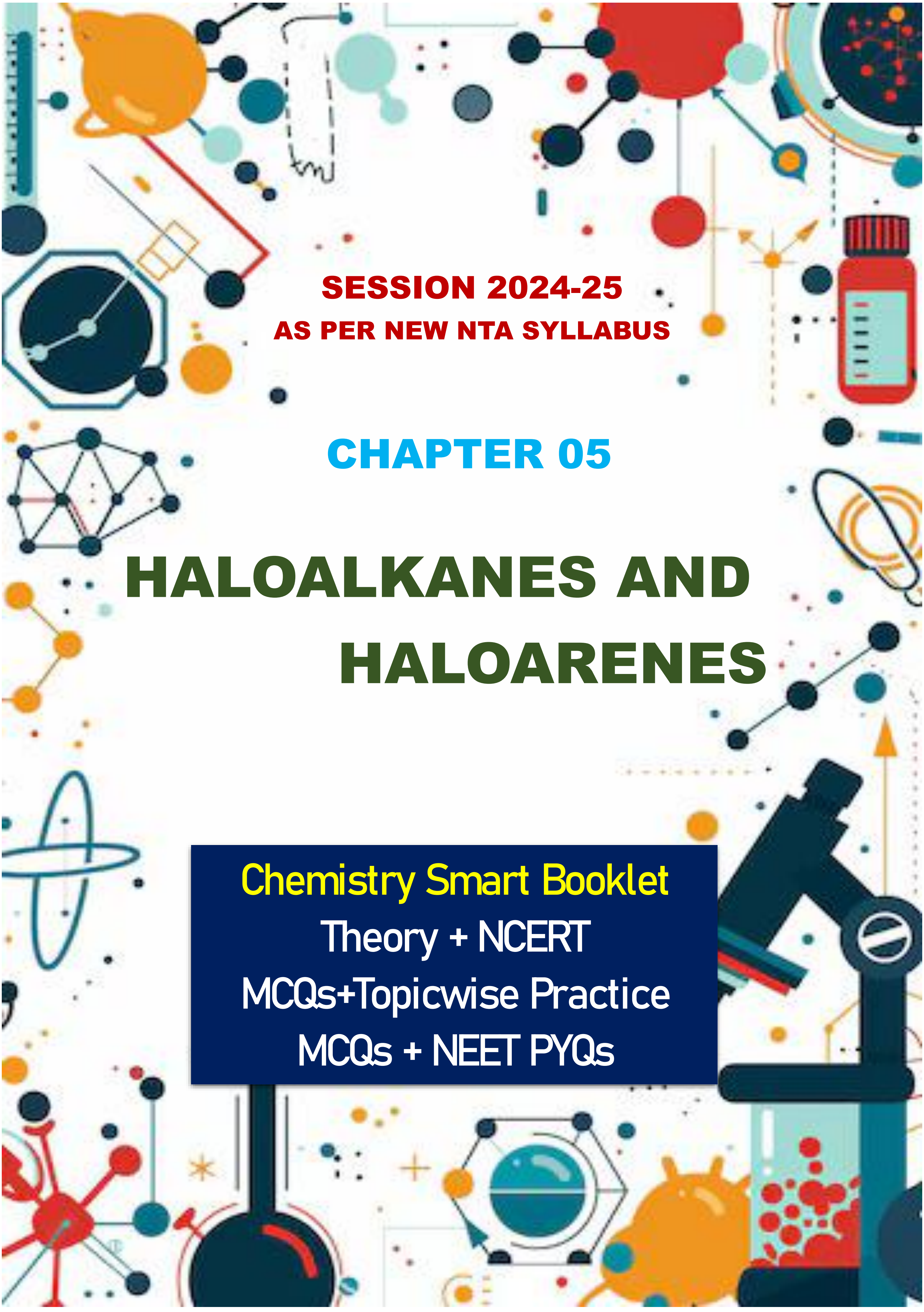


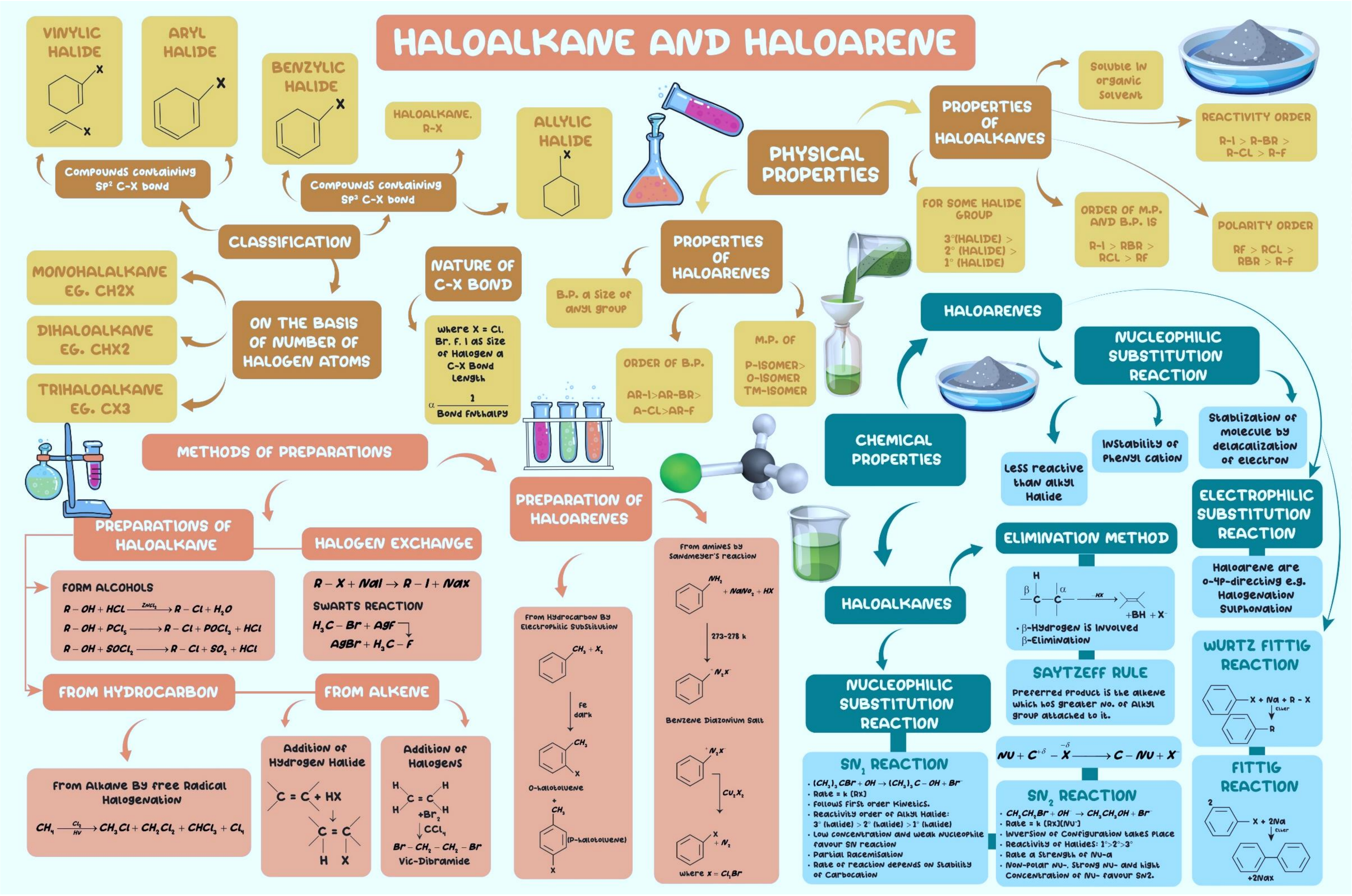
SESSION 2024-25

AS PER NEW NTA SYLLABUS

CHAPTER 05

HALOALKANES AND HALOARENES

Chemistry Smart Booklet
Theory + NCERT
MCQs+Topicwise Practice
MCQs + NEET PYQs



HALOALKANE AND HALOARENE

CLASSIFICATION

Compounds containing Sp^2 C-X bond

- VINYLIC HALIDE
- ARYL HALIDE

Compounds containing Sp^3 C-X bond

- BENZYLIC HALIDE
- HALOALKANE. R-X
- ALLYLIC HALIDE

ON THE BASIS OF NUMBER OF HALOGEN ATOMS

- MONOHALALKANE EG. CH2X
- DIHALOALKANE EG. CHX2
- TRIHALOALKANE EG. CX3

NATURE OF C-X BOND

Where X = Cl. Br. F. I as Size of Halogen α C-X Bond Length

$\alpha \frac{1}{\text{Bond Enthalpy}}$

PHYSICAL PROPERTIES

PROPERTIES OF HALOALKANES

- Soluble in organic solvent
- REACTIVITY ORDER
  R-I > R-BR > R-CL > R-F
- POLARITY ORDER
  RF > RCL > RBR > R-F
- ORDER OF M.P. AND B.P. IS
  R-I > RBR > RCL > RF
- FOR SOME HALIDE GROUP
  3°(HALIDE) > 2° (HALIDE) > 1° (HALIDE)

