10

Organic Compounds Containing Halogens

Organic compounds formed by the replacement of one or more hydrogen atoms from the aliphatic and aromatic hydrocarbons by an equal number of halogen atoms are called **aliphatic** and **aromatic halogen** compounds respectively. Term **alkyl halide** is used for aliphatic halogen derivatives and **aryl halide** is used for aromatic halogen derivatives. Here, halogen atom serves as a functional group.

IN THIS CHAPTER ....

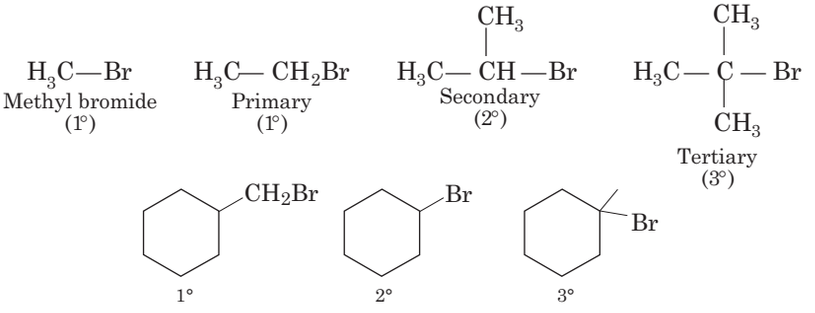
- Classification of Halogen Compounds
- Nomenclature of Halogen Derivatives
- Monohaloalkanes
- Dihaloalkanes
- Trihaloalkanes
- Polyhaloalkanes
- Aryl halides

Classification of Halogen Compounds

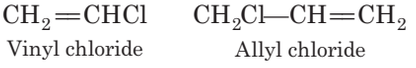
These compounds are classified into following classes depending upon different attributes.

On the Basis of Nature of Carbon Atom

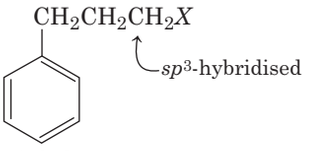
- Halogen derivatives can be classified as *primary, secondary* and *tertiary* halides depending upon the fact that halogen atoms is attached to primary, secondary or tertiary C-atom. e.g.



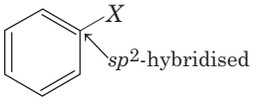
- The halogen derivatives are called **vinylic** and **allylic** derivatives, if the halogen atom is attached to vinyl and allyl group respectively.



- If halogen atom is attached to aliphatic chain, it is called **aliphatic halogen compound** or **haloalkanes** and if it is attached to aromatic carbon, it is called **aromatic halogen compound** or **haloarenes.**



Aliphatic halogen compound because X is attached with the aliphatic chain, not with the aromatic chain

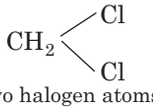


Aromatic halogen compound as X is attached directly to the benzene nucleus

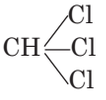
On the Basis of Number of Halogen Atoms

- The halogen derivatives (both aliphatic and aromatic) can also be classified as mono, di, tri and tetra halogen derivatives depending upon the number of halogen atoms present in the molecule, i.e.

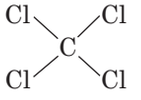
One halogen atom
Monohalogen derivative



Two halogen atoms
Dihalogen derivative



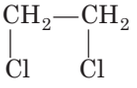
3 halogen atoms
Trihalogen derivative
(chloroform)



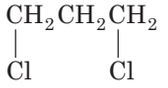
4 halogen atoms
Tetrahalogen derivative
(carbon tetrachloride)

- Remember in halogen derivatives, if both the halogen atoms are present at the same carbon atom, it is called geminal (*gem*-) dihalides and if present at adjacent carbon atoms, it is called vicinal (*vic*) dihalides.
- An another kind of dihalide, in which the two halogen atoms neither occupy the same nor the successive carbon atoms are also known. These are named as α or ω dihalogen derivatives (the halogen atoms occupy the terminal positions), e.g.

gem-dihalide



vic-dihalide



ω-dihalogen derivatives

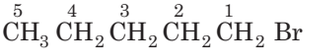
Nomenclature of Halogen Derivatives

In trivial system of nomenclature, halogen derivatives are named as alkyl halide. e.g.

Methyl chloride | Vinyl chloride | Ethylene dibromide

In IUPAC system, alkyl halides are named as 'haloalkanes' and aryl halides as 'haloarenes'.

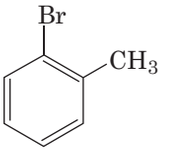
The longest chain is numbered in such a way that the C-atom bearing halogen must get the smallest possible number. If more than one halogen atoms are present then these different substituents are named alphabetically. e.g.



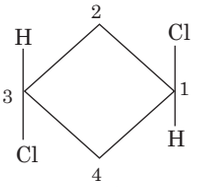
1-bromopentane

1, 1-dibromomethane

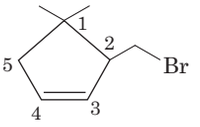
1,1,1-trichloro-methane



1-bromo-2-methyl benzene
or 2-bromotoluene
(*o*-bromotoluene; general name)



trans-1, 3-dichloro cyclobutane



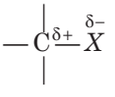
2-bromomethyl-1, 1-dimethyl cyclopentane

Monohaloalkanes

These are the compounds in which only one halogen atom is attached to the alkyl chain. Their general formula is $C_nH_{2n+1}X$.

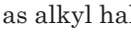
Nature of C—*X* Bond

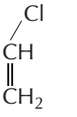
Since, there is a large difference in the electronegativity of halogen atom and carbon so, the C atom of the halogen derivative acquires partial positive charge while the halogen atom gets partial negative charge. Hence, the C—*X* bond is polar in nature. This polar nature of halogen derivatives is responsible for their high reactivity and makes them useful organic compound.

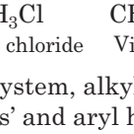


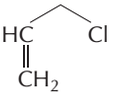
Monohaloalkanes exhibit chain, position, conformations and optical isomerism.

Example 1. *Among the following compounds, which one has the shortest* C—Cl *bond?* ***(JEE Main 2020)***

(a) 

(b) 

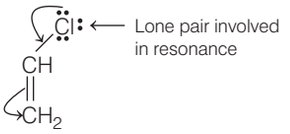
(c) 

(d) 

Sol. (*b*) In vinyl chloride, C—Cl bond is shortest due to resonance of lone pair of — Cl (chlorine atom).

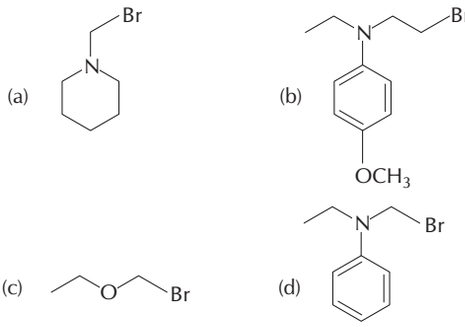
Due to resonance C — Cl bond aquire partial double bond character.

Hence, vinyl chloride have shortest C — Cl bond length.



Example 2. *Which of the following compounds will form the precipitate with aq.* $AgNO_3$ *solution most readily?*

(JEE Main 2020)



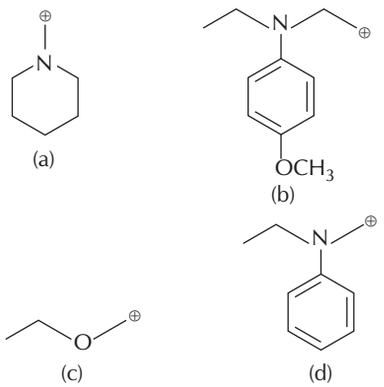
Sol. *(a)* All given species in the question are alkyl halide. They react with aqueous $AgNO_3$ solution with different rate.

Reaction undergoes as follows

$$R\text{—}X + AgNO_3(aq) \xrightarrow{RDS} R^+ + \underset{\text{Precipitate}}{AgX}$$

Hence, rate precipitate formation of Ag*X* depends on stability of carbocation (R^+).

In the given question all formed carbocation will be



Among the above given options, carbocation (a) is most stable due to stronger + *M* effect, so give precipitate with aqueous $AgNO_3$ solution most readily.

Methods of Preparation

Following methods are used for the preparation of monohaloalkanes

1. Halogenation of Alkanes

This reaction takes place in the presence of heat or light and follows free radical mechanism.

$$R\text{H} + X_2 \xrightarrow{h\nu} RX + R\text{H}X \quad \text{(where, } X = \text{Cl, Br, I)}$$

Detailed mechanism of this reaction is given in previous (Hydrocarbon; Alkane) chapter.

Remember that

- reaction of F_2 with alkanes is explosive therefore, fluorides are generally prepared by halogen exchange method which we shall discuss later.
- iodination occurs only in the presence of an oxidising agent such as HgO, HIO_3, HNO_3 because direct iodination is a reversible reaction.

2. Allylic Substitution in Alkenes

In the presence of light and trace of peroxide, allylic bromination takes place with NBS. This reaction also proceeds through free radical mechanism.

$$CH_3CH{=}CH_2 + \text{NBS} \longrightarrow BrCH_2CH{=}CH_2 + \text{HCl}$$

vic-dibromides can be prepared by addition of Br_2 in the presence of CCl_4, to alkenes

$$CH_2{=}CH_2 + Br_2 \xrightarrow{CCl_4} Br_2\text{—}CH_2\text{—}CH_2\text{—}Br$$

For detailed mechanism see previous (Hydrocarbon; Alkene) chapter.

3. Addition of Halogen Acids to Alkenes

It is an electrophilic addition reaction. In case of unsymmetrical alkene, addition takes place according to Markownikoff's rule, i.e. negative part goes to more hydrogenated carbon.

$$R\text{CH}{=}CH_2 + \text{HBr} \longrightarrow R\text{CHBrCH}_3$$

At high temperature the addition of halogens to alkenes becomes reversible and hence, does not occur.

Addition of HBr to alkenes for obtaining haloalkanes can be done in the presence of organic peroxide as well. This reaction is also known as **Kharasch effect**. Here, HBr is obtained *in situ* by reaction of KBr or NaBr with concentrated H_2SO_4. For detailed mechanism see previous (Hydrocarbon, Alkene) chapter.

4. Substitution of —OH Group of Alcohol

These reactions are infact nucleophilic substitution reactions and follow S_N1 or S_N2 mechanisms accordingly depending upon the alcohol used.

The equations of these reactions are

I. $3ROH + PX_3 \longrightarrow 3RX + H_3PO_3$

II. $ROH + PX_5 \longrightarrow RX + POX_3 + HX$

As PBr_5 and PI_5 are highly unstable compounds due to steric hindrance therefore, only chlorides are prepared by this method.

III. $ROH + \text{Dry HCl} \xrightarrow{\text{Anhyd. } ZnCl_2} RCl + H_2O$

A mixture of (1 : 1) dry HCl and anhydrous $ZnCl_2$ is called **Lucas reagent**.

IV. $R—OH + HX \longrightarrow RX + H_2O$

The reactivity of alcohols towards H*X* is **allyl, benzyl** > **3°** > **2°** > **1°** and

the reactivity of halogen acids is **HI** > **HBr** > **HCl** > **HF**.

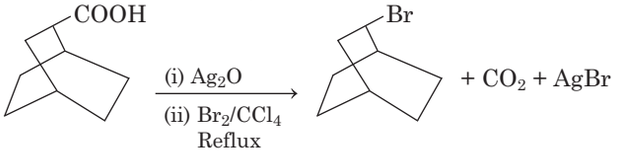
V. $ROH + SOCl_2 \xrightarrow{\text{Pyridine}} RCl + HCl + SO_2$

The reaction of $SOCl_2$ with alcohols is called **Darzens procedure**. *Bromide and iodide are not prepared by this method*, because thionyl bromide is unstable and thionyl iodide does not exist.

5. Borodine-Hunsdiecker Method

This is the decarboxylation of silver salt of fatty acids, when these are treated with Br_2 in refluxing CCl_4.

$$CH_3COOAg + Br_2 \xrightarrow[\text{Reflux}]{CCl_4} CH_3Br + AgBr + CO_2$$



The yield of halide is **1°** > **2°** > **3°**.

The reaction follows free radical mechanism and yield of alkyl chloride is less than alkyl bromide.

If iodine is used in the place of Br_2, the reaction is modified as

$$2\,RCOOAg + I_2 \longrightarrow RCOOR + CO_2 + 2AgI$$

This modified reaction is called **Birnbaurn Simonini reaction.**

6. Halide Exchange Method

Alkyl chloride and bromides are converted into their iodides or fluorides as

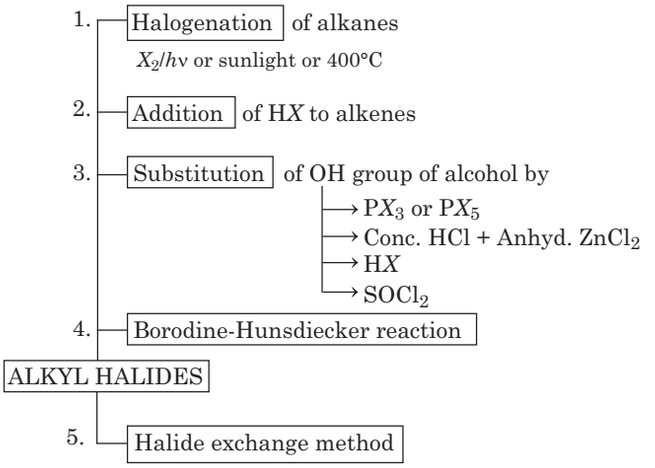
$$\text{Alkyl chloride or bromide} \xrightarrow{NaI/\text{acetone}} \text{Alkyl iodide} + \text{Na chloride or bromide}$$

This reaction is called **Finkelstein reaction**. Alkyl fluorides which can't be prepared by the **Finkelstein reaction**. These may be obtained from corresponding chlorides by the action of mercurous fluoride or antimony trifluoride or AgF. This reaction is called **Swarts reaction**.

$$2CH_3Cl + Hg_2F_2 \longrightarrow 2CH_3F + Hg_2Cl_2$$

$$CH_3Br + AgF \longrightarrow CH_3F + AgBr$$

Summary of methods of preparations of monohaloalkanes is given below



Physical Properties

- Chloride, bromide and fluoride of methane and chloride of ethane are gases at room temperature. Rest alkyl halides up to C_{18} are colourless liquids and beyond that are colourless solids.
- Bromides and particularly iodides develop colour when exposed to light.
- Haloalkanes have polar nature but are insoluble in polar solvents like water as they don't have ability of forming H-bonding with water. However, these are soluble in organic solvents like ether, benzene etc.
- Fluoro and chloro compounds are lighter than water whereas bromo and iodo derivatives are heavier than water. The density of alkyl halides decreases, as the size of alkyl group increases.
- These have higher boiling point than alkanes of comparable molecular weight. For a given alkyl group their boiling points follow the order $RI > RBr > RCl > RF$.
- For a given halogen atom the boiling points of alkyl halides increase with increase in the size of alkyl group.
- Boiling point decreases with branching, e.g.

$$\underset{(351\text{ K})}{CH_3CH_2CH_2CH_2Cl} \qquad \underset{(342\text{ K})}{CH_3—\overset{\overset{CH_3}{|}}{CH}—CH_2Cl}$$

- The dipole moment of halogen derivatives is due to the polar nature of C—*X* bond. Vinyl chloride and chlorobenzene show resonance and have low dipole moment as compared to alkyl halide. It is due to unusual positive charge which decreases the electronegativity of Cl atom and thus, the polarity of the bond.

- Dipole moment of alkyl halides decreases as the electronegativity of halogen atom decreases. However, the dipole moment of fluorides is lower than that of chlorides because of very small size of fluorine.
- Haloalkanes are less inflammable then corresponding hydrocarbons.

Chemical Properties

The chemical reactivity of alkyl halides is due to the presence of polar C—*X* bond in their reactions. The bond strength of C—*X* bond decreases with increase in the size of the halogen. For example, the order of bond strength of methyl halides is $CH_3F > CH_3Cl > CH_3Br > CH_3I$.

So, their reactions can be studied under the following headings.

- Nucleophilic substitution reaction
- Reduction
- Reaction with metals
- Elimination reactions
- Friedel-Crafts' reactions

I. Nucleophilic Substitution Reactions

When a methyl halide or primary alkyl halide reacts with a base such as sodium hydroxide, the base replaces the halogen as halide. This is an example of a very general type of reaction, called a **nucleophilic substitution reaction,** or nucleophilic **displacement reaction** (S_N).

The hydroxide ion is the nucleophile and it substitutes for the bromide which is called the **leaving group**.

Nucleophile

$$Na^+\overline{O}H + Br\text{—}CH_2CH_3 \longrightarrow CH_3CH_2O\text{—}H + Na^+Br^-$$

Leaving group

Alkyl halides react with a large number of nucleophilic reagents, both organic and inorganic, to form various other products. These nucleophilic substitution reactions can be unimolecular (S_N1) or bimolecular (S_N2).

A detailed mechanism of these reactions is given in chapter 15.

A quick recap of these reactions is given below

(i) **S_N2 Reactions**

$$OH^- + R\text{—}X \underset{\text{Slow}}{\rightleftharpoons} HO\cdots R\cdots X \xrightarrow[\text{Fast}]{} R\text{—}OH + X^-$$

The order of reactivity of alkyl halides for S_N2 reaction is 1° > 2° > 3° because transition state is involved which is more stable in case of unhindered carbons.

(ii) **S_N1 Reactions**

$$(CH_3)_3C\text{—}X \underset{\text{Slow}}{\overset{^-OH}{\rightleftharpoons}} (CH_3)_3C^+ + X^- \xrightarrow[\text{Fast}]{^-OH} (CH_3)_3COH$$

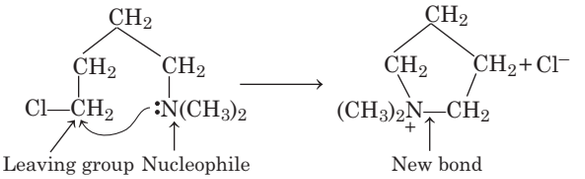
The order of reactivity of alkyl halide for such reaction is 3° > 2° > 1° because 3° carbocation is most stable.

- In all cases, X^- can be a good leaving group when the incoming group can be one of those present at the last of increasing order given below

$$H^-, R^- <<< MeO^-, OH^- < CN^- < MeCOO^- < ROSO_2^- < ArSO_2O^-$$

This order is based upon easiness and leavability of groups.

- The given reaction is an example of an **intramolecular nucleophilic substitutuion reaction**—a reaction in which the nucleophile and the leaving group are a part of the same molecule. In this case, S_N reaction causes ring formation as shown below



Examples of some nucleophilic substitution reactions as shown by alkyl halides are summarised below.

(i) **With aqueous alkali** It is also called "hydrolysis of alkyl halide".

$$RX + KOH\ (aq) \longrightarrow ROH + KX$$

(ii) **With moist silver oxide** Moist silver oxide is AgOH and the equation of reactions look like

$$RX + AgOH \longrightarrow ROH + AgX$$

(iii) **With dry silver oxide** Ether are formed by heating alkyl halides with dry silver oxide.

$$2RX + Ag_2O \xrightarrow{\Delta} ROR + 2AgX$$

(iv) **With sodium alkoxide** This reaction is also called "*Williamson's ether synthesis*".

$$R'O^-Na^+ + R''X \longrightarrow R'OR'' + Na^+X^-$$

(v) **With NH_3** The reaction of alkyl halide and ammonia proceed as,

$$RX + NH_3 \longrightarrow RNH_2 + HX;$$
$$RNH_2 + RX \longrightarrow R_2NH + HX$$
$$R_2NH + RX \longrightarrow R_3N + HX;$$
$$R_3N + RX \longrightarrow R_4N^+X^-$$

Thus, a mixture of primary amine (RNH_2), secondary amine (R_2NH), tertiary amine (R_3N) and quaternary ammonium salt ($R_4N^+X^-$) is obtained.

This reaction is called **Hofmann ammonolysis** of alkyl halides.

(vi) **With NaCN and AgCN** With NaCN, alkyl cyanide and with AgCN, alkyl isocyanide is produced. The reactions looks like

$$RX + Na^+CN^- \longrightarrow RCN + Na^+X^-$$

$$RX + AgCN \longrightarrow N \rightleftharpoons C + AgX$$

The reason is **electrovalent nature of NaCN** and **covalent linear structure of AgCN** where Ag atom is linked to C and N both thus, formation of both the isomers is possible.

(vii) Reaction with sodium alkynide to yield higher alkyne

$$R-X + Na^+ - C \equiv C - R' \longrightarrow R-C \equiv C-R' + NaX$$

(viii) **With *R*COOAg** Equation of this reaction looks like

$$RCOO\,Ag + XR' \longrightarrow RCOOR' + AgX$$

(ix) **With KSH** The euqation of this reaction looks like

$$RX + KSH \longrightarrow \underset{\text{Thioalcohol or mercaptan}}{RSH} + KX$$

(x) **With K_2S** The equation of this reaction looks like

$$2RX + K_2S \longrightarrow \underset{\text{Thioether}}{RSR} + 2KX$$

(xi) **With KNO_2 and $AgNO_2$** With KNO_2, alkyl nitrites ($R-O-N=O$) and with $AgNO_2$, nitro alkanes are produced.

$$NaNO_2 \longrightarrow Na^+ + NO_2^{\ominus}$$

$$O=N-\ddot{\underset{\ominus}{O}}: + R-I \longrightarrow \underset{\text{Alkyl nitrite (major)}}{R-O-N=O} + I^{\ominus}$$

$$Ag-\ddot{O}-N=\ddot{O}: + \overset{\delta+}{R}-\overset{\delta-}{X} \longrightarrow \underset{\text{Nitroalkane}}{R-N\begin{matrix}O^-\\ \\ O\end{matrix}} + AgX$$

The reason is exactly same to the one written in reaction 6 above. $NaNO_2$ is ionic in nature while $AgNO_2$ is linear covalent.

(xii) **With $(C_6H_5)_3P$** The reaction looks like

$$RX + (C_6H_5)_3P \longrightarrow [R(C_6H_5)_3P]^+X^-$$

(xiii) **With NaN_3** It is the sodium salt of hydrazoic acid (N_3H) in which N has the oxidation state of $-\frac{1}{3}$.

$$R\boxed{X + Na}N_3 \longrightarrow RN_3 + NaX$$

Note All the above written reactions proceed through S_N1 or S_N2 mechanisms depending upon the type of alkyl halide.

Example 3. *Which of the following compounds will show retention in configuration on nucleophilic substitution by OH^- ion?* ***(JEE Main 2020)***

(a) $CH_3-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-Br$ (b) $CH_3-\underset{\displaystyle C_2H_5}{\underset{|}{CH}}-CH_2Br$

(c) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-Br$ (d) $CH_3-\underset{\displaystyle C_6H_{13}}{\underset{|}{\overset{\displaystyle Br}{\overset{|}{C}}}}-H$

Sol. *(b)* In (a) and (d), carbon atoms bearing the leaving group (Br atom) are chiral. So, their configurational change will take place with OH^- ion by S_N2 or S_N1 pathway.

In (c), $(CH_3)_2CH-Br$ does not have any chiral centre. So, no comment on configuration will arise with (c).

In option (b), the α-carbon (with respect to $-CH_2Br$ with which S_N2 reaction will take place) is only chiral. This α-carbon remains unaffected in S_N2 pathway. So, it will show retention in configuration.

The major product obtained in the given reaction is 1, 2-dimethyl cyclohexene.

Example 4. *The mechanism of S_N1 reaction is given as*

$$R-X \longrightarrow \underset{\text{Ion pair}}{R^{\oplus}X^{\ominus}} \longrightarrow \underset{\substack{\text{Solvent}\\ \text{Separated ion pair}}}{R^{\oplus}||\,X^{\ominus}} \xrightarrow{Y^{\ominus}} R-Y + X^{\ominus}$$

A student writes general characteristics based on the given mechanism as

A. The reaction is favoured by weak nucleophiles.
B. $R^{\oplus}$ would be easily formed if the substituents are bulky.
C. The reaction is accompanied by recemisation.
D. The reaction is favoured by non-polar solvents.

Which observations are correct? ***(JEE Main 2020)***

(a) (A) and (B) (b) (A) and (C)
(c) (A), (B) and (C) (d) (B) and (D)

Sol. (c) $R-X \longrightarrow \overset{\oplus}{R}\,X^{\ominus} \longrightarrow \overset{\oplus}{R}\,||\,X^{\ominus} \xrightarrow{Y^{\ominus}} R-Y + X^{\ominus}$

It indicates $R^{\oplus}$ (carbocation) formation takes place and $R^{\oplus}$ got stabilised by electronic factors and polar solvent molecules because solvent separation of $R^{\oplus}$ is possible.

So, statement (D) is not correct.

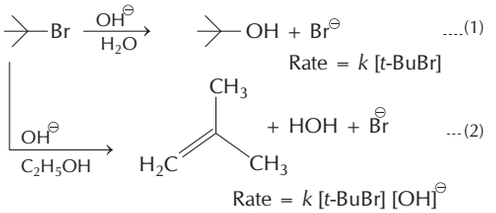
Here, $X^{\ominus}$ (leaving group) of $R-X$ is substituted by $Y^{\ominus}$, (nucleophile) *via* the formation of carbocation ($R^{\oplus}$) intermediate.

So, it is an S_N1 reaction. S_N1 mechanism supports weaker nucleophiles. So, statement (A) is correct.

S_N1 reaction is accompanied by inversion and retention in configuration, i.e. racemisation provided '*R*' of $R-X$ is chiral. So, statement (C) is correct.

Attachment of bulkier substituents or 3°-nature of the carbon atom of C—*X* bond of $R-X$ will favour formation of $R^{\oplus}$ (carbocation). So, statement (B) is also correct.

Example 5. *Consider the reaction sequence given below*



Which of the following statements is true? ***(JEE Main 2020)***

(a) Changing the base from $OH^{\ominus}$ to $^{\ominus}OR$ will have no effect on reaction (2)

(b) Changing the concentration of base will have no effect on reaction (1)

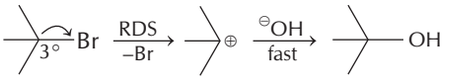
(c) Doubling the concentration of base will double the rate of both the reactions

(d) Changing the concentration of base will have no effect on reaction (2)

Sol. (*b*) **Reaction (1)**

Rate = k[*t*-BuBr], it is a unimolecular nucleophilic substitution reaction (S_N1), so, rate of this reaction will depend only on the concentration of the substrate, i.e. *t*-BuBr.

So, option (b) is correct, but option (c) is not correct.



