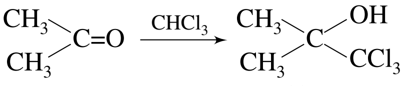
Rate = k[substrate]^1

Independent of concentration of nucleophile

21. The reaction of chloroform with acetone gives

(1) Mesitylene	(2) Ethylidene chloride
(3) Chloretone	(4) Chloral

Sol. **[3]**



Chloretone

22. $CH_3CH_2–OH$ can be converted to CH_3CH_2CN by the following reactions:

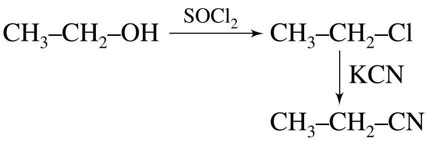
(1) $CH_3CH_2OH + KCN \xrightarrow{\Delta}$

(2) $CH_3CH_2OH + HCN \xrightarrow{\Delta}$

(3) $CH_3CH_2OH \xrightarrow{Na/\Delta} \xrightarrow{KCN}$

(4) $CH_3CH_2OH \xrightarrow{SOCl_2} \xrightarrow{KCN}$

Sol. **[4]**



$CH_3–CH_2–OH \xrightarrow{SOCl_2} CH_3–CH_2–Cl \xrightarrow{KCN} CH_3–CH_2–CN$

23. Which of the following reactions will proceed the fastest?

(1) $CH_3CH_2OH + HCl \longrightarrow CH_3CH_2Cl + H_2O$

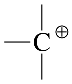
(2) $CH_3CH_2OH + HBr \longrightarrow CH_3CH_2Br + H_2O$

(3) $(CH_3)_2CHOH + HBr \longrightarrow (CH_3)_2CHBr + H_2O$

(4) $(CH_3)_2CHOH + HI \longrightarrow (CH_3)_2CHI + H_2O$

Sol. **[4]**

→ Reactivity of alcohol (towards HX) ∝ stability of carbocation



→ If $-\overset{|}{\underset{|}{C}}^{\oplus}$ is same, then HI > HBr > HCl > HF

24. Major product of which of the following reactions shows zero dipole moment?

(1) $CH_3OH, SOCl_2$

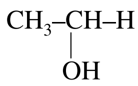
(2) C_2H_5OH, OH^-, Cl_2

(3) $CHCl_3, Cl_2, h\nu$

(4) CHI_3, Zn, HCl

Sol. **[3]**

$$CH_3\text{–}OH \xrightarrow{SOCl_2} CH_3\text{–}Cl \qquad \mu \neq 0$$

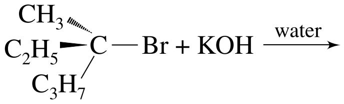


$$CH_3\text{–}\underset{\underset{OH}{|}}{CH}\text{–}H \xrightarrow[\text{Chloroform reaction}]{OH^-/Cl_2} CHCl_3 + H\text{–}COO^- \quad \mu \neq 0$$

$$CHCl_3 \xrightarrow{Cl_2/h\nu} CCl_4 \qquad \mu = 0$$

$$CHI_3 \xrightarrow[\text{reduction}]{Zn/HCl} CH_2Cl_2 \qquad \mu \neq 0$$

25. In the reaction



If the concentration of both the reactants is doubled, the rate of the reaction will

(1) double

(2) quadruple

(3) be reduced to one-fourth

(4) remain unchanged

Sol. **[1]**

Substrate is tertiary halide so reaction is SN_1

Thus $\frac{dx}{dt}$ = K [substrate]

Rate of SN_1 reaction is independent of concentration of alkali.

EXERCISE 1

1. Consider the reaction:

(i) $(CH_3)_2CH\text{–}CH_2Br \xrightarrow{C_2H_5OH} (CH_3)_2CH\text{–}CH_2\,OC_2H_5 + HBr$

(ii) $(CH_3)_2CH\text{–}CH_2Br \xrightarrow{C_2H_5O^-} (CH_3)_2CH\text{–}CH_2\,OC_2H_5 + Br$

The mechanisms of reaction (i) and (ii) are, respectively:

(1) S_N2 and S_N1 (2) S_N1 and S_N2

(3) S_N1 and S_N1 (4) S_N2 and S_N2

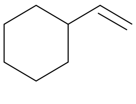
2. 2, 2-Dichloropentane can best be synthesised by:

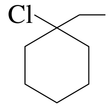
(1) $CH_2CH_2CH_2C{\equiv}CH \xrightarrow{Cl_2}$

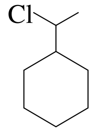
(2) $CH_3CH_2CH_2C{\equiv}CH \xrightarrow{H_2} [A] \xrightarrow{Cl_2}$

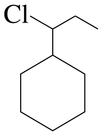
(3) $CH_3CH_2CH_2C{\equiv}CH \xrightarrow{2HCl}$

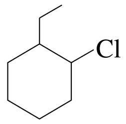
(4) $CH_3CH_2CH{=}CHCH_3 \xrightarrow{HCl}$

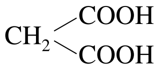
3.  $\xrightarrow{HCl}$ Major product:

(1) 

(2) 

(3) 

(4) 

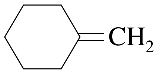
4. 

$$CH_2\begin{matrix}\diagup COOH \\ \diagdown COOH\end{matrix} \xrightarrow{\Delta} (A) \xrightarrow[\text{Reagent}]{\text{Tollen's}} (B) \xrightarrow[CS_2]{Br_2} (C)$$

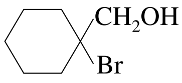
The end product (C) of given sequence of reaction is:

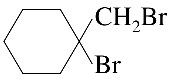
(1) $CH_2BrCOOAg$ (2) CH_3COOBr

(3) CH_3CH_2Br (4) CH_3Br

5.  $\xrightarrow[H_2O]{Br_2}$ A; A is:

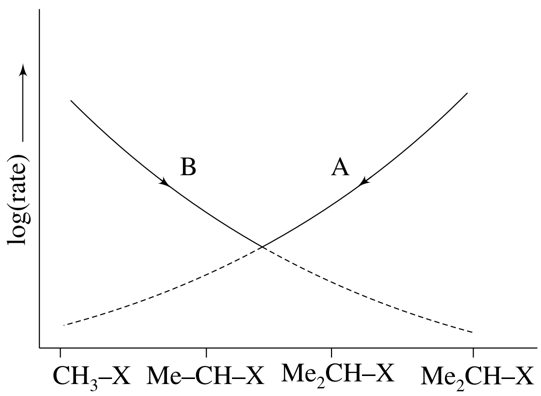
(1) 

(2) 

(3) 

(4) 

6.



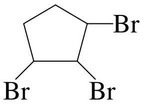
Which of the following is true about given graph A and B?

(1) A → S_N1 B → S_N2 (2) A → S_N2, B → S_N1
(3) A and B → E_1 (4) A and B → E_2

7. Ethyl alcohol reacts at faster rate with HI than with HCl in forming the corresponding ethyl halides under identical conditions mainly because:

(1) HI, being a stronger acid, protonates ethyl alcohol at oxygen much better and helps substitution
(2) the bond length in HI is much shorter than that in HCl
(3) I^- derived from HI is a much better leaving group
(4) I^- derived from HI is a much better nucleophile than Cl^-

8. Identify the correct reaction to synthesise the following compound from cyclopentane.



(1) $\xrightarrow[h\nu]{Cl_2} \xrightarrow{\text{Alc. KOH}} \xrightarrow[CCl_4]{Br_2}$
(2) $\xrightarrow[h\nu]{Br_2} \xrightarrow{C_2H_5O^{\ominus}} \xrightarrow{Br_2,\ CCl_4}$
(3) $\xrightarrow[h\nu]{Br_2} \xrightarrow{\text{Alc. KOH}} \xrightarrow{NBS} \xrightarrow[CCl_4]{Br_2}$
(4) None of these

9. Which of the following reactions will result in the formation of a chiral centre in the product?

(1) $CH_3CH{=}CH_2 + HBr \longrightarrow$
(2) $CH_2{=}CH_2 + HOBr \longrightarrow$
(3) $CH_3CH_2CH{=}CH_2 + HBr \xrightarrow{H_2O_2}$
(4) $CH_3CH_2CH{=}CH_2{+}HBr \longrightarrow$

10. In the presence of dibenzoyl peroxide, addition of HBr to 1-butene produces

(1) 2-bromobutane (2) 1-bromobutane
(3) (±)-2-bromobutane (4) 1-bromobutene

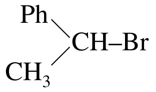
11. The reaction of (S) – 2-bromobutane with OH^- to produce (R)-butan-2-ol will be

(1) first order in 2-bromobutane only
(2) first order in OH^- only
(3) first order in 2-bromobutane and first order in OH^-
(4) second order in OH^-

12. The correct order of increasing reactivity of the substrates (I), (II), (III), and (IV) below, towards S_N1 reaction with a given nucleophile is:

(I) $CH_3CH_2—Br$ (II) $(CH_3)_2CH—Br$

(III) $CH_2{=}CHCH_2—Br$ (IV)

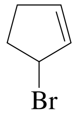


$\begin{matrix}Ph\\CH_3\end{matrix}\!\!>CH{-}Br$

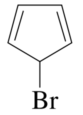
(1) I < II < III < IV (2) II < I < III < IV
(3) IV < II < I < III (4) III < IV < II < I

13. Among the bromides I–III given below, the order of reactivity of S_N 1 reaction is:

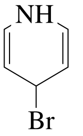
(I)



(II)



(III)

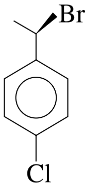


(1) III > I > II (2) III > II > I
(3) II > III > I (4) II > I > III

14. The $S_N{}^2$ reaction of 1-chloro-3-methylbutane with sodium methoxide is relative slow, but can be accelerated by the addition of a small amount of NaI. How this catalysis is best explained?

(1) The sodium cation helps pull off the chloride anion
(2) The iodide anion activates the methoxide nucleophile
(3) $S_N{}^2$ reaction of iodide ion converts the alkyl chloride to the more reactive alkyl iodide
(4) The NaI changes the mechanism to $S_N{}^1$

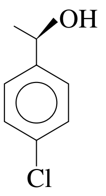
15.



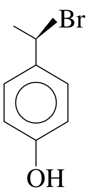
$\xrightarrow[DMF]{\text{aq. KOH}}$ Major product is:

The major product in this reaction is:

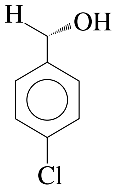
(1)



(2)



(3)



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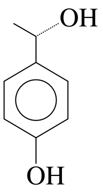
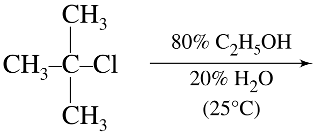


16. Isopropylidene chloride is hydrolysed with aqueous NaOH. The product formed is:

(1) 1-propanal (2) propanal

(3) 2-propanal (4) propanone

17.



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-Cl \xrightarrow[\substack{20\%\ H_2O \\ (25°C)}]{80\%\ C_2H_5OH}$$

The given reaction undergoes

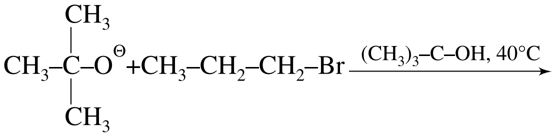
(1) unimolecular substitution predominantly.

(2) unimolecular elimination predominantly.

(3) bimolecular substitution predominantly.

(4) bimolecular elimination predominantly.

18.

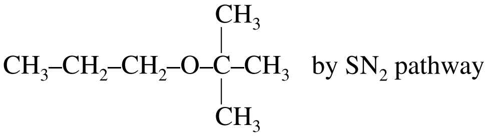


$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-O^{\ominus}+CH_3-CH_2-CH_2-Br \xrightarrow{(CH_3)_3-C-OH,\ 40°C}$$

Major product

(1) $CH_3-CH = CH_2$ by E_2 pathway

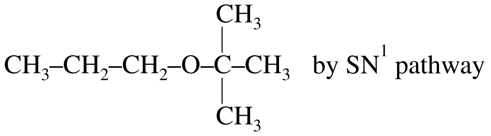
(2)



$CH_3-CH_2-CH_2-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3$ by SN_2 pathway

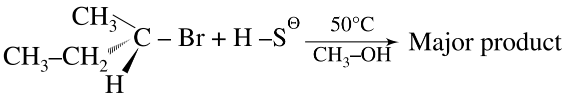
(3) $CH_3-CH = CH_2$ by E1 pathway

(4)



$CH_3-CH_2-CH_2-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3$ by SN^1 pathway

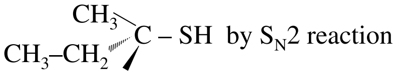
19.



Major product

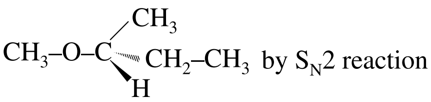
Select the major product and path of mechanism of given reaction

(1)



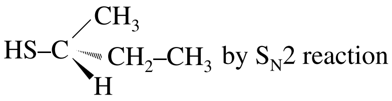
by S_N2 reaction

(2)



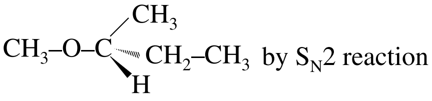
by S_N2 reaction

(3)



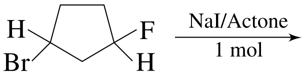
by S_N2 reaction

(4)



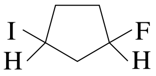
by S_N2 reaction

20.

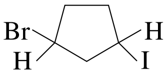


What would be major product of given reaction?

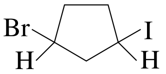
(1)



(2)



(3)



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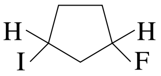
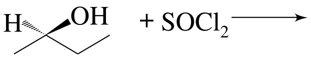
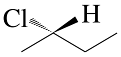


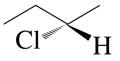
21. The product formed in the reaction is:



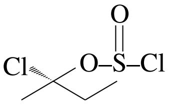
(1)



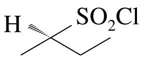
(2)



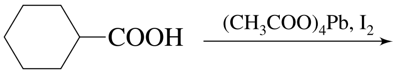
(3)



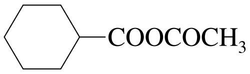
(4)



22. The product formed in the reaction is:



(1)



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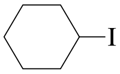

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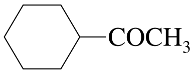

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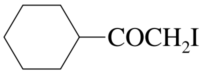
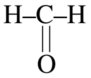


23. $CHCl_3 \xrightarrow{OH^-/H_2O}$ A, A is

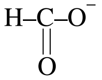
(1) CO_3^{2-}

(2)



$H-\underset{\displaystyle \| \atop O}{C}-H$

(3)



$H-\underset{\displaystyle \| \atop O}{C}-O^-$

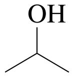
(4) $C_2O_4^{2-}$

24. Identify (X):

$$CHCl_3 \xrightarrow[HF]{SbF_5} CHF_2Cl \xrightarrow{1070K} (X) + 2HCl$$

(1) $F_2C = CF_2$ (2) $ClFC = CFCl$

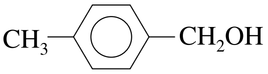
(3) $F_2C = CFCl$ (4) $F_2C = CCl_2$

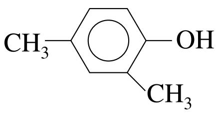
25. 

$+ aI_2 + bNaOH \longrightarrow CHI_3$, ratio of moles (a) and (b) is:

(1) 3:4 (2) 2:3
(3) 3:2 (4) 4:3

26. Chloropicrin is a strong lachrymatory compound and is used in war. It is prepared by:
(1) heating acetone with chloroform in the presence of dilute NaOH.
(2) heating chloroform with HNO_3.
(3) heating nitormethane with carbon tetrachloride.
(4) the reaction of acetylene and arsenic chloride.

27. An aromatic compound A of the molecular formula $C_8H_{10}O$ on reaction with iodine and dilute NaOH gives a yellow precipitate. The structure of the compound is expected to be:
(1) $C_6H_5CH_2CH_2OH$
(2) $C_6H_5CHOHCH_3$
(3) 

(4) 

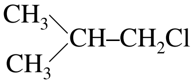
28. Which of the following has zero dipole moment?
(1) *o*-Dichlorobenzene
(2) *m*-Dichlorobenzene
(3) *p*-Dichlorobenzene
(4) *p*-chlorotoluene

29. The boiling points of methyl bromide (I), ethyl bromide (II), n-propyl bromide (III) and n-butyl bromide (IV) decrease in the order:
(1) I > II > III > IV (2) IV > III > II > I
(3) I > III > II > IV (4) III > IV > I > II

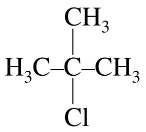
30. The stabilities of alkyl fluorides (I), alkyl chlorides (II), alkyl bromides (III) and alkyl iodides (IV) decrease in the order
(1) I > II > III > IV (2) IV > III > II > I
(3) I > IV > II > III (4) II > I > IV > III

31. The strengths of carbon–halogen bonds follow the order:
(1) R–F > R–Cl > R–Br > R–I
(2) R–I > R–Br > R–Cl > R–F
(3) R–F > R–I > R–Br > R–Cl
(4) R–Cl > R–Br > R–I > R–F

32. Arrange the following compounds in the increasing order of their boiling points:

(a) 
$(CH_3)_2CH–CH_2Cl$

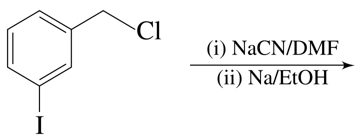
(b) $CH_3CH_2CH_2CH_2Cl$

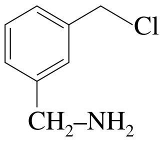
(c) 
$H_3C–C(CH_3)(Cl)–CH_3$

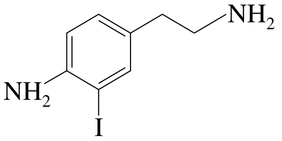
(1) (b) < (a) < (c) (2) (a) < (b) < (c)
(3) (c) < (a) < (b) (4) (c) < (b) < (a)

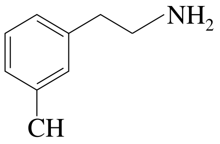
33. Positive Beilstein's test for halogens shows that:
(1) a halogen is definitely present.
(2) a halogen may be present.
(3) a halogen is absent.
(4) None of the above

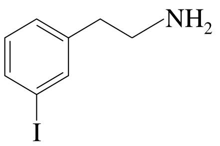
34. The structure of the major product formed in the following reaction is:



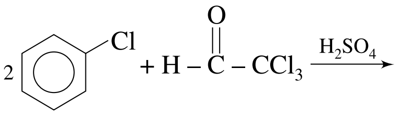
(1) 

(2) 

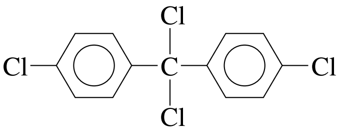
(3) 

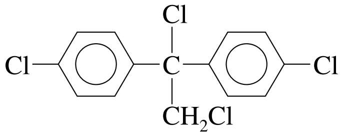
(4) 

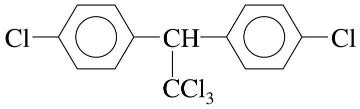
35. Chlorobenzene reacts with trichloro acetaldehyde in the presence of H_2SO_4

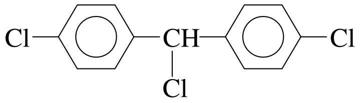


The major product formed is:

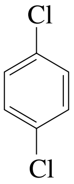
(1) 

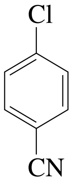
(2) 

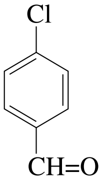
(3) 

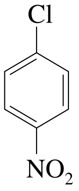
(4) 

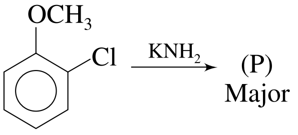
36. Which of the given aryl halide is most readily hydrolysed?