PROPERTIES OF HALOARENES

- B.P. α Size of anyl group
- ORDER OF B.P.
  AR-I>AR-BR>A-CL>AR-F
- M.P. OF
  P-ISOMER> O-ISOMER TM-ISOMER

METHODS OF PREPARATIONS

PREPARATIONS OF HALOALKANE

FORM ALCOHOLS

$R-OH+HCL\xrightarrow{ZnCl_2}R-Cl+H_2O$

$R-OH+PCl_5\longrightarrow R-Cl+POCl_3+HCl$

$R-OH+SOCl_2\longrightarrow R-Cl+SO_2+HCl$

HALOGEN EXCHANGE

$R-X+NaI\rightarrow R-I+NaX$

SWARTS REACTION

$H_3C-Br+AgF\rightarrow AgBr+H_3C-F$

FROM HYDROCARBON

From Alkane By free Radical Halogenation

$CH_4\xrightarrow[hv]{Cl_2}CH_3Cl+CH_2Cl_2+CHCl_3+Cl_4$

FROM ALKENE

Addition of Hydrogen Halide

$>C=C<+HX\rightarrow$ C(H)–C(X)

Addition of Halogens

$H_2C=CH_2 + Br_2 \xrightarrow{CCl_4}$ $Br-CH_2-CH_2-Br$

Vic-Dibramide

PREPARATION OF HALOARENES

From Hydrocarbon By Electrophilic Substitution

$C_6H_5CH_3 + X_2 \xrightarrow[\text{dark}]{\text{Fe}}$ O-halotoluene + (P-halotoluene)

From amines by Sandmeyer's reaction

$C_6H_5NH_2 + NaNO_2 + HX \xrightarrow{273-278\ k} C_6H_5N_2^+X^-$

Benzene Diazonium Salt

$C_6H_5N_2^+X^- \xrightarrow{Cu_2X_2} C_6H_5X + N_2$

where $X = Cl, Br$

CHEMICAL PROPERTIES

HALOARENES

NUCLEOPHILIC SUBSTITUTION REACTION

- Less reactive than alkyl Halide
- Instability of Phenyl cation
- Stablization of molecule by delacalization of electron

ELECTROPHILIC SUBSTITUTION REACTION

Haloarene are o-4p-directing e.g. Halogenation Sulphonation

WURTZ FITTIG REACTION

$C_6H_5-X+Na+R-X\xrightarrow{\text{Ether}}C_6H_5-R$

FITTIG REACTION

$2\,C_6H_5-X+2Na\xrightarrow{\text{Ether}}C_6H_5-C_6H_5+2NaX$

HALOALKANES

ELIMINATION METHOD

$\overset{\beta}{C}(H)-\overset{\alpha}{C}\xrightarrow{-HX}>C=C<\;+BH+X^-$

- β-Hydrogen is Involved β-Elimination

SAYTZEFF RULE

Preferred product is the alkene which hos greater No. of Alkyl group attached to it.

NUCLEOPHILIC SUBSTITUTION REACTION

$NU+C^{+\delta}-\overset{-\delta}{X}\longrightarrow C-NU+X^-$

SN_1 REACTION

- $(CH_3)_3CBr+OH\rightarrow(CH_3)_3C-OH+Br^-$
- Rate = k (RX)
- Follows first order Kinetics.
- Reactivity order of Alkyl Halide: 3° (halide) > 2° (halide) > 1° (halide)
- Low concentration and weak nucleophile favour SN reaction
- Partial Racemisation
- Rate of reaction depends on Stability of Carbocation

SN_2 REACTION

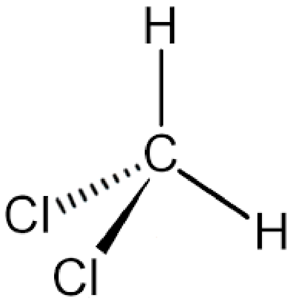
- $CH_3CH_2Br+OH^-\rightarrow CH_3CH_2OH+Br^-$
- Rate = k (RX)(NU⁻)
- Inversion of Configuration takes place
- Reactivity of Halides: 1°>2°>3°
- Rate α Strength of NU-α
- Non-Polar NU-. Strong NU- and hight Concentration of NU- favour SN2.

Polyhalogen Compounds

Polyhalogen compounds: Carbon compounds containing more than one halogen atom permolecule.

Polyhalogen compounds are useful in various industries and in agriculture.
Some important polyhalogen compounds:

Dichloromethane (Methylene chloride)



Uses:

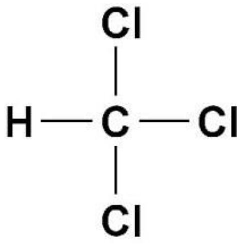
Dichloromethane (methylene chloride) is used as a:

1. Solvent for paint removers
2. Propellant in aerosols
3. Process solvent in the manufacture of drugs
4. Metal cleaning and finishing solvent

Harmful effects:

1. It endangers the human central nervous system.
2. Exposure to lower levels of methylene chloride in air can lead to slightly impaired hearing andvision.
3. High levels of methylene chloride in air cause dizziness, nausea, tingling and numbness in thefingers and toes.
4. In humans, direct skin contact with methylene chloride causes intense burning and mild rednessof the skin.
5. Direct contact with the eyes can burn the cornea.

Trichloromethane (Chloroform)



$$\begin{array}{ccccc} & & Cl & & \\ & & | & & \\ H & - & C & - & Cl \\ & & | & & \\ & & Cl & & \end{array}$$

Uses:

1. Chemically, chloroform is used as a solvent for fats, alkaloids, iodine and other substances.
2. The major use of chloroform today is in the production of the freon refrigerant R-22.

3. It was once used as a general anaesthetic in surgery but has been replaced by less toxic, saferanaesthetics such as ether.

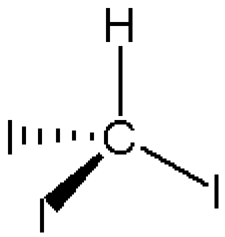
Harmful effects:

1. As might be expected from its use as an anaesthetic, inhaling chloroform vapour depresses the central nervous system.
2. Breathing about 900 parts of chloroform per million parts of air (900 ppm) for a short time can cause dizziness, fatigue and headache.
3. Chronic chloroform exposure may cause damage to the liver (where chloroform is metabolised to phosgene) and to the kidneys. Some people develop sores when the skin is immersed inchloroform.
4. Chloroform is slowly oxidised by air (oxygen) in the presence of light to an extremely poisonous gas, carbonyl chloride, also known as phosgene.

$$2CHCl_3 + O_2 \xrightarrow{\text{light}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

It is therefore stored in closed dark-coloured bottles which are completely filled so that air is keptout.

Triiodomethane (Iodoform)



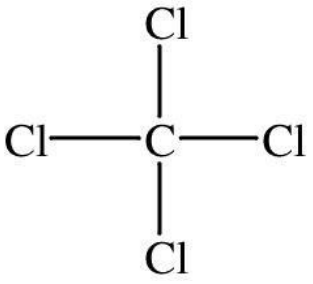
Uses:

- It was used earlier as an antiseptic, but the antiseptic properties are due to the liberation of freeiodine and not due to iodoform itself.

Drawback:

- Because of its objectionable smell, it has been replaced by other formulations containing iodine.

Tetrachloromethane (Carbon tetrachloride)



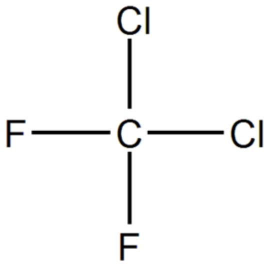
Uses:

1. It is produced in large quantities for use in the manufacture of refrigerants and propellants foraerosol cans.
2. It is also used as feedstock in the synthesis of chlorofluorocarbons and other chemicals, inpharmaceutical manufacturing and general solvent use.
3. Until the mid-1960s, it was also widely used as a cleaning fluid, both in industry, as a degreasingagent, and in the home, as a spot remover and fire extinguisher.

Harmful effects:

1. There is evidence that exposure to carbon tetrachloride causes liver cancer in humans.
2. The most common effects are dizziness, light headedness, nausea and vomiting, which cancause permanent damage to nerve cells.
3. In severe cases, these effects can lead rapidly to stupor, coma, unconsciousness or death. Exposure to CCl_4 can make the heart beat irregularly or stop.
4. The chemical may irritate the eyes on contact. When carbon tetrachloride is released into the air,it rises to the atmosphere and depletes the ozone layer.
5. Depletion of the ozone layer is believed to increase human exposure to ultraviolet rays, leading toincreased skin cancer, eye diseases and disorders, and possible disruption of the immunesystem.