(*t*-BuBr) Carbocation intermediate

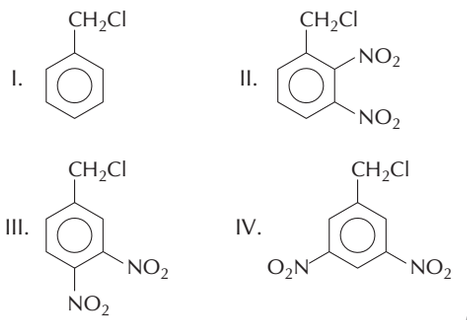
Reaction (2)

Rate = k [*t*-ByBr] [OH^-], it is a second order α, β-elimination reaction (base)

(E_2), because *t*-BuBr undergoes dehydrohalogenation (—HBr) with a strong base (alcoholic or ethanolic OH^-) to give an alkene. So, rate of the reaction depends on concentrations of substrate (*t*-ByBr) and base (OH/alc.). So, option (d) is not correct.

$\overset{\ominus}{O}R$ is a stronger base than $\overset{\ominus}{O}H$. So, use of $\overset{\ominus}{O}R$ will make the E_2 reaction faster. Hence, option (a) is also not correct.

Example 6. *The decreasing order of reactivity of the following compounds towards nucleophilic substitution (S_N2) is…*



(JEE Main 2020)

(a) (II) > (III) > (IV) > (I)

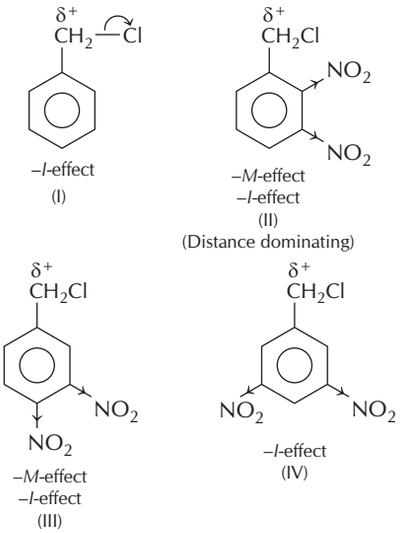
(b) (IV) > (II) > (III) > (I)

(c) (III) > (II) > (IV) > (I)

(d) (II) > (III) > (I) > (IV)

Sol. (*a*) Rate of S_N2 reaction $\propto \dfrac{1}{\text{Stability of carbocation}}$

Stability of carbocation $\propto \dfrac{1}{-I\,/\,-M}$ (effective group)



So, the decreasing order of reactivity of the given compounds toward S_N2 reaction is (II) > (III) > (IV) > (I).

II. Reduction

With Zn/acid or $LiAlH_4$ or catalytic hydrogenation

Alkyl halides on reduction with above written reagents give alkanes as

$$RX \xrightarrow[\text{or } LiAlH_4 \text{ or catalytic hydrogenation}]{\text{Zn/acid}} R\text{—H}$$

III. Reaction with Metals

(i) **With Mg** The reactions proceed as

$$RX + Mg \xrightarrow{\text{Dry ether}} RMgX \qquad \text{(Grignard's reagent)}$$

Reactivity order with Mg is $RI > RBr > RCl$.

(ii) **With Li**

$$RX + 2Li \xrightarrow{\text{Dry ether}} \underset{\text{(Alkyl lithium)}}{RLi} + LiX$$

The application of alkyl lithium is seen in **Corey-House Synthesis** of late 1960s.

The complete process is given in chapter 16.

(iii) **With Na** (Wurtz Reaction)

$$2RX + 2Na \xrightarrow{\text{Dry ether}} \underset{\text{Alkane}}{R\text{—}R} + 2NaX \text{ (Wurtz reaction)}$$

Just like Wurtz reaction, **Wurtz-Fittig** and **Fittig reaction** are shown by haloalkanes (see chapter 16).

TEL (tetra ethyl lead) the antiknock compound of petroleum industry is produced as

$$4C_2H_5Cl + 4Na / 4Pb \longrightarrow (C_2H_5)_4Pb + 4NaCl + 3Pb$$

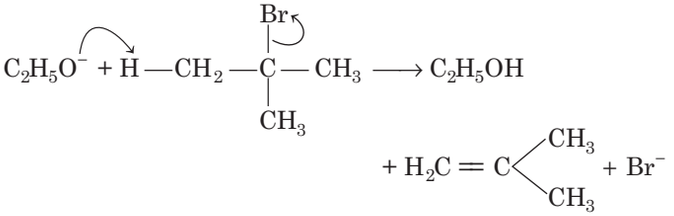
(iv) **With Zn**

$$2\,RX + Zn \xrightarrow[\text{ether}]{\text{Dry}} \underset{\text{Alkane}}{R—R} + ZnX_2 \text{ (Frankland reaction)}$$

Zn also form organometallic compounds like *R*Mg but its reactivity is less than Mg.

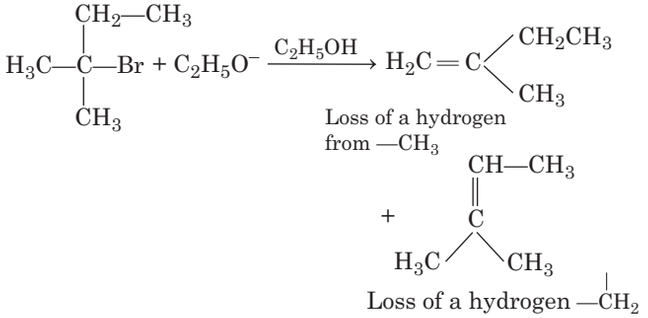
IV. Elimination Reactions

When an alkyl halide reacts with a base such as ethoxide ion ($C_2H_5O^-$, at elevated temperature, elimination reaction takes place. In this reaction, two or more groups are lost from the same molecule.
For example, in the following case H and Br are lost.



Note Reagent wise when, *aq*. KOH is used, substitution becomes predominant. On the other hand when alc. KOH is used then elimination becomes predominant. In alc. KOH, RO^- species works for the purpose.

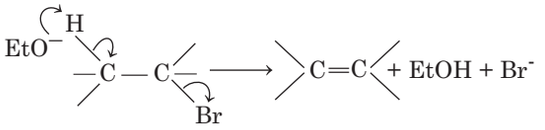
If there are more than one β-hydrogen, it results in more than one elimination products as



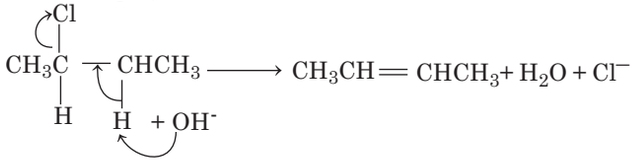
Here, the major and minor products are chosen with the help of Saytzeff or Zaitsev rules.

1. **Elimination can be E_2** (Bimolecular elimination)

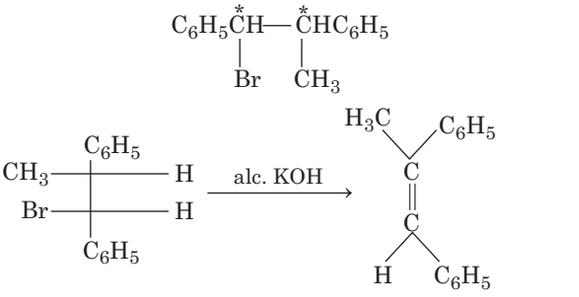
   This E2 reaction is facilitated by the attack of a base on the hydrogen atom which is to be removed.



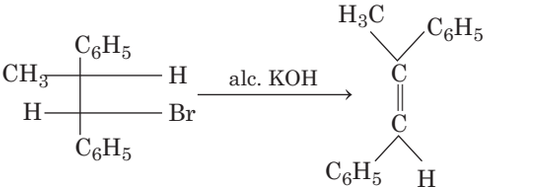
   For example,



   E2 elimination is stereospecific. Like dehydrohalogenation follows ***trans*-elimination.** So, in case of 1-bromo-1,2-diphenyl propane which contains two chiral carbon atoms as denoted by (*).



cis-1,2-diphenyl-prop-1-ene



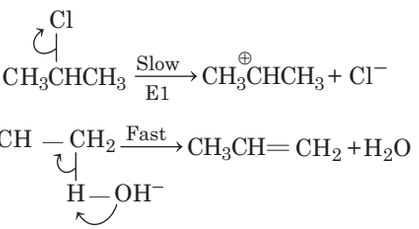
trans 1,2-diphenyl-prop-1-ene

   Reaction rate increases with the increasing strength of the base

$$CH_3CO_2^- < OH^- < EtO^- < Me_3CO^- < NH_2^-$$

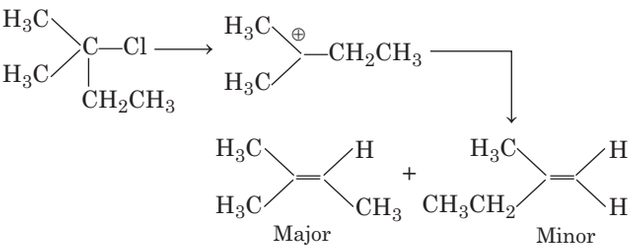
   The ease of the E2 reaction on alkyl halides is — I > — Br > — Cl > — F (bond strengths being in order C —F > C— Cl > C — Br > C — I) and amongst the alkyl groups, the order of reactivity for E2 elimination is primary > secondary > tertiary.

2. **Elimination can be E1** (unimolecular elimination) In which alkyl halide dissociates first to form carbocation and halide ion is removed as shown below



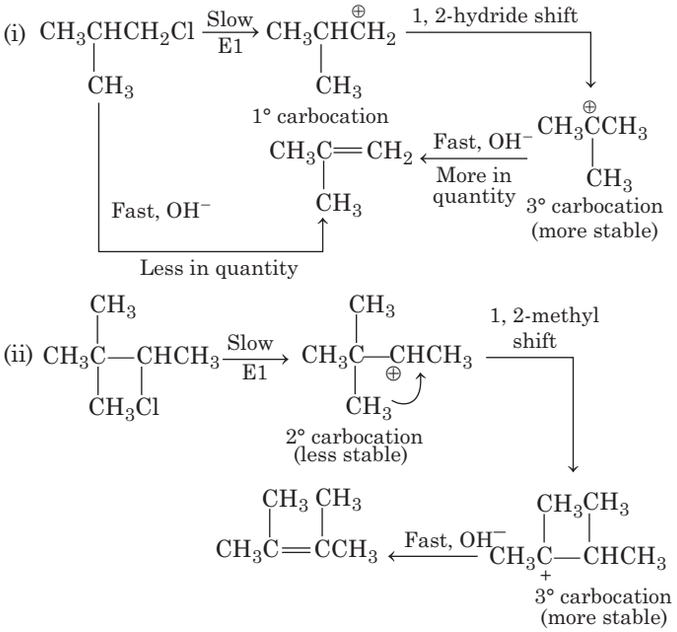
- The order of reactivity of alkyl group is; tertiary > secondary > primary, since, the rate-determining step is the formation of a carbocation, which has stability in order; 3° > 2° > 1°.

  Most substituted alkene is the Saytzeff product and less substituted alkene is the Hofmann product.

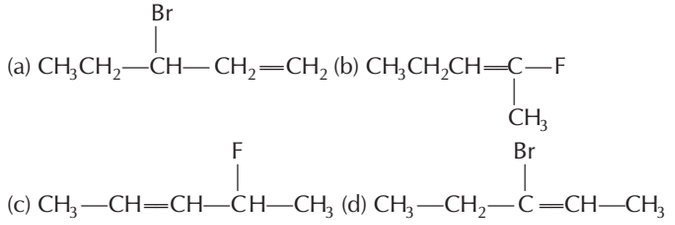


- However, when the product of Saytzeff elimination is more sterically compressed, the less substituted alkene may be formed.
- The carbocation may not only eliminate but may also add a nucleophilic species to give a substitution product by S_N1 reaction. **The E1 and S_N1 reactions are therefore, competitive**.

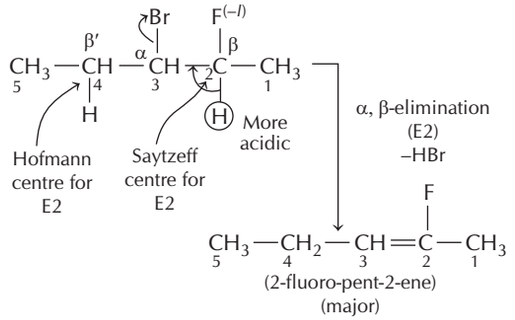
As the reaction involves formation of carbocation so, there can be 1, 2-hydride or 1, 2-methyl shift to attain greater stability of carbocation.



Example 7. *The major product obtained from* E2*-elimination of* 3*-bromo-2-fluoropentane is* ***(JEE Main 2020)***

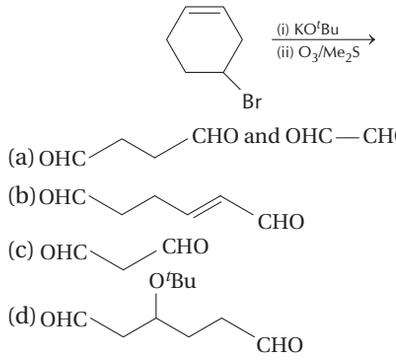


Sol. (*b*) Br atom is larger than F atom. So, C—Br is weaker than C—F bond. In elimination (E2), C—Br bond will break.

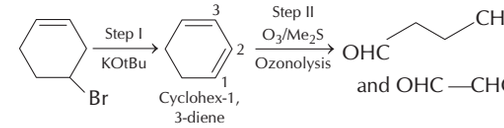


–*I*-effect of F atom makes the β-hydrogen more acidic for its elimination by a strong base used in E2.

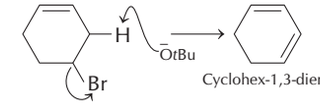
Example 8. *The major product(s) obtained in the following reaction is/are* ***(JEE Main 2019)***



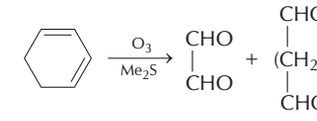
Sol. (*a*)



In step-1 dehydrohalogenation reaction takes place. Here, hydrogen is eliminated from β-carbon and the halogen is lost from α-carbon atom. As a result diene is formed.

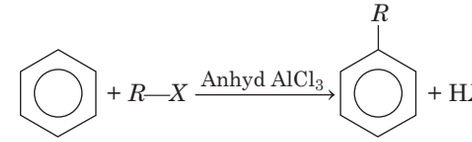


Cyclohex -1, 3-diene on ozonolysis gives butane-1, 4- dial and ethane- 1, 2- dial.



V. Friedel-Crafts Reactions

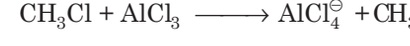
Alkyl benzene are the product of this reaction. The reaction takes place as



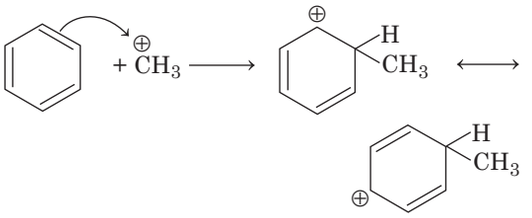
Function of anhydrous $AlCl_3$ (Lewis acid) is to generate electrophile, which is carbocation in this case. It is thus, S_E reaction.

Following steps are followed in the reaction

1. **Generation of electrophile**

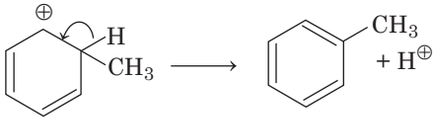


2. **Attack of electrophile or benzene nucleus to form σ-complex**



σ-complex (stable due to resonance)

3. **Removal of H^+ from σ-complex**

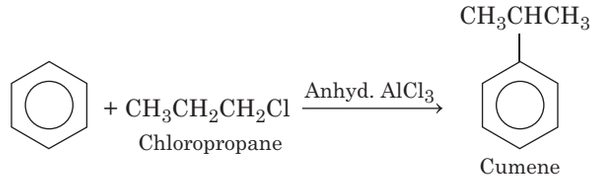


4. **Liberation of catalyst from Nu^- catalyst complex**

$$H^{\oplus} + AlCl_4^{\ominus} \longrightarrow AlCl_3 + HCl$$

In the carbocation, there may be the possibility of 1, 2-hydride or 1, 2-methyl shift to attain its greater stability.

For example chloropropane on reaction with benzene gives cumene instead of propyl benzene.

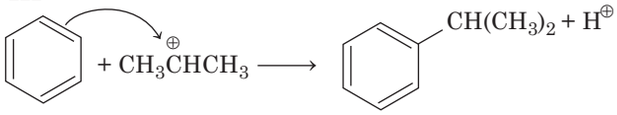


The reason behind it is that due to 1, 2-hydride shift propyl carbonium ion is formed initially.

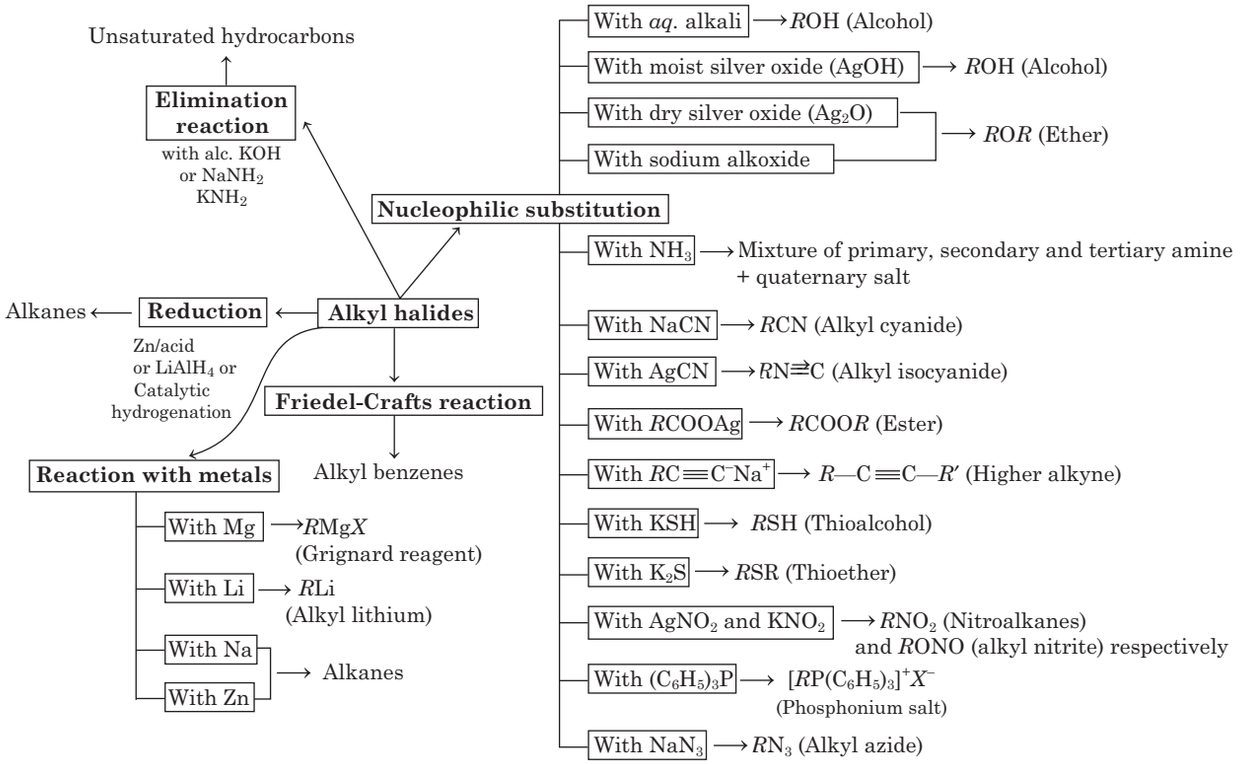
***Step* I** $CH_3CH_2CH_2Cl + AlCl_3 \longrightarrow CH_3\underset{1^\circ}{C}H_2\overset{\oplus}{C}H_2 + AlCl_4^{\ominus}$

***Step* II** $CH_3CH_2\overset{\oplus}{C}H_2 \xrightarrow{\text{1,2-hydride shift}} CH_3\underset{2^\circ}{\overset{\oplus}{C}}HCH_3$ (More stable than 1°)

***Step* III**



The chemical properties of monohaloalkanes can be summarised below



Dihaloalkanes

In these compounds two halogen atoms are present. They have the general formula, $C_nH_{2n}X_2$.

Methods of Preparation

Following methods can be employed to prepare dihalogen derivatives of alkanes.

1. Addition Reactions

(i) **Addition of Br_2 to alkenes** This reaction gives *vic*-dihalides.

$$R\text{—}CH{=}CH_2 + Br_2 \longrightarrow \underset{\displaystyle Br}{\overset{\displaystyle R\,CH\text{—}CH_2Br}{|}}$$

Alkylene bromide
(*vic*- dihalides)

(*gem*-dihalides an not prepared by this method.)

(ii) **Addition of halogen acids to alkynes** By this method only *gem*-dihalides can be prepared.

$$R{-}C{\equiv}CH + H\text{—}X \longrightarrow \underset{\displaystyle X}{\overset{\displaystyle R\text{—}C{=}CH_2}{|}} \xrightarrow{H\text{—}X} \underset{\displaystyle X}{\overset{\displaystyle X}{|}}R\text{—}\overset{\displaystyle X}{\overset{|}{C}}\text{—}CH_3$$

gem-dihalide

2. Substitution Reactions

(i) **Reaction of glycol with H*X*** This method gives *vic*-dihalides.

$$\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix} + 2HX \xrightarrow{200^\circ C} \begin{matrix}CH_2X\\|\\CH_2X\end{matrix} + 2H_2O$$

(ii) **Reaction of glycol with PCl_5** This method also gives only *vic*-dihalides.

$$\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix} + 2PCl_5 \longrightarrow \begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix} + 2POCl_3 + 2HCl$$

(iii) **Reaction of aldehydes and ketones with PCl_5** By this method *gem*-dihalides are prepared.

$$\begin{matrix}R\\R'\end{matrix}\!\!>\!C{=}O + PCl_5 \longrightarrow \begin{matrix}R\\R'\end{matrix}\!\!>\!\overset{\displaystyle Cl}{\overset{\displaystyle Cl}{C}} + POCl_3$$

(where, R' = H or alkyl group)

In reaction (ii) and (iii) PCl_3 and $SOCl_2$ can also be used in the place of PCl_5.

Physical Properties

These are colourless, sweet smelling liquids. The boiling points of CH_2Cl_2 is 313K. Because of its low boiling point and low inflammability, it is an effective extraction solvent used in pharamaceutical and food industries.

Chemical Properties

Chemical properties of dihaloalkanes are as follows:

(i) **Reaction with alcoholic KOH** This is a dehydrohalogenation reaction. Both *gem*-dihalides and *vic* dihalides give alkynes as final product when treated with alc. KOH.

$$\begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix} + \text{Alc.KOH} \xrightarrow[-KCl;\,-H_2O]{} \underset{\text{Vinyl chloride}}{\overset{\displaystyle CH_2}{\overset{\|}{CH\text{—}Cl}}} \xrightarrow[-KCl;\,-H_2O]{\text{Alc. KOH}} \overset{\displaystyle CH}{\overset{\equiv}{CH}}$$

$NaNH_2$, KNH_2 and K_3N can also be used in the place of alc. KOH. In all the above cases alkynes are formed in one step.

(ii) **Reaction with Zn dust** *gem* and *vic*-dihalides when heated with Zn dust, give alkenes by losing both the halogen atoms. Thus, it is a dehalogenation reaction.

$$\begin{matrix}CH_2X\\|\\CH_2X\end{matrix} + Zn \xrightarrow[-ZnX_2]{\Delta} \underset{\text{Ethylene}}{\overset{\displaystyle CH_2}{\overset{\|}{CH_2}}}$$

$$CH_3\text{—}CHX_2 + Zn \xrightarrow[-ZnX_2]{\Delta} \underset{\text{Ethylene}}{CH_2{=}CH_2}$$

(iii) **Reaction with aqueous alkali** *vic*-dihalides give glycol while *gem*-dihalides give aldehyde or ketones when treated with aqueous alkali. e.g.

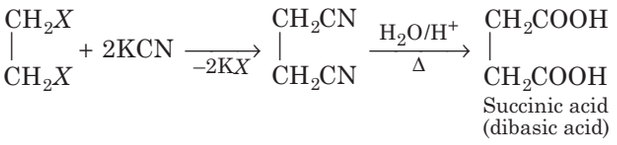
$$\underset{\text{*vic*-dihalide}}{\begin{matrix}CH_2X\\|\\CH_2X\end{matrix}} + 2NaOH(aq) \xrightarrow[-2NaX]{} \begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}$$

$$\underset{\text{*gem*-dihalide}}{CH_3CHX_2} + 2KOH(aq) \xrightarrow[-2NaX]{} \underset{\text{(Unstable)}}{CH_3CH\!\!<\!\!\begin{matrix}O\text{—}H\\|\\OH\end{matrix}} \xrightarrow[-H_2O]{} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

(iv) **Reaction with KCN followed by hydrolysis and heating** *gem*-dihalides when treated with KCN, form alkylidene cyanide which on hydrolysis and heating gives monobasic acid as

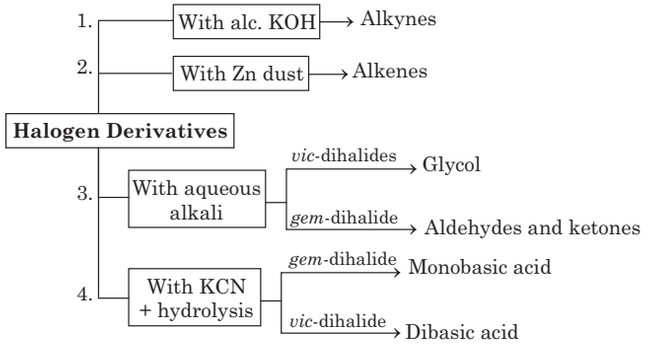
$$CH_3CHX_2 + 2KCN \xrightarrow[-2KX]{} CH_3\text{—}CH\!\!<\!\!\begin{matrix}CN\\CN\end{matrix} \xrightarrow{H_2O/H^+} CH_3\text{—}CH\!\!<\!\!\begin{matrix}COOH\\COOH\end{matrix} \xrightarrow[-CO_2]{\Delta} \underset{\text{(monobasic acid)}}{\underset{\text{Propanoic acid}}{CH_3CH_2COOH}}$$

vic-dihalides on the other hand, when subjected to the same procedure give dibasic acid.

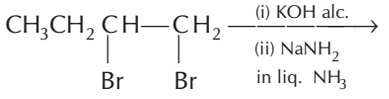


These dibasic acids have —COOH group at successive carbon atoms, so, do not lose —CO_2 on heating.