(1) 

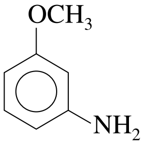
(2) 

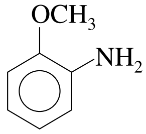
(3) 

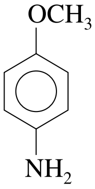
(4) 

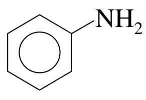
37. 

What is P?

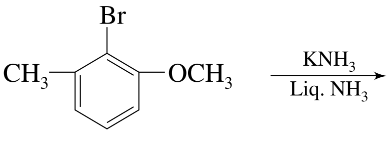
(1) 

(2) 

(3) 

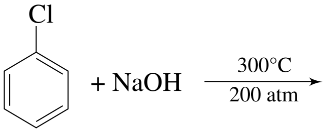
(4) 

38. Which of the following reaction does not takes place?

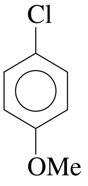
(1) 

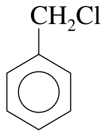
(2) $+$Cl + aq. KOH $\longrightarrow$

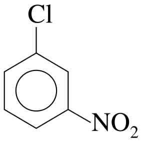
(3) $+$Cl + alc. KOH $\longrightarrow$

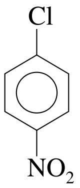
(4) 

39. Among the following compounds, which one undergoes nucleophilic substitution of chlorine atom by OH^- most readily?

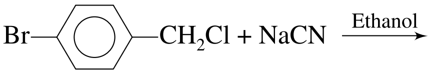
(1) 

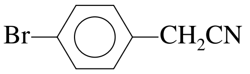
(2) 

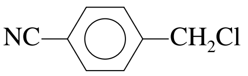
(3) 

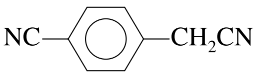
(4) 

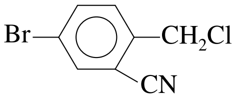
40. The product obtained from the reaction

 is:

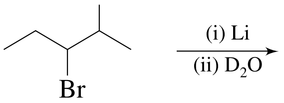
(1) 

(2) 

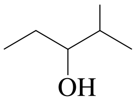
(3) 

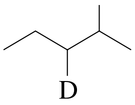
(4) 

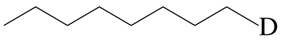
EXERCISE 2

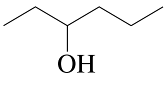
1. 

What is the product in the above reaction?

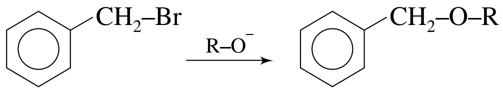
(1) 

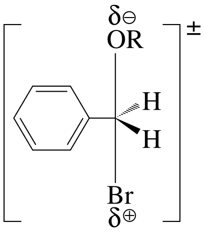
(2) 

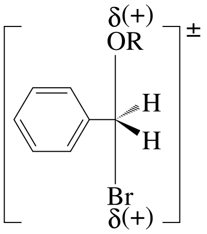
(3) 

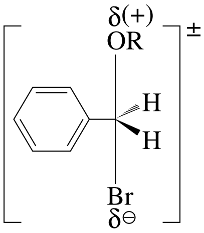
(4) 

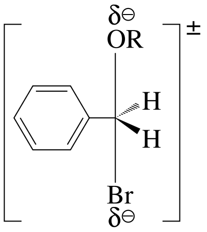
2. Transition state of given S_{N_2} is:



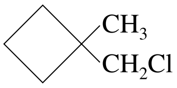
(1) 

(2) 

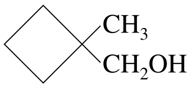
(3) 

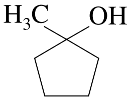
(4) 

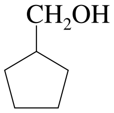
3. Which are possible products in following?

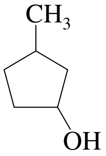


$\xrightarrow[SN_1]{\text{moist } Ag_2O}$ Major product

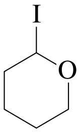
(1) 

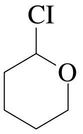
(2) 

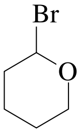
(3) 

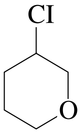
(4) 

4. Arrange the following compound for S_N^1 reactivity order:

(I) 

(II) 

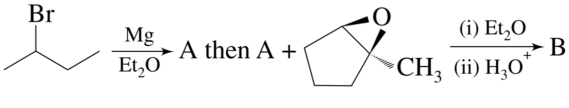
(III) 

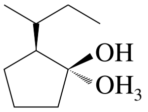
(IV) 

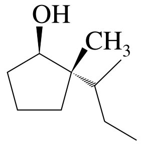
(1) I > II > III > IV (2) I > III > II > IV

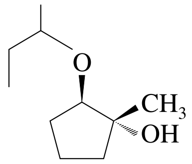
(3) IV > III > II > I (4) II > IV > III > I

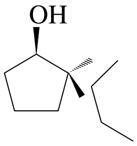
5. What is the product of the given reaction?



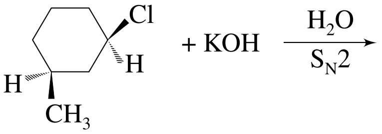
(1) 

(2) 

(3) 

(4) 

6. Consider the following reaction:



(1R, 3S)-Cis-1-chloro-3-methylcyclohexane

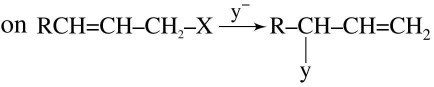
The product formed in the reactions is:

(1) (1R, 3S)-cis-3-methylcyclohexanol

(2) (1S, 3R)-cis-3-methylcyclohexanol

(3) (1S, 3S)-Trans-3-methylcyclohexanol

(4) (1R, 3R)-Trans-3-methylcyclohexanol

7. The reaction  is:

$RCH{=}CH{-}CH_2{-}X \xrightarrow{y^-} R{-}\underset{\substack{|\\ y}}{CH}{-}CH{=}CH_2$

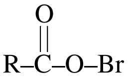
(1) an S_N1 reaction (2) an S_N2 reaction

(3) an S_Ni reaction (4) None of these

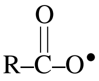
8. In the reaction

$R{-}COOAg + Br_2 \longrightarrow RBr + CO_2 + AgBr$

The reaction proceeds through the intermediate formation of:

(1) 

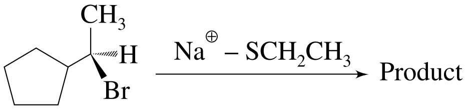
$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}Br$

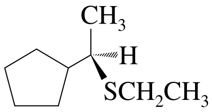
(2) 

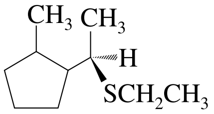
$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^{\bullet}$

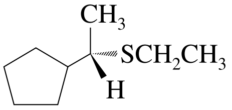
(3) $R^{\bullet}$ (4) All of these

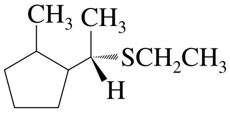
9. Consider the following reaction and select best choice that represents the reaction.



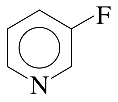
(1) 

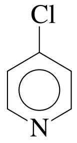
(2) 

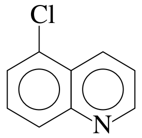
(3) 

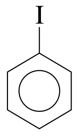
(4) 

10. Which is most reactive towards nucleophilic aromatic substitution?

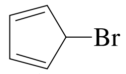
(1) 

(2) 

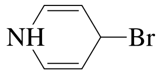
(3) 

(4) 

11. Which of the following statements is correct regarding the rate of hydrolysis of the compounds (A) and (B) by S_N1 reaction?



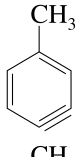
A

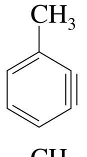


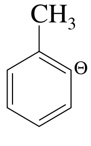
B

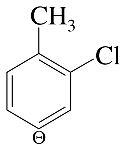
(1) A reacts faster than B
(2) B reacts faster than A
(3) Both A and B reacts at the same rate
(4) Neither A nor B reacts

12. o-Chlorotoluene reacts with $NaNH_2$ in liquid ammonia to give o-toluidine and m-toluidine. This reaction proceeds through the intermediate

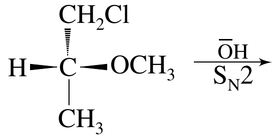
(1) 

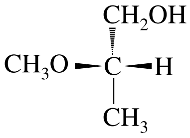
(2) 

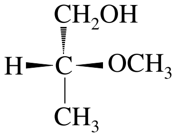
(3) 

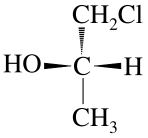
(4) 

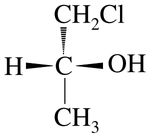
13. What is the major product of the given reaction?


$\mathrm{H{-}\overset{CH_2Cl}{\underset{CH_3}{C}}{-}OCH_3} \xrightarrow[S_N2]{\overline{O}H}$

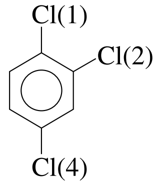
(1) 
$\mathrm{CH_3O{-}\overset{CH_2OH}{\underset{CH_3}{C}}{-}H}$

(2) 
$\mathrm{H{-}\overset{CH_2OH}{\underset{CH_3}{C}}{-}OCH_3}$

(3) 
$\mathrm{HO{-}\overset{CH_2Cl}{\underset{CH_3}{C}}{-}H}$

(4) 
$\mathrm{H{-}\overset{CH_2Cl}{\underset{CH_3}{C}}{-}OH}$

14. Which chlorine is most easily replaced under nucleophilic attack?



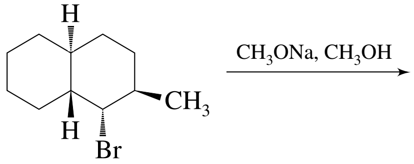
(1) Cl(1)
(2) Cl(2)
(3) Cl(4)
(4) Cl(1) and Cl(4)

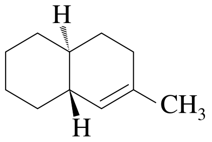
15. Arrange the following compounds in order of increasing dipole moment:

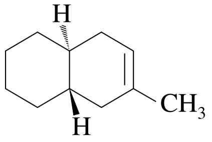
Toluene (I)
m-dichlorobenzene (II)
o-dichlorobenzene (III)
p-dichlorobenzene (IV)

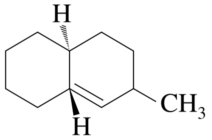
(1) I < IV < II < III
(2) IV < I < II < III
(3) IV < I < III < II
(4) IV < II < I < III

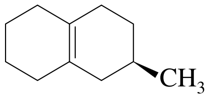
16. Provide the structure of the major organic product which results in the following reaction:



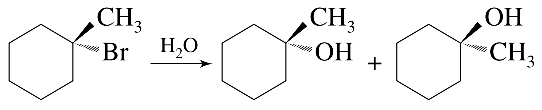
(1) 

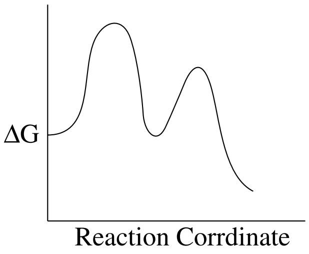
(2) 

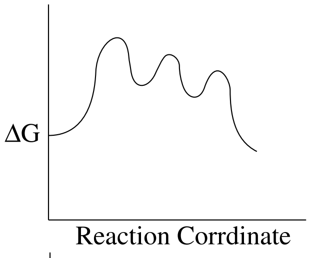
(3) 

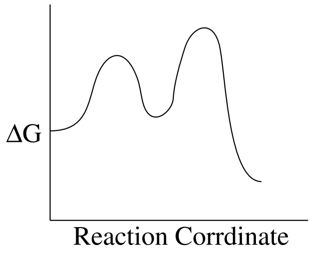
(4) 

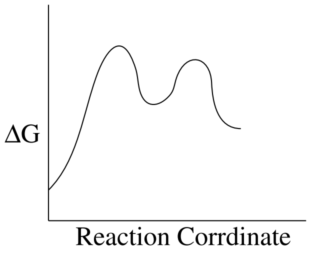
17. Which is the correct reaction coordinate diagram for the following solvolysis reaction?



(1) 

(2) 

(3) 

(4) 

18. Which of the following reagents can be used to distinguish chlorobenzene from chlorocyclohexane?

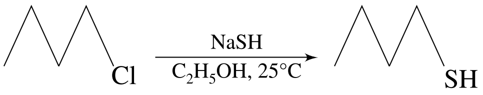
(1) $AgNO_3/C_2H_5OH$

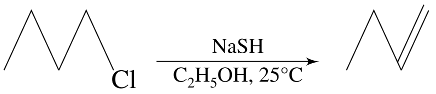
(2) $Ag(NH_3)_2OH$

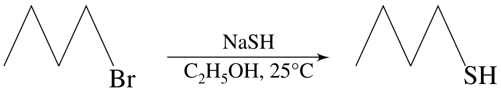
(3) Na fusion; HNO_3, $AgNO_3$

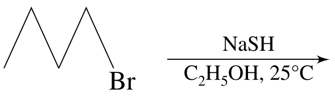
(4) Br_2/CCl_4

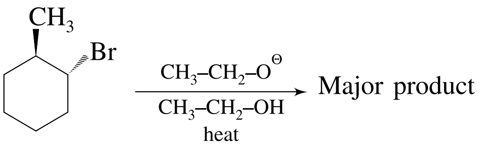
19. Which reaction takes place at the fastest rate?

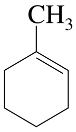
(1) 

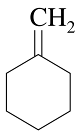
(2) 

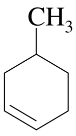
(3) 

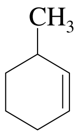
(4) 

20. 

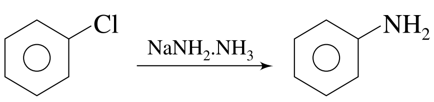
(1) 

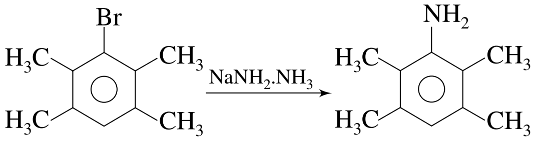
(2) 

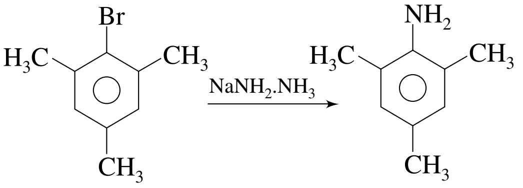
(3) 

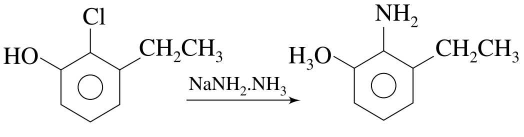
(4) 

21. Which of the following reaction is feasible?

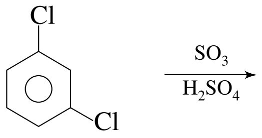
(1) 

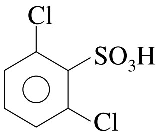
(2) 

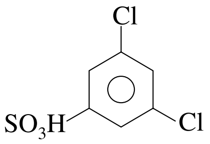
(3) 

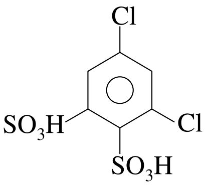
(4) 

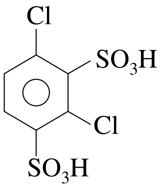
22. The major product obtained in the reaction



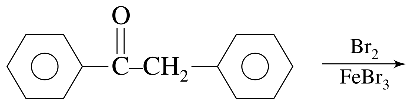
(1) 

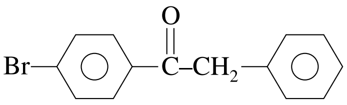
(2) 

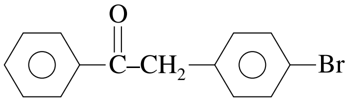
(3) 

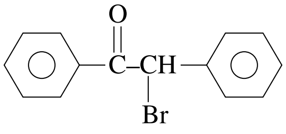
(4) 

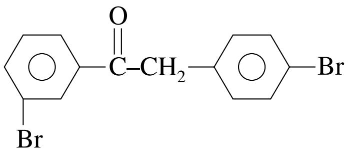
23. The major product obtained in the reaction



(1) 

(2) 

(3) 

(4) 

24. 2-Bromo-1-phenylpropane can be synthesised by

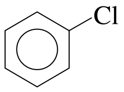
(1) $C_6H_5CH_2CH(OH)CH_3 + HBr \xrightarrow{\Delta}$

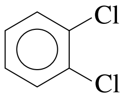
(2) $C_6H_5CH{=}CHCH_3$ + HBr + benzoyl peroxide →

(3) $C_6H_5CH_2CH_2CH_3 + Br_2$ + light $\longrightarrow$

(4) none of these

25. Which of the following substituted benzene derivatives would produce three isomeric products when one more constituent is introduced?