Freons



$$F-\overset{\displaystyle Cl}{\underset{\displaystyle F}{C}}-Cl$$

- The chlorofluorocarbon compounds of methane and ethane are collectively known as freons.
- They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases.
- They are manufactured from tetrachloromethane by Swarts reaction.
- By 1974, the total freon production in the world was about 2 billion pounds annually.

Uses:

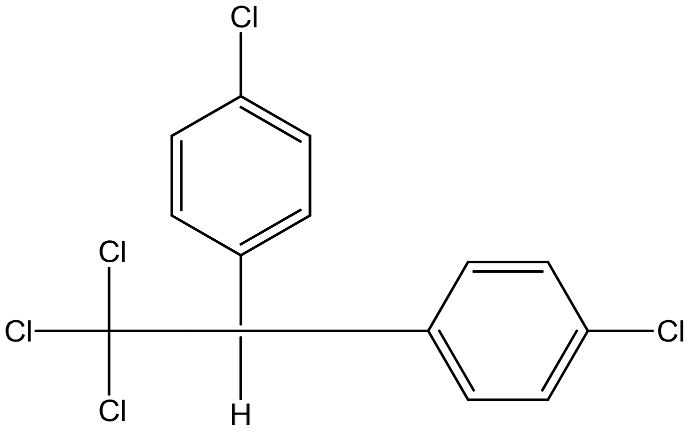
1. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes.
2. Freon 12 (CCl_2F_2) is one of the most common freons in industrial use.
3. Most freons, even those used in refrigeration, eventually make their way

into the atmospherewhere it diffuses unchanged into the stratosphere.

Harmful Effect:

- In stratosphere, freons can initiate radical chain reactions which can upset the natural ozonebalance.

p,p′-Dichlorodiphenyltrichloroethane (DDT)



DDT, the first chlorinated organic insecticide, was originally prepared in 1873. However, it was not until 1939 that Paul Muller of Geigy Pharmaceuticals in Switzerland discovered theeffectiveness of DDT as an insecticide.

Paul Muller was awarded the Nobel Prize in Medicine and Physiology in 1948 for this discovery.

Paul Muller

Uses:

- The use of DDT increased enormously worldwide after World War II, primarily because of itseffectiveness against the mosquito which spreads malaria and lice which carry typhus.

Harmful Effects:

Problems related to extensive use of DDT began to appear in the late 1940s.

1. Many species of insects developed resistance to DDT.

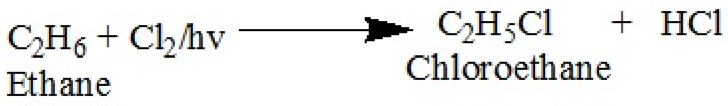
2. It has a high toxicity towards fish.
3. The chemical stability of DDT and its fat solubility compounded the problem. DDT is not metabolised very rapidly by animals. Instead, it is deposited and stored in the fatty tissues. If ingestion continues at a steady rate, DDT builds up within the animal over time.

   The use of DDT was banned in the United States in 1973, although it is still in use in some other parts ofthe world.

Preparation

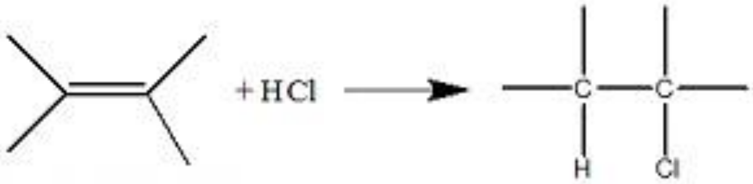
Methods of Preparation of haloalkanes

By halogenations of alkanes in presence of light, catalyst or heat:



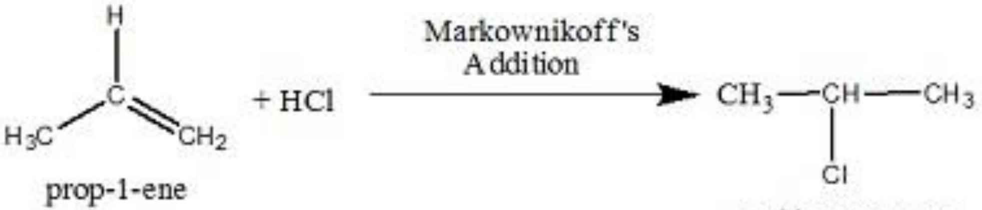
$$\underset{\text{Ethane}}{C_2H_6} + Cl_2/hv \longrightarrow \underset{\text{Chloroethane}}{C_2H_5Cl} + HCl$$

By halogenations of alkenes with HX :



2,3-dimethylbut-2-ene

2-chloro-2,3-dimethylbutane



prop-1-ene

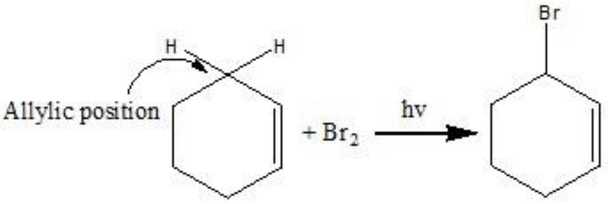
2-chloropropane

Hunsdiecker reactions:

The Hunsdiecker reaction is an instance of a halogenation reaction which involves an organic between silver salts of carboxylic acids and halogens resulting in the formation of organic halides.

$$RCOOAg + Br_2 \longrightarrow RBr + CO_2 + AgBr$$

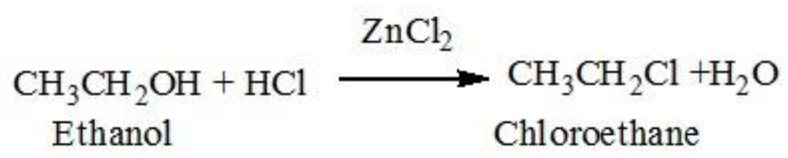
Allylic halogenations:



Preparation of alkyl halides from alcohols:

Treatment of alcohol with HCl in the presence of anhydrous ZnCl2 phosphorous pentachloride, $PX_3(P_4 + X_2)$or $SOCl_2$ leads to the preparation of alkyl halide.

By the action of halogen acids:



$$CH_3CH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2Cl + H_2O$$

Ethanol Chloroethane

1 and 2 degree alcohols require anhydrous $ZnCl_2$ while alcohols do not require $ZnCl_2$. Mixture of conc. HCl and anhydrous $ZnCl_2$ is called Lucas reagent.

Primary and secondary alkyl chlorides are prepared from their respective alcohols by using HCl gas and anhydrous $ZnCl_2$.

By the action of phosphorous halides:

$3ROH + PX_3$ à $3RX + H_3PO_3$.

Alkyl chlorides can be synthesized by the action of PCl_3 or PCl_5.

Methods of Preparation

There are primarily 4 different types of preparation techniques of Haloalkanes and Haloarenes. They include Preparation of Haloalkanes and Haloarenes from:

- Alcohols
- Hydrocarbons
- Alkenes by addition of hydrogen halides and halogens
- Halogen exchange reaction.

Preparation from Alcohols (Haloalkanes):

The most convenient method of preparation of haloalkane is from alcohols. R-OH when reacts with suitable reagents, the reaction results in the formation of R − X. The suitable reagents that help in the reaction are

Concentrated halogen acids (HX)

Phosphorus halides (PX_5 or PX_3)

Thionyl chloride ($SOCl_2$)

i) The Reaction of Alcohols with Halogen Acid

An organic compound derivative of alcohol reacts with halogen acid (H-X) to form haloalkanes as the major product.

$$ROH + HX \xrightarrow{catalyst} RX + H_2O$$

Reaction when Alcohol Reacts with Conc. Halogen Acids

Example-Preparation of Chloroalkanes

Preparation of chloroalkane is an example of the reaction of an alcohol with halogen acid to form haloalkane. In this case, primary alcohol and secondary alcohol react with HCl acid gas to form haloalkane in the presence of anhydrous $ZnCl_2$, which act as a catalyst in this reaction.

$$CH_3CH_2OH + HX \xrightarrow{ZnCl_2} CH_3CH_2X + H_2O$$
$$CH_3CH_2CH(OH)CH_3 + HX \xrightarrow{ZnCl_2} CH_3CH_2CH(X)CH_3 + H_2O$$
$$(CH_3)_3C-OH + HCl \rightarrow (CH_3)_3C-Cl + H_2O$$

Preparation of Chloroalkanes

$$(CH_3)_3C-OH + HCl \rightarrow (CH_3)_3C-O^+H_2$$
$$(CH_3)_3C^+ \xrightarrow{Cl^-} (CH_3)_3C-Cl$$

Mechanism of the Reaction

Preparation of Bromoalkanes

Hydrogen bromide (HBr) reacts with alcohols to form bromoalkanes. Hydrogen bromide synthesis of the reaction takes place by the reaction of sodium bromide or potassium bromide and H_2SO_4 (sulphuric acid). In the reaction below, NaBr and H_2SO_4 react to form HBr which further reacts with alcohol.

$$ROH + NaBr + H_2SO_4 \longrightarrow RBr + NaHSO_4 + H_2O$$

Preparation of Bromoalkanes

Example of Preparation of Bromoethane from Ethanol

$$CH_3CH_2OH + NaBr + H_2SO_4 \longrightarrow CH_3CH_2Br + NaHSO_4 + H_2O$$

Bromoethane from Ethanol

The tertiary carbonation which occurs due to tertiary alcohols is more stable than secondary and primary alcohols. Therefore tertiary carbocations offer more stability in comparison to the primary and secondary form of the compound. Hence, tertiary is more reactive than primary and secondary. The order of reactivity is 30 > 20 > 10.