The summary of their chemical reactions looks as



Example 9. *The major product of the following reaction is*

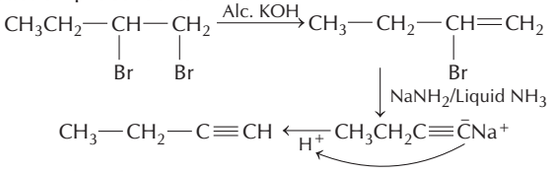


(a) $CH_3CH_2CH(NH_2)-CH_2(NH_2)$ (b) $CH_3CH=CHCH_2NH_2$

(c) $CH_3CH=C=CH_2$ (d) $CH_3CH_2C\equiv CH$ ***(JEE Main 2019)***

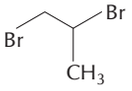
Sol. *(d)* Both alc. KOH and $NaNH_2$ in liquid NH_3 are dehydrohalogenating reagents. On comparative terms $NaNH_2$/liquid NH_3 is stronger in action.

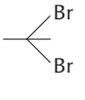
The reaction proceeds as

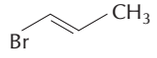


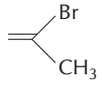
The option (d) is the correct answer.

Example 10. *1-methyl ethylene oxide when treated with an excess of* HBr *produces* ***(JEE Main 2020)***

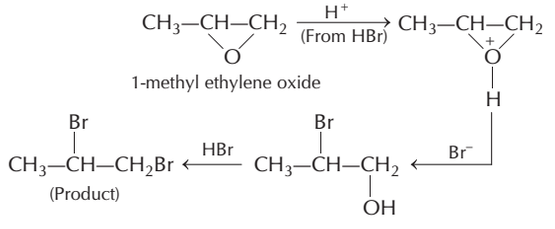
(a) 

(b) 

(c) 

(d) 

Sol. (a) The given reaction is completed as follows



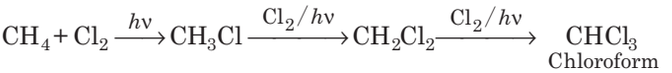
Trihaloalkanes

These compounds are commonly called haloforms, i.e. chloroform, bromoform, iodoform and have general formula CHX_3 (where, X = Cl, Br, I). Chloroform is the first discovered haloform.

Methods of Preparation

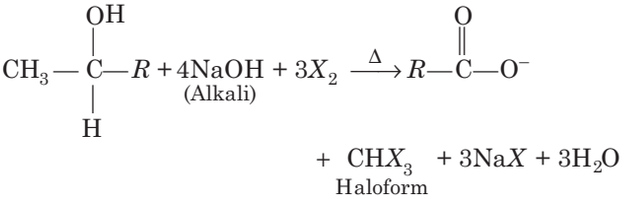
The important methods used to prepare haloform are as follows

1. Halogenation of Alkanes



2. Haloform Reaction

When certains compounds like methyl ketone or 2° alcohol having $CH_3CH(OH)-$ group or ethyl alcohol is treated with halogen, in the presence of alkali, then haloform is obtained. Due to the formation of haloform the reaction is called **haloform reaction**. The equation of complete reaction is shown below



Important facts related to haloform reaction are given below

- The compounds which can give this test must contain either one of these

  $CH_3-C(=O)-$; $CH_3-CH(OH)-$;

  $CH_3-CH(Cl)-$; $CX_3-C(=O)-$;

  $CHX_2-C(=O)-$; $CH_2X-C(=O)-$;

  i.e. any compound containing CH_3CO- group or any compound which on oxidation give such group or their halogen derivatives in which halogen is substituted from CH_3 group give this reaction.
- KOH may also be used as alkali.
- $CH_3COCH_2COOC_2H_5$ does not give haloform reaction

  (↑ Active methylene group)

  inspite of the presence of CH_3CO- group in it. The reason is the presence of active methylene or $-CH_2-$ group in it which prevents the conversion of CH_3CO- to CX_3CO- which is a necessity for the reaction.

The outline of the mechanism of this reaction is as follows

***Step* I** Halogen first oxidises (only in case of alcohols) to carbonyl compounds and then halogenated the compound to get $CX_3C(=O)-$ group.

If $CH_3-\underset{\underset{X}{|}}{CH}-$ is taken, it is first converted to $CH_3-\underset{\underset{OH}{|}}{CH}-$ by alkali and then oxidise which is followed by halogenation, i.e.

$$CH_3-\underset{\underset{X}{|}}{CH}- \xrightarrow{\text{Alkali}} CH_3-\underset{\underset{OH}{|}}{CH}- \xrightarrow[\text{Oxidation}]{X_2}$$

$$CH_3-\overset{\overset{O}{\|}}{C}- \xrightarrow{X_2} CX_3-\overset{\overset{O}{\|}}{C}-$$

Remember If the compound contains $CH_3-\overset{\overset{O}{\|}}{C}-$ group then oxidation does not occur, only halogenation takes place.

***Step* II** $CX_3-\overset{\overset{O}{\|}}{C}-$ formed in step I is then hydrolysed by alkali as

$$CX_3-\overset{H\,|\,OH}{\overset{\overset{O}{\|}}{C}}- \longrightarrow \underset{\text{Haloform}}{CHX_3} + HO-\overset{\overset{O}{\|}}{C}-$$

***Step* III** The $-\overset{\overset{O}{\|}}{C}-OH$ further reacts with alkali to give salt and water as

$$-\overset{\overset{O}{\|}}{C}-OH + NaOH \longrightarrow -\overset{\overset{O}{\|}}{C}-O^-Na^+ + H_2O$$

So, at the end haloform, sodium/potassium salt of a carboxylic acid and water are formed in the reaction.

3. Reaction of Bleaching Powder with Acetone

It is a modified form of haloform reaction in which bleaching powder ($CaOCl_2$) works as the source of halogen (Cl_2) and weak base ($Ca(OH)_2$). The equation of complete reaction is given below

***Step* I** $$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

***Step* II** $$CH_3COCH_3 + 3Cl_2 \xrightarrow{\text{Chlorination}} CCl_3COCH_3 + 3HCl$$

***Step* III** $$2CCl_3COCH_3 + Ca(OH)_2 \xrightarrow{\text{Hydrolysis}} \underset{\text{Chloroform}}{2CHCl_3} + (CH_3COO)_2Ca$$

The reaction is used for the preparation of $CHCl_3$ only.

Remember Preparation of chloroform from ethyl alcohol and bleaching powder involves three more steps, *viz.*, oxidation, chlorination and hydrolysis along with the step I shown above.

4. Reaction of Ethanol or Acetone with Aqueous Na_2CO_3 and KI

It is again a modified form of haloform reaction. In this reaction Na_2CO_3 is taken in the place of NaOH. This Na_2CO_3 on hydrolysis itself give NaOH, H_2O and CO_2 as

$$\text{Acetone} + Na_2CO_3 + KI \xrightarrow[60\text{-}70^\circ]{\text{Electrolysis}} \underset{\text{Yellow ppt.}}{CHI_3\downarrow} + 2H_2O + CO_2$$

$$CH_3CH_2OH + 4I_2 + 3Na_2CO_3 \longrightarrow \underset{\text{Iodoform}}{CHI_3\downarrow} + HCOO^-Na^+ + 5NaI + 2H_2O + 3CO_2$$

The methods of preparation of trihaloalkanes can be summarised as

1. Halogenation of alkanes
2. By haloform reaction
   $CH_3-\overset{\overset{O}{\|}}{C}-$ + alkali + X_2
3. By reacting bleaching powder paste with ethyl alcohol or acetone
4. By reacting ethanol or acetone with *Aq.* Na_2CO_3 and KI through electrolysis at 60-70°C

HALOFORMS

Physical Properties

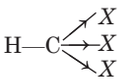
Physical properties of trihaloalkanes are as follows

- $CHCl_3$ and $CHBr_3$ are sickly smelling liquids, while CHI_3 is seen in the form of yellow, hexagonal plates.
- Their boiling point increases with increase in mol. wt. e.g. $CHCl_3$ – 334K, $CHBr_3$ – 422.5 K and CHI_3 – 392 K m.p.
- $CHCl_3$ and $CHBr_3$ are sparingly soluble in water but more soluble in organic solvents.
- However, CHI_3 is insoluble in H_2O but soluble in ether and ethanol.

Chemical Properties

Before going into detail of reactions, remember that the presence of three halogen atoms distort the trihaloalkanes molecule.

The structure looks like as



Their dipole moments are very high thus, here the C—H bond is polar and can be easily broken with the help of any base, resulting to the formation of dihalocarbenes as shown below (for $CHCl_3$).

$$CHCl_3 + \bar{O}H \rightleftharpoons :\bar{C}Cl_3 + H_2O$$

$$:\bar{C}Cl_3 \longrightarrow \underset{\text{Dichlorocarbene}}{:CCl_2} + Cl^-$$

This dihalocarbene is a very good electrophile and most of the reaction of trihalogen derivatives are attributed to it. Their reactivity order follows

$$CHI_3 > CHBr_3 > CHCl_3 >> CHF_3$$

This is because the C—I bond is less stable as compared to C—Cl or C—F bond.

The reactions shown by **chloroform** are as follows

(i) **Oxidation** Chloroform is so sensitive towards oxygen that it get autoxidised in the presence of sunlight and air. This results in the formation of phosgene gas or carbonyl chloride gas.

$$CHCl_3 + \frac{1}{2}O_2 \xrightarrow{h\nu} \underset{\substack{\text{Phogene}\\ \text{gas}}}{COCl_2} + HCl$$

The phosgene gas formed is extremely poisonous. To retard this oxidation we use 1% C_2H_5OH which converts poisonous phosgene to non-poisonous ethyl carbonate as shown below.

$$\underset{(1\%)}{COCl_2 + 2C_2H_5OH} \longrightarrow \underset{\text{Ethyl carbonate}}{(C_2H_5O)_2CO} + 2HCl$$

(ii) **Reduction** On using simple reducing agents/molecular H_2 with **catalyst, dihalogen** and **monohalogen derivatives** of alkanes along with **alkanes can** be produced.

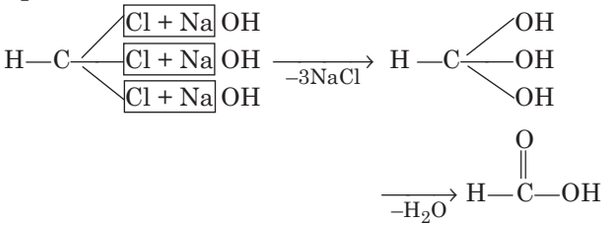
$$CH_4 \xleftarrow[-HCl]{Zn/H_2O} CHCl_3 \xrightarrow{Zn/HCl\text{-}C_2H_5OH} CH_2Cl_2$$

(iii) **Hydrolysis** Sodium or potassium salt of acid is obtained when hydrolysed with NaOH.

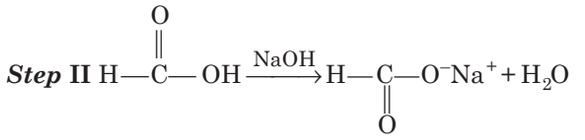
$$CHCl_3 + 4NaOH \longrightarrow HCOO^-Na^+ + 3NaCl + 2H_2O$$

In outline way the reaction proceeds as

***Step* I**



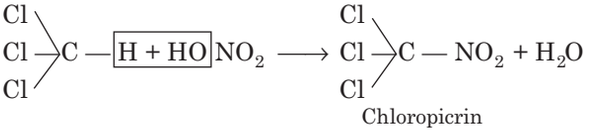
***Step* II**



(iv) **Halogenation** On further halogenation of $CHCl_3$ in presence of light results in the formation of CCl_4.

$$\underset{\text{Chloroform}}{CHCl_3} \xrightarrow{Cl_2/h\nu} \underset{\substack{\text{Tetrachloromethane}\\ \text{(pyrene)}}}{CCl_4}$$

(v) **Nitration** It results in the formation of **chloropicrin**.



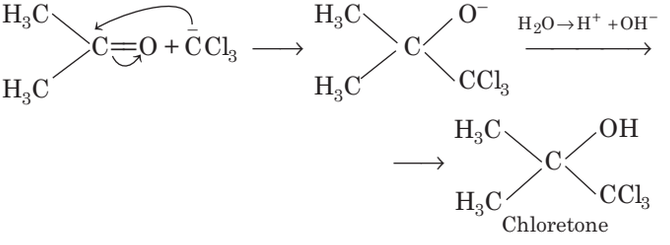
Chloropicrin (nitro chloroform) is used as a broad spectrum **antimicrobial**, **fungicide**, **herbicide**, **insecticide** and **a poisonous war gas.**

(vi) **With Ag** It is an example of dehalogenation reaction and results in the formation of alkyne

$$CHCl_3 + Ag \longrightarrow \underset{\text{Alkyne}}{CH{\equiv}CH}$$

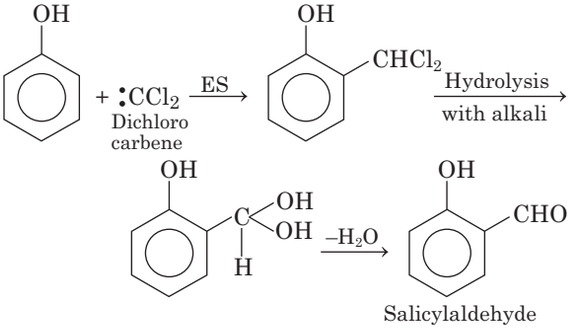
(vii) **With acetone** The reaction occurs in alkaline medium and $\bar{C}Cl_3$ attacks at $\rangle C{=}O$ group of acetone as a nucleophile, i.e.

$$CHCl_3 + \bar{O}H \longrightarrow \bar{C}Cl_3 + H_2O$$

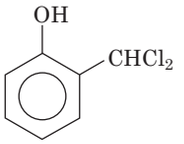


Chloretone is a sleep inducing medicine, (i.e. hypnotic).

(viii) **Reimer-Tiemann reaction** Phenol react with chloroform to form salicylaldehyde. The equation of complete reaction is shown below.



The attacking electrophile in this reaction is $:CCl_2$ (dichlorocarbene) which attacks itself to benzene ring through electrophilic substitution to give



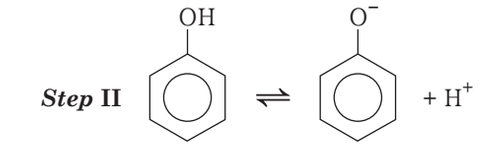
This compound undergoes hydrolysis due in the presence of electrophile to give salicylaldehyde.

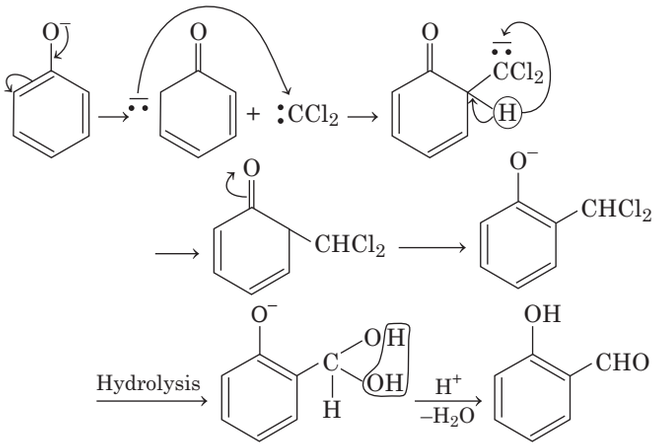
The mechanism of the reaction is as follows

***Step* I** $CHCl_3 + OH^- \rightleftharpoons :CCl_3^- + H_2O$

$:CCl_3^- \longrightarrow :CCl_2 + Cl^-$

***Step* II**



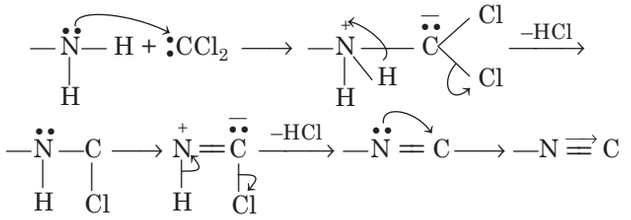


(ix) **Carbylamine reaction** The attacking reagent in this reaction is also $:CCl_2$ which attacks on the lone pair of nitrogen of amino group as

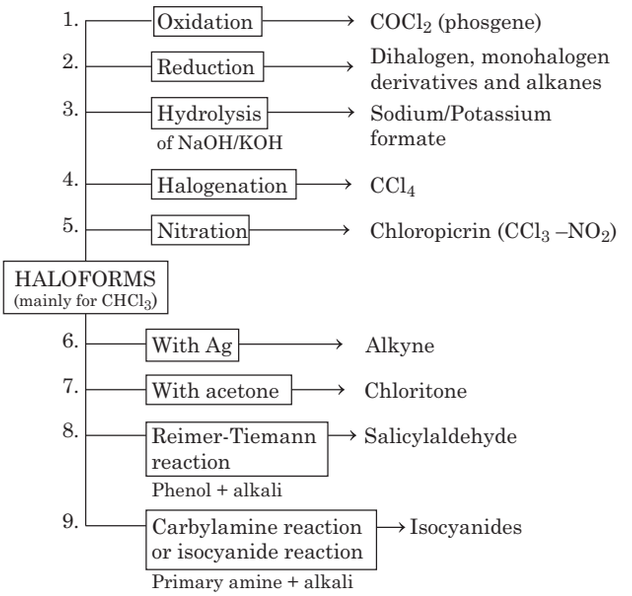
Chloroform react with primary amines in the presence of alkali (KOH or NaOH) to give alkyl cyanides are

$$CHCl_3 + 3KOH + RNH_2 \xrightarrow{\Delta} \underset{\text{Isocyanide or carbylamine}}{RNC} + 3KCl + 3H_2O$$

The reaction proceed as



The summary of chemical properties of haloforms is summarised as follows



Uses of Haloforms

- Chloroform is used for the synthesis of drug like chloretone and insecticide like chloropicrin. Moreover, it was used as an anaesthetic but because of its harmful effects it is not used for this purpose now a days.
- Chloroform is used as a solvent for fats, waxes, rubber, iodine etc.
- Iodoform is extensively used as an antiseptic for wounds. Its antiseptic action is due to liberation of free iodine, not because of the iodoform itself.

Example 11. *The major organic compound formed by the reaction of* 1, 1, 1 *–trichloroethane with silver powder is*

(a) acetylene (b) ethene ***(JEE Main 2014)***

(c) 2 – butyne (d) 2-butene

Sol. (c) $2Cl-\underset{\text{(1, 1, 1-trichloroethane)}}{\overset{Cl}{\underset{Cl}{\overset{|}{\underset{|}{C}}}}-CH_3} \xrightarrow{Ag} \underset{\text{(2-butyne)}}{CH_3-C\equiv C-CH_3} + 6AgCl$

Environmental Effects of Trihalomethanes (THMs)

THMs (trihalomethanes) are also environmental pollutants and are also considered as **carcinogenic.** Their adverse effect on environment are as follows

- **Trifluoromethane** and **chlorodifluoromethane** are both used as **refrigerants** in some applications. Trihalomethanes, released to the environment, break down faster than **chlorofluorocarbons** (CFCs), thereby doing much less damage to the **ozone layer.** However, fluoroform is not ozone depleting.

- Chloroform is a very common **solvent** used in organic chemistry. It is less **polar** solvent than water and is well-suited to dissolving many **organic compounds.** Although still toxic and potentially carcinogenic, chloroform is significantly less harmful than **carbon tetrachloride.** Because of the health and regulatory issues associated with the use of carbon tetrachloride, in laboratories. chloroform is used as a cheaper, cleaner alternative wherever possible.
- **Chloroform** is also formed in **swimming pools** which are disinfected with **chlorine** or **hypochlorite** due to **haloform reaction** with organic substances like **urine, sweat** and **skin** particles.
- Some of the THMs are quite volatile and may easily vaporise into the air. In swimmers uptake of THMs is greatest *via* skin with thermal absorption accounting for 80% of THM uptake.
- Exercising in chlorinated pool increases the toxicity of a "safe" chlorinated pool atmosphere with toxic effects of chlorine byproducts greater in young swimmers than older swimmers.

Polyhaloalkanes

These are the compounds having more than three halogen atoms. Some of such compounds are described below

Carbon Tetrachloride (CCl_4)

It is also known as tetrachloromethane. Until the mid 1960s it was widely used as a cleaning fluid, both in the industry as well as in home.

Methods of Preparation

It is prepared by the chlorination of alkane (methane), chloroform, carbondisulphide or propane under different reaction conditions as

Methane

$$\underset{\text{Methane}}{CH_4} + \underset{\text{(Excess)}}{4Cl_2} \xrightarrow{400^\circ C} CCl_4 + 4HCl$$

$$\underset{\text{Chloroform}}{CHCl_3} + Cl_2 \xrightarrow{h\nu} CCl_4 + HCl$$

Carbon disulphide

$$\underset{\substack{\text{Carbon}\\\text{disulphide}}}{CS_2} + 3Cl_2 \xrightarrow{AlCl_3 \text{ or } SbCl_3} CCl_4 + \underset{\substack{\text{Sulphur}\\\text{monochloride}}}{S_2Cl_2}$$

$$CS_2 + 2S_2Cl_2 \xrightarrow{AlCl_3} CCl_4 + 6S$$

Propane

$$\underset{\text{Propane}}{C_3H_8} + 9Cl_2 \xrightarrow[\text{pressure}]{\Delta} \underset{\substack{\text{Carbon}\\\text{tetrachloride}\\\text{(liquid)}}}{CCl_4} + \underset{\substack{\text{Hexa}\\\text{chloro}\\\text{ethane}\\\text{(solid)}}}{C_2Cl_6} + 8HCl$$

Physical Properties

CCl_4 is a colourless, non-inflammable and poisonous liquid with a characteristic odour. Its boiling point is 77°C. It is insoluble in water but soluble in a organic solvents. It is also resistant towards boiling water due to the non-availability of *d*-orbitals in carbon.

Chemical Reactions

Chemical properties of polyhaloalkanes are as follows

(i) **Reduction** With different reducing agents, CCl_4 gives different products as

$$CH_2Cl_2 \xleftarrow{Fe/H_2O} CCl_4 \xrightarrow{Fe/HCl} CHCl_3$$

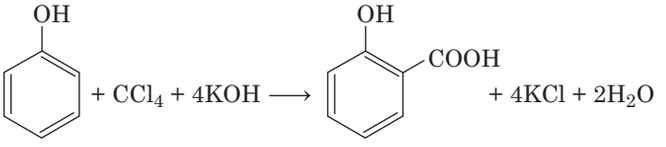
(ii) **Hydrolysis** The equation of this reaction looks like

$$CCl_4 \xrightarrow[-KCl]{4KOH(aq)} \underset{\substack{\text{(Highly unstable)}}}{\begin{matrix} & OH & \\ & | & \\ HO-C-OH & & \\ & | & \\ & OH & \end{matrix}} \xrightarrow[-2H_2O]{} CO_2 \xrightarrow[-H_2O]{2KOH} K_2CO_3$$

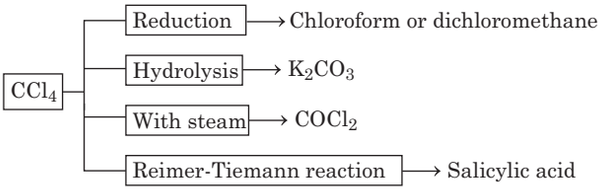
(iii) **With steam** CCl_4 gets oxidised to phosgene when reacts with steam at 500°C.

$$CCl_4 + H_2O \xrightarrow[\text{steam, } 500^\circ C]{\text{Superheated}} COCl_2 + 2HCl$$

(iv) **Reimer-Tiemann reaction** The reaction follows equation of the same mechanism as in case of chloroform and the net reaction looks as



The summary of chemical properties of CCl_4 is



Uses of CCl_4

- CCl_4 is used as a fire extinguisher under the name **pyrene**.
- It is used in medicines and as a solvent for fats, oils, waxes, greases etc.
- It is also used in the manufacture of refrigerants and propellants for aerosol cans.
- It is used in the synthesis of CFCs (chloro fluorocarbons) and other chemicals and in pharmaceutical manufacturing.

Harmful Effects

- Exposure to CCl_4 may cause irregular heart beat or heart failure. It may irritate the eyes on contact.
- It causes dizzines, light-headedness, nausea, vomitting which can cause permanent damage to nerve cells.

- Subsequently, these effects may lead to stupor, coma, unconsciousness, or death.
- In air, it deplets the ozone layer which increases the level of ultraviolet rays, causing skin cancer, eye diseases and disruption of the human immune system.

Freons

These are **chlorofluorocarbon** (CFC), i.e. contain, **carbon, chlorine,** and **fluorine** and produced as a **volatile** derivatives of **methane** and **ethane.**

A common subclass is the **hydro chloro fluorocarbons** (HCFCs), which contain hydrogen, as well. The most common representative is **dichlorodifluoromethane**.

Nomenclature of Freon

Freon-12 Here, the first number, i.e. 1, denotes C-atom, whereas the second number, i.e. 2, denotes the number of F-atoms and remaining H-atoms in CH_4 or C_2H_6 are replaced by Cl-atoms. Number of Cl-atoms is not mentioned.

Various freons obtained from methane and ethane are given in table below

Alkane	Freon
CH_4	**Freon-11** $CFCl_3$ (1 C, 1F, 3 Cl)
	Freon-12 CF_2Cl_2 (1 C, 2 F, remaining H-atoms are replaced by 2 Cl atoms)
	Freon-13 CF_3Cl (1C, 3F, 1 Cl)
C_2H_6	**Freon-22** $C_2F_2Cl_4$ (2C, 2F, remaining 2H-atoms replaced by Cl atoms)
	Freon-23 $C_2F_3Cl_3$ (2 C, 3F, 3Cl)
	Freon-24 $C_2F_4Cl_2$ (2 C, 4F, 2Cl)

- CFCs and HCFCs are usually produced by halogen exchange (Swarts reaction) starting from chlorinated methanes and ethanes. Following reaction is the synthesis of chlorodifluoromethane from **chloroform.**

$$HCCl_3 + 2HF \longrightarrow HCF_2Cl + 2HCl$$

The brominated derivatives are generated by free-radical reactions of the chlorofluorocarbons, replacing C—H bonds with C—Br bonds.

- The most important reaction of the CFCs is the photo-induced cleavage of a C—Cl bond

$$CCl_3F \longrightarrow CCl_2F^{\bullet} + Cl^{\bullet}$$

It is given in detail with in the "Environmental Chemistry" Chapter.