(I)


(II)


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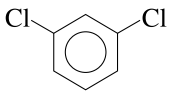
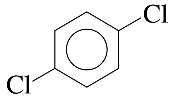
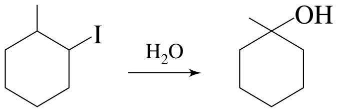
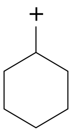


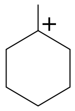
(IV)


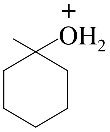
(1) I, II and III
(2) I
(3) II and IV
(4) I and III

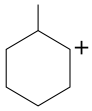
26. Which of the following is not expected to be an intermediate of the following reaction?



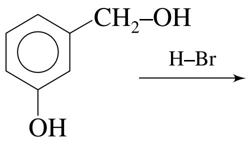
(1)


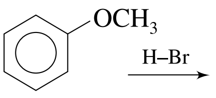
(2)


(3)


(4)


27. In which reaction Halide is not obtained?

(1)


(2)


(3) $CH_3–CH_2–OH + SOCl_2 \longrightarrow$

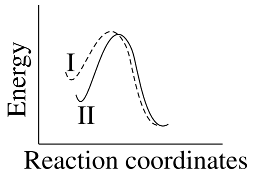
(4) $CH_3–CH_2–OH + KBr \longrightarrow$

28. What is the correct increasing order of reactivity of the followings in S_N2 reaction?

(I) $CH_2=CH–CH_2–Br$
(II) $CH_2=CH–I$
(III) $CH_3CH_2CH_2–I$
(IV) $CH_3OCH_2CH_2–I$

(1) I < II < III < IV
(2) III < II < I < IV
(3) II < III < IV < I
(4) III < I < II < IV

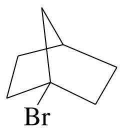
29. Consider the two lines shown in the diagram given below



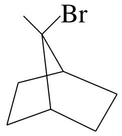
Which of the following apply appropriately to a S_N2 reaction?

(1) Graph I could represent Cl^- and Graph II represents I^- leaving group
(2) Graph I could represent HO^- and Graph II represents CH_3COO^- nucleophile
(3) Graph I could represent H_2O and Graph II H_2S as nucleophile
(4) Graph I could represent $(CH_3)_2NH$ and Graph II to $(CH_3)_2N–$ nucleophiles

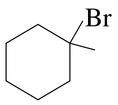
30. Which of the following alkyl halides is respectively most and least electrophilic in S_N1 reaction?



(I)

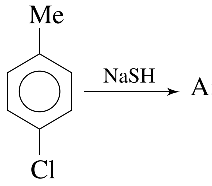


(II)

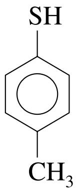


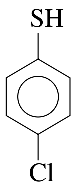
(III)

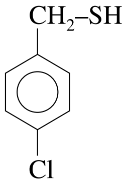
(1) Both I and III
(2) Both II and III
(3) Both III and I
(4) Both I and II

31.


A; Product (A) of the reaction is:

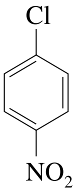
(1)


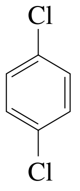
(2)


(3)


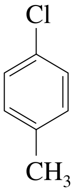
(4) no reaction

32. Which one of the following undergoes nucleophilic aromatic substitution at the fastest rate?

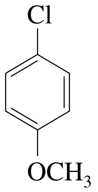
(1)


(2)


(3)

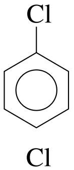


(4)

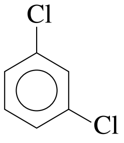


33. Arrange the following compounds in the increasing order of their densities:

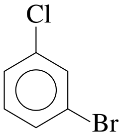
(a)



(b)



(c)

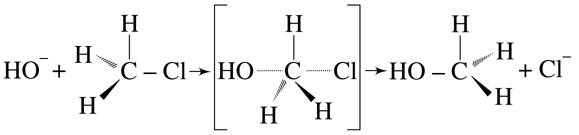


(1) (a) < (b) < (c)
(2) (a) < (c) < (b)
(3) (c) < (b) < (a)
(4) (b) < (c) < (a)

34. Among the following halides, the one which reacts most readily with ethanol is

(1) *p*-nitrobenzyl bromide
(2) *p*-chlorobenzyl bromide
(3) *p*-methoxybenzyl bromide
(4) *p*-methylbenzyl bromide

35. Which of the statements is incorrect about below reaction?



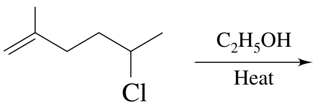
(a) (b) (c) (d) (e)

(1) The given reaction follows S_N2 mechanism.
(2) In (c) carbon atom is sp^3 hybridised.
(3) In (c) carbon atom is sp^2 hybridised.
(4) (b) and (d) have opposite configuration.

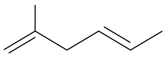
EXERCISE 3

One and More than One Option Correct Type Question

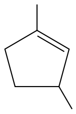
1. Consider the following elimination reaction:



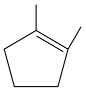
(1)



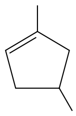
(2)



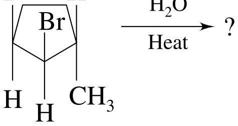
(3)



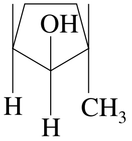
(4)



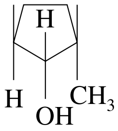
2. When the reactants shown below undergo substitution, which of the products will form?



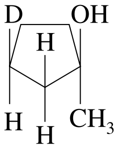
(1)



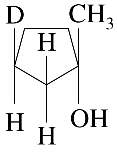
(2)



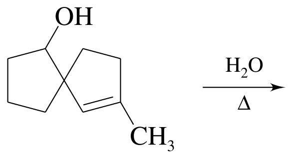
(3)



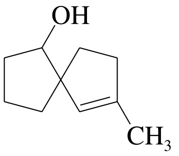
(4)



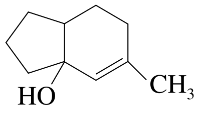
3. What is/are the expected solvolysis product(s) in the following reaction?



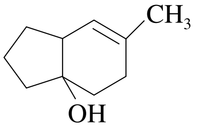
(1)



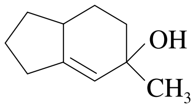
(2)



(3)

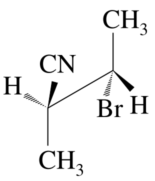


(4)

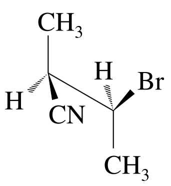


4. Which of the following on treatment with NaCN(aq) results in a chiral product?

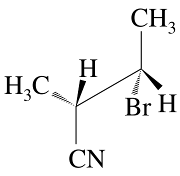
(1)



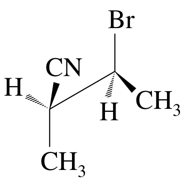
(2)



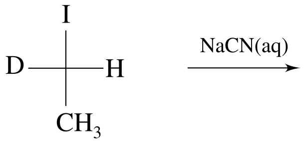
(3)

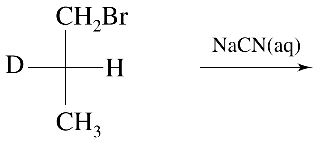


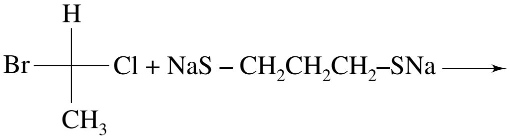
(4)

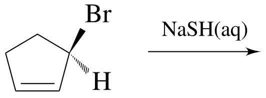


5. In which of the following reaction, inversion of configuration at chiral carbon takes place?

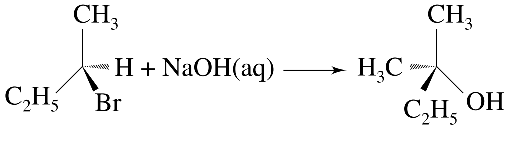
(1) 

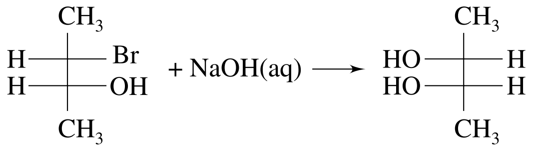
(2) 

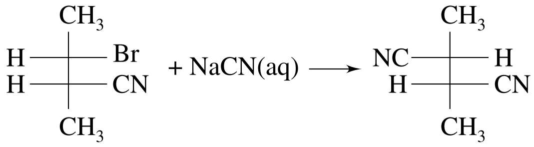
(3) 

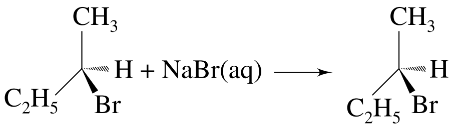
(4) 

6. In which of the following reaction(s), reactant and product are correctly matched?

(1) 

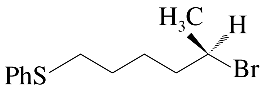
(2) 

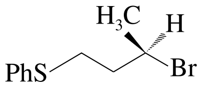
(3) 

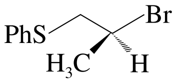
(4) 

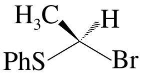
(+)-dextro (±)-racemic

7. Pick out the alkyl bromides which proceed with retention of configuration in an S_N2 reaction with CH_3ONa(aq):

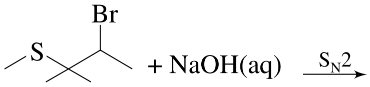
(1) 

(2) 

(3) 

(4) 

8. Consider the following substitution reaction



The correct statement(s) is/are:

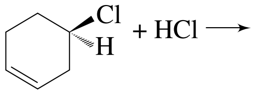
(1) reaction occur at much faster rate than when substrate is 2-bromo-3, 3-dimethyl pentane

(2) reaction occur with inversion of configuration

(3) reaction occur with retention of configuration

(4) E2 product is preferred over S_N2

9. Consider the following reaction



X

When a pure enantiomer of X is taken in the above reaction, correct completion regarding is/are

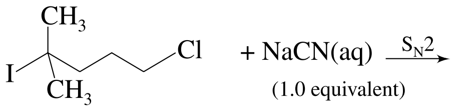
(1) Four different dichlorocyclohexane are formed as significant products

(2) a pair of enantiomers is formed

(3) two pairs of diastereomers are formed

(4) product mixture has zero specific rotation

10. Consider the reaction given below:



The correct statement(s) applicable to the above reaction is/are:

(1) Cl^- is substituted predominantly

(2) Cl^- is a better leaving group

(3) substitution of I^- in the above reaction required greater activation energy than for Cl^-

(4) addition of some NaI catalyse the substitution reaction

11. Which one of the following statements is true?

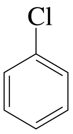
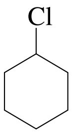
(1) Major part of energy needed for the heterolysis of C–X bond in S_N1 reaction mechanism is obtained by the solvation of X^- by the polar protic solvent.

(2) Greater solvation of attacking nucleophile & poor solvation of transition state promotes the reaction by S_N2 mechanism.

(3) Increase in the number of phenyl ring at C of C–X causes a shift in mechanism from S_N2 to S_N1.

(4) Allyl and benzyl halides undergo S_N1 reactions as they give resonance stabilized carbocation.

12. Which of the statements is correct?

(1)  is more reactive than  towards S_N1 mechanism due to aromaticity.

(2) Inversion of configuration takes place during S_N2 mechanism at α-chiral carbon.

(3) Formation of R–CI from R–OH by reaction with $SOCI_2$ is best method because byproducts are gases.

(4) CH_4 can be prepared by decarboxylation of carboxylic acid.

13. Which of the following reactions yield an alkyl halide?

(1) $CH_3CH_2OCH_2CH_3 \xrightarrow[h\nu]{Cl_2}$

(2) $CH_3CH_2OCH_2CH_3 \xrightarrow[heat]{Conc.\ HI}$

(3) $CH_3CH_2OCH_2CH_3 \xrightarrow[heat]{PCl_5}$

(4) $CH_3CH_2OH \xrightarrow{SOCl_2}$

14. $(CH_3–CH_2)_3–C–Br \xrightarrow[25°C]{CH_3OH} (CH_3–CH_2)_3–C–O–CH_3$

$+ CH_3–CH = C(CH_2–CH_3)_2$

Pick out correct statement for given reaction.

(1) Major product is $(CH_3–CH_2)_3–C–O–CH_3$

(2) At low temperature reaction preceding through SN_1

(3) On increasing temperature major product is $CH_3–CH = C(CH_2–CH_3)_2$

(4) At high temp reaction preceding through E_2

Statement Type Question

(1) If both Statement-I and Statement-II are correct and Statement-II is the correct explanation for Statement-I

(2) If both Statement-I and Statement-II are correct and Statement-II is not the correct explanation for Statement-I

(3) If Statement-I is correct and Statement-II is incorrect

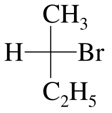
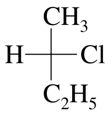
(4) If Statement-I is incorrect and Statement-II is correct

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

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

16. **Statement I:** Aryl halides undergo nucleophilic substitution with ease.

Statement II: The carbon halogen bond in aryl halides has partial double bond character.

17. **Statement I:** If the mixture of  $H–\overset{CH_3}{\underset{C_2H_5}{C}}–Br$ and  $H–\overset{CH_3}{\underset{C_2H_5}{C}}–Cl$ reacts with the excess of NaSH in DMF, the molecularity of the SN^2 reaction will be two but not three.

Statement II: In the SN^2 reaction two molecules e.g. R–X and Nu take part in the formation of transition state.

18. **Statement I:** Aryl halides are extremely less reactive towards nucleophilic substitution reactions.

Statement II: In haloarenes the electron pairs of halogen atom are in conjugation with π electrons of the ring. More over due to more 'S' character of sp^2 carbon of ring, the C–X bond strength increases and cleavage becomes difficult.

19. **Statement I:** n-Butyl chloride has higher boiling point than n-butyl bromide.

Statement II: C–Cl bond is more polar than C–Br Bond.

20. **Statement I:** The London force of attraction and the dipole–dipole attraction (of C – X bond) are two types of forces which influence boiling point of alkyl halides.

Statement II: The London force is a surface attraction.

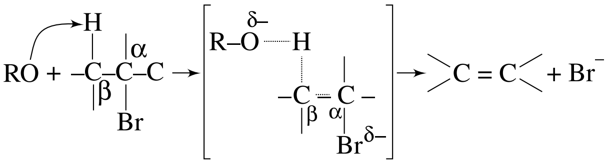
21. **Statement I:** Aryl halide cannot be prepared by Gabriel phthalamide method.

Statement II: Aryl halide does not give substitution reaction in ordinary condition.

Comprehension Type Question

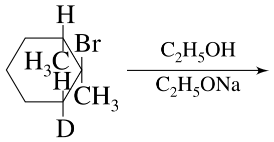
Comprehension (Q. 22–24)

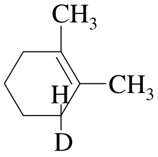
In an E2 reaction, following one step mechanism is involved.

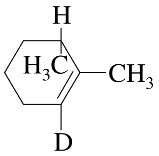


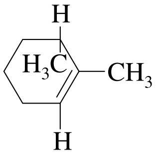
As shown in the above mechanism, a β-proton anti to leaving group is abstracted by the alkoxide base. If a less bulky base is used, β-proton is eliminated giving most substituted, most stable product as the major product. On the other hand if a bulky base is used, β-proton is abstracted from β-carbon where there is least steric hindrance and this gives least substituted, although least stable, alkene as the major product.

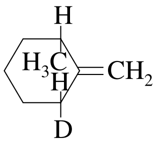
22. What is the major product in the following elimination reaction?



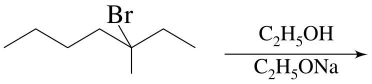
(1) 

(2) 

(3) 

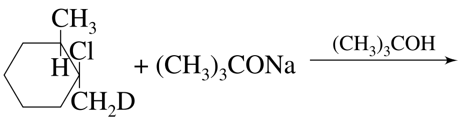
(4) 

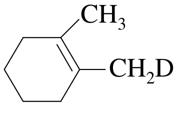
23. In the following reaction, how many elimination products would be formed in principle by E2 mechanism?

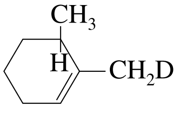


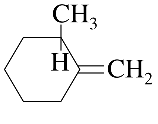
(1) 2 (2) 3
(3) 4 (4) 5

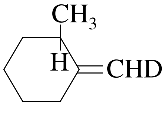
24. What is the major elimination product in the following reaction?



(1) 

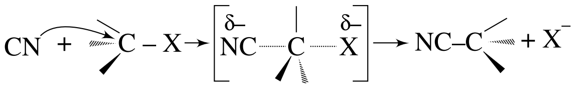
(2) 

(3) 

(4) 

Comprehension (Q. 25–27)

The general mechanism of a S_{N_2} reaction is as follows



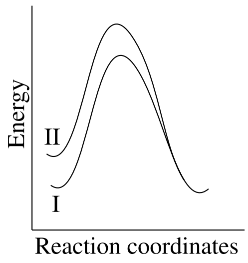
Factors that limit the rate of reaction are steric hindrance at α-carbon of substrate and strength of C–X bond. Any factor which stabilises transition state increases the rate of reaction.