Additionally, the reactivity of haloacids follows the order HI > HBr > HCl > HF. HI is easily and highly reacting haloacid among all of them because the HI bond is weaker than the other three. Therefore, it can be broken easily in comparison to the other halogen bonds to form H+ and I− ions.

However, this preparation method will not be able to synthesize aryl halides/haloarenes. C-OH bond in the phenol structure contains partial double bond character because of the delocalization of lone pair of electrons present on the oxygen atom of the benzene ring. Therefore, the bond formed in the structure cannot be easily broken down by any sort of reaction with haloacids.

$Ar - OH + HX \rightarrow$ No reaction

ii) The Reaction of Alcohols with Phosphorus halides (PX_5 or PX_3)

This reaction helps in the formation of Chloroalkanes, bromoalkanes, and iodoalkanes. In this reaction phosphorus halides interchange the functional group of alcohols (–OH) with the corresponding halides. The reaction is as follows:

$ROH + PCl_5 \rightarrow RCl + POCL_3 + HCl$

The above reaction is for the formation of alkyl chloride. Similarly, alkyl bromide or alkyl iodide formation is possible by the reaction of an alcohol with phosphorus tribromide and triiodide. To achieve the reaction, red phosphorus reacts with bromine or iodine by in-situ preparation (during the reaction) of phosphorus tribromide and triiodide.

$$ROH \xrightarrow{\textit{Red phosphorus}/Br_2} R - Br$$

$$ROH \xrightarrow{\textit{Red Phosphorus}/I_2} R - I$$

In-situ Preparation of Phosphorus Tribromide and Triiodide

Note: Fresh preparation of the phosphorus tribromide and phosphorus triiodide is made with red phosphorus and bromine or iodine due to the instability of the compounds. Thus, alcohol reacts with phosphorus trihalides (PX3) to obtain three molecules of alkyl halide. The general overall reaction is.

$$3R - OH + PX_3 \rightarrow 3R - X + H_3PO_3, \text{ Here } X = Cl, Br$$

Example: Reaction of ethanol with PCl_3 for the formation of chloroethane

$$3CH_3CH_2OH + PCl_3 \longrightarrow 3CH_3CH_2Cl + H_3PO_3$$

Reaction of Ethanol with PCl_3

iii) The Reaction of Alcohols with Thionyl chloride as Suitable Reagent

This reagent is the most preferred and suitable in between the three reactions of alcohols. Alcohol reacts with Thionyl chloride (SOCl2) to form alkyl chlorides. However, the by-products formed in this reaction are gaseous in nature. Therefore, the by-products can easily escape into the atmosphere, leaving the pure alkyl halide. This method helps in the generation of pure alkyl halide.

$$CH_3CH_2OH + SOCl_2 \rightarrow \mathbf{CH_3CH_2Cl} + SO_2\uparrow + HCl\uparrow$$

Reaction of Ethanol with $SOCl_2$

2) Preparation of Haloalkanes & Haloarenes from Hydrocarbons

Preparation of Haloalkanes and haloarenes from hydrocarbons is possible by 3 different methods. They are

- Free radical halogenation of haloalkanes
- Electrophilic Substitution Reactions
- Sandmeyer reaction

i) Free Radical Halogenation

Alkyl bromides and alkyl chloride formation are possible by the free radical halogenation reaction. However, radicals are very non-selective in nature. Moreover, radicals are non-specific and highly reactive intermediates that result in the formation of the mixture of products.

For instance bromination or chlorination of free radical results in the formation of a number of haloalkanes. This causes difficulty in the isolation of a single product. Therefore it is not the preferred method for the preparation of haloalkanes. Example- When butane reacts with chlorine in the presence of light as energy, a mixture of product formation takes place.

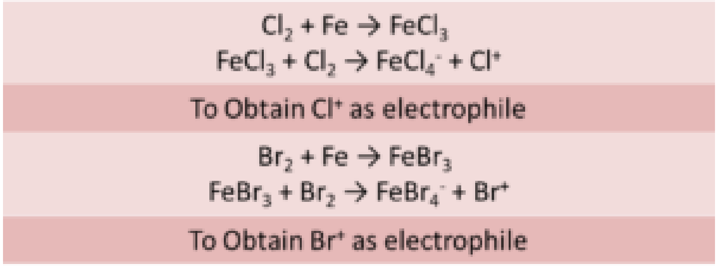
$$CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2/h\nu} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CH(Cl)CH_3$$

Free Radical Halogenation

ii) Electrophilic Substitution Reaction

This method helps in the preparation of haloarenes such as aryl bromides and aryl chlorides. Electrophilic substitution forms the aryl bromides and aryl chlorides by using halogens such as chlorine and bromine in the presence of Lewis acid. However, the reaction requires the following of certain specific condition for the generation of proper electrophile.

For example, the reaction should be conducted in presence of Lewis acid. Additionally, the reaction must be carried out in the dark. The reactions to obtain the electrophiles are



$Cl_2 + Fe \rightarrow FeCl_3$

$FeCl_3 + Cl_2 \rightarrow FeCl_4^- + Cl^+$

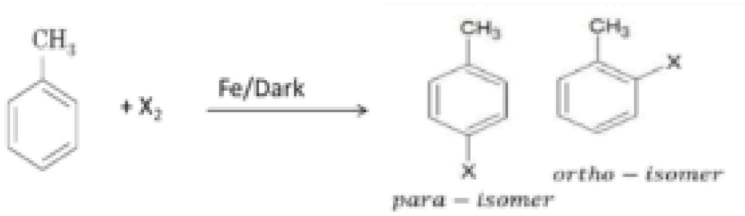
To Obtain Cl^+ as electrophile

$Br_2 + Fe \rightarrow FeBr_3$

$FeBr_3 + Br_2 \rightarrow FeBr_4^- + Br^+$

To Obtain Br^+ as electrophile

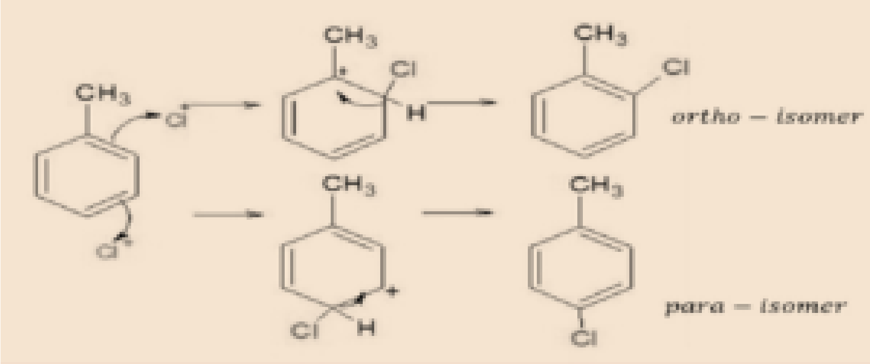
The electrophiles in the above reactions are Cl+ and Br+ and HCl and HBr are the by-products of the reaction. Therefore, the electrophilic substitution reaction for the preparation of aryl bromide and aryl chloride is



Mechanism of Electrophilic Substitution Reaction

In the above reaction, two different isomers of the aryl chlorides are formed. They are Ortho and Para isomer. The π-electron in the benzene ring attacks the Cl+ electrophile to produce an intermediate complex. However, the H+ bond from the intermediate complex moves in order to compensate for the positive charge of the carbon atom.

Thus the reaction forms two different isomers of the product-ortho and para. The melting points of both the isomer differ significantly. And para-isomer has the higher boiling point than ortho-isomer. Therefore, they can be easily separated from each other.