Applications

- Their uses include **refrigerants, blowing agents,** propellants in medicinal applications, and degreasing solvents.
- Billions of kilograms of chlorodifluoromethane are produced annually as a precursor to **tetrafluoroethylene,** the monomer that is converted into **teflon.**

Effect Upon Environment

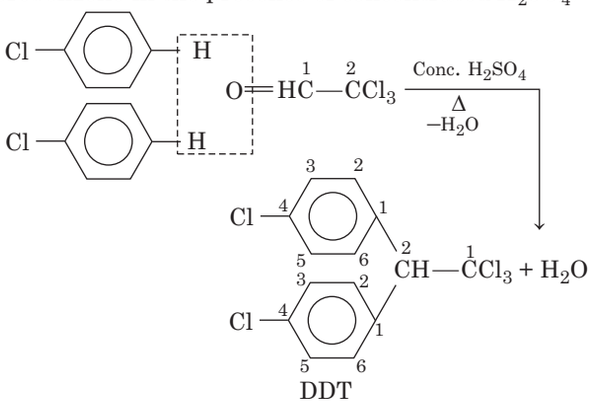
- The decomposition of freons in the atmosphere contributes to the destruction of the ozone layer.
- Overexposure may cause dizziness, loss of concentration, central nervous system depression and/or cardiac arrhythmia.
- Vapours displace air and can cause asphyxiation in confined spaces. Although being non-flammable, their combustion products include hydrofluoric acid, phosgene, and related species.

DDT (*p*,*p*'-Dichlorodiphenyl trichloroethane)

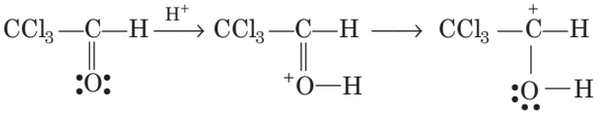
Its **IUPAC name** is 2,2-*bis* (4-chlorophenyl)-1,1,1-trichloroethane.

Method of Preparation

It is prepared by heating chloral, i.e. trichloro acetaldehyde or 2,2,2-trichloroethanal with two moles of chlorobenzene in the presence of concentrated H_2SO_4.

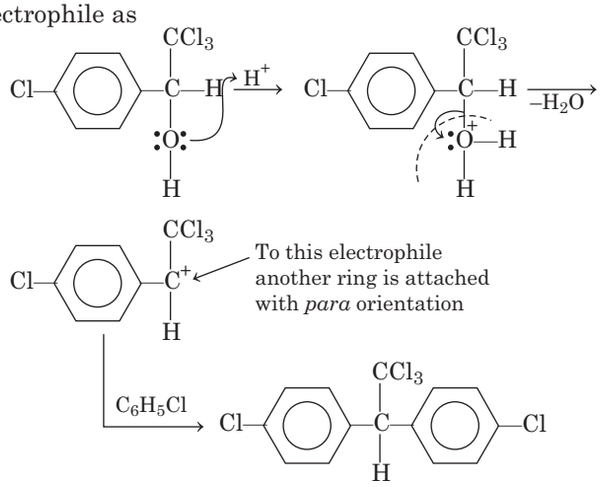


Mechanism It follows electrophilic substitution mechanism in which electrophile is generated as



After its attachment with one chloro benzene at para position H^+ of acid further takes lone pair from oxygen

resulting to removal of water and generation of another electrophile as



Note In chloral hydrate two —OH groups are present at the same carbon atom but still it is a stable compound. This is because of the existence of intramolecular H-bonding between Cl and H-atom of OH group.

Uses

It is a cheap but powerful insecticide for mosquitoes that spread malaria and lice that carry typhus.

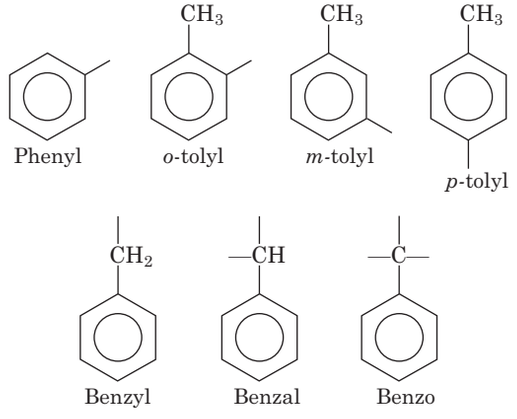
Harmful Effects

DDT has high toxicity towards fish. Due to its stability and fat solubility, it is not metabolised rapidly by animals but is deposited and stored in the fatty tissues. It was banned in the USA in 1973, but is still used in many parts of the word due to the non-availability of any other better and cheaper insecticides.

Aryl Halides

Aryl halides are the compounds having halogen atoms directly attached to the aromatic ring. These compounds are represented by Ar—*X* where Ar represents phenyl, substituted phenyl or any other aryl ring.

Before going in detail explore the below written terms and their usage.



Methods of Preparation of Aryl Halides

General methods used for the preparation of alkyl halide are usually not applied to synthesise **aryl halides.**

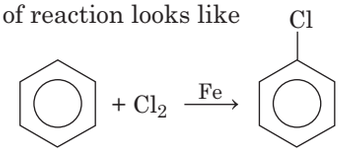
So, these are prepared by the following additional methods.

1. Halogenation

Low temperature and presence of a halogen carrier, i.e. Lewis acid favours this substitution. The chlorides or bromides of Al, Fe, Sb, Sn, etc., may also be used as halogen carriers. Fe is most commonly used among them as it is converted into following Lewis acid.

$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3 \text{ (Lews acid)}$$

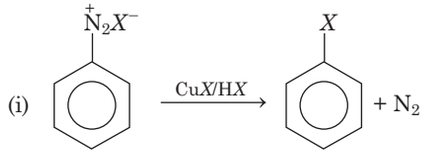
The equation of reaction looks like



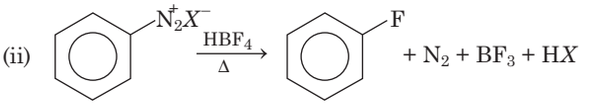
Without halogen carrier halonium ion (X^+) is not formed, thus, above reaction is not possible.

2. Decomposition of Diazonium Salt

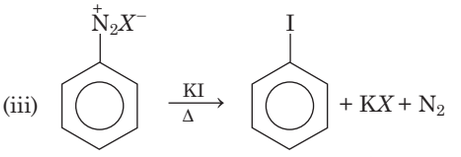
The equations of these reactions look like



Sandmeyer reaction [X = Cl, Br]



Sandmeyer reaction



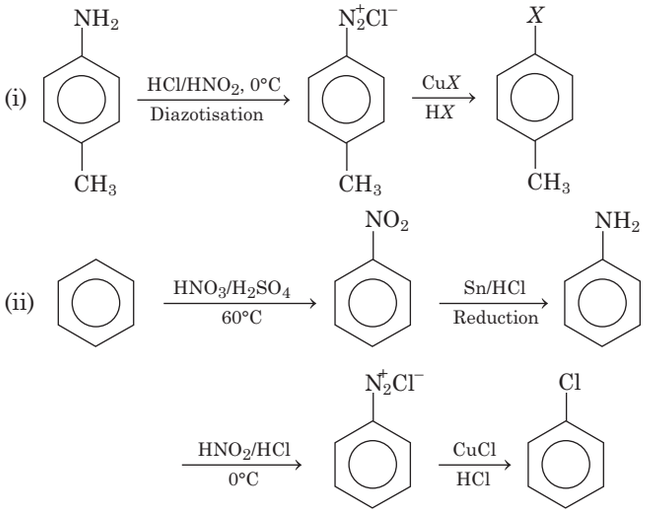
Gattermann reaction

Thus, fluorides, chlorides, bromides and iodides all can be prepared with the same method due to their differential reactivity.

Remember, above written (i) reaction is used to prepare **chlorides** and **bromides** (ii) reaction is used to prepare **fluorides** and (iii) reaction is used to prepare **aryl iodides.**

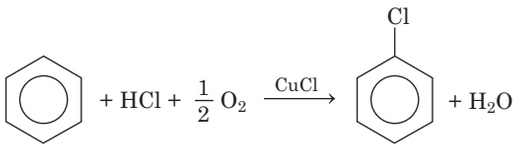
3. From Aromatic Amino and Nitro Compounds

A better yield of aryl halides is obtained through this reaction which is summarised as. It is the laboratory method



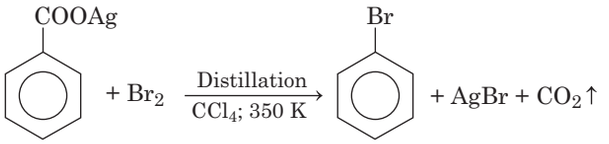
4. Raschig Process

It is the commercial method of the preparation chlorobenzene. The equation of complete reaction looks like

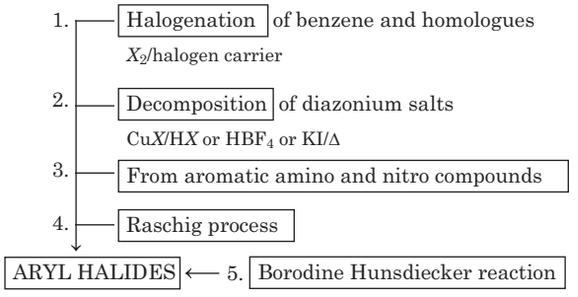


5. Borodine Hunsdiecker Reaction

This reaction is used to prepare haloalkanes also. The equation of complete reaction looks like



The summary of methods of preparation of aryl halides is as follows



Physical Properties

- Aryl halides are heavier than water. These are though polar but immiscible with water due to their incapability of forming H-bonds.
- The boiling points of haloarenes are nearly same as that of haloalkanes with same number of carbon atoms.
- For the same aryl group, the melting and boiling points increase as the size of the halogenation increases. For the same haloarenes melting and boiling points increase as size of the aryl group increases.

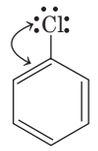
Chemical Properties

Chemical properties of aryl halides are as follows

Nucleophilic Substitution Reactions

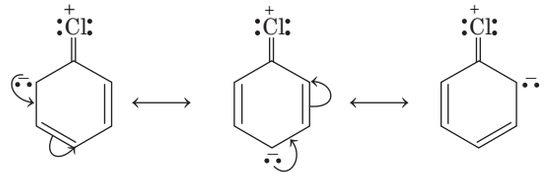
Aryl halides are less reactive towards nucleophilic substitution reactions as compared to alkyl halides under normal conditions due to the following reasons.

- The C—*X* bond in aryl halides have double bond character due to conjugation between lone pair of halogen and benzene ring as shwon below.



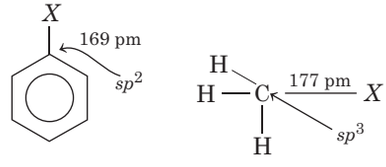
Conjugation of result in the following

3 resonating structures.



Due to the presence of such double bond character, it is difficult to break C—*X* bond in favour of *X*-atoms. Hence, aryl halides does not give the normal reactions of X^- (halides) ions. This rules out the possibility of nucleophilic substitutions under normal conditions.

- Moreover in halobenzene, C atom holding the halogen atom is sp^2-hybridised and in alkyl halide it is sp^3-hybridised.
- Since, an sp^2-hydridised orbital is smaller in size as compared to an sp^3-hybridised orbital therefore, the (C—*X*) bond in halobenzene should be shorter and hence stronger than that in alkyl halide. e.g.



- The sp^2-hybrid C-atom is more electronegative as compared to sp^3-hybrid C-atom, therefore, the sp^2-hybrid (of C —*X* bond) in aryl halide is less willing to release electron to the halogen than an sp^3-hybrid C atom in alkyl halide.

- As a result, we can conclude that (C—*X*) bond in an aryl halide is less polar than in alkyl halides, This is supported by the observation that dipole moment of chlorobenzene is 1.7 D as compared to the dipole moment CH_3Cl, i.e. 1.94 D. Consequently, the halogen atom present in aryl halides cannot be easily replaced by nucleophiles.

$$H_5\overset{+\delta}{C}_6—\overset{-\delta}{Cl} \qquad H_3\overset{+\delta}{C}—\overset{-\delta}{Cl}$$

It is difficult for the electron rich nucleophile to approach electron rich arenes because of repulsion between them.

Chloride Ion Test

Chlorobenzene does not give test for $Cl^{\ominus}$ ions when treated with *aq.* NaOH (or with KOH) and then with $AgNO_3$, whereas CH_3Cl gives this test.

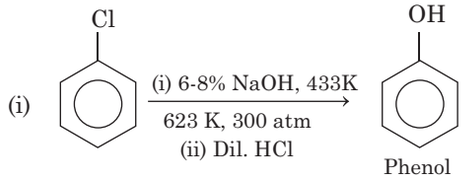
$$C_6H_5Cl + aq.\ KOH \xrightarrow{AgNO_3} \text{No. ppt.}$$

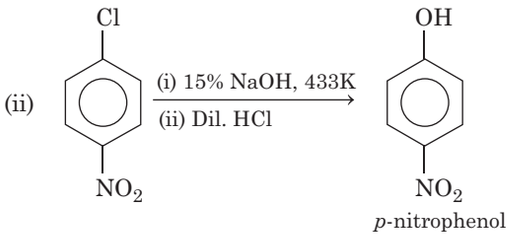
$$CH_3Cl + aq.\ KOH \longrightarrow CH_3OH + Cl^- \xrightarrow{AgNO_3} AgCl$$

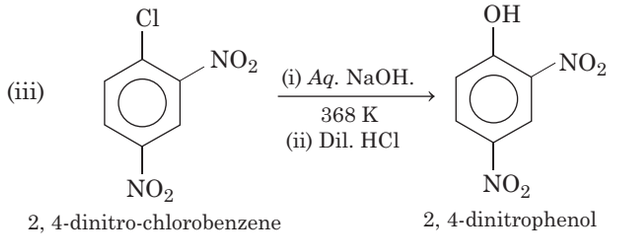
(White ppt. soluble in NH_4OH)

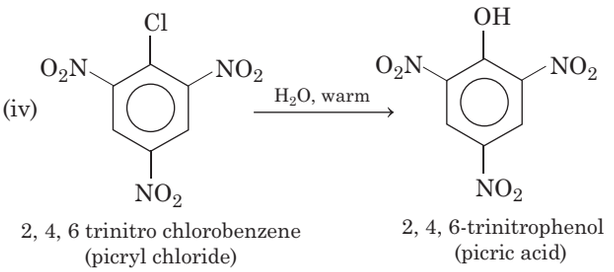
Under Drastic Conditions

However, aryl halides can be made to undergo nucleophilic substitution either under drastic conditions (such as the use of high temperature, pressure, or very strong nucleophile) or by the presence of electron-withdrawing group (e.g. — NO_2, —COOH, etc.) at the *o*-and *p*-positions to the nuclear halogen. The equations of some such reactions are shown below









Explanation The presence of nitro group at *ortho*- and *para* positions withdraws the electron density from the benzene ring and thus facilitates the attack of the nucleophile on haloarene.

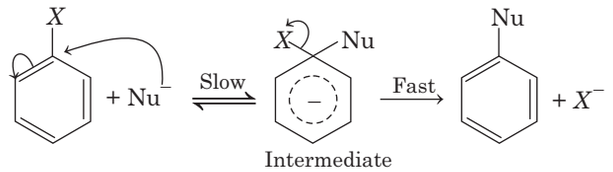
The carbanion thus formed is stabilised through resonance. The negative charge appearing at *ortho*- and *para*-positions with respect to the halogen substituent is stabilised by (—NO_2) group.

However, the presence of nitro group at *meta*- position does not stabilise the negative charge and no effect on reactivity is observed by the presence of (—NO_2) group at *meta*-position.

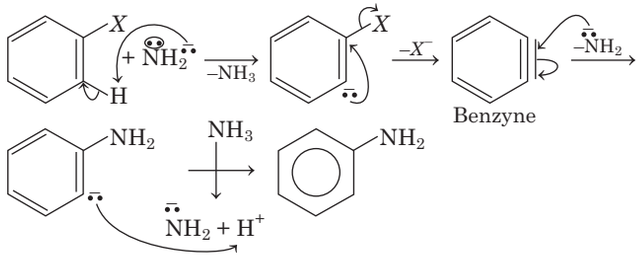
In general **nucleophilic substitution** reactions does not take place through straight S_N mechanism but alternate benzyne or bimolecular mechanisms are suggested for it.

These mechanisms are summarised as follows.

(i) **Bimolecular mechanism**



(ii) **Benzyne mechanism**



Nucleophilic substitution of NH_2 can also perform by reacting aryl halides with $NaNH_2$ or KNH_2 in liquid NH_3. The equation of all these reactions is given in the flow chart that is given on page 949.

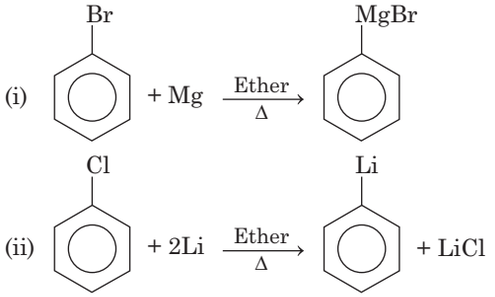
Remember In the absence of electron withdrawing groups or in the presence of electron donating groups, the nucleophilic substitution reactions in aryl halides occur preferably by the benzyne mechanism.

2. Reaction with Metals

Following reactions shown by aryl halides with metals

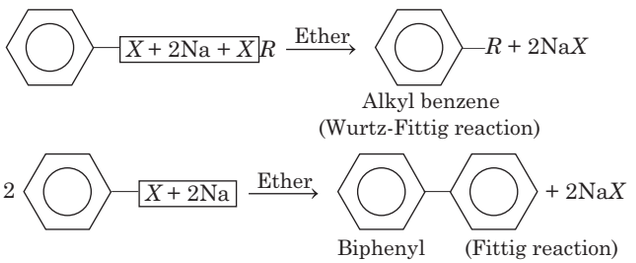
Formation of Organometallic Compounds

By this reaction, organometallic compounds are formed. The reactions looks like



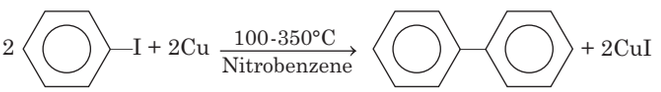
The reaction with Mg can also take place in the presence of THF.

Wurtz-Fittig and Fittig Reaction

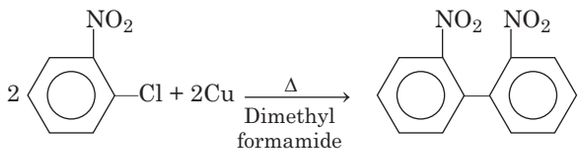


Ullmann Reaction

The reaction is successful with aryl iodides in the presence of Cu as C—I bond is weakest among all C—*X* bonds in aryl halides and the equation looks like

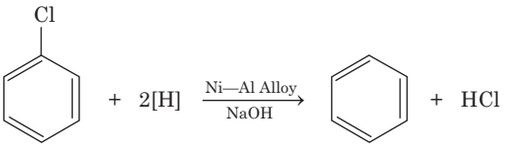


However, aryl chlorides and bromides also react, when some electronegative substituent with ability to activate the halogen is present. e.g.



Reduction

Haloarenes can be converted into corresponding arenes by reduction with Ni—Al alloy in the presence of an alkali

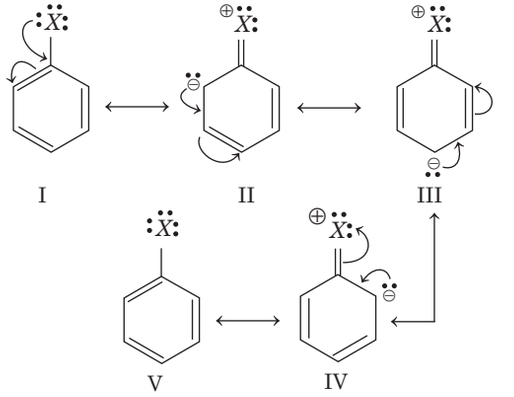


Electrophilic Substitution Reactions

Ar*X* undergoes the usual electrophilic substitution reactions of the benzene ring such as halogenation, sulphonation, nitration, and Friedel-Crafts' reactions.

Although slightly deactivating (due to –*I* effect), yet they are *o*, *p*-directing. Orientation (*o*-,*p*-directing) influence of halogens is explained by the resonance.

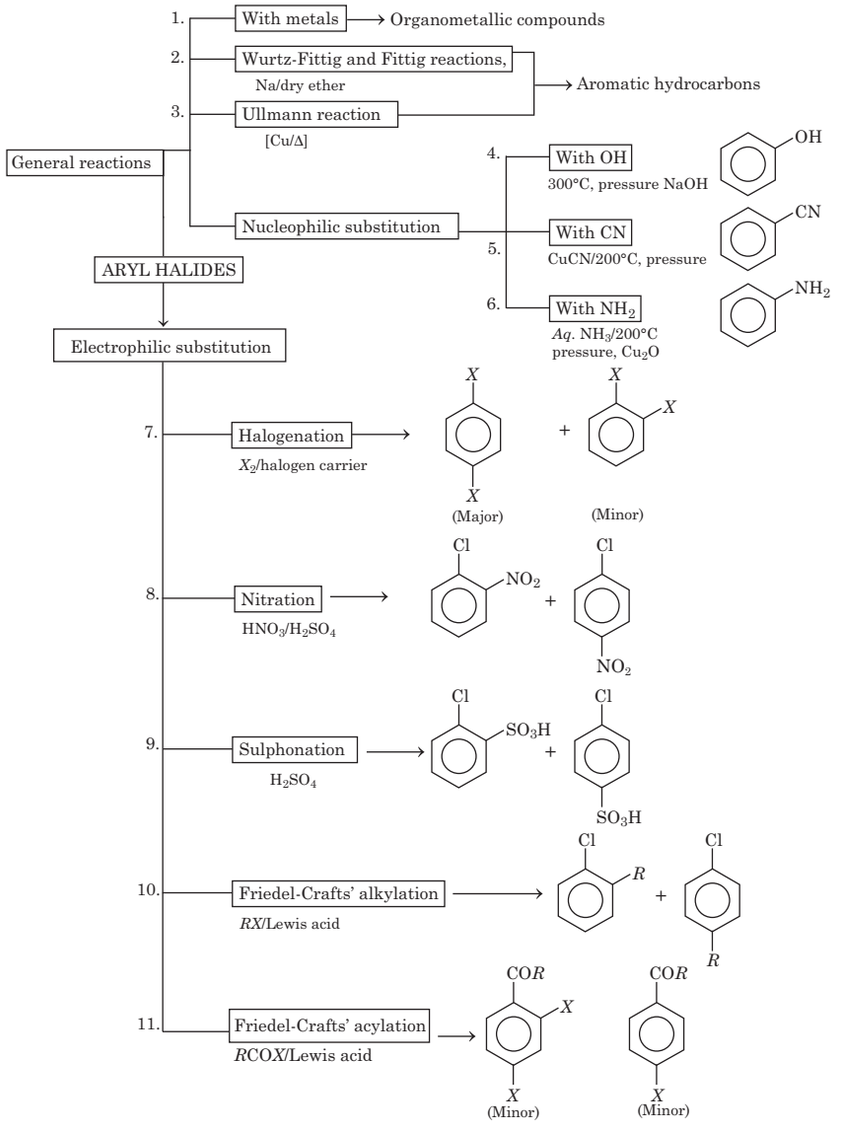
Due to + *M* effect, Ar*X* show resonance stabilisation in following structures



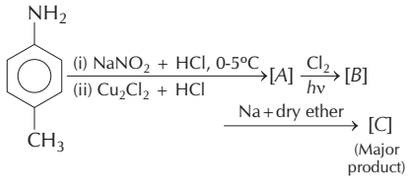
So, due to resonance, benzene ring is activated due to increase in the electron density more at *o*-and *p*-positions than at *m*-position.

Moreover, due to –*I* effect of *X*, there is some tendency to withdraw electron from the benzene ring; as a result the ring gets slightly deactivated as compared to benzene and hence, **electrophilic substitution reaction in Ar*X* occurs slowly** and **drastic conditions are required as compared** to those in benzene.