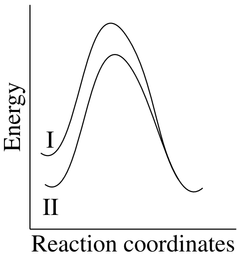
25. Consider the following S_N2 reaction

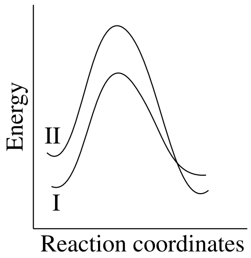
$$CH_3 - I + HO^- \xrightarrow{K_1} CH_3 - OH + I^- \qquad (I)$$

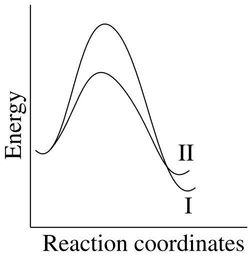
$$CH_3 - Cl + HO^- \xrightarrow{K_2} CH_3 - OH + Cl^- \qquad (II)$$

Which of the following energy diagram is correctly labeled?

(1) 

(2) 

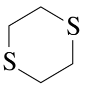
(3) 

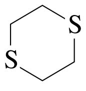
(4) 

26. In the previous question, under identical reaction condition, i.e., temperature, concentration of substrate and nucleophile, the correct relationship between rate constant is

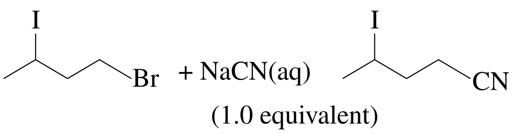
(1) $k_I < k_{II}$ (2) $k_I = k_{II}$
(3) $k_I > k_{II}$ (4) $k_I = k_{II}$

27. Which of the following is not a correct representation of S_N2 reaction?

(1) $Br–CH_2CH_2–Br + NaS–CH_2CH_2–SNa \rightarrow$ 

(2) $Br–CH_2CH_2CH_2CH_2–Br + NaS \rightarrow$ 

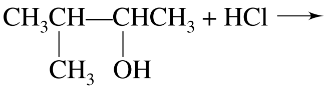
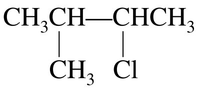
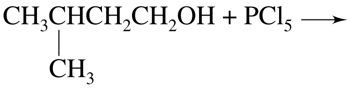
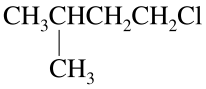
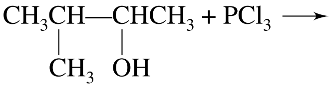
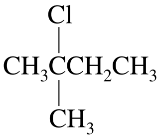
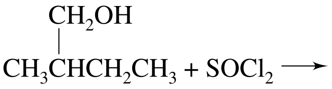
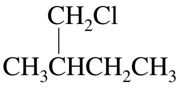
(3) $CH_3CH_2OH + NaNH_2 \rightarrow CH_3CH_2NH_2$

(4) 

(1.0 equivalent)

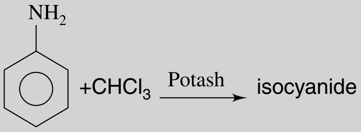
Column Matching Type Question

28. Match the following

	Column-I		**Column-II**
(A)	 $CH_3\underset{CH_3}{\underset{\mid}{C}}H-\underset{OH}{\underset{\mid}{C}}HCH_3 + HCl \longrightarrow$	(p)	 $CH_3\underset{CH_3}{\underset{\mid}{C}}H-\underset{Cl}{\underset{\mid}{C}}HCH_3$
(B)	 $CH_3\underset{CH_3}{\underset{\mid}{C}}HCH_2CH_2OH + PCl_5 \longrightarrow$	(q)	 $CH_3\underset{CH_3}{\underset{\mid}{C}}HCH_2CH_2Cl$
(C)	 $CH_3\underset{CH_3}{\underset{\mid}{C}}H-\underset{OH}{\underset{\mid}{C}}HCH_3 + PCl_3 \longrightarrow$	(r)	 $CH_3\overset{Cl}{\overset{\mid}{\underset{CH_3}{\underset{\mid}{C}}}}CH_2CH_3$
(D)	 $CH_3\overset{CH_2OH}{\overset{\mid}{C}}HCH_2CH_3 + SOCl_2 \longrightarrow$	(s)	 $CH_3\overset{CH_2Cl}{\overset{\mid}{C}}HCH_2CH_3$

(1) A → r; B → q; C → p; D → s
(2) A → q; B → p; C → s; D → r
(3) A → s; B → r; C → q; D → p
(4) A → p; B → s; C → r; D → q

29. Make the correct match of the following from List-I and List-II.

List-I		**List-II**	
(A)	$RCCOAg + Br_2 \xrightarrow{CCl_4} RBr + CO_2 + AgBr$	(P)	Carbylamine
(B)	 $C_6H_5NH_2 + CHCl_3 \xrightarrow{Potash}$ isocyanide	(Q)	Hundiecker Reaction
(C)	$2R–COOAg + I_2 \longrightarrow RCOOR + CO_2 + AgI$	(R)	Baurn Simonini Reaction
(D)	$2CH_3Cl + HgF_2 \longrightarrow 2CH_3 - F + HgCl_2$	(S)	Swarts Reaction

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

30. Make the correct match of the following from List-I and List-II.

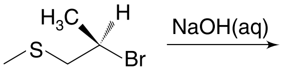
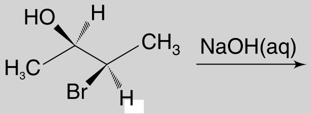
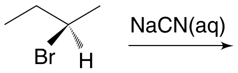
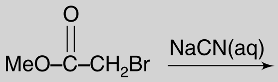
List-I		**List-II**	
(A)	Gammexane	(P)	Pesticide
(B)	D.D.T.	(Q)	Insecticide
(C)	Chloroform	(R)	Anesthetic Agent
(D)	Westron	(S)	Solvent

(1) A → Q, B → R, C → S, D → P
(2) A → P, B → Q, C → S, D → R

(3) A → R, B → S, C → Q, D → P

(4) A → P, B → Q, C → R, D → S

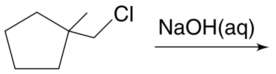
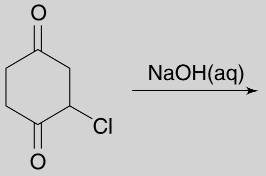
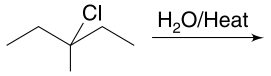
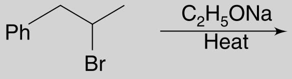
31. Match the column-I with Column-II and mark the correct option from the codes given below

	Column-I		Column-II
i.		p.	Net inversion of configuration in S_N2 reaction
ii.		q.	Net retention of configuration in S_N2 reaction
iii.		r.	Formation of achiral product
iv.	 $MeO-\overset{\overset{O}{\parallel}}{C}-CH_2Br \xrightarrow{NaCN(aq)}$	s.	Neighbouring group participation

Codes

	i	ii	iii	iv
(1)	q, s	p, r	p	r, s
(2)	q, s	s	p, s	q, s
(3)	p	q, r	s	p
(4)	p, r	q, s	p, r	q

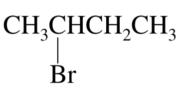
32. Match the reaction from Column-I with the type of mechanism from Column-II and mark the correct option from the codes given below.

	Column-I		Column-II
i.		p.	S_N1
ii.		q.	S_N2
iii.		r.	E2
iv.		s.	E1cb

Codes

	i	ii	iii	iv
(1)	p	p, q	p, q, r	r, s
(2)	q	q, r, s	p	p, q, r, s
(3)	s	p	r, s	p, q
(4)	p, q	r, s	q, s	p, r, s

33. Match the reactions in Column-I with the appropriate name in the Column-II.

Column-I	Column-II
(A) $C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$	(p) Elimination reaction
(B) $C_6H_5N_2^+Cl^- + HBr \xrightarrow{Cu} C_6H_5Br + N_2 + HCl$	(q) Finkelstein reaction
(C)  $\underset{\underset{Br}{\vert}}{CH_3CHCH_2CH_3} \xrightarrow{alc.KOH} CH_3–CH = CHCH_3$	(r) Groove's process
(D) $CH_3CH_2CH_2Cl+NaI \xrightarrow{Acetone} CH_3CH_2CH_2I + NaCl$	(s) Gattermann reaction

(1) A → r; B → s; C → p; D → q

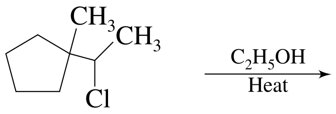
(2) A → r ; B → p; C → q; D → s

(3) A → p; B → q; C → s; D → r

(4) A → q; B → s; C → r; D → p

Single Digit Integer Type Question

34. Consider the following reaction,

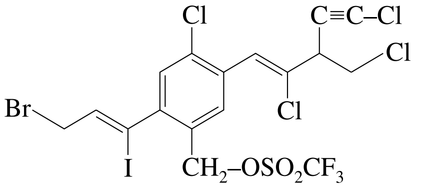


In principle, how many different alkenes are possible by the above elimination reaction?

35. How many of the following are denser than water?

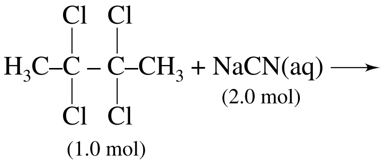
(i) CCl_4
(ii) $CH_3CH_2CH_2CH_2Cl$
(iii) Bromocyclohexane
(iv) Chlorocyclopentane
(v) 1,3-difluorocyclopentane
(vi) CH_3I
(vii) 1-fluorodecane
(viii) CH_2Br_2
(ix) CH_3Cl
(x) $CHCl_3$

36. Consider the following compound



If the above compound is treated with excess of NaCN (aq), how many CN^- group would be incorporated by S_N2 reaction?

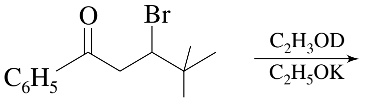
37. In the following reaction



$$\underset{(1.0\ \text{mol})}{H_3C\text{–}\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}\text{–}CH_3} + \underset{(2.0\ \text{mol})}{NaCN(aq)} \longrightarrow$$

How many different dicyano products are expected?

38. In the reaction given below how many elimination products are formed in principle if reaction proceeds by E1cb mechanism?



EXERCISE 4

1. The reaction is a **[AIEEE-2002]**

$(CH_3)_3\ CBr + H_2O \longrightarrow (CH_3)_3\ COH + HBr$

(1) Substitution reaction
(2) Debromination reaction
(3) Rearrangement reaction
(4) Elimination reaction

2. The correct order of the thermal stability of hydrogen halides (H–X) is **[AIEEE-2005]**

(1) HF > HCl > HBr > HI
(2) HI > HBr > HCl > HF
(3) HI > HCl < HF > HBr
(4) HCl < HBr > HBr < HI

3. Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of **[AIEEE-2005]**

(1) Instability (2) Insolubility
(3) Steric hindrance (4) Inductive effect

4. Alkyl halides react with dialkyl copper reagents to give **[AIEEE-2005]**

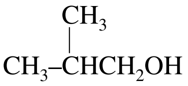
(1) Alkyl copper halides
(2) Alkenes
(3) Alkenyl halides
(4) Alkanes

5. Elimination of HBr from 2-bromobutane results in the formation of **[AIEEE-2005]**

(1) Predominantly 2-butene
(2) Equimolar mixture of 1 and 2-butene
(3) Predominantly 2-butyne
(4) Predominantly 1-butene

6. Among the following the one that gives positive iodoform upon reaction with I_2 and NaOH is **[AIEEE-2006]**

(1) $C_6H_5CH_2CH_2OH$

(2) 

$CH_3\text{–}\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2OH$

(3) $PhCHOHCH_3$
(4) $CH_3CH_2CH(OH)CH_2CH_3$

7. Which of the following is the correct order of decreasing SN^2 reactivity? **[AIEEE-2007]**

(1) $RCH_2X > R_3CX > R_2CHX$
(2) $RCH_2X > R_2CHX > R_3CX$
(3) $R_3CX > R_2CHX > RCH_2X$
(4) $R_2CHX > R_3CX > RCH_2X$

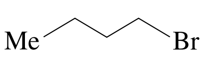
8. The organic chloro compound, which shows complete stereochemical inversion during a S_N2 reaction is: **[AIEEE-2008]**

(1) $(CH_3)_3CCl$ (2) $(CH_3)_2CHCl$
(3) CH_3Cl (4) $(C_2H_5)_2CHCl$

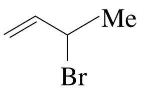
9. Which of the following on heating with aqueous KOH, produces acetaldehyde? **[AIEEE-2009]**

(1) CH_3COCl (2) CH_3CH_2Cl
(3) CH_2ClCH_2Cl (4) CH_3CHCl_2

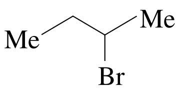
10. Consider the following bromides **[AIEEE-2010]**



Ⓐ



Ⓑ



Ⓒ

The correct order of S_N1 reactivity is

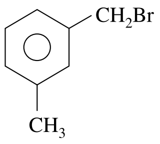
(1) A > B > C (2) B > C > A
(3) B > A > C (4) C > B > A

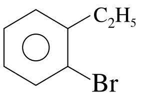
11. By heating which mixture, propane nitrile will be obtained? **[AIEEE-2011]**

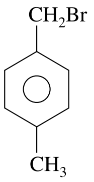
(1) Ethyl alcohol + KCN
(2) Propyl alcohol + KCN
(3) Ethyl chloride + KCN
(4) Propyl chloride + KCN

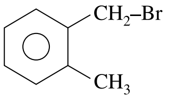
12. Compound A, (C_8H_9Br) gives a white precipitate when warmed with alcoholic $AgNO_3$ oxidation of A gives an acid B, $(C_8H_6O_4)$ B easily forms anyhydride on heating. Identify the compound A.

[JEE Main-2011]

(1)


(2)


(3)


(4)


13. Iodoform can be prepared from all except **[AIEEE-2012]**

(1) Isopropyl alcohol (2) 3-Methyl-2-butanone
(3) Isobutyl alcohol (4) Ethyl methyl ketone

14. $C_2H_5Br \xrightarrow{AgCN} X \xrightarrow[Zn–Hg/HCl]{Reduction} Y$; Here, Y is:

[JEE Main Online-2012]

(1) n-propylamine (2) Isopropylamine
(3) Ethyl methyl amine (4) Ethylamine

15. Copper wire test for halogens is known as: **[JEE Main Online-2012]**

(1) Duma's Test (2) Beilstein's Test
(3) Lassigne's Test (4) Liebig's Test

16. Among the following the molecule with the lowest dipole moment is: **[JEE Main Online-2012]**

(1) $CHCl_3$ (2) CH_2Cl_2
(3) CCl_4 (4) CH_3Cl

17. Beilstein test is used for estimation of which one of following elements? **[JEE Main Online-2012]**

(1) S (2) Cl
(3) C and H (4) N

18. The conversion of benzene diazonium chloride to bromobenzene can be accomplished by

[JEE Main Online-2012]

(1) Azo coupling reaction
(2) Friedel–Crafts reaction
(3) Reimer–Tiemann reaction
(4) Gattermann reaction

19. Aryl fluoride may be prepared from arene diazonium chloride using **[JEE Main Online-2013]**

(1) HBF_4/Δ (2) $HBF_4/NaNO_2$, Cu, Δ
(3) CuF/HF (4) Cu/HF

20. In Williamson synthesis of mixed ether having a primary and tertiary alkyl group if tertiary halide is used, then **[JEE Main Online-2013]**

(1) Rate of reaction will be slow due to slow cleavage of carbon-halogen bond
(2) Alkene will be the main product
(3) Simple ether will form instead of mixed ether
(4) Expected mixed ether will be formed

21. The Wurtz–Fittig reaction involves combination of

[JEE Main Online-2013]

(1) Two molecules of aryl halides
(2) One molecule of each of aryl halide and alkyl-halide
(3) One molecule of each aryl-halide and phenol
(4) Two molecules of alkyl-halides

22. Carbylamine forms from aliphatic or aromatic primary amine via which of the following **[JEE Main Online-2013]**

(1) Carbanion (2) Carbene
(3) Carbocation (4) Carbon radical

23. A solution of (–)-chloro-1-phenylethane in toluene racemises slowly in the presence of a small amount of $SbCl_5$, due to the formation of

[JEE-Main-2013]

(1) Carbanion (2) carbene
(3) carbocation (4) free radical

24. On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is: **[JEE Main-2014]**

(1) An alkane diol (2) an alkyl cyanide
(3) an alkyl isocyanide (4) an alkanol

25. In S_N2 reaction, the correct order of reactivity for the following compounds:

$CH_3Cl, CH_3CH_2Cl, (CH_3)_2CHCl$ and $(CH_3)_3CCl$ is **[JEE Main-2014]**

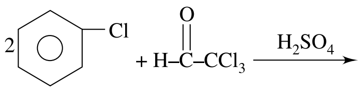
(1) $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > (CH_3)_3CCl$
(2) $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$
(3) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$
(4) $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$

26. In a nucleophilic substitution reaction:

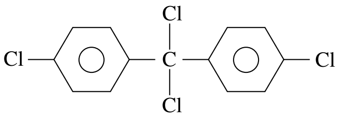
$R–Br + Cl^- \xrightarrow{DMF} R–Cl + Br^-$, which one of the following undergoes complete inversion of configuration? **[JEE Main Online-2014]**

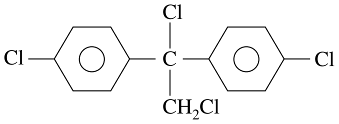
(1) $C_6H_5CHC_6H_5Br$ (2) $C_6H_5CH_2Br$
(3) $C_6H_5CHCH_3Br$ (4) $C_6H_5CCH_3C_6H_5Br$

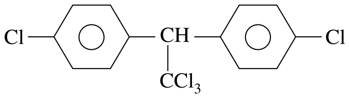
27. Chlorobenzene reacts with trichloro acetaldehyde in the presence of H_2SO_4

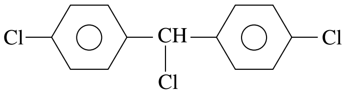


The major product formed is: **[MEE Main Online-2014]**

(1) 

(2) 

(3) 

(4) 