Mechanism of Electrophilic Substitution Reaction

Preparation of aryl chloride and bromide is possible from this reaction. Aryl fluoride formation is not possible due to the high reactivity of the halogen fluorine. Additionally, iodine reaction is also not possible as iodine is reversible in nature. Thus, it requires a strong oxidizing agent such as Conc. HNO_3 or HIO_4 for the oxidation of HI and converting it to I2. Therefore, driving the reaction in forwarding direction is difficult and requires a strong oxidizing agent

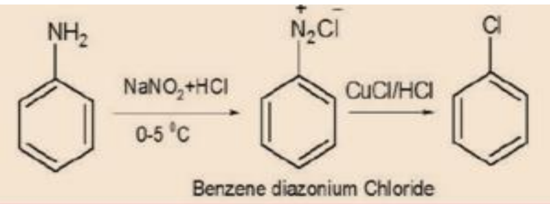
iii) Sandmeyer's Reaction

Sandmeyer's Reaction is a two-step method which includes:

Diazonium salt formation

Diazonium salt reaction with a cuprous halide (Cu_2X_2)

Primary aromatic amine reacts with sodium nitrite in the presence of cold mineral acid to form the diazonium salt. In this case, HNO_2 is prepared within the reaction by reacting sodium nitrite and HX in the temperature of 273-278K.



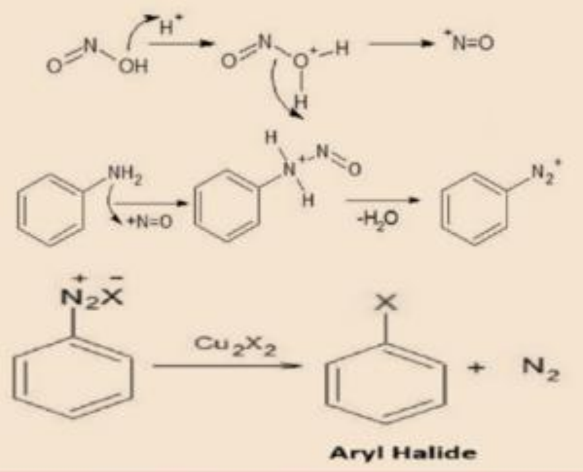
Sandmeyer's Reaction

Mechanism of the Sandmeyer's Reaction

In the first step

$NaNO_2 + HCl \rightarrow HNO_2 + NaCl$

The HNO_2 formed in the presence of H+ undergo protonation to form NO+ as the electrophile. The lone pair of the atom from the primary amine will react with the electrophile.to form an intermediate compound which further gives diazonium salt after elimination of H_2O. In the second step, the diazonium salt reacts with cuprous halide to form the respective aryl halide



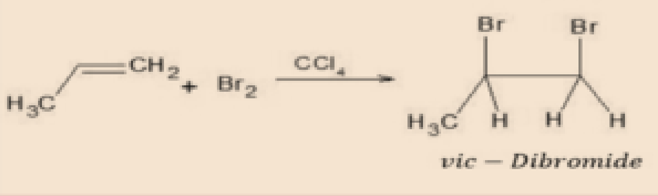
Mechanism of the Sandmeyer's Reaction

3) Haloalkanes & Haloarenes from Alkenes

Haloalkanes and haloarenes preparation is possible by the addition of halogens (X2) across the double bond of the alkene. It is also possible by the addition of hydrogen halides (HX). In this halogen can be chlorine, bromine or even iodine.

i) Addition of HX

Alkene can be converted to haloalkane by an electrophilic addition reaction. Alkene reacts with HX to form R-X. The order of reactivity of halides with respect to alkenes follows the order HI > HBr > HCl > HF. The general reaction will be



Formation of Haloalkane by Addition of Halogen to an Alkene

The reaction, in this case, is an example of a regioselective reaction. In this type of reaction, we get products in major and minor quantity. Additionally, the reaction follows Markovnikov's rule of addition for the determination of the major product by the addition of across the double bond of the alkene.

According to Markovnikov's rule, in an addition reaction of unsymmetrical alkenes, the negative part of the reagent or halogen will attach itself to the carbon that contains less number of hydrogen atoms. For example, prop-1-ene reacts with hydrogen bromide to form 2-bromopropane as a major product.

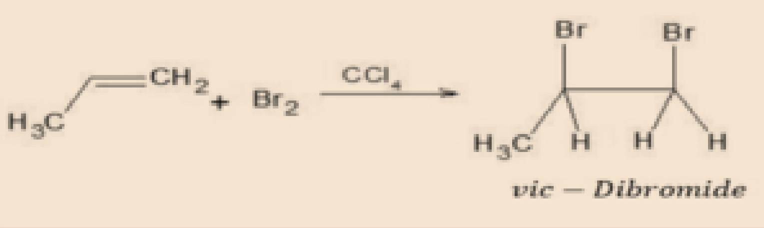
Peroxide effect (Kharash effect)

There is another possibility where the reaction contradicts Markovnikov's rule. This effect is known as Peroxide effect/ Kharash effect/ anti-markovnikov's rule. In this reaction, alkene reacts with HBr in the presence of peroxide. The Br- or the negative part of the reagent will attach itself to the carbon having more number of hydrogen atoms. For example, Prop-1-ene reacts with hydrogen bromide to form 1-bromopropane as a major product in the presence of peroxide.

$$CH_3CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3\text{-}CH_2\text{-}CH_2\text{-}Br$$

ii) Addition of Halogens

Similarly, alkenes can also react with halogens (X2). For example, Bromine reacts with an alkene in the presence of carbon tetrachloride (CCl4) to form vic-dibromide. It is a common test to determine a double bond or an alkene compound. The reaction will release reddish brown colour during the reaction.



Formation of Haloalkane by Addition of Halogen to an Alkene

4) Haloalkanes and Haloarenes from Halogen exchange reaction

i) Finkelstein Reaction

The last method of preparation of haloalkane and haloarene is halogen exchange reaction. In this reaction, an alkyl chloride or alkyl bromide reacts with sodium iodide in acetone to form alkyl iodides.

$$R - X + NaI \rightleftharpoons R - I + NaX$$
$$C_2H_5 - Cl + NaI \rightleftharpoons C_2H_5 - I + NaCl$$

Halogen Exchange Reaction

The reaction is an equilibrium reaction so there is a possibility of forming other products. The solubility difference of alkyl halides in acetone is used for driving the reaction in the forward direction. We know that sodium iodide is soluble in acetone but NaCl or NaBr are insoluble. Therefore, they precipitate out in the reaction which is easy to remove from the reaction mixture.

ii) Swartz Reaction

In this reaction, alkyl fluorides formation is possible by heating of Alkyl fluorides RBr/RCl. The reaction is carried out in the presence of metallic fluoride such as SbF_3, Hg_2F_2, AgF, CoF_2.

$$CH_3Br + AgF \rightarrow CH_3F + AgBr$$

Swartz Reaction

Darzen method: Darzens halogenation is a chemical processs involving the preparation of alkyl halides from alcohols by treating with reflux of thionyl chloride or bromide (SOX_2) in the presence of small quantity of a nitrogen base like tertiary amine or pyridine, or the equivalent hydrochloride.

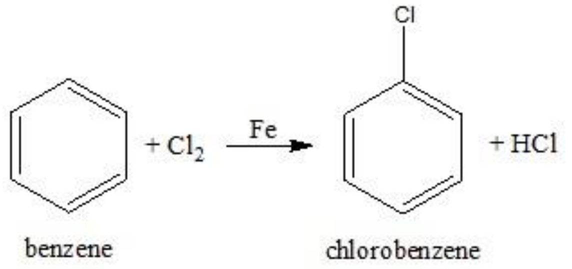
Alkyl bromides and iodides cannot be prepared by this method. The reason behind this is that thionyl bromide is unstable and thionyl iodide does not exist. This method is preferred for preparing alkyl chlorides because here by-products are gaseous SO_2 and HCl which escape easily. But this does not happen in the method involving phosphorous chloride; hence it is not used for preparing alkyl chlorides.

$$ROH + SOCl_2 \xrightarrow[\text{Reflux}]{\text{Pyridine}} RCl + SO_2 + HCl$$

Methods of Preparation of aryl halides

Nuclear halogenations:

This method can be used to prepare aryl chlorides and bromides. This is done by treatment of arene with chlorine or bromine in the absence of sunlight and in the presence of halogen carrier like $AlCl_3$, $FeCl_3$ etc. at low temperatures. It is an electrophilic substitution.