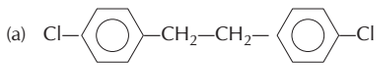
The chemical properties of aryl halides can also be summarised as

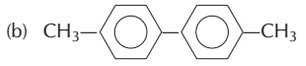


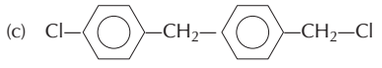
Example 12. *In the following reaction sequence,* [C] *is*

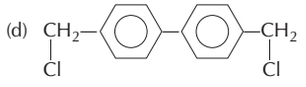


(JEE Main 2020)

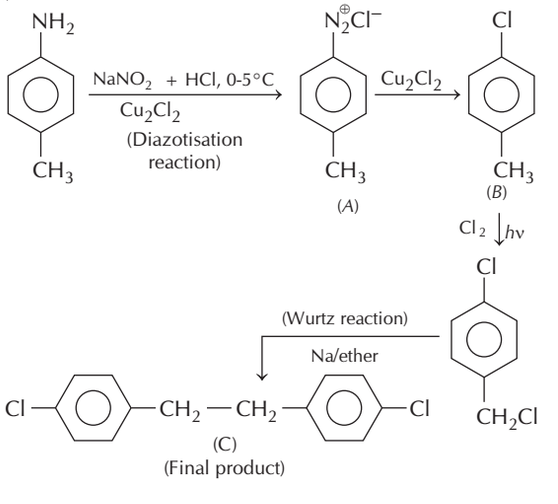
(a) 

(b) 

(c) 

(d) 

Sol. (a)



Practice Exercise

ROUND I Topically Divided Problems

General Characteristics and Preparation of Monohaloalkanes

1. Which of the following is an example of *vic*-dihalide? *[NCERT Exemplar]*

(a) Dichloromethane (b) 1, 2-dichloroethane
(c) Ethylidene chloride (d) Allyl chloride

2. What should be the correct IUPAC name for diethylbromomethane? *[NCERT Exemplar]*

(a) 1-bromo-1, 1-diethylmethane
(b) 3-bromopentane
(c) 1-bromo-1-ethylpropane
(d) 1-bromopentane

3. When hydrochloric acid gas is treated with propene in the presence of benzoyl peroxide, it gives

(a) 2-chloropropane (b) allyl chloride
(c) *n*-propyl chloride (d) *iso*-propyl chloride

4. Grignard reagents should be prepared under anhydrous conditions because *(NCERT Exemplar)*

(a) it is highly reactive towards protonic substances
(b) it reacts with ether
(c) Both (a) and (b)
(d) None of the above

5. Sulphuric acid cannot be used during the reaction of alcohols with KI because it is a *(NCERT)*

(a) strong oxidant (b) strong reductant
(c) weak oxidant (d) it can be used

6. The reagents required to obtain 1-iodobutane from but-1-ene is/are *(NCERT)*

(a) I_2 / red P
(b) KI
(c) HI / H_2O_2
(d) HBr / H_2O_2 and KI/acetone

7. Alkyl iodides can be prepared by

(a) $R\text{CH}_2\text{COOAg} + \text{I}_2 \xrightarrow[\Delta]{\text{CCl}_4} R\text{CH}_2\text{I}$

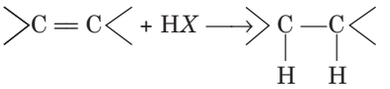
(b) $R\text{CH}_2\text{Cl} + \text{NaI} \xrightarrow[\Delta]{\text{Acetone}} R\text{CH}_2\text{I} + \text{NaCl}$

(c) $R - \text{OH} + \text{I}_2 \longrightarrow R\text{I} + \text{H}_2\text{O}$

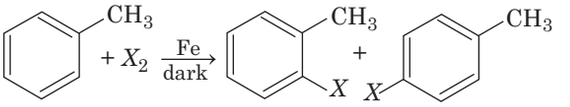
(d) $\text{CH}_4 + \text{I}_2 \longrightarrow \text{CH}_3\text{I}$

8. Which of the following is halogen exchange reaction ? *(NCERT Exemplar)*

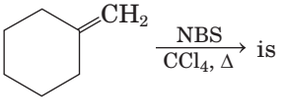
(a) $RX + \text{NaI} \longrightarrow RI + \text{Na}X$

(b) 

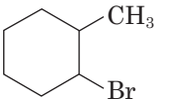
(c) $R\text{—OH} + HX \xrightarrow{\text{ZnCl}_2} R\text{—}X + \text{H}_2\text{O}$

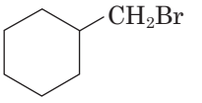
(d) 

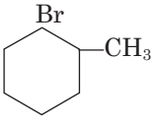
9. The major product formed in the reaction

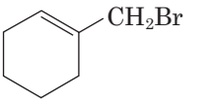


is

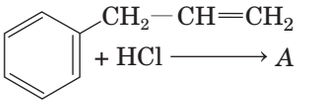
(a) 

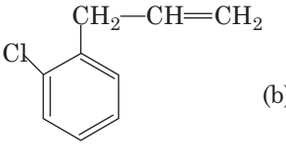
(b) 

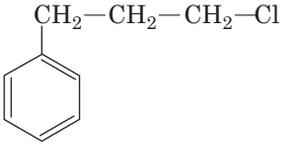
(c) 

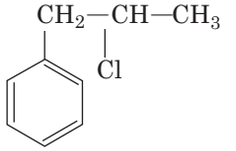
(d) 

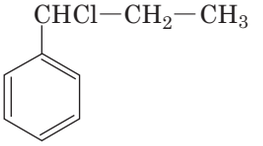
10. What is '*A*' in the following reaction? *(NCERT Exemplar)*



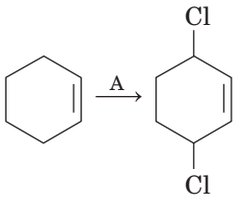
(a) 

(b) 

(c) 

(d) 

11. Consider the following *(JEE Main 2021)*



Identify the reagent(s) '*A*' and condition(s) for the reaction:

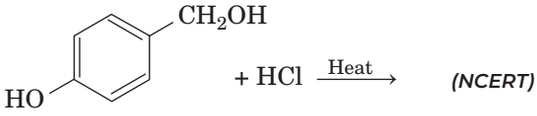
(a) $A = HCl$; anhydrous $AlCl_3$

(b) $A = HCl, ZnCl_2$

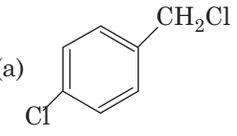
(c) $A = Cl_2$; UV light

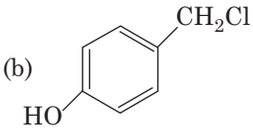
(d) $A = Cl_2$; dark, anhydrous $AlCl_3$

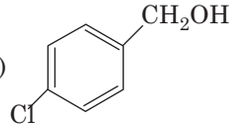
12. Find the structure of the product

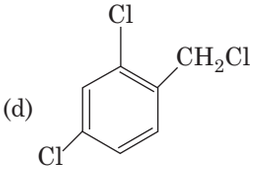


(NCERT)

(a) 

(b) 

(c) 

(d) 

13. Among the isomeric alkanes of molecular formula C_5H_{12} identify the one that on photochemical chlorination yields four isomeric monochlorides. *(NCERT)*

(a) 2-methylbutane (b) 2, 2-dimethylpropane

(c) 3-methylbutane (d) *n*-pentane

14. Which of the following alcohols will yield the corresponding alkyl chloride on reaction with concentrated HCl at room temperature? *(NCERT Exemplar)*

(a) $CH_3CH_2 - CH_2 - OH$ (b) $CH_3CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - OH$

(c) $CH_3CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2OH$ (d) $CH_3CH_2 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - OH$

15. The order of reactivity of the following alcohols with halogen acids is *(NCERT Exemplar)*

$\underset{(A)}{CH_3CH_2 - CH_2 - OH}$; $\underset{(B)}{CH_3CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - OH}$

$\underset{(C)}{CH_3CH_2 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - OH}$

(a) $A > B > C$ (b) $C > B > A$

(c) $B > A > C$ (d) $A > C > B$

16. A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon. *(NCERT)*

(a) 

(b) $CH_3CH_2 - CH = CHCH_2Cl$

(c) $CH_3CH = CHCH_2CH_2Cl$

(d) 

17. Which reagent will you use for the following reaction ?

$CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$

(a) Cl_2 / UV light (b) $NaCl + H_2SO_4$ *(NCERT)*

(c) Cl_2 gas in dark

(d) Cl_2 gas in the presence of iron in dark

18. The reaction of propene with HOCl ($Cl_2 + H_2O$) proceeds through the intermediate. That intermediate is *(JEE Main 2016)*

(a) $CH_3\overset{+}{C}HCH_2Cl$ (b) $CH_3CH(OH)\overset{+}{C}H_2$

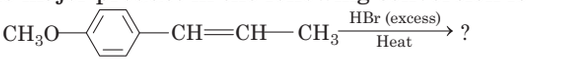
(c) $CH_3CHCl\overset{+}{C}H_2$ (d) $CH_3\overset{+}{C}HCH_2OH$

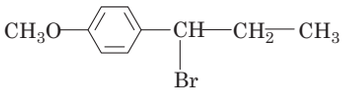
19. The synthesis of alkyl fluorides is best accomplished by *[JEE Main 2015]*

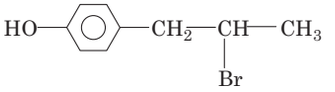
(a) free radical fluorination (b) Sandmeyer's reaction

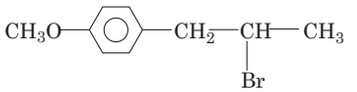
(c) Finkelstein reaction (d) Swarts reaction

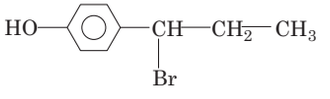
20. The major product in the following conversion is



(a) 

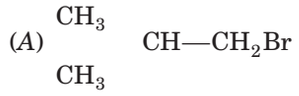
(b) 

(c) 

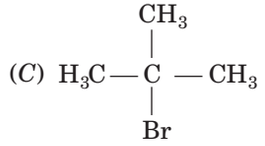
(d) 

Physical and Chemical Properties of Haloalkanes

21. Arrange the following compounds in the increasing order of their boiling points. *(NCERT Exemplar)*

(*A*) 

(*B*) $CH_3CH_2CH_2CH_2Br$

(*C*) 

(a) (*B*) < (*A*) < (*C*) (b) (*A*) < (*B*) < (*C*)
(c) (*C*) < (*A*) < (*B*) (d) (*C*) < (*B*) < (*A*)

22. Which is the correct increasing order of boiling points of the following compounds ?

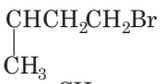
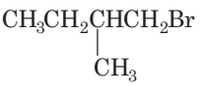
1-iodobutane, 1-bromobutane, 1-chlorobutane, Butane *(NCERT Exemplar)*

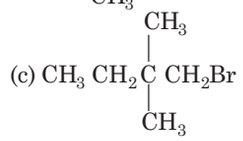
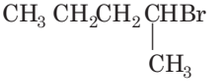
(a) Butane < 1-chlorobutane < 1-bromobutane <1-iodobutane
(b) 1-iodobutane < 1-bromobutane < 1-chlorobutane < butane
(c) Butane < 1- iodobutane < 1-bromobutane < 1-chlorobutane
(d) Butane <1-chlorobutane < 1-iodobutane <1-bromobutane

23. The alkyl halide that undergoes S_N1 reaction more readily is

(a) ethyl bromide (b) *iso*-propyl bromide
(c) vinyl bromide (d) *t*-butyl bromide

24. Which alkyl halide from the following pairs would you expect to react more rapidly by an S_N2 mechanism?

(a)  (b) 

(c)  (d) 

25. The increasing order of reactivity of the following halides for the S_N1 reaction is

I. $CH_3CH(Cl)CH_2CH_3$
II. $CH_3CH_2CH_2Cl$
III. *p* - $H_3CO—C_6H_4—CH_2Cl$ *[JEE Main 2017]*

(a) (III) < (II) < (I) (b) (II) < (I) < (III)
(c) (I) < (III) < (II) (d) (II) < (III) < (I)

26. The order of reactivities of the following alkyl halides for a S_N2 reaction is

(a) *R*F > *R*Cl > *R*Br > *R*I (b) *R*F > *R*Br > *R*Cl > *R*I
(c) *R*Cl > *R*Br > *R*F > *R*I (d) *R*I > *R*Br > *R*Cl > *R*F

27. $CH_3Br + Nu^- \longrightarrow CH_3—Nu + Br^-$

The decreasing order of the rate of the above reaction with nucleophile (Nu^-) *A* to *D* is

[Nu = (*A*) PhO^-, (*B*)AcO^-, (*C*)HO^-, (*D*) CH_3O^-] *(AIEEE 2006)*

(a) *D* > *C* > *A* > *B* (b) *D* > *C* > *B* > *A*
(c) *A* > *B* > *C* > *D* (d) *B* > *D* > *C* > *A*

28. Acetyl bromide reacts with excees of CH_3MgI followed by treatment with a saturated solution of NH_4Cl gives

(a) acetone (b) acetamide
(c) 2-methyl-2-propanol (d) acetyl ioide

29. Among the following the most reactive towards alcoholic KOH is

(a) $CH_2=CHBr$ (b) $CH_3COCH_2CH_2Br$
(c) CH_3CH_2Br (d) $CH_3CH_2CH_2Br$

30. An alkyl halide with molecular formula, $C_6H_{13}Br$ on treatment with alcoholic KOH gave two isomeric alkenes, *A* and *B*. Ozonolysis of the mixture gave the following compounds. CH_3COCH_3, CH_3CHO, CH_3CH_2CHO and $(CH_3)_2CHCHO$.

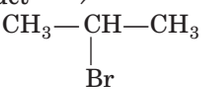
The alkyl halide is

(a) 2-bromohexane
(b) 3-bromo-2-methylpentane
(c) 2, 2-dimethyl-1-bromobutane
(d) 2-bromo-2, 3-dimethylbutane

31. The treatment of tertiary butyl chloride with 80% aqueous ethanol at 140°C gives

(a) $(CH_3)_3C—OH$ (b) $(CH_3)_3C—OCH_2CH_3$
(c) $CH_2=C(CH_3)_2$ (d) All of these

32. Identify the set of reagent/reaction conditions '*X*' and '*Y*' in the following set of transformations.

$CH_3—CH_2—CH_2Br \xrightarrow{X}$ Product $\xrightarrow{Y}$ 

(a) *X* = dilute aqueous NaOH, 20°C; *Y* = HBr/acetic acid, 20°C
(b) *X* = concentrated alcoholic NaOH, 80°C; *Y* = HBr/acetic acid, 20°C
(c) *X* = dilute aqueous NaOH, 20°C; *Y* = $Br_2/CHCl_3$, 0°C
(d) *X* = concentrated alcoholic NaOH, 80°C; *Y* = $Br_2/CHCl_3$, 0°C

33. *trans*-2-phenyl-1-bromocyclopentane on reaction with alcoholic KOH produces *(AIEEE 2006)*

(a) 4-phenylcyclopentene (b) 2-penylcyclopentene
(c) 1-phenylcyclopentene (d) 3-phenylcyclopentene

34. Identify (*C*) in

$$CH_3CH_2CH_2Br \xrightarrow{Aq.\,NaOH} A \xrightarrow{Al_2O_3} B \xrightarrow{Cl_2/H_2O} C$$

(a) $CH_3CHOHCH_2Cl$
(b) $CH_3CHClCH_2Cl$
(c) mixture of $CH_3CHCl\cdot CH_2Cl$ and $CH_3CHOHCH_2Cl$
(d) $CH_3CH_2ClCH_2OH$

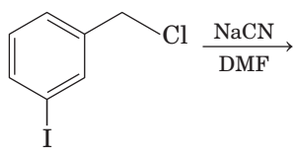
35. The Friedel-Crafts reactions of *n*-propylbromide with benzene in the presence of anhydrous $AlCl_3$ gives

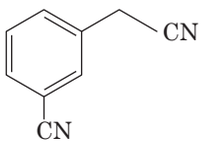
(a) *n*-propyl benzene (b) *iso*-propyl benzene
(c) 1,4-dipropyl benzene (d) 1,2-dipropyl benzene

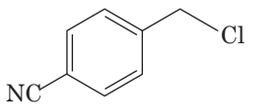
36. Butanenitrile may be prepared by heating

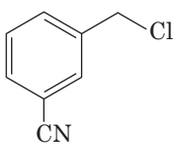
(a) propyl alcohol with KCN
(b) butyl alcohol with KCN
(c) propyl chloride with KCN
(d) butyl chloride with KCN

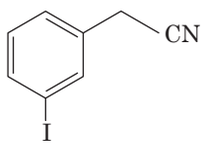
37. The structure of the major product formed in the following reaction is *(AIEEE 2006)*



(a) 

(b) 

(c) 

(d) 

38. The reaction of ethyl bromide and silver cyanide results in the formation of

(a) ethylene (b) ethyl cyanide
(c) ethyl isocyanide (d) ethyl alcohol

39. An alkyl halide (*RX*) reacts with Na to form 4, 5-diethyloctane. Compound *RX* is

(a) $CH_3(CH_2)_3Br$
(b) $CH_3(CH_2)_2CH(Br)CH_2CH_3$
(c) $CH_3(CH_2)_3CH(Br)CH_3$
(d) CH_3Br

40. In the reaction,

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

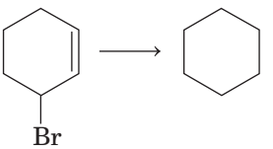
C is

(a) $CH_3CH_2CH_2I$ (b) $CH_3-\underset{\displaystyle I}{\underset{|}{C}}H-CH_3$
(c) $CH_3-\underset{\displaystyle I}{\underset{|}{C}}H-CH_2I$ (d) $CH_3CH=CHI$

41. Wet ether is not used as a solvent in Wurtz reaction, because the water present in it

(a) hydrolyses *RX* to *R*OH
(b) reduces *RX* to *R*H
(c) destroy the Na metal
(d) reacts with *R*—*R*

42. The transformation



can be brought about using

(a) Zn/H^+ (b) CuI
(c) Na (d) $(CH_3)_2CuLi$

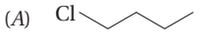
43. 2-bromopentane is heated with potassium ethoxide in ethanol. The major product obtained is

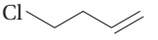
(a) pentene-1
(b) 2-ethoxypentane
(c) *trans*-pentene-2
(d) *cis*-pentene-2

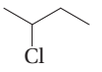
44. In the reaction,
$CH_3CH_2CHBrCH_3 + (CH_3)_3COK \longrightarrow$
the main product is

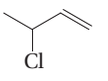
(a) $CH_3CH_2\underset{\displaystyle OC(CH_3)_3}{\underset{|}{C}}HCH_3$ (b) $CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}H\ CH_3$
(c) $CH_3CH_2CH=CH_2$ (d) $CH_3CH=CHCH_3$

45. The decreasing order of reactivity towards dehydrohalogenation (E1) reaction of the following compounds is *(JEE Main 2020)*

(*A*) 

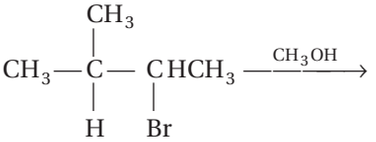
(*B*) 

(*C*) 

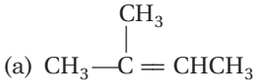
(*D*) 

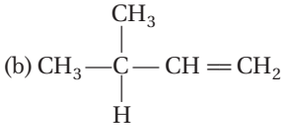
(a) $B > A > D > C$
(b) $B > D > A > C$
(c) $D > B > C > A$
(d) $B > D > C > A$

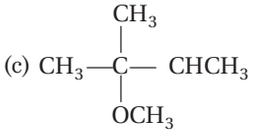
46. The major product of the following reaction is

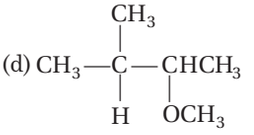


(JEE Main 2019)

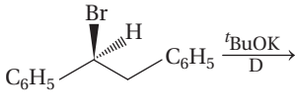
(a) 

(b) 

(c) 

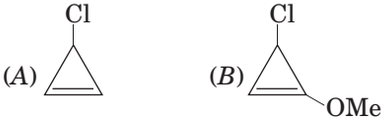
(d) 

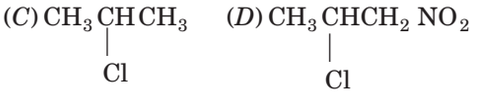
47. The major product obtained in the following reaction is *(JEE Main 2017 (Offline))*



(a) (±) $C_6H_5CH(O^tBu)CH_2C_6H_5$
(b) $C_6H_5CH=CHC_6H_5$
(c) (+) $C_6H_5CH(O^tBu)CH_2C_6H_5$
(d) (–) $C_6H_5CH(O^tBu)CH_2C_6H_5$

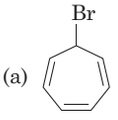
48. The decreasing order of reactivity of the following organic molecules towards $AgNO_3$ solution is *(JEE Main 2020)*

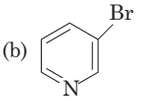


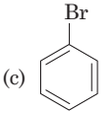


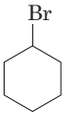
(a) (*A*) > (*B*) > (*C*) > (*D*)
(b) (*C*) > (*D*) > (*A*) > (*B*)
(c) (*B*) > (*A*) > (*C*) > (*D*)
(d) (*A*) > (*B*) > (*D*) > (*C*)

49. Which of the following compounds will produce a precipitate with $AgNO_3$? *(JEE Main 2019)*

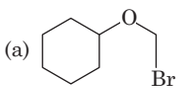
(a) 

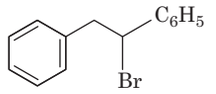
(b) 

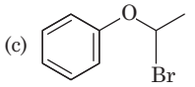
(c) 

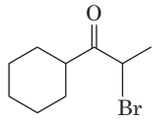
(d) 

50. Which of the following, upon treatment with *tert*-BuONa followed by addition of bromine water, fails to decolourise the colour of bromine ?
[JEE Main 2017 (Offline)]

(a) 

(b) 

(c) 

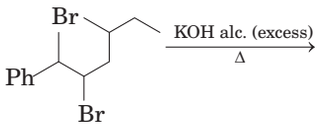
(d) 

Di, tri and Polyhalogen Compounds

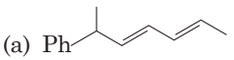
51. Which one of the following has the highest dipole moment ? *(NCERT)*
(a) CH_2Cl_2
(b) $CHCl_3$
(c) CCl_4
(d) All have equal dipole moment

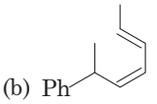
52. 1, 2-dibromoethane reacts with alcoholic KOH to yield a product *X*. The hybridisation state of the carbons present in *X* respectively, are
(a) *sp*, *sp* (b) sp^3, sp^3 (c) sp^3, sp^2 (d) sp^3, sp^2

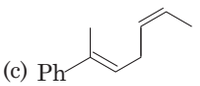
53. The major product of the following reaction is

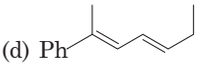


(JEE Main 2019)

(a) 

(b) 

(c) 

(d) 

54. Chloroform reacts with conc. HNO_3 to give
(a) water gas (b) tear gas
(c) laughing gas (d) producer gas

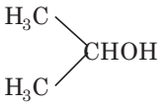
55. The bad smelling substance formed by the reaction of chloroform with methyl amine and alcoholic KOH will be
(a) methyl amine (b) methyl alcohol
(c) methyl cyanide (d) methyl isocyanide

56. If chloroform is left open in air in presence of sun, rays
(a) polymerisation taken place
(b) no reaction takes place
(c) explosion takes place
(d) phosgene gas is formed

57. The trade name of trichloroethylene is
(a) freon (b) westron
(c) westrosol (d) DDT

58. The compound which does not give iodoform with I_2 and alkali is

(a) CH_3CH_2OH (b) CH_3COCH_3

(c)  (d) CH_3OH

59. Haloform reaction cannot be used to prepare

(a) CHF_3 (b) $CHCl_3$

(c) $CHBr_3$ (d) CHI_3

60. Which is not the correct statement ?

(a) Chloretone is an insecticide

(b) $COCl_2$ is called phosgene

(c) Chloropicrin is used as an insecticide

(d) CCl_4 is used as fire extinguisher under the name pyrene

61. The main product of the reaction,

2-butene + chloroform $\xrightarrow{NaOH}$ would be

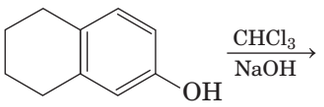
(a) butanoic acid

(b) 2-methylbutanoic acid

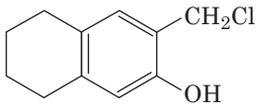
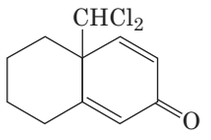
(c) 1,1,1-trichloro-2-methylbutane

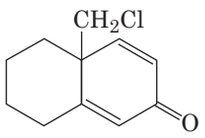
(d) 1,4-butanediol

62. The product obtained in the reaction,

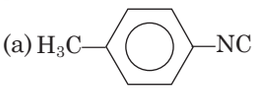
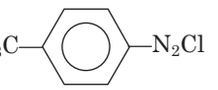


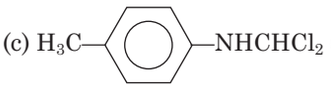
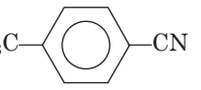
are

(a)  (b) 

(c)  (d) None of these

63. The reaction of chloroform with alcoholic KOH and *p*-toluidine form

(a)  (b) 

(c)  (d) 

64. The compound formed on heating chlorobenzene with chloral in the presence of concentrated sulphuric acid is

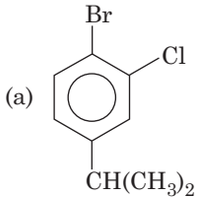
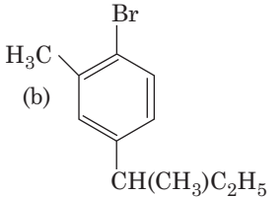
(a) gammexane (b) DDT

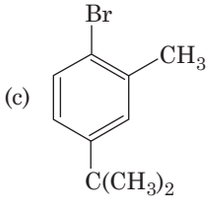
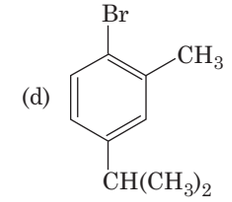
(c) freon (d) hexachloroethane

General Characteristics and Preparation of Aryl Halides

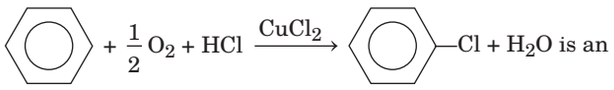
65. Write the structure of the following compounds.

1-bromo-4-*sec*-butyl-2-methylbenzene

(a)  (b) 

(c)  (d) 

66. Conversion of,



example of which of the following reaction?

(a) Nucleophilic substitution

(b) Electrophilic substitution

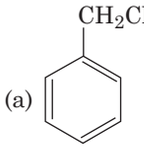
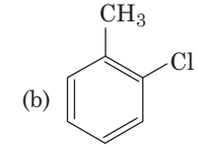
(c) Free radical addition

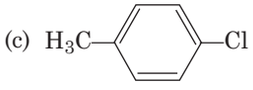
(d) Free radical substitution

67. Chlorobenzene is formed by reaction of chlorine with benzene in the presence of $AlCl_3$. Which of the following species attacks the benzene ring in this reaction ? *(NCERT Exemplar)*

(a) Cl^- (b) Cl^+ (c) $AlCl_3$ (d) $(AlCl_4)^+$

68. The reaction of toluene with chlorine in the presence of iron and in the absence of light yields. ..... *(NCERT Exemplar)*

(a)  (b) 

(c)  (d) Mixture of (b) and (c)

69. The yield of chlorobenzene obtained by reaction of phenol with PCl_5 is less due to the formation of

(a) *p*-chlorophenol

(b) *o*-chlorophenol

(c) triphenyl phosphate

(d) phosphorus oxychloride

70. The compound

$C_7H_8 \xrightarrow{3Cl_2/\Delta} X \xrightarrow{Br_2/Fe} Y \xrightarrow{Zn/HCl} Z.$

The compound Z is

(a) *m*-bromotoluene (b) *p*-bromotoluene

(c) *o*-bromotoluene *(d) 2,4,6-trichlorotoluene*

Physical and Chemical Properties of Aryl Halides

71. *p*-dichlorobenzene has higher melting point and lower solubility than those of *o*-and *m*-isomers. This is because *p*-isomer is

(a) more symmetrical (b) resonance stabilised

(c) stabilised by + *I* effect (d) Both (a) and (b)

72. Which of the following sequence of reactions will give 1-bromo-4-trichloromethylbenzene ?

(a) Toluene $\xrightarrow[Fe]{Br_2}$ *o*-bromotoluene $\xrightarrow[h\nu \text{ or heat}]{Cl_2}$

(b) Toluene $\xrightarrow[Fe]{Br_2}$ *p*-bromotoluene $\xrightarrow[h\nu \text{ or heat}]{Cl_2}$

(c) Toluene $\xrightarrow[h\nu \text{ or heat}]{Cl_2}$ trichloromethyl benzene $\xrightarrow[Fe]{Br_2}$

(d) None of the above

73. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with

$\underset{I}{SO_2Cl_2}$; $\underset{II}{SOCl_2}$; $\underset{III}{Cl_2/h\nu}$; $\underset{IV}{NaOCl}$

(a) I, II and III (b) I and III

(c) II and III (d) All the four

74. Arrange *m*-nitrochlorobenzene (I), 2, 4-dinitrochloro- benzene (II) *p*-nitrochlorobenzene (III) according to reactivity with sodium ethoxide.