28. Conversion of benzene diazonium chloride to chlorobenzene is an example of which of the following reaction? **[JEE Main Online-2014]**

(1) Claisen (2) Friedel–Craft
(3) Sandmeyer (4) Wurtz

29. The major product formed when 1, 1, 1-trichloropropane is treated with aqueous potassium hydroxide is **[JEE main Online-2014]**

(1) Propyne (2) 1-Propanol
(3) 2-Propanol (4) Propionic acid

30. The major organic compound formed by the reaction of 1, 1, 1-trichloroethane with silver powder is **[JEE Main-2014]**

(1) acetylene (2) ethane
(3) 2-butyne (4) 2-butene

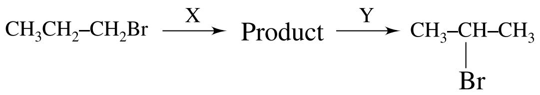
31. The synthesis of alkyl fluorides is best accomplished by **[JEE main-2015]**

(1) Free radical fluorination
(2) Sandmeyer's reaction
(3) Finkelstein reaction
(4) Swarts reaction

32. The order of reactivity of the following alkyl halides for a S_N2 reaction is **[IIT-2000]**

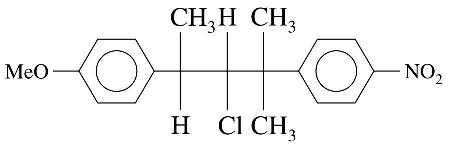
(1) RF > RCl > R–Br > R-I
(2) R-F > R-Br > R-Cl > R-I
(3) R–Cl > R–Br > RF > RI
(4) R–I > R–Br > R–Cl > R–F

33. Identify the set of reagents/reaction of the following alkyl halides for a S_N2 reaction is **[IIT-2002]**

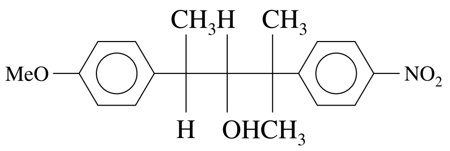


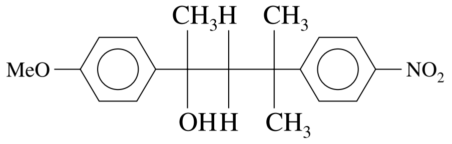
$$CH_3CH_2-CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$$

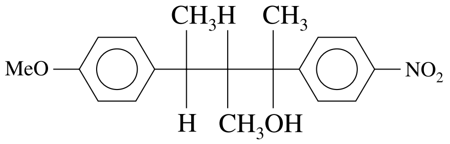
(1) X = dilute aqueous NaOH, 20°C
Y = HBr/acetic acid, 20°C
(2) X = concentrated alcoholic NaOH, 80°C
Y = HBr/acetic acid, 20°C
(3) X = dilute aqueous NaOH, 20°C
Y = $Br_2/CHCl_3$, 0°C
(4) X = concentrated alcoholic NaOH, 80°C
Y = $Br_2/CHCl_3$, 0°C

34.  **[IIT-2005]**

on hydrolysis in presence of acetone?

(A) 

(B) 

(C) 

(1) A & B
(2) Only B
(3) Only C
(4) A & C

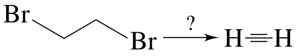
35. Match the Column-I with Column-II and mark the correct option from the codes given below. **[JEE Adv.-2006]**

	Column-I		Column-II
(A)	CH_3–CHBr–CD_3 on treatment with alc. KOH Gives CH_2=CH–CD_3 as the major product.	(p)	E1 reaction
(B)	Ph–CHBr–CH_3–reacts Faster than Ph–CHBr–CD_3	(q)	E2 reaction
(C)	Ph–CH_2–CH_2Br on treatment with $C_2H_5OD/C_2H_5O^-$ gives Ph–CD=CH_2 as the major product.	(r)	E1cb reaction
(D)	$PhCH_2CH_2Br$ and $PhCD_2CH_2Br$ react with same rate.	(s)	First order reaction

Codes

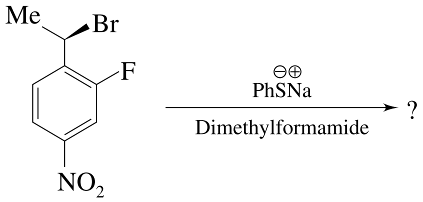
	A	B	C	D
(1)	q	q	r	p, s
(2)	p, s	p	q	r, s
(3)	q	q, r	p, q, r	q
(4)	q	s	q, r	p, r, s

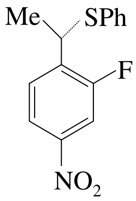
36. The reagent in form the following conversion is/are **[IIT-2007]**

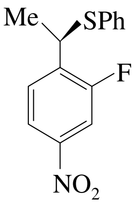


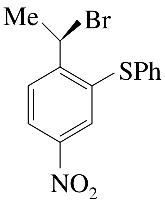
(1) Alcoholic KOH
(2) Alcoholic KOH followed by $NaNH_2$
(3) Aqueous KOH followed by $NaNH_2$
(4) Zn/CH_3OH

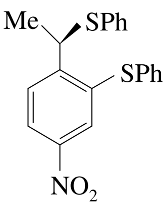
37. The major product of the following reaction is: **[IIT-2008]**



(1) 

(2) 

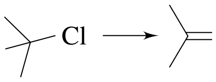
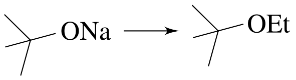
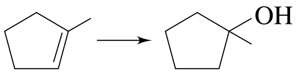
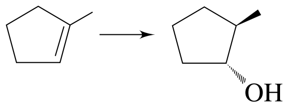
(3) 

(4) 

38. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is

[JEE Adv.-2011 (integer type)]

39. Match the chemical conversion in Column-I with the appropriate reagents in Column-II and select the correct answer using the code given below the lists **[JEE Adv.-2013]**

Column-I	**Column-II**
(A) 	(p) (I) $Hg(OAc)_2$; (ii) $NaBH_4$
(B) 	(q) NaOEt
(C) 	(r) Et-Br
(D) 	(s) (i) BH_3; (ii) H_2O_2/NaOH

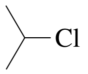
Codes

	A	B	C	D
(1)	q	r	p	s
(2)	r	q	p	s
(3)	r	q	s	p
(4)	r	q	s	p

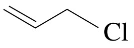
40. KI in acetone, undergoes S_N2 reaction with each P, Q, R and S. The rates of the reaction vary as **[JEE Adv. Only-2013]**

$H_3C–Cl$

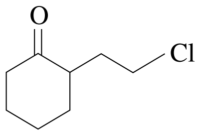
(P)



(Q)



(R)



(S)

(1) P > Q > R > S (2) S > P > R > Q
(3) P > R > Q > S (4) R > P > S > Q

ANSWER KEY

EXERCISE # 1

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

EXERCISE # 2

1. (2) 2. (4) 3. (2) 4. (2) 5. (1)
6. (3) 7. (1) 8. (4) 9. (3) 10. (2)
11. (2) 12. (2) 13. (2) 14. (1) 15. (2)
16. (3) 17. (2) 18. (1) 19. (3) 20. (4)
21. (1) 22. (1) 23. (2) 24. (2) 25. (4)
26. (1) 27. (4) 28. (3) 29. (2) 30. (3)
31. (4) 32. (1) 33. (1) 34. (3) 35. (2)

EXERCISE # 3

1. (1,2,4) 2. (1,2,3,4) 3. (1,2,4) 4. (1,3,4) 5. (1,4)
6. (1,3,4) 7. (1,2,3) 8. (1,3) 9. (1,3) 10. (1,2,4)
11. (1,2,4) 12. (2,3,4) 13. (2,3,4) 14. (1,3) 15. (2)
16. (4) 17. (2) 18. (1) 19. (4) 20. (2)
21. (2) 22. (3) 23. (4) 24. (4) 25. (2)
26. (3) 27. (3) 28. (1) 29. (3) 30. (4)
31. (1) 32. (2) 33. (1) 34. (8) 35. (6)
36. (3) 37. (4) 38. (4)

EXERCISE # 4

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

HINT AND SOLUTION

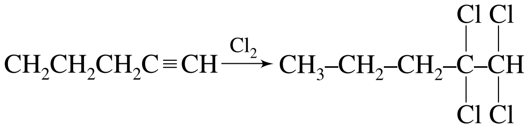
EXERCISE # 1

1. [4]

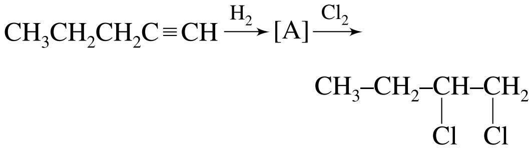
S_N2 Reaction does not involve rearrangement.

Product of (i) and (ii) reaction formed without rearrangement, so that both reaction involve S_N2 mechanism.

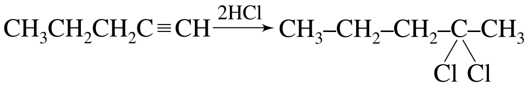
2. [3]

(1) 

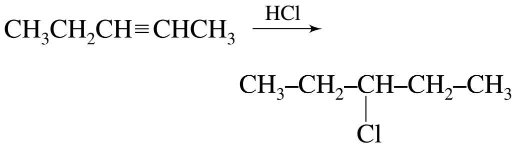
$$CH_2CH_2CH_2C\equiv CH \xrightarrow{Cl_2} CH_3-CH_2-CH_2-\underset{Cl}{\overset{Cl}{C}}-\underset{Cl}{\overset{Cl}{CH}}$$

(2) 

$$CH_3CH_2CH_2C\equiv CH \xrightarrow{H_2} [A] \xrightarrow{Cl_2} CH_3-CH_2-\underset{Cl}{CH}-\underset{Cl}{CH_2}$$

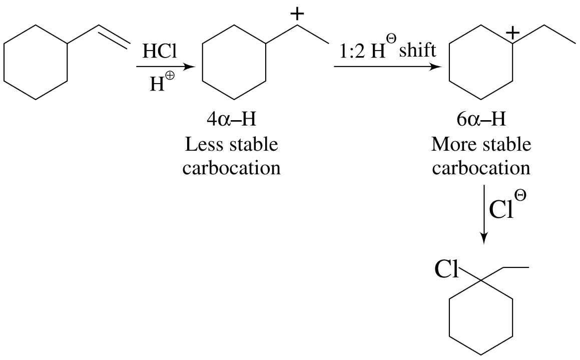
(3) 

$$CH_3CH_2CH_2C\equiv CH \xrightarrow{2HCl} CH_3-CH_2-CH_2-\underset{Cl\ Cl}{C}-CH_3$$

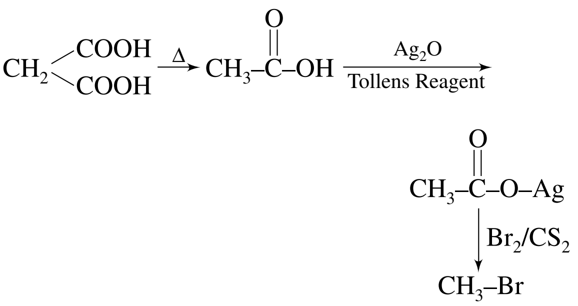
(4) 

$$CH_3CH_2CH\equiv CHCH_3 \xrightarrow{HCl} CH_3-CH_2-\underset{Cl}{CH}-CH_2-CH_3$$

3. [1]

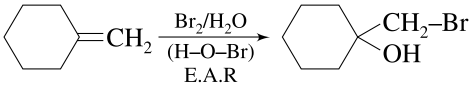


4. [4]



$$CH_2\begin{matrix}COOH\\COOH\end{matrix} \xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{Tollens Reagent}]{Ag_2O} CH_3-\overset{O}{\overset{\|}{C}}-O-Ag \xrightarrow{Br_2/CS_2} CH_3-Br$$

5. [1]



'Markownikov's rule'

6. [1]

Rate of $S_N1 \propto C^{\oplus}$ stability

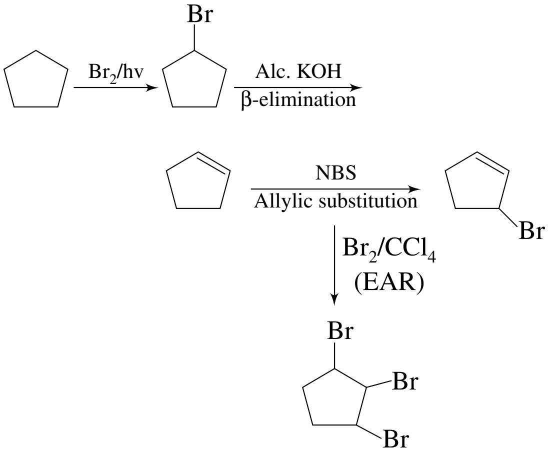
$$\text{Rate of } S_N2 \propto \frac{1}{\text{Steric crowding}}$$

7. [4]

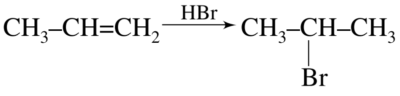
Nucleophilic strength ∝ size

$$\left.\begin{matrix}HCl \rightarrow H^+ + Cl^{\ominus}\\ HI \rightarrow H^+ + I^{\ominus}\end{matrix}\right] \begin{matrix}\text{Size}\uparrow\\ \text{Base strength}\downarrow\\ \text{Nucleophilic strength}\uparrow\end{matrix}$$

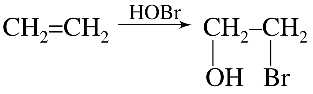
8. [3]



9. [4]

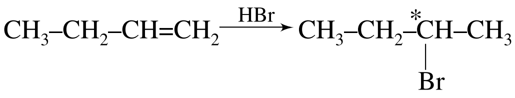


$$CH_3-CH=CH_2 \xrightarrow{HBr} CH_3-\underset{Br}{CH}-CH_3$$



$$CH_2=CH_2 \xrightarrow{HOBr} \underset{OH}{CH_2}-\underset{Br}{CH_2}$$

$$CH_3-CH_2-CH=CH_2 \xrightarrow[H_2O_2]{HBr} CH_3-CH_2-CH_2-CH_2-Br$$



$$CH_3-CH_2-CH=CH_2 \xrightarrow{HBr} CH_3-CH_2-\underset{Br}{\overset{*}{CH}}-CH_3$$

(chiral C-present)

10. [2]

$$CH_3–CH_2–CH{=}CH_2 \xrightarrow[C_6H_5–O–O–C_6H_5]{HBr}$$

Antimarkownikoff addition

$$CH_3–CH_2–CH_2–CH_2–Br$$

1-bromobutane

11. [3]

In given reaction configuration of product opposite as reactant, i.e., inversion takes place so that it must be SN_2 reaction.

$$\frac{dx}{dt} = k\ [\text{substrate}]^1\ [OH^-]^1$$

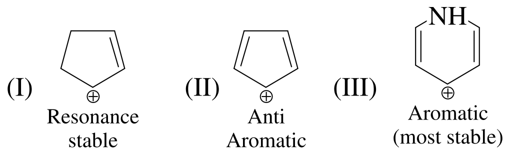
12. [1]

Rate of SN_1 reaction ∝ stability of carbocation

$CH_3-\overset{\oplus}{C}H_2$	$CH_3–\overset{\oplus}{C}H–CH_3$	$CH_2{=}CH–\overset{\oplus}{C}H_2$	$Ph–\overset{\oplus}{C}H–CH_3$
(I)	(II)	(III)	(IV)
(3α–H)	(6α–H)	(Resonance)	(Resonance + H-effect) most stable

13. [1]

Reactivity of SN_1 Reaction ∝ Stability of carbocation



III > I > II

14. [3]

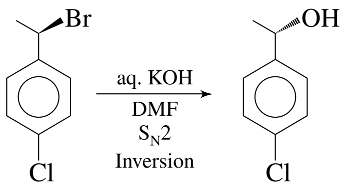
S_N2 reaction of iodide ion converts the alkyl chloride to the more reactive alkyl iodide

$$R–Cl \xrightarrow{NaI} R–I \text{ (Finkeltein reaction)}$$

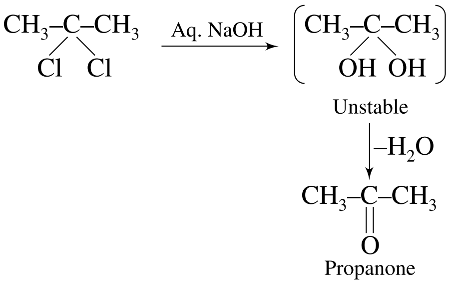
R–I > R–Br > R–Cl > R–F

Reactivity ↓

15. [3]



16. [4]

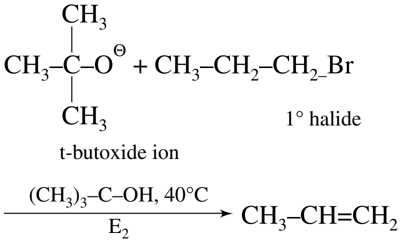


17. [1]

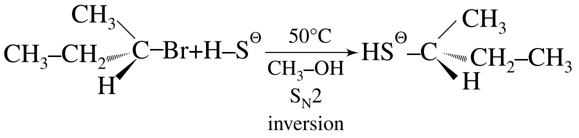
In polar protic solvent 3° halide will give unimolecular substitution (SN_1)

18. [1]

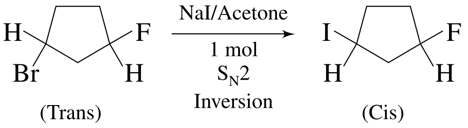
In strangest base (t-Buō) β-elimination predominantly takes place.



19. [3]



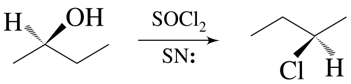
20. [1]



Reactivity of alkyl halides,

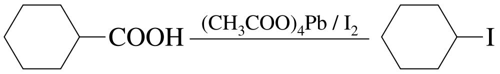
R – I > R – Br > R – Cl > R – F

21. [2]



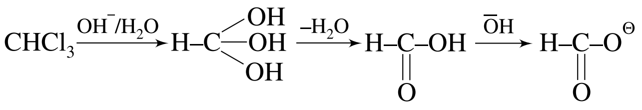
Retention takes place, i.e., configuration of product and reactant are same.