From phenol:

$$\underset{\text{Phenol}}{C_6H_5OH} \xrightarrow[\text{or } SOCl_2]{HX,\ PX_3} \text{No Reaction}$$

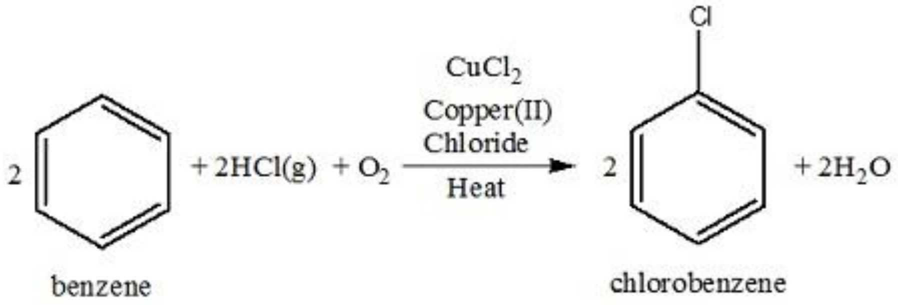
$$\underset{\text{Phenol}}{C_6H_5OH} + \underset{\text{Phosphorus pentachloride}}{PCl_5} \longrightarrow \underset{\text{chlorobenzene}}{C_6H_5Cl} + HCl + \underset{\text{Phosphoryl Chloride}}{POCl_3}$$

However the yield of Chlorobenzene is very poor as the main product is Triphenyl phosphate.

By Hunsdiecker reaction:

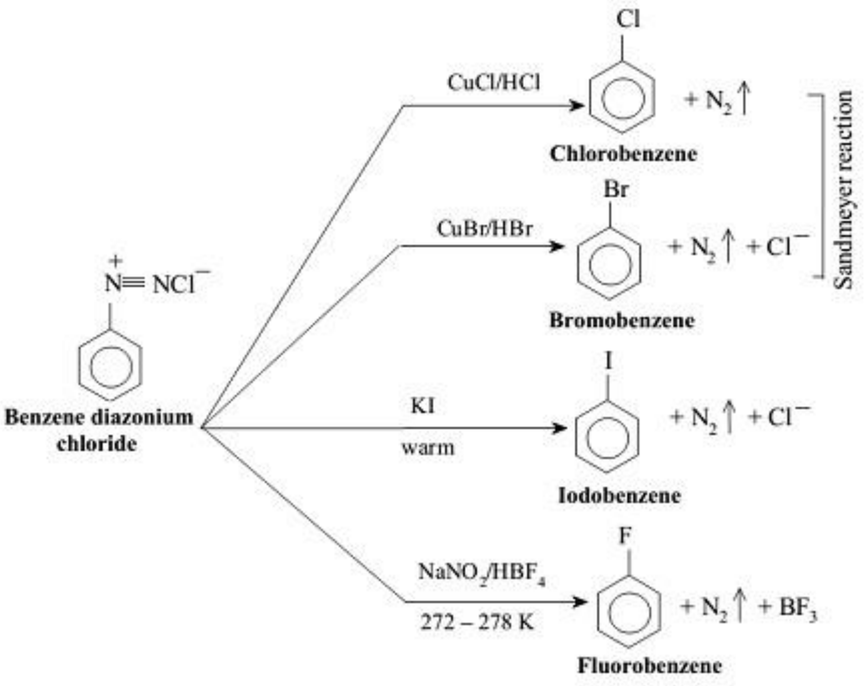
$$\underset{\text{Silver propionate}}{C_2H_5COOAg} + Br_2 \xrightarrow[\text{CCl}_4\text{ as solvent}]{\text{Acetone or}} \underset{\text{Bromoethane}}{C_2H_5Br} + CO_2 + \underset{\text{Silver bromide}}{AgBr}$$

Raschig process:



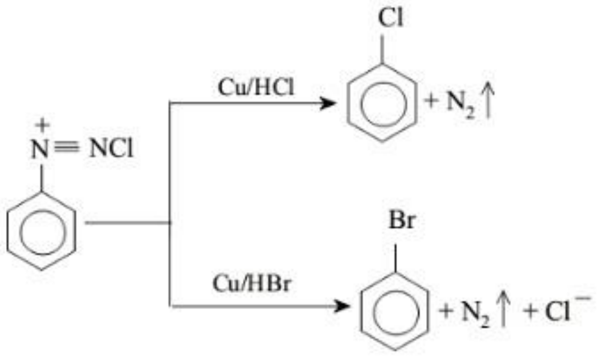
Sandmeyer reaction:

Diazonium salts are highly reactive compounds used to prepare arene derivatives. Treating diazonium salt with copper (I) chloride (Cu_2Cl_2) or copper (I) bromide (Cu_2Br_2) leads to the formation of corresponding haloarene. This reaction is known as Sandmeyer reaction.



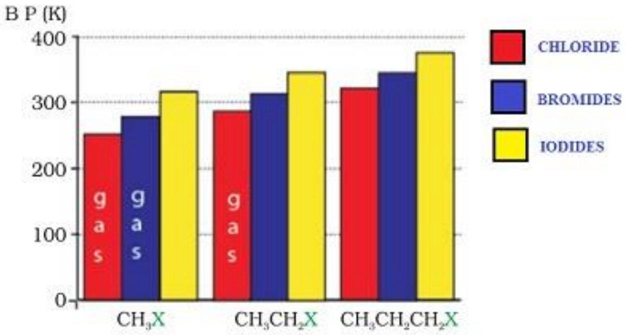
Gattermann reaction:

Haloarenes can also be prepared by reaction of benzene diazonium chloride with copper powder in the presence of corresponding halogen acid. This reaction is termed as Gattermann reaction.

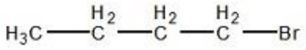


Physical Properties of haloalkanes

- Alkyl halides are colorless in pure state. Bromides and iodides cultivate colour on exposure to light
- Volatile halogen compounds possess a sweet smell.
- Intermolecular forces of attraction of halogen derivatives are stronger due to greater polarity and molecular mass as well compared to the parent hydrocarbon thereby resulting in higher boiling points of chlorides, bromides and iodides compared to hydrocarbons of equivalent molecular mass.
- The boiling points of alkyl halides for same alkyl group follow the order: RI> RBr> RCl> RF due to the increase in size and mass of halogen atom thereby increasing the extent of van der Waal forces.

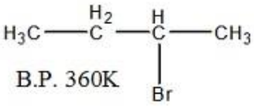


In isomeric haloalkanes the boiling points decreases with increase in branching.



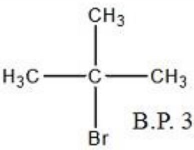
$H_3C-\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-Br$

1-bromobutane B.P. 375K



B.P. 360K

2-bromobutane



B.P. 346K

2-bromo-2-methy lpropane

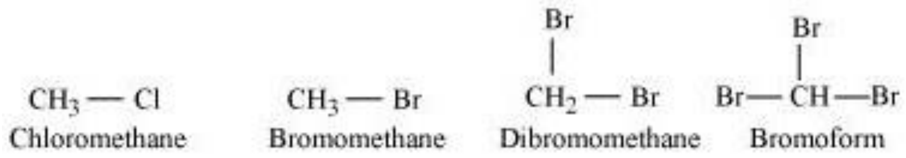
- Para-isomers possess high melting point compared to ortho and meta-isomers due to the symmetry of para-isomers fitting in crystal lattice better than ortho- and meta-isomers.
- Density increases with increase in number of carbon atoms, halogen atoms and atomic mass of the halogen atoms. Consequently the density of Bromo, iodo and polychloro derivatives of hydrocarbons is greater than water.
- The haloalkanes are only very slightly soluble in water due to release of less energy during the setup of new attractions between the haloalkane and the water molecules which in turn is insufficient to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules.
- Haloalkanes dissolves easily in organic solvents due to the new intermolecular forces of attractions between haloalkanes and solvent molecules having equivalent strength as the one that is broken in separate haloalkane and solvent molecules.

Problem: Arrange each set of compounds in order of increasing boiling points.

1. Bromomethane, Bromoform, Chloromethane, Dibromomethane.

2. 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.

Solution:



Haloalkanes are hydrocarbons in which hydrogen in a normal alkane is replaced by a halogen (group 17 elements). In this article, we will discuss the physical properties of haloalkanes. The physical properties of haloalkanes are mostly like a normal covalent compound. Halogens not being much reactive functional group as a carboxyl group or aldehyde doesn't affect the overall physical properties by much. Still, few differences can be seen as we move down in the homologous series of haloalkanes group due to the difference in atomic masses of the compound.

Chemical Properties of Haloalkanes

Haloalkanes are quite reactive compounds. They undergo substitution, elimination and reduction reactions. They also react with some metals to form organometallic compounds. The reactivity of haloalkanes is mainly due to the polar nature of the carbon halogen bond.

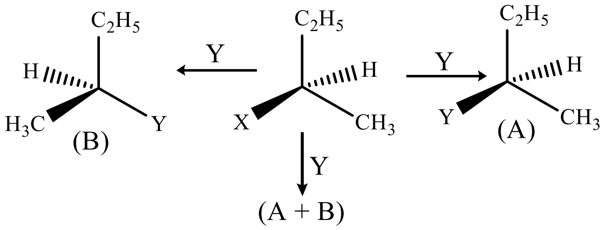
The stability of alkyl halides generally decreases as the strength of the C-X bond decreases. Iodides generally liberate iodine due to their low stability and acquire brown or violet colour.