(a) I > II > III (b) III > I > II

(c) II > III > I (d) II = III > I

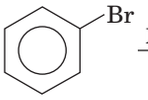
75. Arrange the following in order of increasing ease of nucleophilic substitution reaction

Chlorobenzene (I), 2, 4, 6-trinitrochlorobenzene (II), 2, 4- dinitrochlorobenzene (III) and 4-nitrochloro- benzene (IV)

(a) I < IV < III < II (b) I < III < IV < II

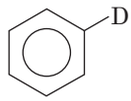
(c) II < III < IV < I (d) IV < III < II < I

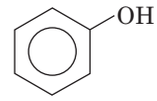
76. The final product obtained in the reaction

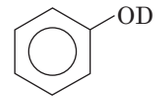


$\xrightarrow{Mg/ether}$ *A* $\xrightarrow{Heavy\ water}$ is

(a) 

(b) 

(c) 

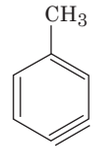
(d) 

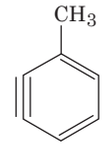
77. A convenient reagent for the conversion of bromobenzene into benzonitrile is

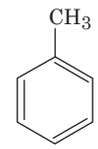
(a) alc. KCN alone (b) KCN and pyridine

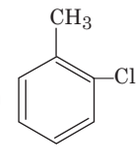
(c) silver cyanide (d) CuCN and pyridine

78. *o*-chlorotoluene reacts with sodamide in liquid NH_3 to give *o*-toluidine and *m*-toluidine. This proceeds through an intermediate

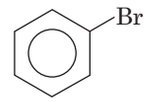
(a) 

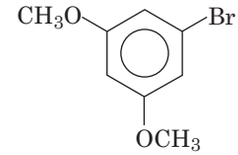
(b) 

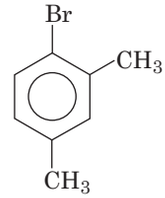
(c) 

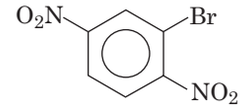
(d) 

79. Which of the following compounds is the most likely to undergo a bimolecular nucleophilic substitution reaction with aqueous NaOH?

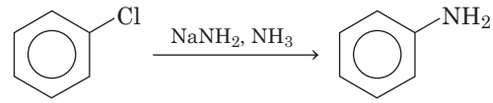
(a) 

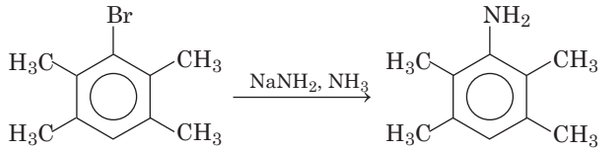
(b) 

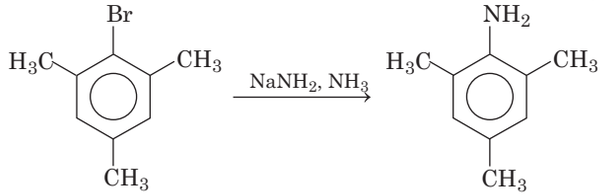
(c) 

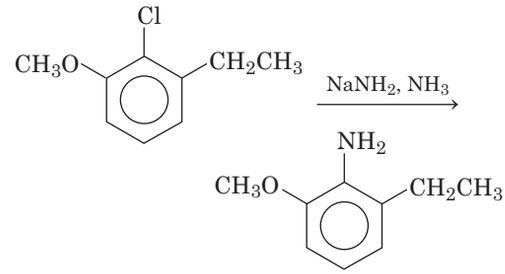
(d) 

80. Which of the following reactions is feasible ?

(a) 

(b) 

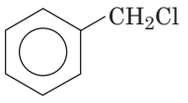
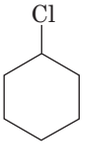
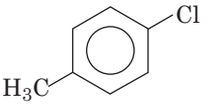
(c) 

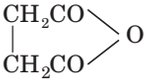
(d) 

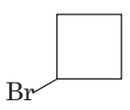
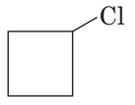
ROUND II Mixed Bag

1. Chlorine is the most reactive towards aqueous NaOH in
(a) methyl chloride
(b) chlorobenzene
(c) vinyl chloride
(d) benzyl chloride

2. Which of the following reagents can be used to distinguish chlorobenzene from chlorocyclohexane ?
(a) $AgNO_3$ / C_2H_5OH
(b) $Ag(NH_3)_2OH$
(c) Na fusion; HNO_3 ; $AgNO_3$
(d) Br_2 / CCl_4

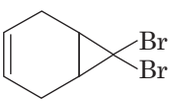
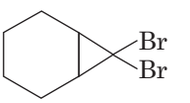
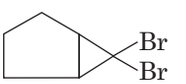
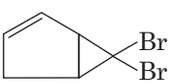
3. Which of the following will be the least reactive towards nucleophilic substitution ?
(a) 
(b) 
(c) 
(d) C_2H_5Cl

4. The product of which of the following reactions on dehydration gives

(a) 1,2-dibromoethane $\xrightarrow{KCN}$ $\xrightarrow[\Delta]{H_3O^+}$
(b) 1,1,-dibromoethane $\xrightarrow{KCN}$ $\xrightarrow[\Delta]{H_3O^+}$
(c) 1,1,1-trichloroethane $\xrightarrow[\text{hydrolysis}]{\text{Alkaline}}$
(d) None of the above

5. What would be the product formed when 1-bromo-3-chlorocyclobutane reacts with two equivalents of metallic sodium in ether?
(a) 
(b) 
(c) 
(d) 

6. The product of which of the following reaction gives the acid catalysed elimination most readily?
(a) $(CH_3)_3COMgBr \xrightarrow{H_3O^+}$
(b) $CH_3CH_2CH_2OMgBr \xrightarrow{H_3O^+}$
(c) $(CH_3)_2CHOMgBr \xrightarrow{H_3O^+}$
(d) $CH_3CH_2OMgBr \xrightarrow{H_3O^+}$

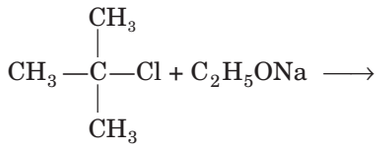
7. Identify *Z* in the following sequence of reactions
$C_3H_7I \xrightarrow{\text{Alc. KOH}} X \xrightarrow[\Delta]{\text{NBS, } h\nu} Y \xrightarrow{\text{Alc. KCN}} Z$
(a) $(CH_3)_2CH—CN$
(b) $Br — CH = CH — CN$
(c) $CH_2 = CH — CH_2CN$
(d) $CH_2 = CH — CHBr — CN$

8. CBr_4 + MeLi +  ⟶ ?
Identify the end product.
(a) 
(b) 
(c) 
(d) 

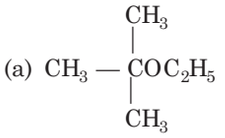
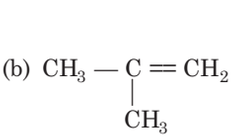
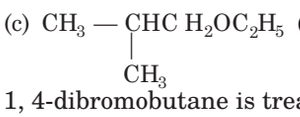
9. A new carbon-carbon bond formation is possible in
(a) Cannizzaro reaction
(b) Reimer-Tiemann reaction
(c) Clemmensen reduction
(d) None of the above

10. A compound obtained by the hydrolysis of the substance *A,* on reduction forms 2-hexanol. Hence, the substance *A* is
(a) 3,3-dichlorohexane (b) 2,3-dichlorohexane
(c) 2,2-dichlorohexane (d) 1,1-dichlorohexane

11. A dihaloalkane '*X*', having formula $C_3H_6Cl_2$, on hydrolysis gives a compound, that can reduce Tollen's reagent. The compound '*X*' is
(a) 1, 2-dichloropropane
(b) 1, 1-dichloropropane
(c) 1, 3-dichloropropane
(d) 2, 2-dichloropropane

12. 

Major product of this reaction is

(a) 
(b) 
(c) 
(d) None of these

13. 1, 4-dibromobutane is treated with Na_2S in aqueous ethanol. The product formed is

(a) $BrCH_2CH_2CH_2CH_2OH$ (b) $HSCH_2CH_2CH_2SH$

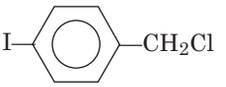
(c) $BrCH_2CH_2CH_2S^-Na^+$ (d) 

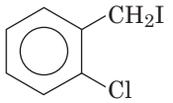
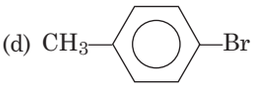
14. The reactivity of the compounds

(i) MeBr (ii) $PhCH_2Br$ (iii) MeCl (iv) *p* - $MeOC_6H_4Br$ decreases as

(a) (i) > (ii) > (iii) > (iv)
(b) (iv) > (ii) > (i) > (iii)
(c) (iv) > (iii) > (i) > (ii)
(d) (ii) > (i) > (iii) > (iv)

15. Which of the following will give yellow precipitate on shaking with an aqueous solution of NaOH followed by acidification with dil. HNO_3 and addition of $AgNO_3$ solution ?

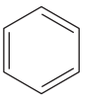
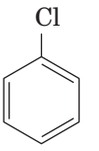
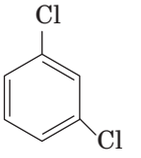
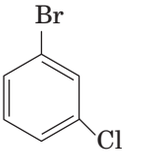
(a) C_2H_5I (b) 

(c)  (d) 

16. A hydrocarbon of molecular mass 72 g mol^{-1} gives a single monochloro derivative and two dichloro derivatives on photochlorination. Give the name of the hydrocarbon.

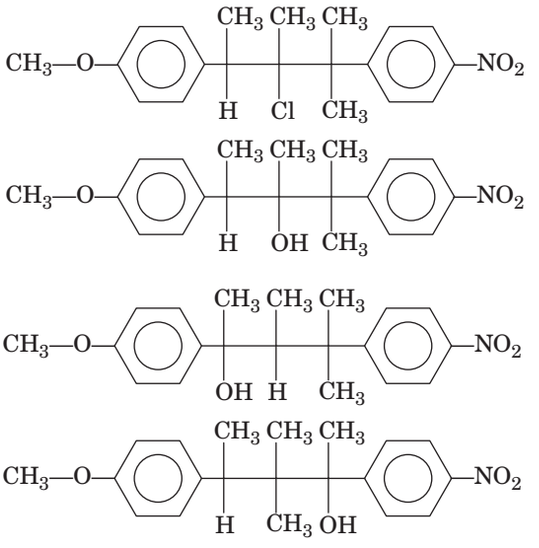
(a) *n*-pentane
(b) 2, 2-dimethyl propane
(c) 2, 2-dimethyl pentane
(d) *iso*-pentane

17. Arrange the following compounds in the increasing order of their densities.

(*A*) 
(*B*) 
(*C*) 
(*D*) 

(a) (*A*) < (*B*) < (*C*) < (*D*)
(b) (*A*) < (*C*) < (*D*) < (*B*)
(c) (*D*) < (*C*) < (*B*) < (*A*)
(d) (*B*) < (*D*) < (*C*) < (*A*)

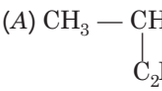
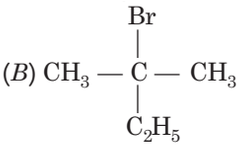
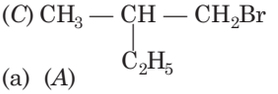
18. The following compound on hydrolysis in aqueous acetone will give



(a) mixture of (*K*) and (*L*)
(b) mixture of (*K*) and (*M*)
(c) only (*M*)
(d) only (*K*)

19. Which of the following compounds will give racemic mixture on nucleophilic substitution by OH^- ion ?

(NCERT Exemplar)

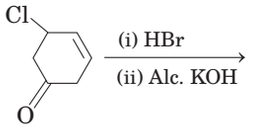
(*A*) 
(*B*) 
(*C*) 

(a) (*A*) (b) (*A*), (*B*), (*C*)
(c) (*B*), (*C*) (d) (*A*), (*C*)

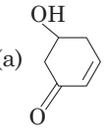
20. The dihalogen derivative '*X*' of a hydrocarbon with three carbon atoms reacts with alcoholic KOH and produces another hydrocarbon which forms a red precipitate with ammoniacal Cu_2Cl_2. '*X*' gives an aldehyde on reaction with aqueous KOH. The compound '*X*' is

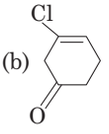
(a) 1, 3-dichloropropane (b) 1, 2-dichloropropane
(c) 2, 2-dichloropropane (d) 1, 1-dichloropropane

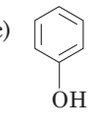
21. The major product of the following reaction is

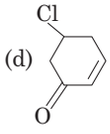


(JEE Main 2019)

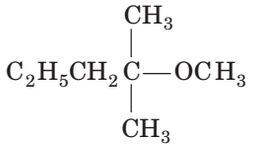
(a) 

(b) 

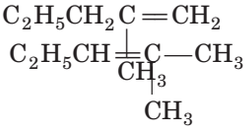
(c) 

(d) 

22. 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields *[JEE Main 2016 (Offline)]*

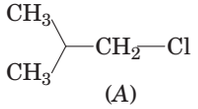
I. 

II.

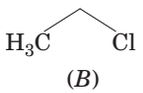
III. 

(a) Both I and III
(b) Only III
(c) Both I and II
(d) All of these

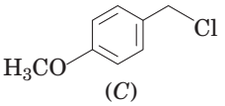
23. Increasing order of reactivity of the following compounds for S_N1 substitution is



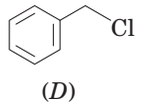
(*A*)



(*B*)



(*C*)

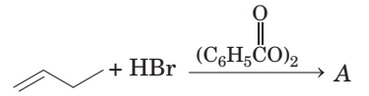


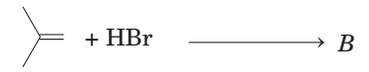
(*D*)

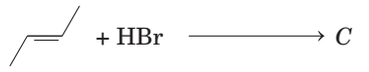
(JEE Main 2019)

(a) (*A*) < (*B*) < (*D*) < (*C*)
(b) (*B*) < (*C*) < (*D*) < (*A*)
(c) (*B*) < (*A*) < (*D*) < (*C*)
(d) (*B*) < (*C*) < (*A*) < (*D*)

24. The increasing order of the boiling points of the major products *A*, *B* and *C* of the following reactions will be *(JEE Main 2020)*

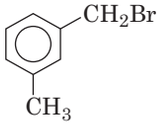
I. 

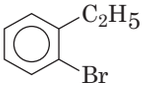
II. 

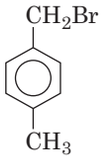
III. 

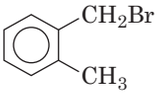
(a) II < III < I (b) III < I < II
(c) I < II < III (d) I < III < II

25. 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 2013]*

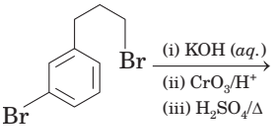
(a) 

(b) 

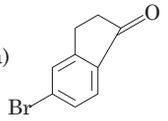
(c) 

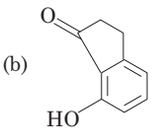
(d) 

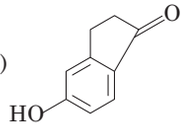
26. The major product of the following reaction is

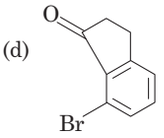


(JEE Main 2019)

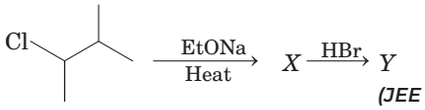
(a) 

(b) 

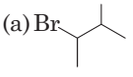
(c) 

(d) 

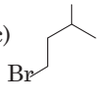
27. The major product *Y* in the following reaction is

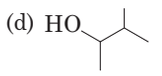


(JEE Main 2019)

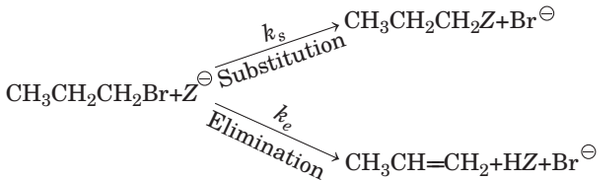
(a) 

(b) 

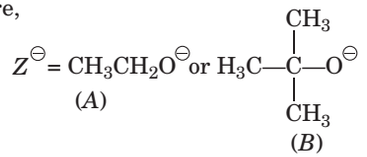
(c) 

(d) 

28. For the following reactions :



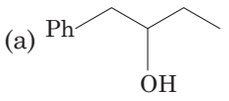
where,

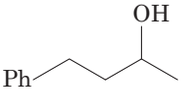


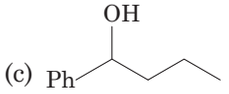
k_s and k_e, are respectively the rate constants for substitution and elimination, and $\mu = \frac{k_s}{k_e}$, the correct option is ..... . *(JEE Main 2020)*

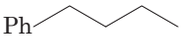
(a) $\mu_B > \mu_A$ and $k_e\,(B) > k_e\,(A)$
(b) $\mu_B > \mu_A$ and $k_e\,(A) > k_e\,(B)$
(c) $\mu_A > \mu_B$ and $k_e\,(A) > k_e\,(B)$
(d) $\mu_A > \mu_B$ and $k_e\,(B) > k_e\,(A)$

29. Heating of 2-chloro-1-phenyl butane with EtOK/EtOH gives X as the major product. Reaction of X with $Hg(OAc)_2$ / H_2O followed by $NaBH_4$ gives Y as the major product. Y is *(JEE Main 2019)*

(a) 

(b) 

(c) 

(d) 

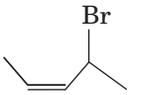
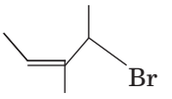
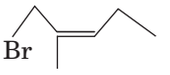
30. Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original labels. They were labelled A and B for testing. A and B were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and then some $AgNO_3$ solution was added. Substance B gave a yellow precipitate. Which one of the following statements is true for this experiment ?

(a) A was C_6H_5I
(b) A was $C_6H_5CH_2I$
(c) B was C_6H_5I
(d) Addition of HNO_3 was unnecessary

31. An alkyl chloride (A) on reaction with magnesium in dry ether followed by treatment with ethanol gave 2-methylbutane. Give the possible structure of (A).

(a) $(CH_3)_2C(Cl)CH_2CH_3$ (b) $(CH_3)_2CHCH_2CH_2Cl$
(c) $CH_3CH_2CH_2CH_2CH_2X$ (d) Both (a) and (b)

32. Match the structures given in Column I with the names in Column II.

Column I	Column II
(A) 	(p) 4-bromopent-2-ene
(B) 	(q) 4-bromo-3-methylpent-2-ene
(C) 	(r) 1-bromo-2-methylpent-2-ene

Codes

	A	B	C
(a)	q	r	p
(c)	p	q	r

	A	B	C
(b)	q	p	r
(d)	r	p	q

Numeric Value Questions

33. Consider the given compounds $NH_3, CCl_4, CF_4, CF_2Cl_2, CH_2F_2$ the number of compound used as refrigerants is x. The value of $x \times 2.4$ will be ..... .

34. Among the reagent given below

I. Br_2/CCl_4.
II. shaking with an aqueous solution of $AgNO_3$
III. boiling with aqueous solution of KOH solution followed by acidification with dil. HNO_3 and addition of $AgNO_3$ solution.
IV. fusion with Na followed by acidification with dilute HNO_3 and addition of $AgNO_3$ solution.

The number of reagents that can be used to distinguish allyl bromide from n-propyl bromide are ..... .

35. The total number of lone pair in the compound Z which is formed is the reaction.

$CH_3CH_2CH_2Br \xrightarrow{Aq.\,NaOH} X \xrightarrow{Al_2O_3} Y \xrightarrow{Cl_2/H_2O} Z$ is y. The value of y + 4.2 will be ..... .

36. In the following sequence of reactions

$CH_3CH_2OH \xrightarrow{P + I_2} A \xrightarrow[ether]{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_2O} D$ the total number of —OH group in compound D is ..... .

37. Among the following compounds, $C_6H_5COCH_3$, CH_3CH_2Br, $CH_3CHClCH_3$, CH_3COCH_2I, the compounds will given haloform test is/are ..... .

38. Among the haloalkanes 2-bromopentane, vinyl chloride, 2-chloroacetophenone, trichloromethane, the number of haloalkane contain halogen atom(s) attached to the sp^3-hybridised carbon atom of an alkyl group is/are ..... .

39. In the following sequence of reaction

$$CH_3CH_2OH \xrightarrow{P/I_2,\Delta} A \xrightarrow{KOH(alc),\ \Delta} B \xrightarrow{Br_2/CCl_4} C \xrightarrow{KOH(alc.),\ \Delta} D \xrightarrow[196\ K_2]{NaNH_2,\ liq.\ NH_3} E \xrightarrow{CH_3I\ (excess)} F$$

the number of carbon atom present in compound F is ..... .

Answers

Round I

1. (b)	**2.** (b)	**3.** (a)	**4.** (a)	**5.** (a)	**6.** (d)	**7.** (b)	**8.** (a)	**9.** (d)	**10.** (d)
11. (c)	**12.** (b)	**13.** (a)	**14.** (d)	**15.** (b)	**16.** (a)	**17.** (a)	**18.** (a)	**19.** (d)	**20.** (d)
21. (c)	**22.** (a)	**23.** (d)	**24.** (a)	**25.** (b)	**26.** (d)	**27.** (a)	**28.** (c)	**29.** (d)	**30.** (b)
31. (b)	**32.** (b)	**33.** (d)	**34.** (a)	**35.** (b)	**36.** (c)	**37.** (c)	**38.** (c)	**39.** (b)	**40.** (a)
41. (c)	**42.** (a)	**43.** (c)	**44.** (d)	**45.** (c)	**46.** (c)	**47.** (b)	**48.** (c)	**49.** (a)	**50.** (a)
51. (a)	**52.** (a)	**53.** (d)	**54.** (b)	**55.** (d)	**56.** (d)	**57.** (c)	**58.** (d)	**59.** (a)	**60.** (a)
61. (b)	**62.** (c)	**63.** (a)	**64.** (b)	**65.** (b)	**66.** (b)	**67.** (b)	**68.** (d)	**69.** (c)	**70.** (a)
71. (a)	**72.** (b)	**73.** (b)	**74.** (c)	**75.** (a)	**76.** (b)	**77.** (d)	**78.** (b)	**79.** (d)	**80.** (a)

Round II

1. (a)	**2.** (a)	**3.** (c)	**4.** (a)	**5.** (d)	**6.** (a)	**7.** (c)	**8.** (b)	**9.** (b)	**10.** (c)
11. (b)	**12.** (b)	**13.** (d)	**14.** (d)	**15.** (c)	**16.** (b)	**17.** (a)	**18.** (a)	**19.** (a)	**20.** (d)
21. (c)	**22.** (d)	**23.** (c)	**24.** (a)	**25.** (d)	**26.** (a)	**27.** (b)	**28.** (d)	**29.** (c)	**30.** (a)
31. (d)	**32.** (c)	**33.** (4.8)	**34.** (3)	**35.** (8.2)	**36.** (1)	**37.** (2)	**38.** (2)	**39.** (4)	

Solutions

Round I

1. 1, 2-dichloroethane $\left(\begin{matrix}Cl & Cl\\ | & |\\ CH_2 & -CH_2\end{matrix}\right)$ is an example of *vic*-dihalide because two halogen atoms occupy successive positions.

2. Correct IUPAC name for diethylbromomethane is 3-bromopentane.

$$\underset{1}{CH_3}-\underset{2}{CH_2}-\underset{3}{\overset{\overset{Br}{|}}{C}H}-\underset{4}{CH_2}-\underset{5}{CH_3}$$

3-bromopentane

3. Peroxide effect is observed only in case of HBr. Therefore, addition of HCl to propene even in the presence of benzoyl peroxide occurs according to Markownikoff's rule.

$$CH_3CH=CH_2 \xrightarrow[(C_6H_5COO)_2]{HCl} \underset{2\text{-chloropropane}}{CH_3-\overset{\overset{Cl}{|}}{C}H-CH_3}$$

4. Grignard reagents (R—Mg —X) are readily decomposed by water to produce alkanes. That is why they should be prepared under anhydrous conditions. Instead, ether is used as a solvent during the preparation of Grignard reagent as these are inert towards it.

$$R\text{—Mg—}X + H_2O \longrightarrow \underset{\text{Alkane}}{R\text{—H}} + Mg\begin{matrix}\nearrow X\\ \searrow OH\end{matrix}$$

5. When KI reacts with H_2SO_4, it produces HI. In order to produce alkyl iodides (R—I), this HI should react with alcohols (R—OH). But the reaction does not take place in this manner as H_2SO_4 oxidises HI to I_2 which in turn does not react with alcohol.

$$KI + H_2SO_4 \xrightarrow{Heat} KHSO_4 + HI$$

$$H_2SO_4 \longrightarrow H_2O + SO_4 + [O]$$

$$2HI + [O] \longrightarrow H_2O + I_2$$

Note Instead of H_2SO_4, H_3PO_4 can be used to produce alkyl iodides.

6. Alkene is first reacted with HBr to form alkyl bromide.

$$CH_3CH_2CH{=}CH_2 \xrightarrow[H_2O_2]{HBr} CH_3CH_2CH_2 - CH_2Br$$

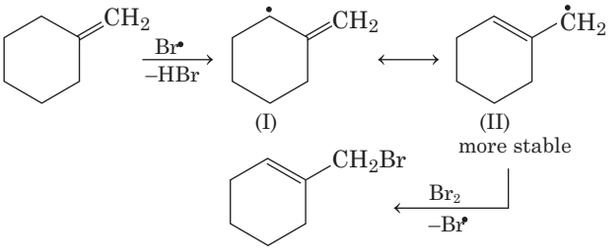
Alkyl bromide formed reacts with potassium iodide to form alkyl iodide.

$$CH_3CH_2CH_2CH_2Br \xrightarrow[Acetone]{KI} CH_3CH_2CH_2CH_2I + KBr$$

7. $RCH_2Cl + NaI \xrightarrow[\Delta]{Acetone} RCH_2I + NaCl$

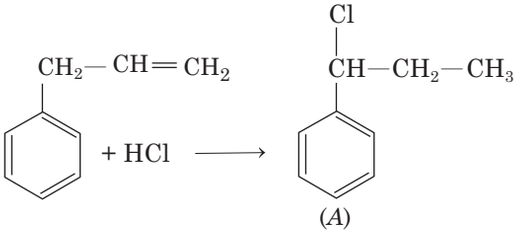
All other reactions are not feasible.

9. The mechanism of allylic bromination is



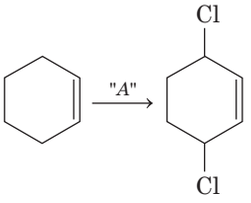
Since, endocyclic double bond is more stable than exocyclic double bond, therefore initially formed less stable free radical (I) gets converted into the more stable free radical (II) which then reacts with Br_2 to give the product.

10.