22. [2]



De-carboxylation followed by iodination takes place.

23. [3]



$$\mathrm{CHCl_3} \xrightarrow{\mathrm{\bar{O}H/H_2O}} \mathrm{H{-}C(OH)_3} \xrightarrow{-\mathrm{H_2O}} \mathrm{H{-}\underset{\underset{O}{\|}}{C}{-}OH} \xrightarrow{\mathrm{\bar{O}H}} \mathrm{H{-}\underset{\underset{O}{\|}}{C}{-}O^{\ominus}}$$

24. [1]

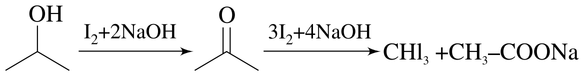
$$\mathrm{CHCl_3} \xrightarrow[\mathrm{HF}]{\mathrm{SbF_5}} \underset{\text{(2 mole)}}{\mathrm{CHF_2Cl}} \xrightarrow{\mathrm{1070K}} \mathrm{CF_2{=}CF_2\,(X) + 2HCl}$$

25. [2]

$$2\mathrm{NaOH} + \mathrm{I_2} \longrightarrow \mathrm{NaOI} + \mathrm{NaI} + \mathrm{H_2O}$$

$$\downarrow$$

$$\mathrm{NaI} + [\mathrm{O}]$$



a = 4, (I_2 molecule used)
b = 6 (NaOH molecule used)

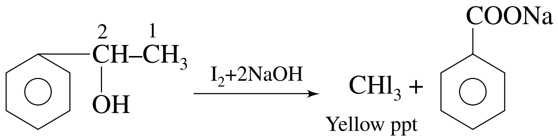
$$\frac{a}{b} = \frac{4}{6} = 2:3$$

26. [2]

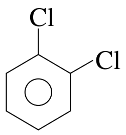
$$\mathrm{CHCl_3} \xrightarrow[\text{Nitration}]{\text{Conc. } \mathrm{HNO_3}} \underset{\text{Chloropicrin}}{\mathrm{CNO_2{\cdot}Cl_3}}$$

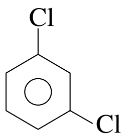
27. [2]

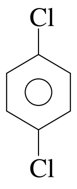
A will give positive iodoform test, so it must be 2-alkanol of $C_8H_{10}O$.

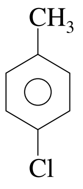


28. [3]









$\mu \neq 0$ $\mu \neq 0$ $\mu = 0$ $\mu \neq 0$

Magnitude of equal vector at 180°, Cancelled by each other.

29. [2]

Boiling point ∝ molecular weight.

30. [1]

Stability of R–X

$$\underrightarrow{\mathrm{R{-}F > R{-}Cl > R{-}Br > R{-}I}}$$

E.N.↓ Polarity↓ stability↓

31. [1]

Bond strength ∝ Electronegativity.

32. [3]

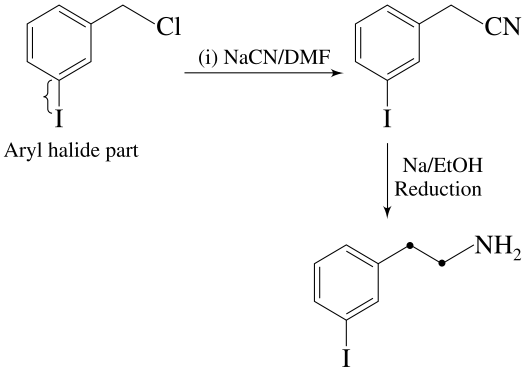
Boling point ∝ Molecular weight

$$\propto \frac{1}{\text{Branching (for isomer)}}$$

33. [2]

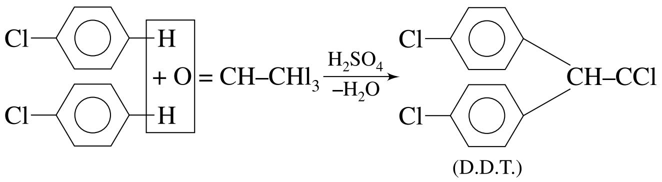
$\mathrm{R{-}X} \xrightarrow[\text{Beilstein's test}]{\text{Cu-wire}}$ Green flame (A halogen may be present.)

34. [4]



1° halide undergoes SN reaction but aryl halides do not give SN reaction in ordinary condition.

35. [3]

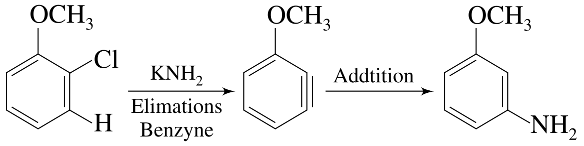


36. [4]

$$\text{Rate of Ar SN} \propto \text{EWG} \propto \frac{1}{\text{ERG}}$$

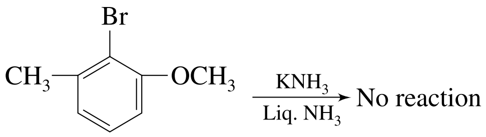
Thus presence of strong EWG increases the rate of hydrolysis.

37. [1]



(Elimination addition reaction
Benzyne mechanism refer keyconcept)

38. [1]

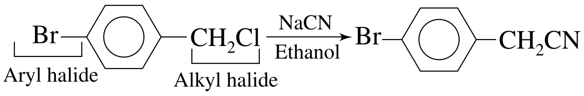


- Aryl substitution reaction takes place by benzyne mechanism; needed H at *ortho* position which is not present in option (1). So no reaction takes place.

39. [2]

Rate of nucleophilic substitution in Ar–Cl < R–Cl

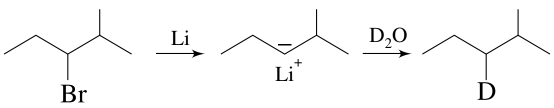
40. [1]



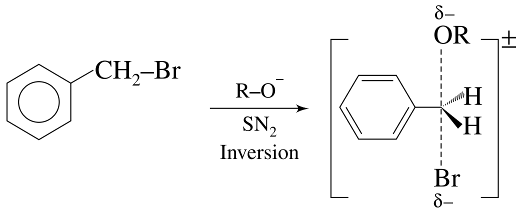
In ordinary condition aryl halide do not give SN reaction

EXERCISE # 2

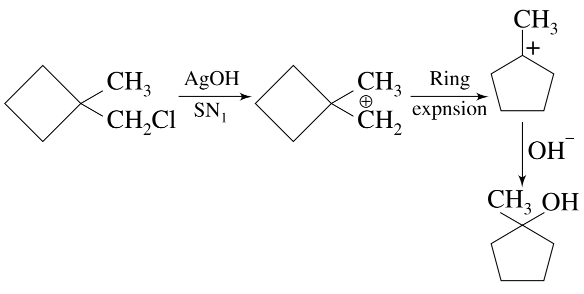
1. [2]



2. [4]



3. [2]



4. [2]

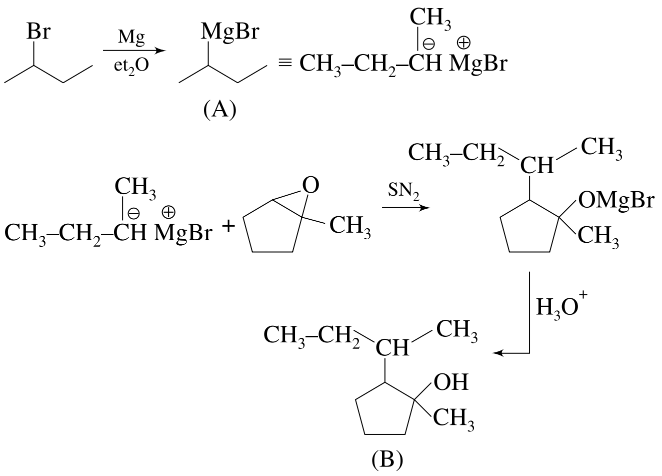
Rate of S_N1 reaction α stability of $-\overset{|}{\underset{|}{C}}{}^{\oplus}$

If carbocation is same, than

R–I > R–Br > R–Cl > R–F

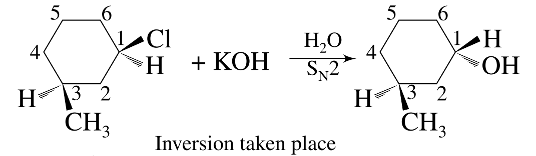
∴ I > III > II > IV

5. [1]



Since breaking of cyclic ether in alkaline media accompanied by SN_2, so that nucleophile added at least stericly hindred position.

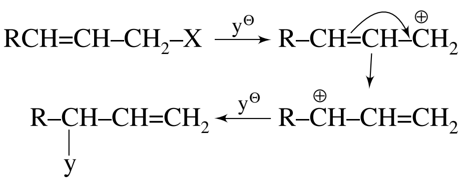
6. [3]



(1R, 3S) Cis   Inversion taken place at 1st carbon   (1S, 3S) Trans

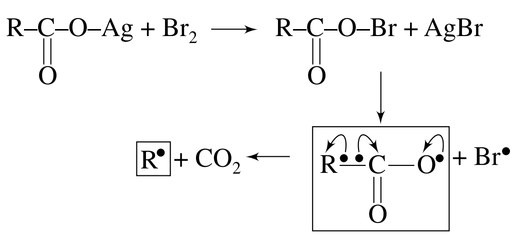
Hence configiration of only 1st carbon will revert.

7. [1]

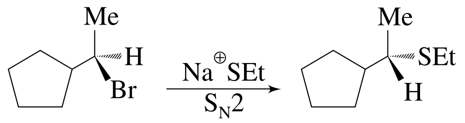


This reaction happened by stable carbocation so it is S_N1 reaction.

8. [4]



9. [3]

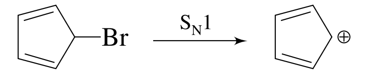


10. [2]

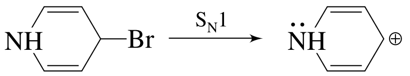
Rate of Ar-SN ∝ – M, – I

→ Lone pair of $\ddot{N}$ atom does not delocalize. So it works as –I group Thus it increases the rate of Ar–SN (aromatic nucleophlilic substitution) reaction.

11. [2]



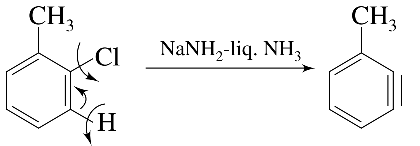
A Antiaromatic



B Aromatic

Rate of S_N1 reaction α stability of carbocation

12. [2]



β-elimination (refer keyconcept)

13. [2]

α-carbon is achiral, hence retention of configuration at β-carbon.

14. [1]

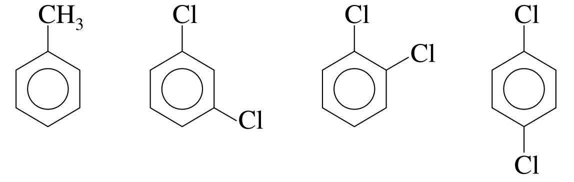
For Cl(1), other two Cl present at either *ortho* or *para* position; so it works as Electron Withdrawing Group.

Rate of Ar–S_N2 ∝ power of EWG

15. [2]

Dipole moment depends upon magnitude as well direction, and also it is calculated by the vector sum of two dipoles.

Angle (θ) ↑ dipole moment (μ) ↓

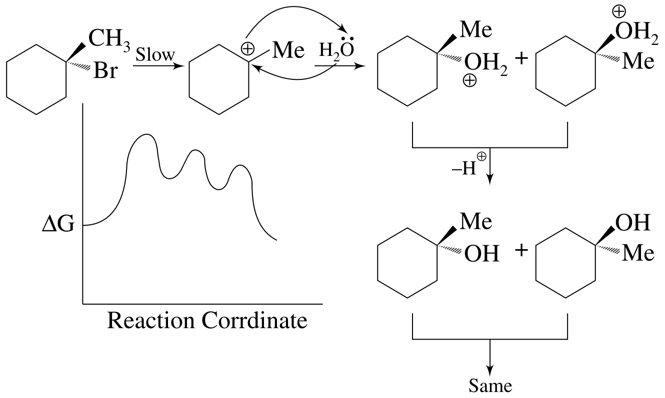


(I)	(II)	(III)	(IV)
(Polar)	(θ = 120)	(θ = 60)	(θ = 180)

16. [3]

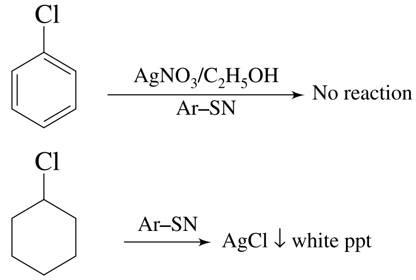
β-H at the bridging carbon is anti to leaving group, lost in E2 reaction

17. [2]



Two intermediate formed carbocation and oxoniumion.

18. [1]

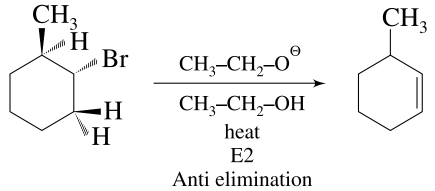


19. [3]

→ 1° halide will gives S_N2 reaction predominantly with $\overset{\ominus}{S}H$ ion.

→ If alkyl halide is same then R–Br is more reactive than R–Cl.

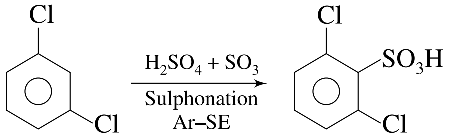
20. [4]



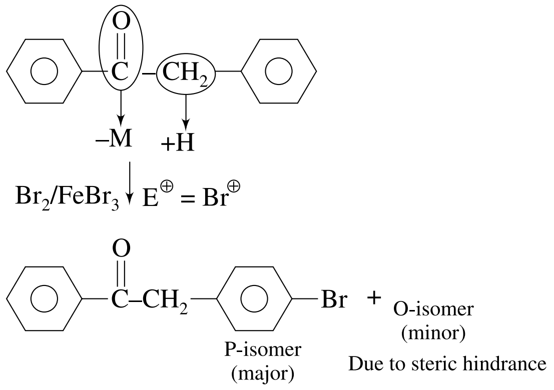
21. [1]

Arylic substitution takes place by benzyne mechanism, for this presence of H-atom at ortho position must be essential which is available only in option (1).

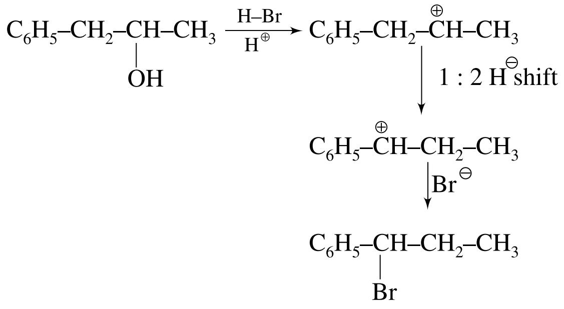
22. [1]



23. [2]

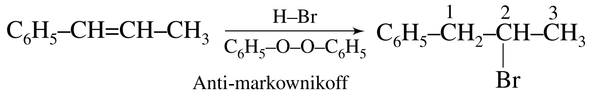


24. [2]



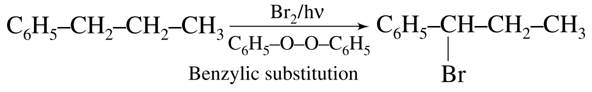
$$C_6H_5–CH_2–\underset{|}{\underset{OH}{CH}}–CH_3 \xrightarrow[H^{\oplus}]{H–Br} C_6H_5–CH_2–\overset{\oplus}{C}H–CH_3 \xrightarrow{1:2\ H^{\ominus}\ \text{shift}} C_6H_5–\overset{\oplus}{C}H–CH_2–CH_3 \xrightarrow{Br^{\ominus}} C_6H_5–\underset{Br}{\underset{|}{CH}}–CH_2–CH_3$$

1-brano-1-phenyl propanea



$$C_6H_5–CH=CH–CH_3 \xrightarrow[C_6H_5–O–O–C_6H_5]{H–Br} C_6H_5–\overset{1}{C}H_2–\underset{Br}{\underset{|}{\overset{2}{C}H}}–\overset{3}{C}H_3$$

Anti-markownikoff

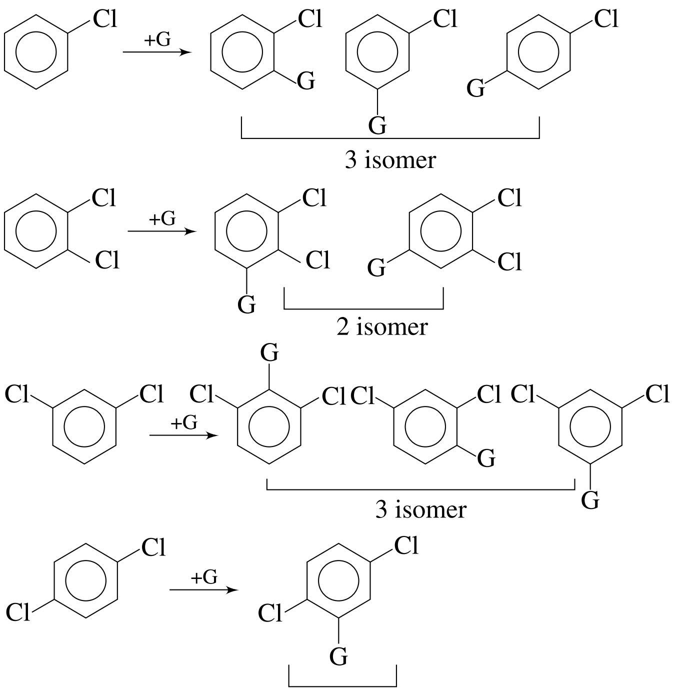


$$C_6H_5–CH_2–CH_2–CH_3 \xrightarrow[C_6H_5–O–O–C_6H_5]{Br_2/h\nu} C_6H_5–\underset{Br}{\underset{|}{CH}}–CH_2–CH_3$$

Benzylic substitution

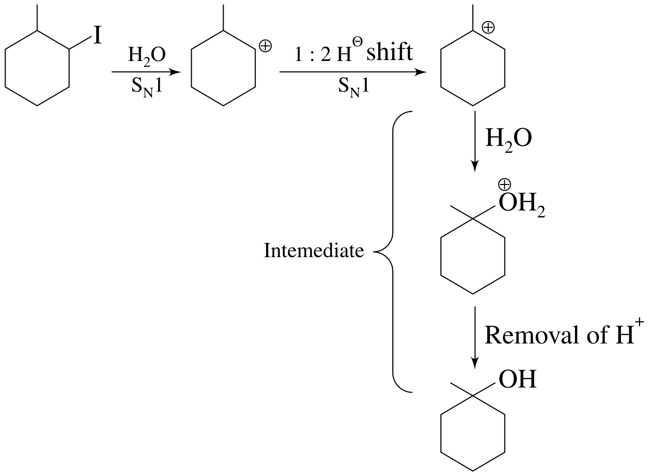
via stable ($C_6H_5–\dot{C}H–CH_2–CH_3$) radical

25. [4]

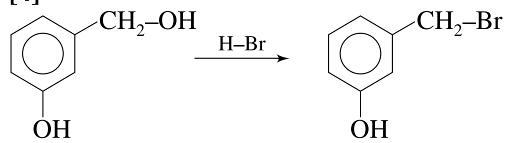


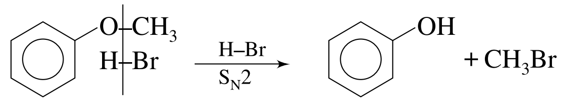
Single isomer

26. [1]



27. [4]





$CH_3–CH_2–OH \xrightarrow{SOCl_2} CH_3–CH_2–Cl$

$CH_3–CH_2–OH \xrightarrow{KBr}$ no reaction

Poor
Leaving
group

28. [3]

Allyl bromide (I) is most reactive among the given halides as pi bonds from alylic position stabilizes the transition state. Vinyl iodide (II) is least reactive due double bond character. Electron withdrawing inductive effect of CH_3O^- increase reactivity of (IV) over (III)

29. [2]

HO^- is stronger nucleophile than CH_3COO^-. Hence, lower is the activation energy of (i) than (ii).