$2R\text{-}I \rightarrow R\text{-}R + I_2$

Iodoform shows the antiseptic properties due to the liberation of iodine.

NCERT LINE BY LINE QUESTIONS

(1.) Consider the following reactions [Page: 307]



Here A+B is

(a.) Racemic mixture (b.) Inversion

(c.) Retention (d.) None of these

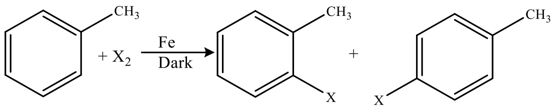
(2.) In which of the following solvents, the solubility of haloalkanes is low? [Page: 299]

(a.) water (b.) ethanol

(c.) benzene (d.) chloroform

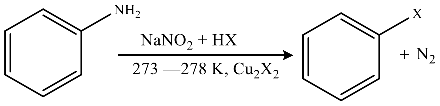
(3.) Which of the following reaction is Sandmeyer's reaction?

(a.)



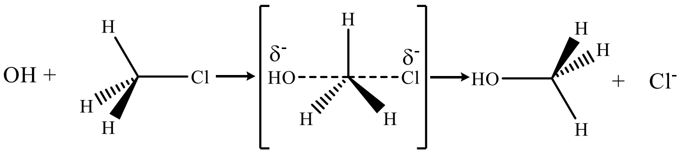
(b.) $H_3C - Br + AgF \longrightarrow H_3C - F + AgBr$

(c.)



(d.) $H_3C - X + NaI \longrightarrow H_3C - I + Nax$

(4.) Consider the following reaction [Page: 301]



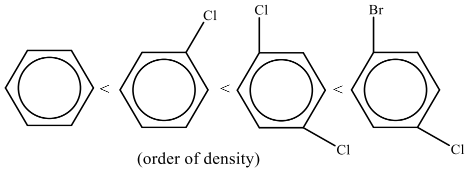
The reaction represents

(a.) S_N2 mechanism (b.) S_N1 mechanism

(c.) S_Ni mechanism (d.) none of these

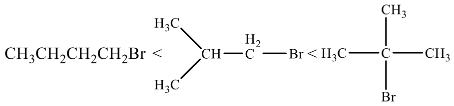
(5.) Which of the following is in correct [QR code, NCERT Exemplar, Page: 304]

(a.)



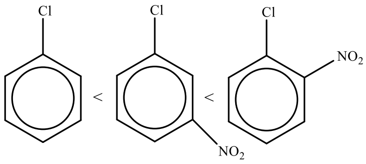
(order of density)

(b.)



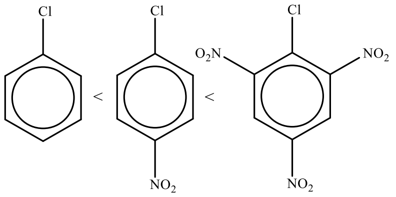
(order of Boiling point)

(c.)



(order of rate of reaction towards nucleophilic substitution)

(d.)



(order of rate of reaction towards nucleophilic substitution)

(6.) An alkyl chloride produces a single alkene on reaction with sodium ethoxide and ethanol. The alkene further undergoes hydrogenation to yield 2-methylbutane. Identify the alkyl chloride from amongst the following.

(a.) $ClCH_2(CH_3)_2CH_3$

(b.) $ClCH_2CH_2CH_2CH_3$

(c.) $ClCH_2CH(CH_3)CH_2CH_3$

(d.) $CH_3C(Cl)(CH_3)CH_2CH_3$

(7.) Which of the following statement is incorrect? [Page: 291]

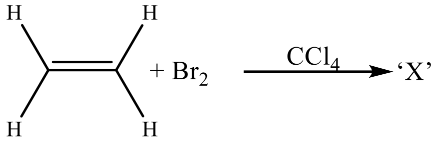
(a.) The common name of alkyl halides are derived by naming the alkyl group followed by the name of halide.

(b.) For monohalogen substituted derivatives of benzene, common and IUPAC names are used.

(c.) For dihalogen derivatives, the prefixes o-, mand p- are used in IUPAC system.

(d.) The dihaloalkanes having the same type of halogen atoms are named as alkylide.

(8.) Consider the following reaction [Page: 295]

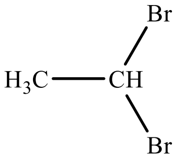


Here, 'X' is

(a.) $Br\,CH_2-CH_2\,Br$

(b.) CH_3- CH_2 Br

(c.)



(d.) both (a) and (b)

(9.) Carbon compounds containing more than one halogen atom are usually referred to as [Page: 317]

(a.) polyhalogen compounds

(b.) hydrocarbon

(c.) haloalkane

(d.) haloarene

(10.) Match the organic compounds given in column I with their effects given in column II. [Page: 289]

(Column I)	**(Column I)**
Organic compounds	**Effects**
(I) Chloramphenicol	(p) treatment of malaria
(II) Thyroxine	(q) antibiotic
(III) Chloroquine	(r) Iodine containing hormone
(IV) Halothane	(s) Anaesthetic

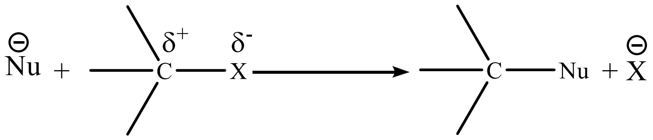
Codes

I II III IV

(a.) r q p s　　(b.) p q r s

(c.) q r p s　　(d.) p q s r

(11.) Consider the following reaction [Page: 300]

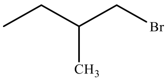
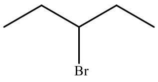


The type of reaction shown by the reaction is

(a.) nucleophilic substitution　　(b.) electrophilic substitution

(c.) addition reaction　　(d.) elimination reaction

(12.) Match the following. [Page: 292]

Column I (IUPAC)	**(Name) Column II**
(i) 	(p) Bromobutane
(ii) 	(q) 1-Bromo-2-methylbutane
(iii) $CH_3-CH_2CH_2CH_2\ Br$	(r) 3-bromopentane

Codes

	I	II	III
(a.)	r	p	q
(b.)	p	q	r
(c.)	q	p	r
(d.)	q	r	p

(13.) $C_7H_8 \xrightarrow{3Cl_2,Heat} A \xrightarrow{Zn/Br_2} B \xrightarrow{Zn/HCl}$, Here, the correct compound C is

(a.) 3-Bromo-2,4,6-trichlorotoluene　　(b.) o-bromotoluene

(c.) p-bromotoluene　　(d.) m-bromotoluene

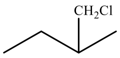
(14.) Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to [Page: 311]

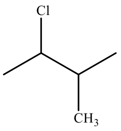
(a.) Resonance effect　　(b.) Difference in hybridisation

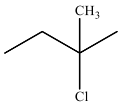
(c.) Instability of phenyl cation　　(d.) All of these

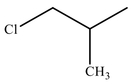
(15.) An alkene ‘A’ on reaction with O₂ and $Zn\ /H_2O$ gives propanone and ethanol in equimolar ratio. Addition of HCl to alkene ‘A’ gives ‘B’ as the major product. [NEET-2019]

The structure of product ‘B’ is

(a.) 

(b.) 

(c.) 

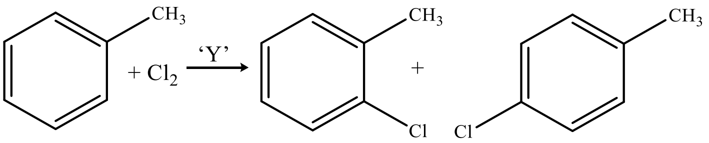
(d.) 

(16.) The number of isomers for the compound with molecular formula C2BrClFI is

(a.) 3 (b.) 4

(c.) 5 (d.) 6

(17.) The reagent 'Y' in the reaction is [Page: 296]



(a.) Fe dark

(b.) Fe + sunlight

(c.) $FeCl_3$

(d.) $FeBr_3$

(18.) Thionyl chloride is preferred because [Page: 294]

(a.) alkyl halide and H_3PO_3 formed (b.) alkyl halide is formed along with SO_2 and HCl gas

(c.) alkyl halide and $POCl_3$ are formed (d.) alkyl halide and H_2O are formed

(19.) Chlorination of toluene in presence of light and heat followed by treatment with aq. NaOH and acidification gives

(a.) o-cresol (b.) p-cresol

(c.) 2,4-dihydroxytoluene (d.) benzoic acid

(20.) The alkane that gives only one mono-chloro product on chlorination with Cl_2 in presence of diffused sunlight is [Odisha NEET-2019]

(a.) 2,2-dimethylbutane (b.) neopentane

(c.) n-pentane (d.) isopentane

(21.) Name the polyhalogen compound which is employed as a solvent for fats, alkaloids, iodine and other substances. [Page: 317]

(a.) chloroform (b.) methylene chloride

(c.) iodoform (d.) None of these

(22.) Consider the following statements [Page: 292]

(I) The dihalo compounds is classified as geminal halide.
(II) In common system, gem-dihalides are named as alkylidene halides.
(III) Vic-dihalides are named as alkylene dihalides.
(IV) IUPAC name of $H_3C-CHCl_2$ is ethylidene chloride.