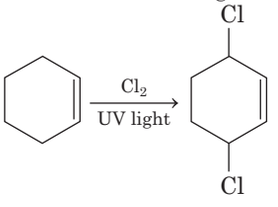
It is an addition reaction and addition occurs according to Markownikoff's rule.

11.

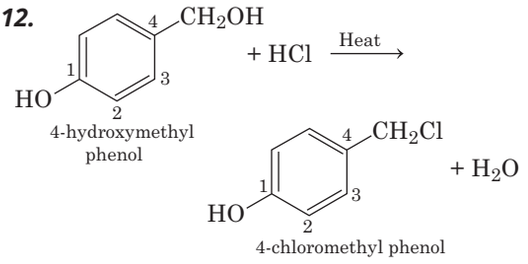


For substitution at allylic position in the given compound, the reagent used is Cl_2/UV light.

The reaction is free radical halogenation.

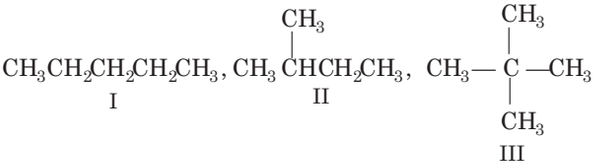


12.



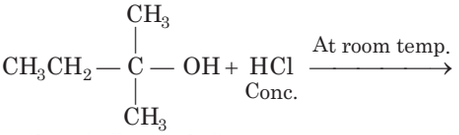
Note Phenolic —OH group is not replaced by —Cl group.

13. The possible isomers of C_5H_{12} are

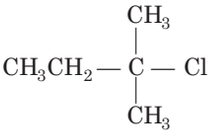


Isomer [II] has four groups of equivalent hydrogen atoms. Therefore, it can produce four isomeric monochlorides.

14.

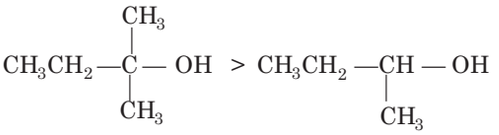


(2-methylbutan-2-ol)
(because it is a 3° alcohol)



2-chloro-2-methyl-butane

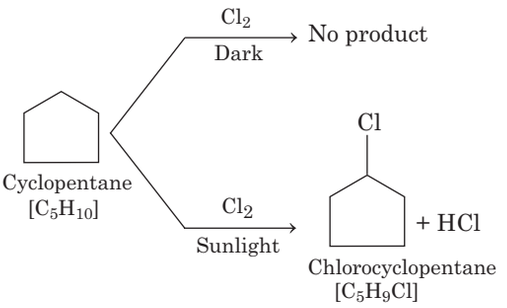
15. The order of reactivity of alcohols wih halogen acid is



> CH_3CH_2—CH_2—OH
(1°) (*A*)

16. Molecular formula C_5H_{10} can be either alkene or cycloalkane. Since, the hydrocarbon does not react with chlorine in dark, it is not an alkene. So, it is a cycloalkane, i.e. cyclopentane.

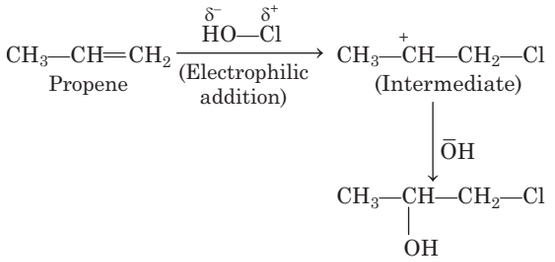
Since, it forms only single monochloro derivative in bright sunlight, all the H-atoms should be identical. So, it is cyclopentane.



17. $CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2/UV\ light} CH_3CH_2CH_2CH_2Cl$ (1-chlorobutane) + $CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3$ (2-chlorobutane)

Butane

18.



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

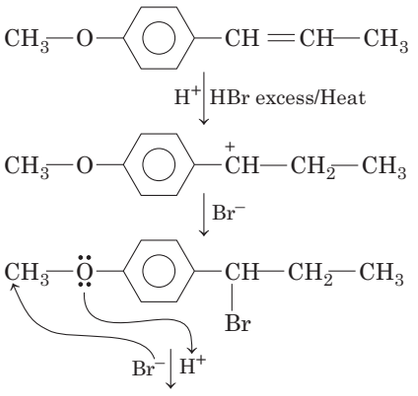
$$CH_3Br + AgF \longrightarrow \underset{\text{Methyl fluoride}}{CH_3F} + AgBr$$

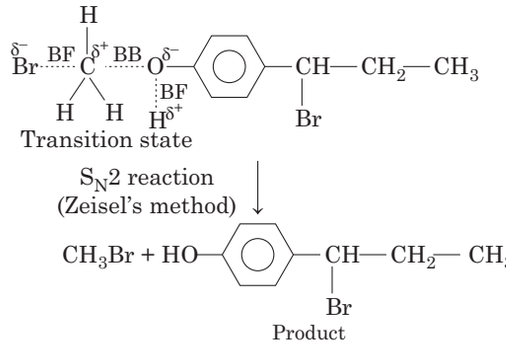
20. The excess of HBr and high temperature in given reaction serves for dual purpose

(i) Markownikoff addition occurs at double bond of the branch.

(ii) Hydrolysis of ether *via* S_N2 mechanism, i.e. Zeisel's method.

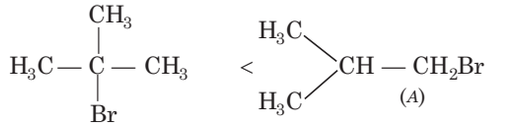
The road map of complete reaction is as follows





Here, BB = Bond breakage, BF = Bond formation

21. Increasing order of the boiling points of the compounds are



$< CH_3CH_2CH_2CH_2Br$ (*B*) (no branching)

22. The correct increasing order of boiling points of the compounds are

butane < 1 - chlorobutane < 1 - bromobutane < 1 - iodobutane because boiling point increases with increase in the size of halogen atom.

23. *t*-butyl bromide gives the most stable carbocation, i.e. 3° carbocation, so it readily undergoes S_N1 reaction.

24. $\overset{4}{C}H_3\ \overset{3}{\underset{\displaystyle CH_3}{\underset{|}{C}}}H\overset{2}{C}H_2\overset{1}{C}H_2Br$

Out of the give compounds three are primary halides. The presence of methyl group closer to halide group increases the steric hindrance and decreases rate in

$\overset{4}{C}H_3\ \overset{3}{C}H_2\overset{2}{\underset{\displaystyle CH_3}{\underset{|}{C}}}H\overset{1}{C}H_2Br$ or $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}—CH_2Br$

25. The rate of S_N1 reaction depends only upon the following

(i) concentration of the alkyl halide.

(ii) the formation of stable carbocation.

The reactivity is decided by ease of dissociation of alkyl halide.

$$R—X \rightleftharpoons R^{\oplus} + X^{\ominus}$$

Higher the stability of R^+ (carbocation), higher would be the reactivity towards S_N1 reaction.

p-$H_3CO—C_6H_4—CH_2^{\oplus}$ is the most stable carbocation due to resonance and then $CH_3\overset{\oplus}{C}HCH_2CH_3$ (2° carbocation) while $CH_3CH_2\overset{\oplus}{C}H_2$(1°) is least stable.

Thus, the correct increasing order of the reactivity of the given halides towards the S_N1 reaction is

$$\underset{\text{(II)}}{CH_3CH_2CH_2Cl} < \underset{\text{(I)}}{CH_3\underset{\displaystyle Cl}{\underset{|}{CH}}CH_2CH_3} < \underset{\text{(III)}}{p\text{-}H_3CO—C_6H_4—CH_2Cl}$$

29. The polarity between the C—*X* bond increases by increasing +*I* effect. The +*I* effect also increases by increasing the alkyl group, therefore in $CH_3CH_2CH_2Br$ the polarity is more than CH_3CH_2Br. While in rest the polarity decreases due to the presence of = bond and $\begin{matrix}O\\\|\\-C-\end{matrix}$ group.

30. Out of CH_3COCH_3, CH_3CHO, CH_3CH_2CHO and $(CH_3)_2CHCHO$ two pairs containing a total six carbon atoms are

(i) $CH_3COCH_3 + CH_3CH_2CHO$

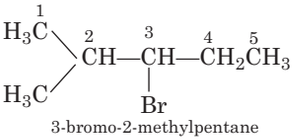
(ii) $CH_3CHO + (CH_3)_2CHCHO$

The alkenes which will give these pairs of compound on ozonolysis are

$$\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>\!C=CHCH_2CH_3 \text{ and}$$

$$\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>\!CH-CH=CHCH_3$$

These two alkenes can be obtained on dehydrogenation if the alkyl halide is $(CH_3)_2CHCH(Br)CH_2CH_3$.



3-bromo-2-methylpentane

31. $$H_3C-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Cl \xrightarrow[140°C]{80\%\ C_2H_5OH} H_3C-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OC_2H_5$$

32. $$CH_3CH_2CH_2Br \xrightarrow[\text{(Dehydrobromination)}\ -HBr]{\text{Conc. alc. NaOH, 80°C}(X)} CH_3CH=CH_2$$

$$CH_3CH=CH_2 \xrightarrow[20°C\ (Y)]{HBr,\ \text{aceticacid}} CH_3-CHBr-CH_3$$

34. $$CH_3CH_2CH_2Br \xrightarrow{Aq.\ NaOH} \underset{(A)}{CH_3CH_2CH_2OH} \xrightarrow[-H_2O]{Al_2O_3,\ \Delta} \underset{(B)}{CH_3CH=CH_2} \xrightarrow{Cl_2\ /\ H_2O} \underset{(C)}{CH_3-CHOH-CH_2Cl}$$

35. $$C_6H_6 + C_3H_7Br \xrightarrow{\text{Anhyd. } AlCl_3} C_6H_5CH(CH_3)_2 + HBr$$

The 1° carbonium ion isomerizes to the more stable 2° carbonium ion, which in turn reacts with benzene in the Friedel-Crafts reaction to give *iso*-propyl benzene.

36. $$\underset{\text{Propyl chloride}}{CH_3CH_2CH_2Cl} \xrightarrow[-KCl]{KCN} \underset{\text{Butane nitrile}}{CH_3CH_2CH_2CN}$$

38. Alkyl halides react with silver cyanide to give isocyanides.

$$CH_3CH_2Br + AgCN \longrightarrow \underset{\text{Ethyl isocyanide}}{CH_3CH_2NC} + AgBr$$

39. Since, the alkyl halide *RX* gives 4, 5-diethyloctane, when reacts with Na, it must be $CH_3(CH_2)_2CH(Br)CH_2CH_3$.

$$2\underset{\displaystyle CH_2CH_3}{\underset{|}{CH_3CH_2CH_2CH}}-Br \xrightarrow[\text{Dry ether}]{Na}$$

3-bromohexane

$$CH_3(CH_2)_2\underset{\displaystyle CH_2CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_2CH_3}{\underset{|}{CH}}-(CH_2)_2-CH_3$$

4, 5-diethyloctane

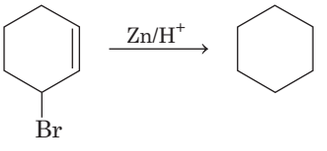
This reaction is known as Wurtz reaction.

40. $$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3 \xrightarrow[KOH]{Alc.} \underset{(A)}{CH_3-CH=CH_2} \xrightarrow{HBr\ \text{peroxide}}$$

$$CH_3-\underset{(C)}{CH_2}-CH_2I \xleftarrow[\text{Acetone}]{NaI} \underset{(B)}{CH_3-CH_2}-CH_2Br$$

41. In Wurtz reaction, wet ether is not used because wet ether destroy the sodium metal.

42.

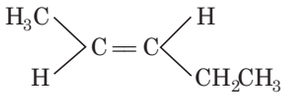


43. Secondary alkyl halides on treatment with alcoholic KOH preferably undergo elimination rather than substitution to give alkenes in accordance with Saytzeff rule.

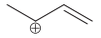
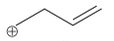
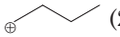
Usually the more stable *trans*-alkenes predominate in this reaction.

Thus, 2-bromopentane gives *trans*-pentene-2

2-Bromopentane

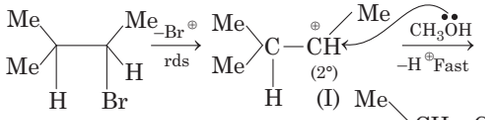


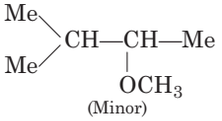
trans-pen-2-ene

45. E_1 reaction proceeds *via* carbocation formation, therefore, greater the stability of carbocation faster is the reaction. Carbocation formed by *D*, (2°, resonance stabilised and the product is diene) is most stable followed by *B*,  (1° and the product formed is diene). Further among C and *A*, the  carbocation formed by *C* is more stable  (2°) than *A*,  (1°). Thus, the reactivity towards dehydrohalogenation follows the order

$$D > B > C > A$$

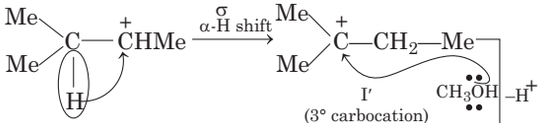
46. In the given question, the substrate is a 2°-halide (bromide) and the medium, CH_3OH (as well as a poor nucleophile) is protic in nature, So, the reaction will follow mainly S_N1 pathways *via* the formation of a carbocation intermediate (I).

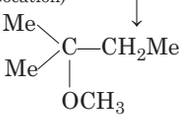




(Minor)

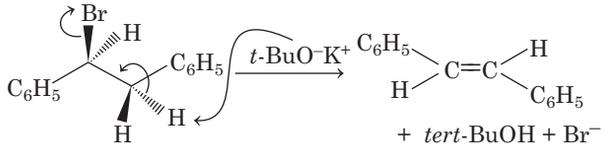
The intermediate, I can be rearranged into the more stable form I′ (3°) by α-hydride shift.
I ′ will give the major product.





(Major)

47. An alkyl halide in presence of a bulkier base removes a proton from a carbon adjacent to the carbon bonded to the halogen. This reaction is called E2 (β-elimination reaction).



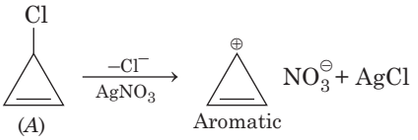
48. General reaction :

$$AgNO_3 + X(\text{Halogen}) \longrightarrow AgX + NO_3^{1-}$$

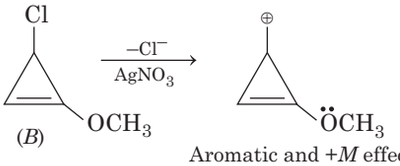
It follows S_N1 reaction.

In S_N1 reaction,

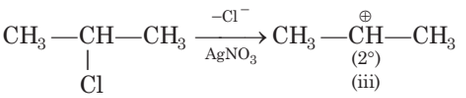
Rate of reaction ∝ stability of carbocation



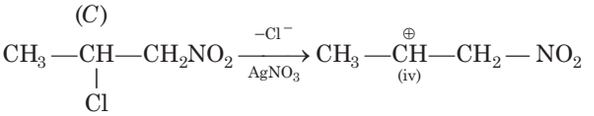
(*A*) Aromatic
(i)



(*B*)
Aromatic and +*M* effect
(ii)



(*C*) (iii)

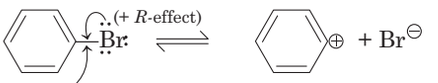


(*D*) NO_2 shows $-M$ effect

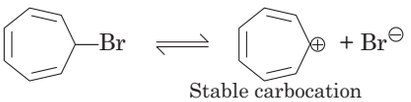
Stability of carbocation is (ii) > (i) > (iii) > (iv)

So, the reactivity order towards $AgNO_3$ solution is (*B*) > (*A*) > (*C*) > (*D*).

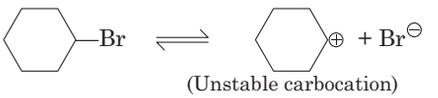
49. Only ionic halides (X^-) give precipitate of Ag*X* on reaction with $AgNO_3$ solution. So, an organic bromide able to produce $R^{\oplus}$ (stable carbocation) and Br^- in aqueous solution will give precipitate of AgBr with $AgNO_3$.

(c) 

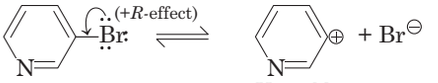
(Bond energy also increases) Unstable (Aryl carbocation)

(a) 

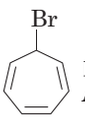
Stable carbocation (Aromatic, 6π system)

(d) 

(Unstable carbocation)

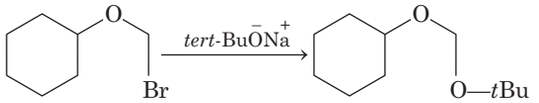
(b) 

Unstable (Aryl carbocation)

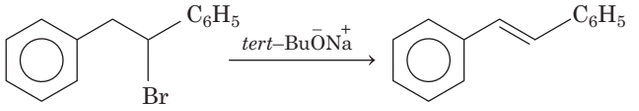
So, only 

produces a precipitate of AgBr with $AgNO_3$ solution.

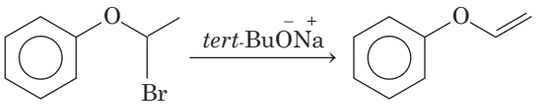
50. To show decolourisation, compound must be unsaturated.



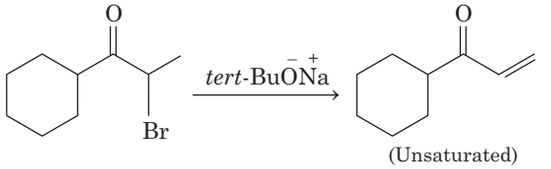
(Saturated)
(cannot decolourise Br_2 water)



(Unsaturated)
(decolourise Br_2 water)

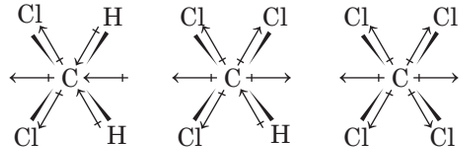


(Unsaturated)
(decolourise Br_2 water)



(Unsaturated)
(decolourise Br_2 water)

51.



$\mu = 1.62$ D $\quad \mu = 1.03$ D $\quad \mu = 0.0$ D

CCl_4 (tetrachloromethane) is a symmerical molecule so, it has zero dipole moment.

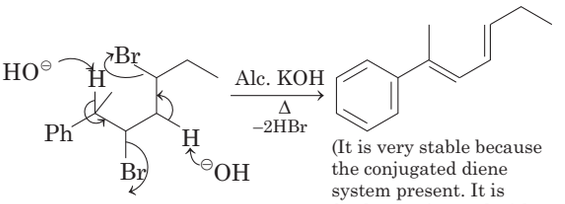
In $CHCl_3$ (trichloromethane/chloroform), the resultant of two C—Cl dipole moments is opposed by the resultant of C—H and C—Cl bond. Since, the letter resultant dipole moment is smaller than the former, $CHCl_3$ has a dipole moment = 1.03 D.

In CH_2Cl_2 (dichloromethane), the resultant of two C—Cl dipole moments is reinforced by the resultant of two C—H bonds. Thus, CH_2Cl_2 has a dipole moment = 1.62 D. Therefore, CH_2Cl_2 has the highest dipole moment amongst the above three molecules.

52. Alkyl halides give elimination reaction with alcoholic KOH and yield an alkene or alkyne (from dihalides).

e.g. $\underset{\text{1, 2-dibromoethane}}{Br—CH_2—CH_2—Br} \xrightarrow[\Delta]{\text{Alc. KOH}} \underset{\text{Acetylene}\ (X)}{\overset{sp}{CH}\equiv\overset{sp}{CH}}$

53. The reaction follows α, β-elimination mechanism to give a more substituted stable alkene as a major product. As the substrate is a α, γ -dibromo (1, 3-) compound it gives a conjugated diene.



(It is very stable because the conjugated diene system present. It is further conjugated with the benzene ring.)

54. Chloroform reacts with conc. HNO_3 to give chloropicrin or tear gas.

$$\underset{\text{Chloroform}}{CHCl_3} + \underset{\text{Conc.}}{HNO_3} \longrightarrow \underset{\substack{\text{Chloropicrin}\\ \text{or}\\ \text{Tear gas}}}{CCl_3NO_2} + H_2O$$

55. $\underset{\substack{\text{Methyl}\\ \text{amine}}}{CH_3NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH \longrightarrow \underset{\substack{\text{Methyl}\\ \text{isocyanide}}}{CH_3N\rightleftarrows C} + 3KCl + 3H_2O$

56. Chloroform undergoes oxidation in the presence of light and air to form phosgene gas.

$$2CHCl_3 + \frac{1}{2}O_2 \longrightarrow \underbrace{COCl_2}_{\text{Phosgene gas}} + 2HCl$$

58. On heating with I_2 and NaOH, methanol (CH_3OH) does not give yellow compound, i.e. iodoform.

59. F_2 reacts with NaOH to give oxygen difluoride (OF_2) and not hypofluorite ion (OF^-) needed for haloform reaction. Hence, CHF_3 cannot be prepared.

60. When acetone reacts with chloroform in alkaline solution, chloretone is obtained which is used as a hypnotic drug.

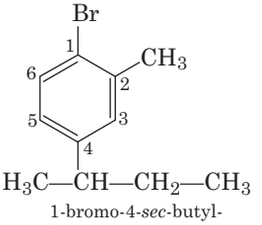
$$CHCl_3 + CH_3COCH_3 \xrightarrow{KOH} CH_3—\overset{\overset{OH}{|}}{\underset{\underset{CCl_3}{|}}{C}}—CH_3$$

Chloretone

61. $\underset{\text{2- butene}}{CH_3CH=CH—CH_3} + \underset{\text{Chloroform}}{CHCl_3} \longrightarrow$

$$\underset{\underset{CCl_3}{|}}{CH_3CH}— CH_2CH_3 \xrightarrow[\text{hydrolysis}]{\text{NaOH}} CH_3—\underset{\underset{C(OH)_3}{|}}{CH}— CH_2CH_3 \xrightarrow[-H_2O]{} \underset{\text{2-methylbutanoic acid}}{CH_3—\overset{\overset{COOH}{|}}{CH}—CH_2CH_3}$$

65.



1-bromo-4-*sec*-butyl-2-methylbenzene

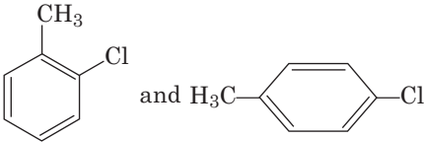
66. Replacement of H of benzene by any atom/group is called electrophilic substitution reaction. The

electrophile in this reaction is Cl^+. The Cl^+ is produced as a result of redox reaction,

$$O_2 + 2Cl^- + 4H^+ \longrightarrow 2H_2O + 2Cl^+$$

67. $AlCl_3 + Cl_2 — AlCl_4^- + \underset{\text{Electrophile}}{Cl^+}$

68. The reaction of toluene with chlorine in the presence of iron and in the absence of light yields the mixture of

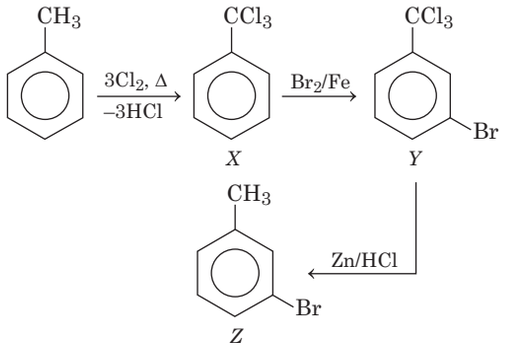


69. $C_6H_5OH + PCl_5 \longrightarrow C_6H_5Cl + POCl_3 + HCl$

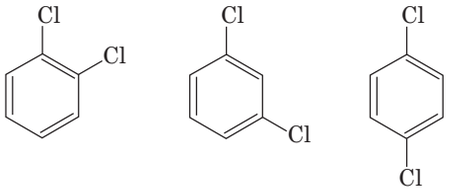
$3C_6H_5OH + POCl_3 \longrightarrow (C_6H_5)_3PO_4 + 3HCl$

The yield of phenol is poor because the main product is triphenyl phosphate.

70.



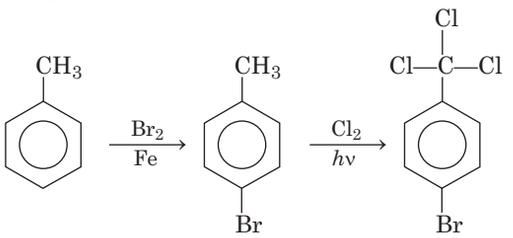
71. Symmetry of the molecule is related to its crystal lattice structure and hence, to its melting point and solubility. A highly symmetrical structure has a higher melting point.



o-dichlorobenzene *m*-dichlorobenzene *p*-dichlorobenzene

Out of the above three isomers of dichlorobenzene, the *p*-isomer is more symmetrical than other two isomers. i.e. it has more closely packed arrangement of molecules in its crystal lattice. So, *p*-dichlorobenzene has a higher melting point and lower solubility as compared to *ortho* and *meta* isomers.

72.

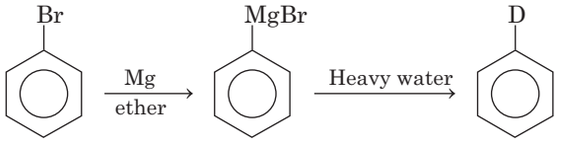


73. $C_6H_5CH_3 \xrightarrow[\text{or } Cl_2/h\nu]{SO_2Cl_2/\text{peroxide}} C_6H_5CH_2Cl$

74. *m*-nitrochlorobenzene is however less reactive than the *p*-nitrochlorobenzene since the NO_2 group at *m*-position can't stabilise the intermediate carbanion by resonance. Thus, the correct option is II > III > I.

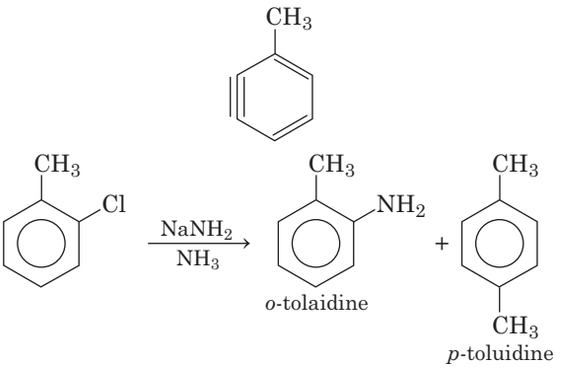
75. Reactivity decreases as the number of NO_2 groups at *o* and *p*-position with respect to chlorine decreases. Thus, the correct order is II > III > IV > I.

76.