30. [3]

(III) forms tertiary carbocation, hence most reactive, (I) is the least reactive as highly unstable carbocation is formed at bridge head carbon of bicyclic compound.

31. [4]

In ordinary condition aryl halide do not give SN reaction.

32. [1]

Rate of Ar–S_N2 $\propto$ Electron Withdrawing Group ($-NO_2$)

33. [1]

Density $\propto$ Molecular weight

34. [3]

Reactivity of S_N1 reaction $\propto$ stability of carbocation

$$\propto \text{ERG}$$

$$\propto \frac{1}{\text{EWG}}$$

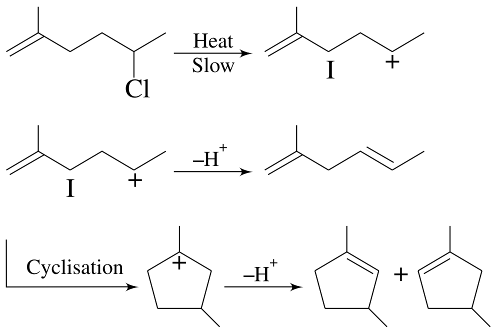
35. [2]

Theory based.

EXERCISE # 3

1. [1, 2, 4]

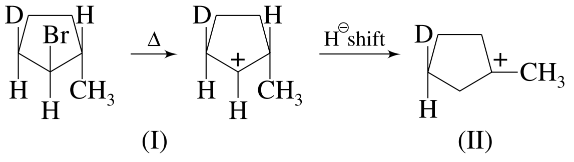
Reaction proceeds by E1 mechanism.



2. [1, 2, 3, 4]

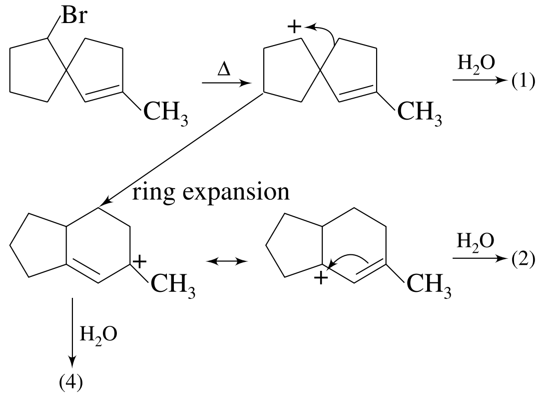
H_2O (Protic Solvent)

Hence SN_1 reaction takes place

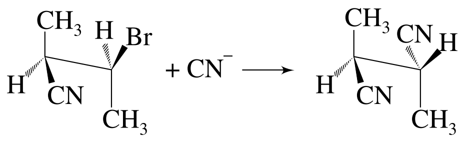


(I) gives (1) and (2) while (II) gives (3) and (4).

3. [1, 2, 4]



4. [1, 3, 4]



Meso achiral

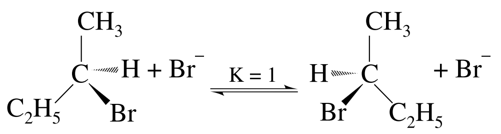
Rest 1, 3, 4 give chiral product

5. [1, 4]

In both option (1) and option (4) α-carbon is chiral, hence S_N2 reaction will lead to inversion of configuration. In option (2), α-carbon is achiral, configuration of chiral β-carbon will not be affected. In option (3) S_N2 reaction occur twice at the same α-carbon hence, double inversion will give not retention of configuration.

6. [1, 3, 4]

In both option (1) and option (4) products have inverted configuration but at α-carbon only. In option (2) product has inverted configuration at both α and β-carbons, hence not true in S_N2 reaction. In case of option (4), an equilibrium will be established with K = 1.



At equilibrium both enantiomers exist in equal amounts giving racemic mixture.

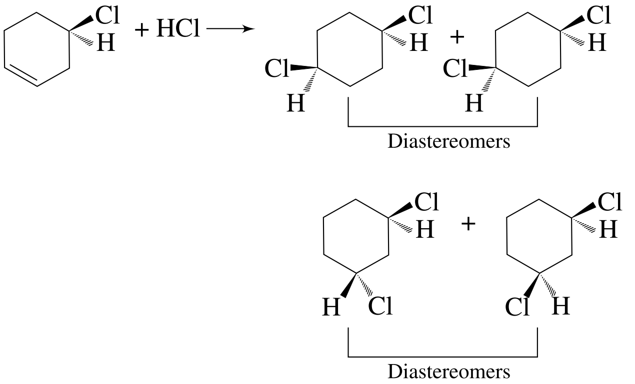
7. [1, 2, 3]

All will react via cyclic sulphonium ion intermediate involving S_N2 reaction twice giving over all retention of configuration.

8. [1, 3]

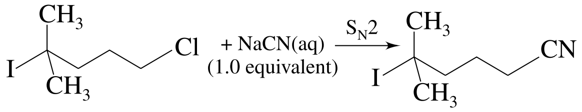
Due to neighbouring group participation, reaction occurs at much faster rate than 2-bromo-3, 3-dimethylpentane. Also it involves S_N2 reaction twice, overall retention of configuration is observed.

9. [1, 3]



10. [1, 3, 4]

Steric hindrance plays the most important role in S_N2 reaction. Hence, although Cl is poorer leaving group than I, Cl is substituted predominantly in the above reaction due to less steric hindrance at α-carbon. Addition of NaI replace Cl by I and substitution becomes easier.



11. [1, 3, 4]

Theory based

12. [2, 3, 4]

Theory based.

13. [2, 3, 4]

(1) $CH_3CH_2OCH_2CH_3 \xrightarrow[h\nu]{Cl_2} C_2Cl_5\text{–}O\text{–}C_2Cl_5$

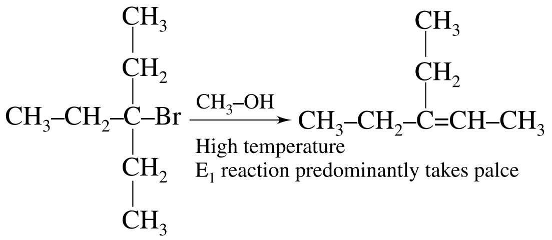
Not alkyl halide

(2) $CH_3CH_2OCH_2CH_3 \xrightarrow[\text{heat}]{\text{conc. HI}} CH_3\text{–}CH_2\text{–}OH + CH_3\text{–}CH_2\text{–}I$

(3) $CH_3CH_2OCH_2CH_3 \xrightarrow[\text{heat}]{PCl_5} 2CH_3\text{–}CH_2\text{–}Cl + POCl_3$

(4) $CH_3CH_2OH \xrightarrow{SOCl_2} CH_3\text{–}CH_2\text{–}Cl + SO_2 + HCl$

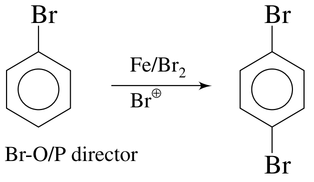
14. [1, 3]



$$CH_3\text{–}CH_2\text{–}\underset{\underset{CH_3}{|}{CH_2}}{\overset{\overset{CH_3}{|}{CH_2}}{C}}\text{–}Br \xrightarrow[\text{High temperature}]{CH_3\text{–}OH} CH_3\text{–}CH_2\text{–}\overset{\overset{CH_3}{|}{CH_2}}{C}=CH\text{–}CH_3$$

E$_1$ reaction predominantly takes palce

15. [2]



16. [4]

Aryl halide do not give nucleophilic substitution in ordinary condition to because partial double bond character develop due to resonance.

17. [2]

refer key concept.

18. [1]

refer key concept.

19. [4]

Boiling point ∝ molecular weight.

So R–Br has higher b.pt. than R–Cl.

20. [2]

refer key concept.

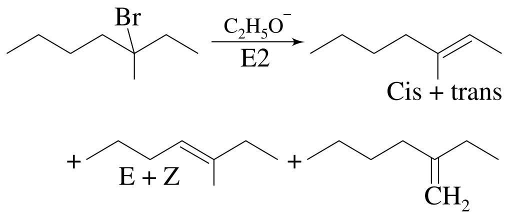
21. [2]

In aryl halide C–X bond have partial double bond character due to resonance, so bond energy increase thus removal of X as leaving group is difficult in ordinary condition. Hence aryl halide do not give substitution reaction easily.

22. [3]

Only deuterium is present at anti position of a β-carbon, it is abstracted by base, although giving less substituted alkene as the major product. On tertiary β-carbon, hydrogen is not available in *anti* position to leaving group.

23. [4]



24. [4]

Bulky base takes β-H from least hindered β-carbon, giving least substituted alkene as the major product.

25. [2]

Products are same in both reaction, hence same potential energies of products are shown, Also I^- is better leaving group, has lower activation energy in S_N2 reaction as indicated by curve-I in diagram.

26. [3]

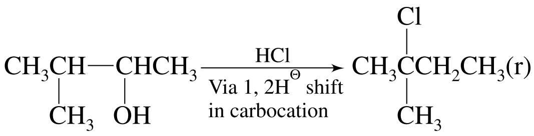
Since I^- is better leaving group, $k_I > k_{II}$

27. [3]

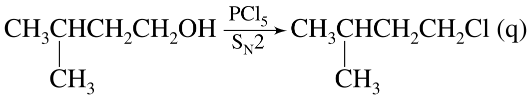
Following neutralisation is preferred over S_N2 reaction:

$$CH_3—CH_2—OH + NaNH_2 \longrightarrow CH_3— CH_2—O^- Na^+ NH_3$$

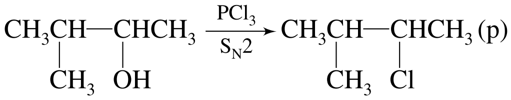
28. [1]

(A)


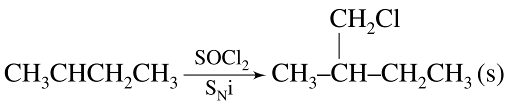
$$CH_3\underset{\underset{CH_3}{|}}{CH}—\underset{\underset{OH}{|}}{CH}CH_3 \xrightarrow[\text{Via 1, 2H}^{\ominus}\text{ shift in carbocation}]{HCl} CH_3\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2CH_3\text{(r)}$$

(B)


$$CH_3\underset{\underset{CH_3}{|}}{CH}CH_2CH_2OH \xrightarrow[S_N2]{PCl_5} CH_3\underset{\underset{CH_3}{|}}{CH}CH_2CH_2Cl\text{ (q)}$$

(C)


$$CH_3\underset{\underset{CH_3}{|}}{CH}—\underset{\underset{OH}{|}}{CH}CH_3 \xrightarrow[S_N2]{PCl_3} CH_3\underset{\underset{CH_3}{|}}{CH}—\underset{\underset{Cl}{|}}{CH}CH_3\text{ (p)}$$

(D)


$$CH_3CHCH_2CH_3 \xrightarrow[S_Ni]{SOCl_2} CH_3–\overset{\overset{CH_2Cl}{|}}{CH}–CH_2CH_3\text{ (s)}$$

29. [3]

Theory based.

30. [4]

Theory based.

31. [1]

(i) Due to 'S' at β-position, neighbouring group participation occur giving net retention (twice inversion).

(ii) S_N2 at a-carbon gives inversion and product is meso diol.

(iii) Only S_N2 hence inversion

(iv) Show neighbouring group effect

Hence, (i) → (q, s); (ii) → (p, r); (iii) → (p); (iv) → (r, s)

32. [2]

(i) Given halide is a primary, predominantly undergo S_N2 reaction.

(i) → (q)

(ii) Given halide is secondary, can undergo S_N2 reaction. Also, E2 reaction leads to a conjugated system. Also, it any react by E1cb mechanism because it forms resonance stabilised carbanion.

(ii) → (q, r, s)

(iii) It is a 3° halide and in the presence of weak base H_2O, weak nucleophile H_2O, it may undergo unimolecular substitution (S_N1) and elimination (E1) reaction.

(iii) → (p)

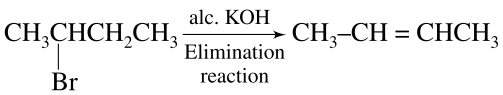
(iv) It may form a stable benzylic carbocation after hydride shift, hence any react by $S_N1$mechanism. Also, it is a secondary halide, may undergo S_N2 reaction. It may also react by E2 reaction at it gives conjugated system. Carbanion, formed at β-C will be stabilized by resonance from ring, hence may undergo E1cb mechanism.

(iv) → (p, q, r, s)

33. [1]

(A) $C_2H_5OH + HCl \xrightarrow[\text{Groove reaction}]{ZnCl_2} C_2H_5Cl + H_2O$

(B) $C_6H_5\overset{+}{N_2}Cl^- + HBr \xrightarrow[\text{Gattermann reaction}]{Cu} C_6H_5Br + N_2 + HCl$

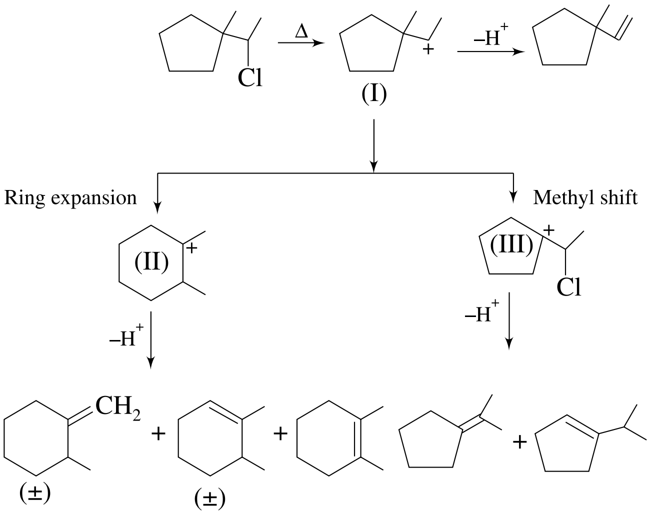
(C)


$$CH_3\underset{\underset{Br}{|}}{CH}CH_2CH_3 \xrightarrow[\text{Elimination reaction}]{\text{alc. KOH}} CH_3–CH = CHCH_3$$

(D) $CH_3CH_2CH_2Cl+NaI \xrightarrow[\text{Frenkelstein reaction}]{\text{Acetone}} CH_3CH_2CH_2I + NaCl$

34. [8]

Total 8 alkenes

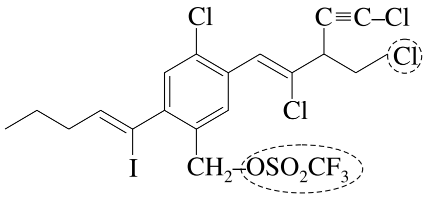


35. [6]

Only (ii), (iv), (vii) and (ix) are less dense than water. Alkyl bromides, alkyl iodides and all alkyl halides containing two or more halogen atoms.

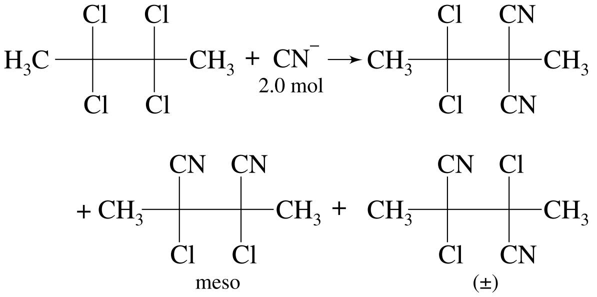
36. [3]

Only the circled groups are substituted in S_N2

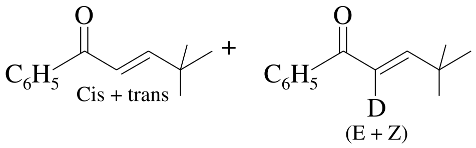


37. [4]

Any of the two Cl can be substituted by CN^- as:



38. [4]



EXERCISE # 4

1. [1]

Replacement of Br by –OH group takes place.

So that it is substitution reaction.