(*A*) (*B*)

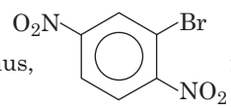
78. The formation of a mixture of *ortho* and *meta*-toluidine certainty suggests that the triple bond in benzyne is between *o*- and *m*-positions and hence the structure of intermediate is



o-tolaidine *p*-toluidine

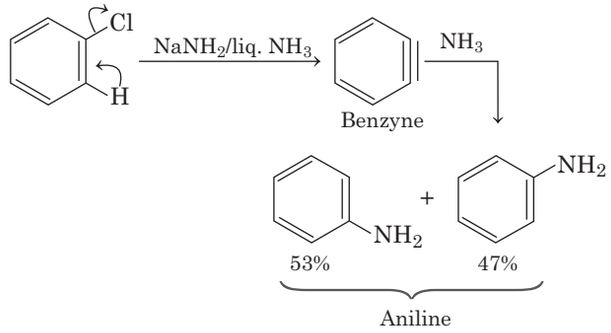
For the formation of benzyne intermediate, it is essential that an hydrogen should be available at an *ortho* position to the halogen.

79. The reactivity of substance for Ar S_N2 reaction depends on the $-R$ and $-I$ powers of the group present at *o*-and/or *p*-position. Thus,



is most reactive for S_N2 reaction.

80. When chlorobenzene is treated with sodamide in liquid ammonia at 196 K, the reaction occurs through the intermediate benzyne formation and finally gives aniline.



Benzyne

53% 47%

Aniline

Round II

2. Chlorocyclohexane behaves like an aliphatic halogen substituted hydrocarbon and can, therefore reacts with alcoholic $AgNO_3$.

3. ArS_N reactions are accelerated by electron withdrawing groups, especially at the *o*-and *p*-positions to the leaving group and retarded by electron-donating groups.

4. $CH_2Br-CH_2Br \xrightarrow{KCN} CH_2CN-CH_2CN \xrightarrow{H_3O^+} CH_2COOH-CH_2COOH$

1,2-dibromoethane — Succinic acid

Succinic acid $\xrightarrow{\Delta}$ CH_2CO-CH_2CO (O)

5. 1-bromo-3-chloro cyclobutane $\xrightarrow[\text{Ether}]{2Na \rightarrow 2Na^+ + 2e^-}$ (Cl)

6. $(H_3C)_3C-OMgBr \xrightarrow{H_3O^+} (H_3C)_3C-OH$ (t-alcohol) $\xrightarrow{\text{Dehydration, elimination}} (H_3C)_2C=CH_2 + H_2O$

Order of elimination (dehydration) of alcohol is

$$3^\circ > 2^\circ > 1^\circ$$

7. $CH_3CH_2CH_2I \xrightarrow{\text{Alc. KOH}} CH_3CH=CH_2$ (X)

$\xrightarrow[\Delta]{NBS,\ h\nu} CH_2Br-CH=CH_2$ (Y)

$\xrightarrow{\text{Alc KCN}} CH_2CN-CH=CH_2$ (Z)

8. $CBr_4 + MeLi \longrightarrow MeBr + LiCBr_3$

$LiCBr_3 \longrightarrow LiBr + :CBr_2$

$+ :CBr_2$ (Electrophile, carbene) $\longrightarrow$ 7,7-dibromo [4,1,0] bicycloheptane (Br, Br)

9. In the Reimer-Tiemann reaction, new C—C bond is formed between the carbon of benzene ring and —CHO group.

Phenol (OH) + $CHCl_3$ + 3NaOH (Chloroform) $\longrightarrow$ Salicylaldehyde (OH, CHO) + 3NaCl + $2H_2O$

10. $CH_3-C(Cl)_2-CH_2-CH_2-CH_2-CH_3 \xrightarrow[Aq.\ KOH]{\text{Hydrolysis}}$

2,2-dichlorohexane (A)

$CH_3-C(=O)-CH_2-CH_2CH_2CH_3$ (2-hexanone)

$\xrightarrow[2[H]]{\text{Reduction}}$ $CH_3-CH(OH)-CH_2-CH_2-CH_2-CH_3$ (2-hexanol)

11. Since, the obtained compound reduces Tollen's reagent, it must be an aldehyde. Thus, it is obvious that both the —Cl atoms are present at C_1. Hence, the compound 'X' is 1,1-dichloropropane and the reactions are as follows

$CH_3CH_2CHCl_2$ (1, 1-dichloropropane, 'X') $\xrightarrow{\text{Hydrolysis}}$ $CH_3CH_2CH(OH)_2$ (Unstable) $\xrightarrow{-H_2O}$ CH_3CH_2CHO (Propanaldehyde) $\xrightarrow{\text{Tollen's reagent}}$ $CH_3CH_2COOH + Ag\downarrow$ (Propanoic acid)

12. $(H_3C)_2C(CH_3)-Cl + C_2H_5O^-Na^+ \longrightarrow (H_3C)_2C=CH_2 + C_2H_5OH + NaCl$

13. $BrCH_2CH_2CH_2CH_2Br \xrightarrow[-NaBr]{Na_2S}$ Br—CH_2 CH_2 CH_2 CH_2 Na^+S^-

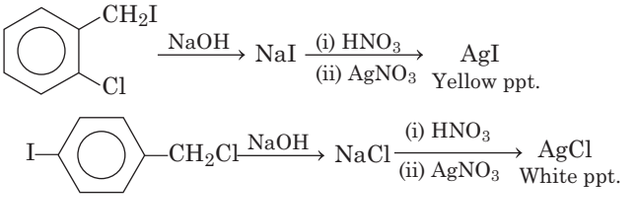
$\xrightarrow{-NaBr}$ S

14. The order of reactivity follows the sequence, benzyl halides > alkyl halides > aryl halides.

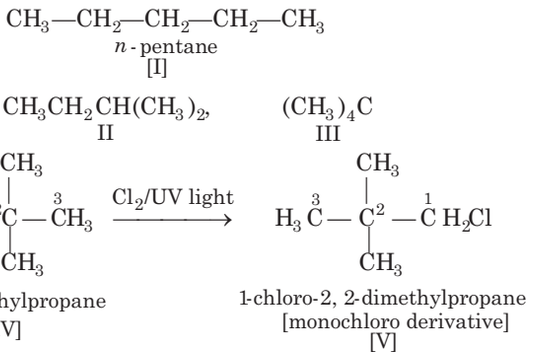
Out of chlorides and bromides, bromides are more reactive. Therefore, the correct order of reactivity is

$$PhCH_2Br > MeBr > MeCl > p\text{ - }MeOC_6H_4Br$$

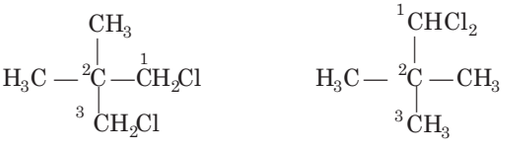
15. Only benzyl halide, i.e. *p*-iodobenzyl chloride and *o*-chlorobenzyl iodide undergo hydrolysis on shaking with an aqueous solution of NaOH.



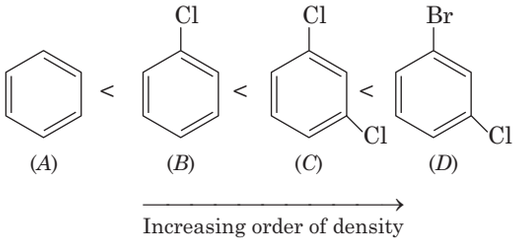
16. Hydrocarbon C_5H_{12} has molecular mass 72 g mol^{-1}. It has three isomers.



Out of the three isomers [V] structure is correct. Its two dichloroderivatives are

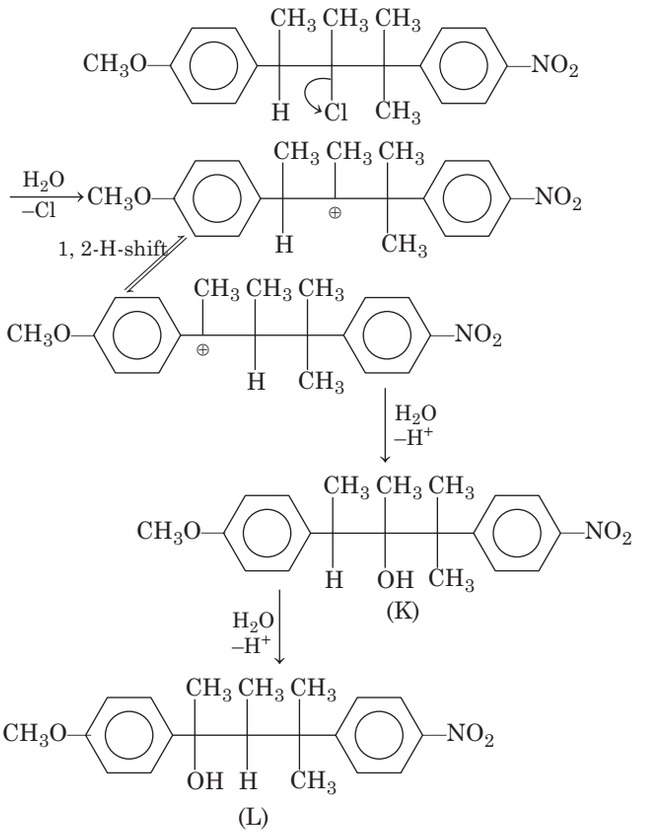


17. Increasing order of the density of the compounds are



Because density increases with increase in mass (molar mass) or size.

18. The product (*K*) is formed through simple nucleophilic substitution while major product (*L*) is formed through H^- shift *via* S_N1 reaction and methoxy group stabilises the carbocation intermediate of product (*L*).



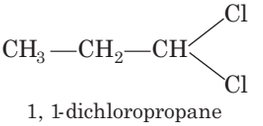
19. '*A*' 2-bromobutane $\left(\begin{array}{c} CH_3 - CH - Br \\ \quad\quad | \\ \quad\quad C_2H_5 \end{array}\right)$ gives racemic mixture on nucleophilic substitution by OH^- ion.

20. '*X*' is a three carbon compound with two halogen atom, so its molecular formula is $C_3H_6Cl_2$. Only terminal alkynes give red ppt with ammoniacal Cu_2Cl_2, so the hydrocarbon produced by the reaction of '*X*' with alc KOH must be a terminal alkyne (i.e. $CH_3C{\equiv}CH$).

$$C_3H_6Cl_2 \xrightarrow{\text{Alc. KOH}} CH_3C{\equiv}CH \xrightarrow{\text{Amm. } Cu_2Cl_2} CH_3C{\equiv}CCu\downarrow$$

Red ppt.

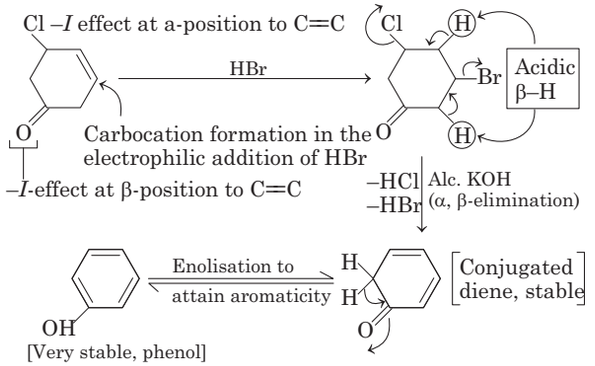
Compound (*X*) gives an aldehyde when reacts with aqueous KOH. This suggests that both the halogens are present on same terminal carbon atom. Thus, the formula of compound (*X*) is



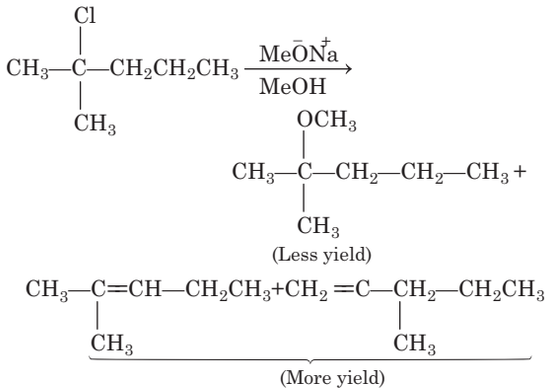
1, 1-dichloropropane

21. In presence of HBr, reactant containing undergoes electrophilic addition reaction and give substituted alkyl halide. On further reaction with alc. KOH, α,β-elimination takes place that give corresponding diene.

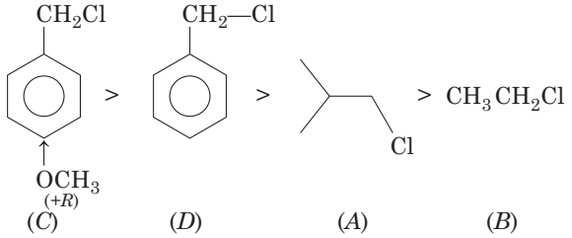
The diene undergoes enolisation to give stable product (phenol).



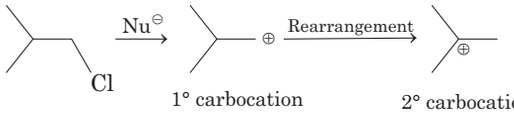
22. Strong nucleophile ($\bar{O}Me$) in polar solvent (MeOH) gives elimination products over substitution products but all products are possible in different yields.



23. Reactivity of substitution nucleophilic unimolecular (S_N1) reaction depends on the formation of carbocation. Greater the stability of carbocation, greater will be its ease of formation of alkyl halide and faster will be the rate of reaction. So, the correct order of (S_N1) reactivity is

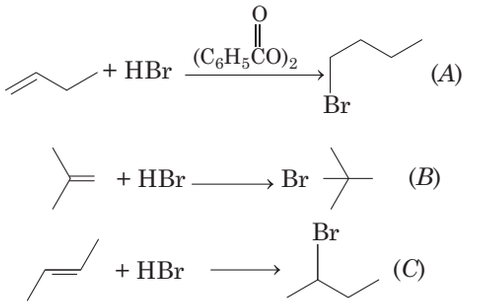


In compound *C*, the carbocation formed is stabilised by activating group (—OCH_3). Compound *D* forms benzyl carbocation ($C_6H_5—\overset{+}{C}H_2$) that is stabilised by resonance. Compound *A* produces a primary carbocation that further rearranges itself to secondary carbocation.



Compound *B* produces primary carbocation which is least stable among all the given options.

24. Complete reaction of I, II and III are as follow



RX are polar, therefore intermolecular forces of attraction (e.g. dipole-dipole and van der Waals') are stronger in *RX*. Hence, the boiling point of *RX* is greater than those of hydrocarbons of comparable molecular masses. Branching decreases the surface area as in alkane because the branched *C* chains are more spherical -like, which results in lower boiling point.

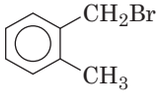
$$BP \propto \frac{1}{\text{Branching}}$$

Hence, the boiling point of isomeric *RX* decreases within increase in branching, hence the order will be $B < C < A$.

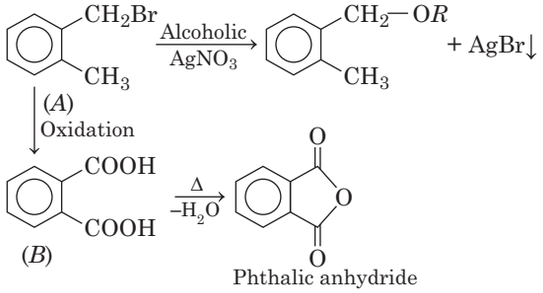
25. Compound *A* gives a precipitate with alcoholic $AgNO_3$ (here white is misprinting because the colour of ppt. is light yellow), so it must contains Br in side chain.

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



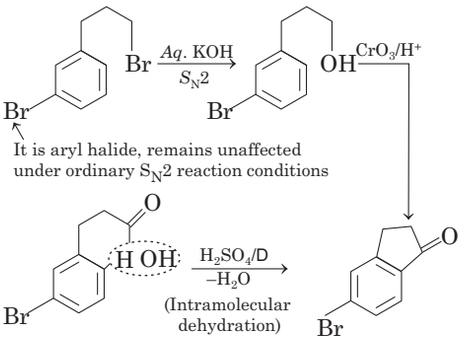
and the reactions are as follows



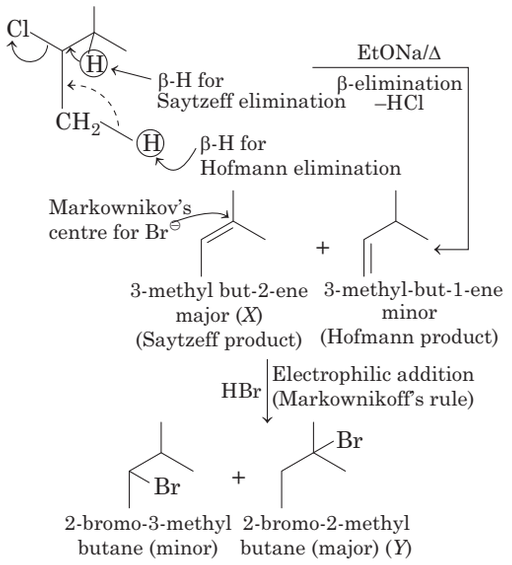
26. The reaction involves hydrolysis or nucleophilic substitution in first step followed by oxidation and dehydration in last step. The most important fact is

that, the Br group attached directly to aromatic ring will not undergo substitution in step 1.

The road map of the given reaction is as follows



27. The given reaction takes place as follows



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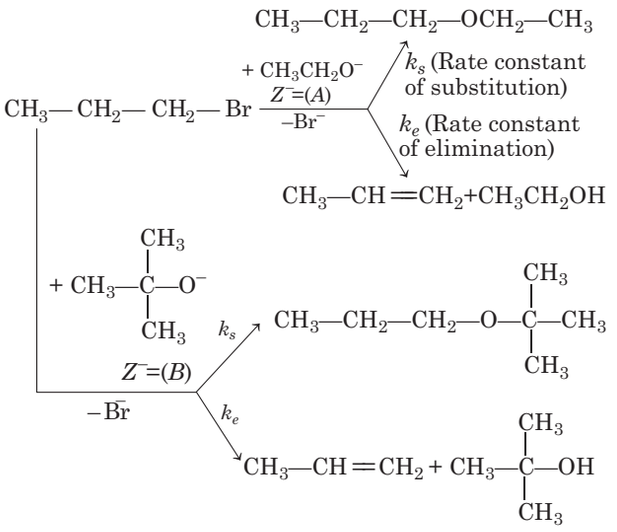


When alkyl halides react with nucleophiles (Z^-), both substitution and elimination reactions can be expected.

1° alkyl halides generally favour substitution, but stronger bases favour elimination.

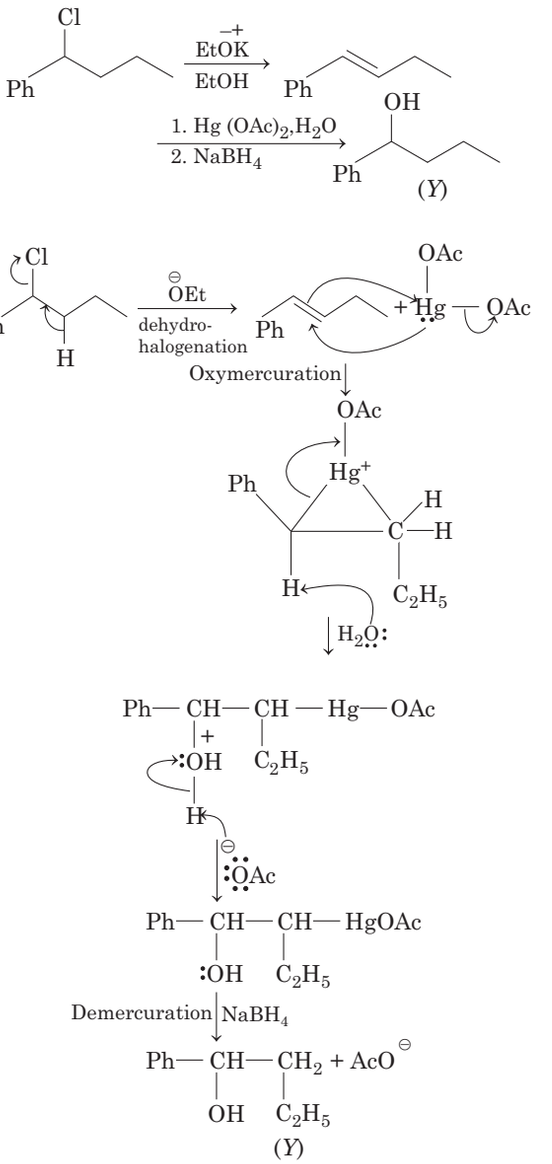
So, in the above reactions in which ($CH_3—CH_2—CH_2—Br$ is 1° alkyl halide, $CH_3CH_2—O^-$ is a strong base), reasonable amounts of substitution and elimination products can form between $A = CH_3CH_2O^-$ and alkyl halide.

(A) is an unhindered nucleophile, so it can give substitution better than (B) which is hindered (more crowded or sterically hindered). But (B) tends to give elimination better than (A) due to the same reason also.

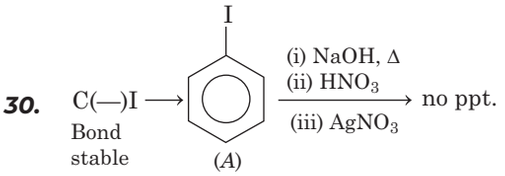
$$\therefore \qquad \mu = \frac{k_s}{k_e} \text{ is in the order } A > B$$

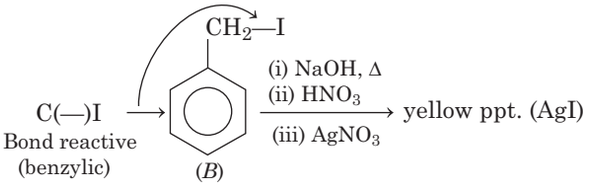
and k_e is in the order $B > A$.

29.

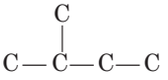


30.





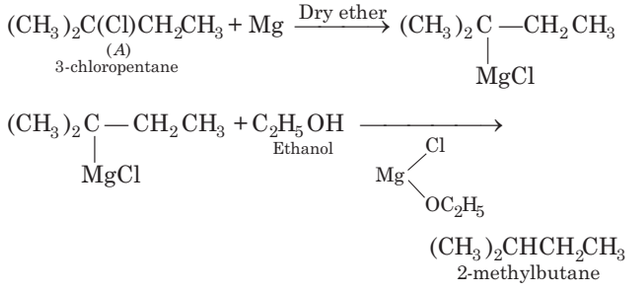
31. Since, the compound gives 2-methyl butane, it must contain the following carbon skeleton.

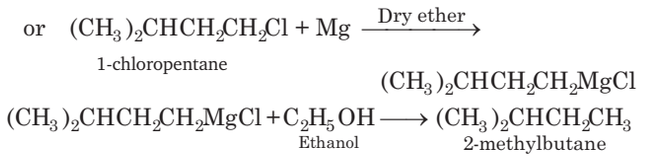


Thus, the structure of chloride may be

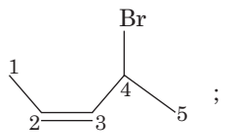
$(CH_3)_2C(Cl)CH_2CH_3$ or $(CH_3)_2CHCH_2CH_2Cl$

and reactions are as follows

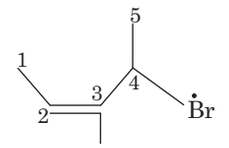




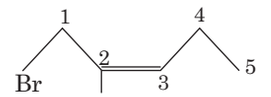
32.



4-bromo-pent-2-ene (*p*) ;



4-bromo-3-methylpent-2-ene (*q*)



1-bromo-2-methylpent-2-ene(*s*)

33. NH_3 and CF_2Cl_2.

34. Br_2 / CCl_4 can be used to distinguish between allyl bromide and *n*-propyl bromide, as allyl bromide being unsaturated will discharge its colour while *n*-propyl bromide does not.

On shaking with *aq*. $AgNO_3$, allyl bromide being more reactive will give pale yellow ppt. of AgBr but *n*-propyl bromide will not.

On boiling with *aq*. KOH, both will undergo hydrolysis, hence give ppt. of AgBr.

Fusion with Na also converts the Br of both the compounds into NaBr, thus both give ppt with $AgNO_3$.

Hence, reagents given in III and IV cannot be used to distinguish between allyl bromide and *n*-propyl bromide.

35. $CH_3CH_2CH_2Br \xrightarrow{Aq,\ NaOH} \underset{(X)}{CH_3CH_2CH_2OH} + NaBr$

$\xrightarrow{Al_2O_3} \underset{(Y)}{CH_3CH=CH_2} \xrightarrow{Cl_2/H_2O} CH_3-\underset{\underset{\ddot{O}H}{|}}{CH}-\underset{\underset{\ddot{C}l}{|}}{CH_2}$ (Z)

36. $CH_3CH_2OH \xrightarrow{P + I_2} \underset{(A)}{CH_3CH_2I} \xrightarrow{Mg\ ether}$

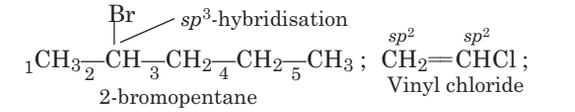
$\underset{(B)}{CH_3CH_2MgI} \xrightarrow{HCHO} \underset{(C)}{CH_3CH_2CH_2OMgI} \xrightarrow{H_2O}$

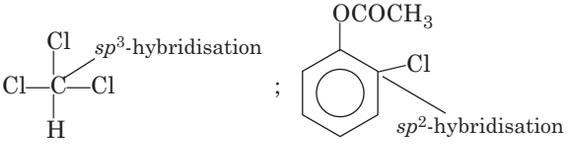
$\underset{(D)}{CH_3CH_2CH_2OH} + Mg(OH)I$

37. CH_3COCH_3I and $C_6H_5COCH_3$ will give haloform test

Further under the basic conditions of the reaction, both $CH_3CHClCH_3$ and CH_3CH_2Br will undergo hydrolysis to give $CH_3CHOHCH_3$ and CH_3CH_2OH respectively which will give iodoform test.

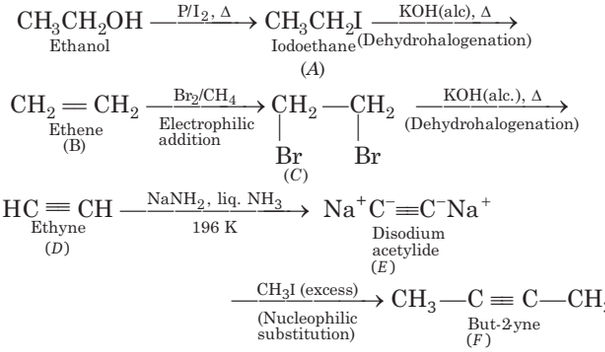
38.





Thus, 2-bromopentane and trichloromethane haloalkanes contain halogen atom attached to the sp^3-hybridised carbon atom of an alkyl group.

39.



The number of carbon atom in (*F*) is 4.