2. [2]

Reactivity of HX is HI > HBr > HCl > HF

3. [3]

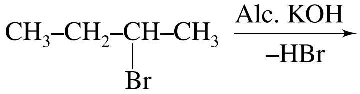
$$\text{Reactivity of } S_N2 \propto \frac{1}{\text{steric hindrance}}$$

Reactivity order 1° halide > 2° halide > 3° halide.

4. [4]

$$\underset{\text{(Dialkyl copper lithium)}}{R_2CuLi} + R'X \longrightarrow \underset{\text{(alkane)}}{R - R'} + R - Cu + LiX$$

5. [1]



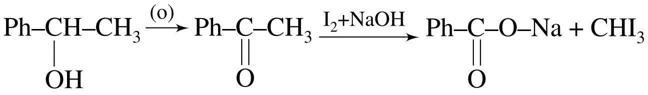
$$CH_3–CH_2–\underset{\underset{Br}{|}}{C}H–CH_3 \xrightarrow[-HBr]{\text{Alc. KOH}}$$

$CH_3–CH=CH–CH_3 + CH_3–CH_2–CH=CH_2$

More substitute	Less substitute
(I)	(II)
Major	Minor

Stability of (I) > (II) hence (I) is predominant.

6. [3]



$$Ph–\underset{\underset{OH}{|}}{C}H–CH_3 \xrightarrow{(o)} Ph–\underset{\underset{O}{||}}{C}–CH_3 \xrightarrow{I_2+NaOH} Ph–\underset{\underset{O}{||}}{C}–O–Na + CHI_3$$

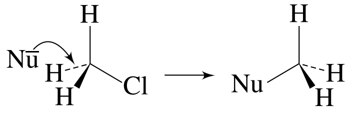
7. [2]

$$\text{Reactivity of } S_N2 \propto \frac{1}{\text{steric hindrance}}$$

Reactivity order 1° halide > 2° halide > 3° halide.

8. [3]

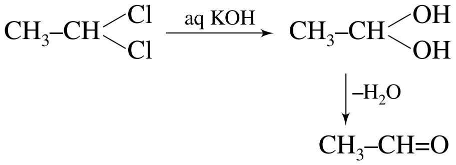
Nucleophilic substitution bimolecular (S_N2) prefers less sterically hindered site to attack. Lesser the steric hindrance, faster is the S_N2 reaction. So ease of reaction is 1° > 2° > 3°.



S_N2 involves inversion of configuration stereo, chemically.

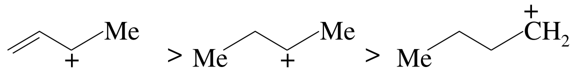
Since 1° alkyl halides are preferred to S_N2 reactions, therefore CH_3Cl undergoes complete stereochemical inversion.

9. [4]



10. [2]

The reactivity of S_N1 reaction depends upon the stability of the intermediate, carbocation formed during these reactions. The stability order of the carbocation formed from the given species is



Allylic carbocation (stabilizes through resonance due to conjugation)	2° carbocation (stabilizes by hyperconjugation due to 5α-H atoms)	1° carbocation (stabilizes by hyperconjugation due to 2α-H-atom)

Hence, the reactivity order of the given bromide towards S_N1 reaction is

11. [3]

$$\underset{\text{Ethyl chloride}}{CH_3–CH_2–Cl} \xrightarrow[S_N2]{KCN} \underset{\text{Propane nitrile}}{CH_3–CH_2–CN}$$

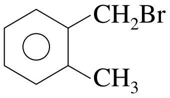
12. [4]

Compound A gives a precipitate with alcoholic $AgNO_3$ (here white is misprinting because the colour of ppt. is light yellow), so it must contain Br in side chain.

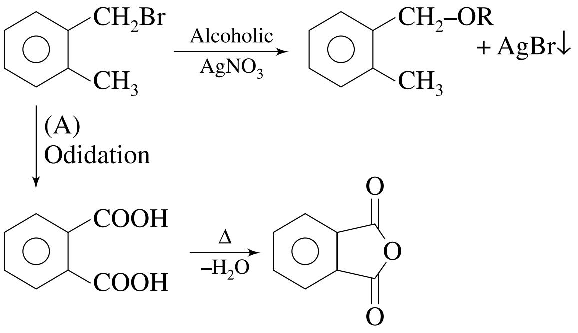
On oxidation, it gives $C_8H_6O_4$, which shows the presence of two alkyl chains attached directly with the benzene nucleus.

Since compound B gives anhydride on heating, the two alkyl substituent must occupy adjacent (1, 2) position.

Thus, A must be

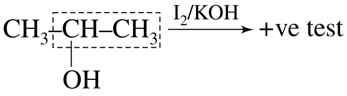


And the reactions are as follows



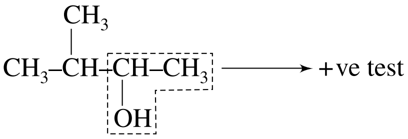
Phthalic anhydride

13. [3]

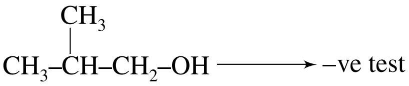


$\underset{OH}{CH_3–CH}–CH_3 \xrightarrow{I_2/KOH}$ +ve test

Isopropyl alcohol 2-alkanol

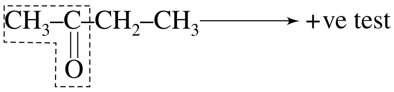


$CH_3–\underset{CH_3}{CH}–\underset{OH}{CH}–CH_3 \longrightarrow$ +ve test



$CH_3–\underset{CH_3}{CH}–CH_2–OH \longrightarrow$ –ve test

Isobutyl alcohol



$CH_3–\underset{O}{\overset{}{C}}–CH_2–CH_3 \longrightarrow$ +ve test

Ethyl methyl ketone

2-alkanol or methyl ketone will give positive iodoform test, isobutyl alcohol is not 2-alkanol type, hence gives negative iodoform test.

14. [3]

$$CH_3–CH_2–Br \xrightarrow[\text{Covalent nature}]{AgCN} CH_3–CH_2–N \equiv C$$

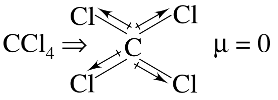
$$\xrightarrow{\text{Reduction Zn–Hg/HCl}} CH_3–CH_2–NH–CH_3$$

Ethyl methyl amine

15. [2]

Copper wire test for halogens is known as Beilstein's Test.

16. [3]



Equal and opposite dipole cancelled by each other.

17. [2]

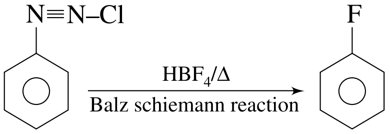
Beilstein test is used for estimation of Cl.

$$R–\boxed{Cl} \xrightarrow[\text{(Beilstein test)}]{\text{Cu-wire}} \text{Green flame}$$

18. [4]

$$Ph–N{=}N–Cl \xrightarrow[\text{Gattermann reaction}]{Cu/HBr} Ph–Br$$

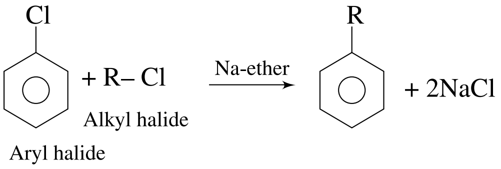
19. [1]



20. [2]

Tertiary alkyl halide mainly give β-elimination reaction so alkene will be formed as major product.

21. [2]



22. [2]

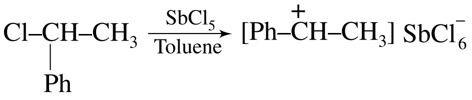
$$R–NH_2 \xrightarrow{CHCl_3/KOH} R–N \equiv C$$

$$CHCl_3 + KOH \longrightarrow \ddot{C}Cl_2 + KCl + H_2O$$

α-elimination (dichloro carbene)

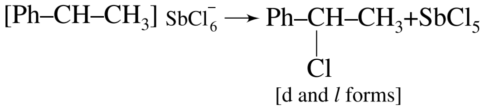
23. [3]

The given compound, (–)– chloro-1-phenylethane in the presence of $SbCl_5$ forms a carbocation.



$$\underset{Ph}{Cl–CH}–CH_3 \xrightarrow[\text{Toluene}]{SbCl_5} [Ph–\overset{+}{C}H–CH_3]\ SbCl_6^-$$

Since, the carbocation is a planar species, therefore it can be attacked by $SbCl_6^-$ either from the front or back side of the carbocation with equal ease. As a result, 50:50 mixture of two enantiomers of 1-choro-1-phenylethane undergoes racemisation due to the formation of a carbocation intermediate.



$$[Ph\text{–}CH\text{–}CH_3]\,SbCl_6^- \longrightarrow \underset{\text{[d and } l \text{ forms]}}{Ph\text{–}\underset{|}{\underset{Cl}{C}}H\text{–}CH_3} + SbCl_5$$

24. [3]

$$R\text{–}NH_2 \xrightarrow{CHCl_3/KOH} \underset{\text{Alkyl isocyanide}}{R\text{–}N \overset{\rightarrow}{=} C} + KCl + H_2O$$

$$CH\text{–}CH_3 + KOH \longrightarrow \ddot{C}Cl_2 + KCl + H_2O$$

α-elimination (dichloro carbene)

25. [1]

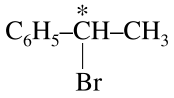
$$\text{Reactivity of } S_N2 \propto \frac{1}{\text{steric hindrance}}$$

Reactivity order 1° halide > 2° halide > 3° halide.

26. [3]

When alkyl halide having chiral carbon then only complete inversion takes place.

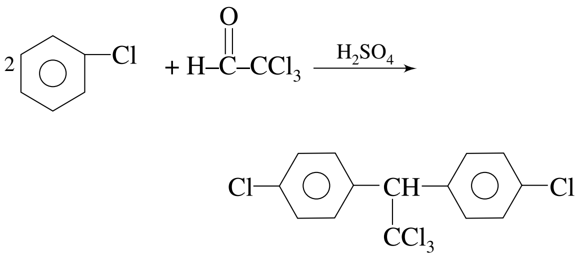
In option 3



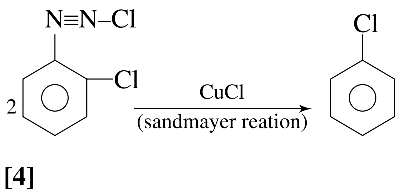
$$C_6H_5\text{–}\overset{*}{\underset{\underset{Br}{|}}{C}}H\text{–}CH_3$$

hence it gives complete inversion of configuration

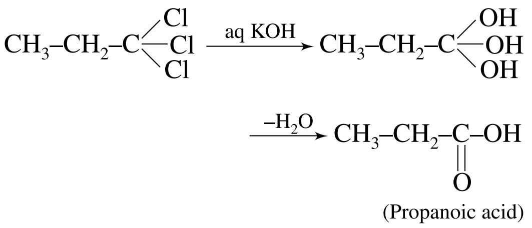
27. [3]



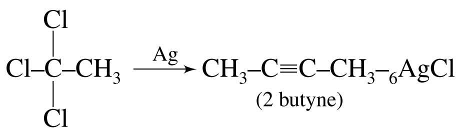
28. [3]



29. [4]



30. [3]



$$Cl\text{–}\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}\text{–}CH_3 \xrightarrow{Ag} \underset{\text{(2 butyne)}}{CH_3\text{–}C{\equiv}C\text{–}CH_3} – {}_6AgCl$$

(1, 1, 1-trichliroethane
2 mole)

31. [4]

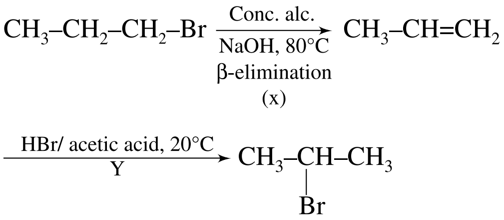
Alkyl fluorides can be prepared by action of mercurous fluoride or antimony trifluorides (inorganic fluorides) on corresponding alkyl halide. It is known as Swarts reaction.

32. [4]

Reactivity of alkyl halide ∝ power of leaving group.

$$\frac{I^{\ominus}\ Br^{\ominus}\ Cl^{\ominus}\ F^{\ominus}}{\text{size}\downarrow \text{ Base strength}\uparrow \text{ leaving tendency}\downarrow}$$

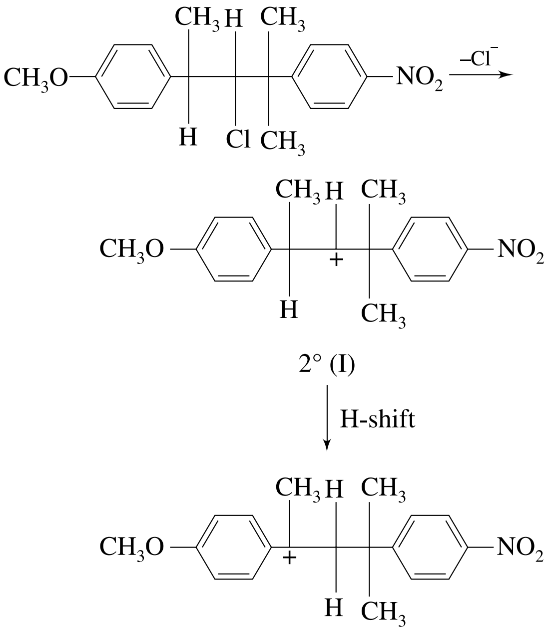
33. [2]



$$CH_3\text{–}CH_2\text{–}CH_2\text{–}Br \xrightarrow[\substack{\text{NaOH, 80°C} \\ \beta\text{-elimination} \\ (x)}]{\text{Conc. alc.}} CH_3\text{–}CH{=}CH_2$$

$$\xrightarrow[\text{Y}]{\text{HBr/ acetic acid, 20°C}} CH_3\text{–}\underset{\underset{Br}{|}}{C}H\text{–}CH_3$$

34. [1]



Stabilized by +R effect of $–OCH_3$

$$(I) \xrightarrow{H_2O} K$$

$$(II) \xrightarrow{H_2O} L$$

35. [1]

(A) $CH_3\text{–}CHBr\text{–}CD_3 \xrightarrow[\text{E2}]{\text{Alc. KOH}} CH_2\text{=}CH\text{–}CD_3$

E2 reaction is a single-step reaction in which both deprotonation from β-C and loss of leaving group from α-C occur simultaneously in the rate-determining step. C–D bond is stronger than C–H bond. C–H is preferably broken in elimination.

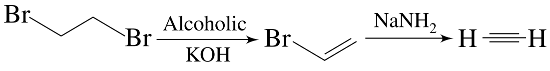
(B) $Ph\text{–}CHBr\text{–}CH_3$ reacts faster than $Ph\text{–}CHBr\text{–}CD_3$ in E2 reaction because in latter case, stronger C–D bond is to be broken in the rate determining step.

(C) $Ph\text{–}CH_2\text{–}CH_2Br \xrightarrow[C_2H_5O^-]{C_2H_5OD} Ph\text{–}CD\text{=}CH_2$

(D) Both $PhCH_2CH_2Br$ and $PhCD_2CH_2Br$ will react at same rate in E1 reaction because C–H bond is broken in fast non-determining.

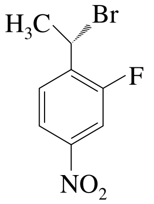
Thus, (A) → q; (B) → q; (C) → r; (D) → p, s

36. [2]



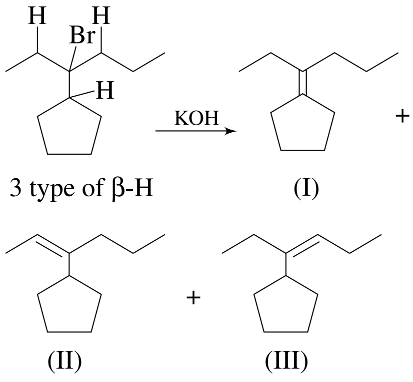
37. [1]

Nucleophile PhS^- substitute the Br^- through S_N2 mechanism with inversion of configuration at α-C



38. [5]

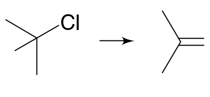
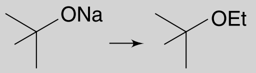
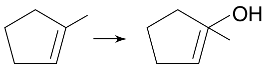
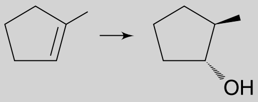
The substrate has three different types of B–H, therefore, first, three structural isomers of alkenes are expected as



3 type of β-H (I) (II) (III)

The last two alkenes (II) and (III) are also capable of showing geometrical isomerism; hence, two geometrical isomers for each of them will be counted giving a total of five isomers

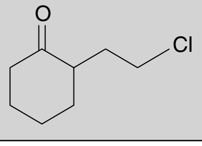
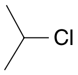
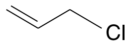
39. [1]

	Column-I	Column-II	Explanation
(A)		NaOEt	$\overline{O}$Et (strong nucleophile) causes dehydrohalogenation of 3° alkyl halide
(B)		Et-Br	3° butoxide undergoes S_N2 reaction with 1° alkyl halide
(C)		(i) $Hg(OAc)_2$; (ii) $NaBH_4$	Mercuration–demercuration adds H_2O by Markownikoff's rule without rearran-gement
(D)		(i) BH_3; (ii) H_2O_2/NaOH	Hydroboro-oxidation adds H_2O by anti-Markownikoff's rule

40. [2]

Acetone is an aprotic solvent and can dissolve both the nucleophile and the substrate and thus S_N2 reaction is favoured. Also rate of $S_N2 \propto -$ I power. Also

$$S_N2 \xleftarrow{1^\circ \quad 2^\circ \quad 3^\circ} \text{Alkyl halides}$$
$$\xrightarrow{\qquad\qquad\qquad\qquad} S_N1$$

S		1° alkyl halide but (C–Cl). BE is decreased by electron withdrawing [C_6H_5CO] group, (a case of I-effect). Thus, maximum rate in SN2 reaction
Q		2° alkyl halide, rate is minimum
P	$CH_3\text{–}Cl$	1° alkyl halide
R		1° allylic halide but allylic 1° carbocation is resonance stabilised in SN1 reaction

Thus, reactivity order is S > P > R > Q