Choose the correct option.

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

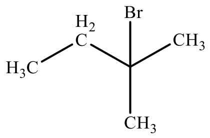
(c.) II, III and IV

(d.) II and III

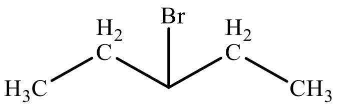
(23.) Which of the following has highest boiling point? [Page: 298]

(a.) $CH_3CH_2CH_2CH_2CH_2Br$

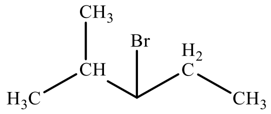
(b.)



(c.)



(d.)



(24.) When a compound rotates the plane of plane polarised light to the right, then it is called [Page: 305]

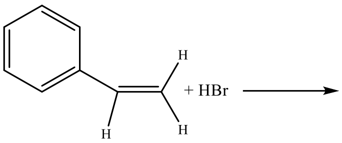
(a.) racemised

(b.) leavorotatory

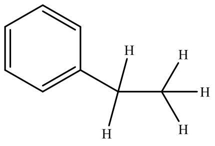
(c.) dextrorotatory

(d.) inverated

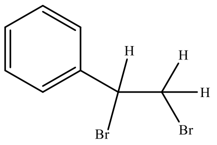
(25.) The product of the following reaction [Page: 297]



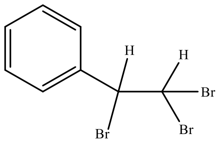
(a.)



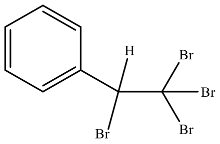
(b.)



(c.)



(d.)



(26.) Which of the following is used as feedstock in the synthesis of chlorofluorocarbons and other chemicals in pharmaceutical manufacturing? [Page: 317]

(a.) CCl_4

(b.) Iodoform

(c.) Chloroform

(d.) Methylene chloride

(27.) The compound C_7H_8 undergoes the following reactions: [NEET-2018, Page: 296]
The product 'C' is

(a.) 3-bromo-2,4,6-trichlorotoluene

(b.) o-bromotoluene

(c.) m-bromotoluene

(d.) p-bromotoluene

(28.) **Assertion**: Vinyl chloride is less reactive than alkyl chloride.
Reason: Stability of alkyl halide decreases as the strength of $C-X$ bond decreases. [Page: 293]

(a.) Both A and R are correct and R is correct explanation of A.

(b.) Both A and R are correct but R is not correct explanation of A.

(c.) A is correct but R is incorrect.

(d.) Both A and R are false.

(29.) Assertion: Chloral reacts with phenylchloride to form DDT. [Page: 318]
Reason: It is an electophilic substitution reaction.

(a.) Both A and R are correct and R is correct explanation of A.

(b.) Both A and R are correct but R is not correct explanation of A.

(c.) A is correct but R is incorrect.

(d.) Both A and R are false.

(30.) **Assertion**: Low member of alkyl halides are colourless gases.
Reason: Alkyl iodides in general turn black on exposure to air and light. [Page: 297]

(a.) Both A and R are correct and R is correct explanation of A.

(b.) Both A and R are correct but R is not correct explanation of A.

(c.) A is correct but R is incorrect.

(d.) Both A and R are false.

(31.) Consider the following statements: [Page: 303]

(I) In S_N1, the rate of reaction depends upon the concentration of only one reactant.

(II) $S_N1$reaction occur in two steps.

(III) The rate of reaction depends only on the concentration of $R-X$ and not on the concentration of hydroxide ion.

Read the given statements and then choose the correct option

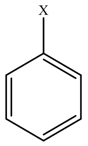
(a.) Only I

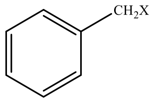
(b.) Only II

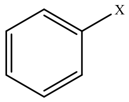
(c.) Both I and II

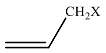
(d.) All of these

(32.) Which of the following is not correct match? [Page: 291]

(a.) Allylic halide -


(b.) Benzylic halide-


(c.) Aryl halide -


(d.) Vinyl halide -


(33.) Assertion: CCl_4 is a fire extinguisher.
Reason: CCl_4 is insoluble in water. [Page: 317]

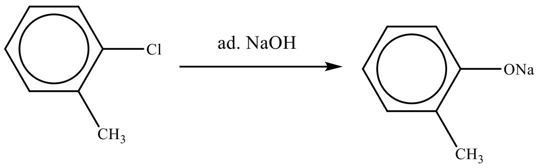
(a.) Both A and R are correct and R is correct explanation of A.

(b.) Both A and R are correct but R is not correct explanation of A.

(c.) A is correct but R is incorrect.

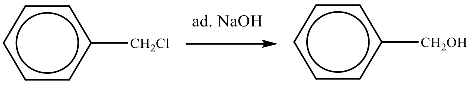
(d.) Both A and R are false.

(34.) The hydrolysis reaction that takes place at the slowest rate, among the following is

(a.) 

(b.) $H_3C-CH_2-Cl \xrightarrow{\text{aq. NaOH}} H_3C-CH_2-OH$

(c.) $H_2C=CH-CH_2-Cl \xrightarrow{\text{aq. NaOH}} H_2C=CH-CH_2OH$

(d.) 

(35.) The boiling points of chlorides are higher than those of hydrocarbons of comparable molecular mass. It is due to [Page: 298]

(a.) dipole−dipole forces of attraction
(b.) van der Waal's attraction
(c.) Both (a) and (b)
(d.) none of these

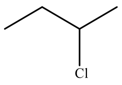
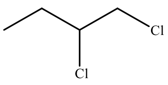
(36.) Replacement of Cl of chlorobenzene to give phenol requires drastic conditions but chlorine of 2,4-dinitrochlorobenzene is readily replaced because

(a.) NO_2 makes the electron rich ring at ortho and para positions
(b.) NO_2 withdraw electrons at metaposition
(c.) NO_2donates electrons at m-position
(d.) NO_2withdraws electrons at ortho and para positions

(37.) Consider the following reaction [Page: 295]

$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{Cl_2\ /\text{UVLight}}$ 'X' and 'Y'

Product 'X' and 'Y' are

(a.)  and 

(b.) $CH_3CH_2CH_2CH_2Cl$ and $CH_3CH_2CHClCH_3$
(c.) $CH_3CH_2CHCl_2CH_3$ only
(d.) $CH_3CH_2CH_2CH_2Cl$ only

(38.) Which of the following is the correct order of reactivity of alkyl halides toward S_N1 reaction? [Page: 303]

(a.) $3° > 2° > 1° > CH_3X$
(b.) $2° > 3° > 1° > CH_3X$
(c.) $1° > 2° > 3° > CH_3X$
(d.) $CH_3X > 1° > 2° > 3°$

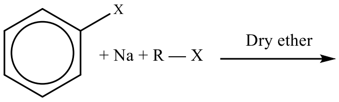
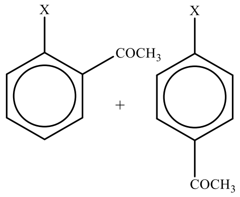
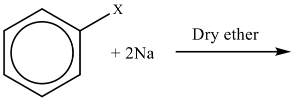
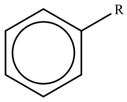
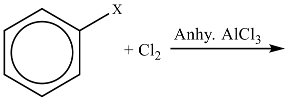
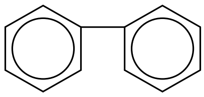
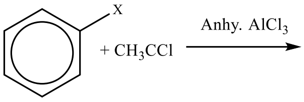
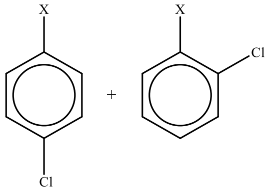
(39.) The compound in which the halogen atom is bonded to an sp^3 hybridised carbon atom adjacent to $C=C$ double bond is

(a.) Benzylic halide
(b.) Aryl halide
(c.) Allylic halide
(d.) Vinylic halide

(40.) **Assertion**: Alkyl iodide can be prepared by treating alkyl chloride/bromide with NaI in acetone. **Reason**: NaCl/NaBr are soluble in acetone while NaI is not. [Page: 295]

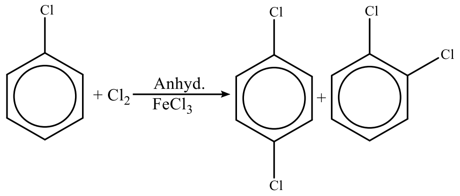
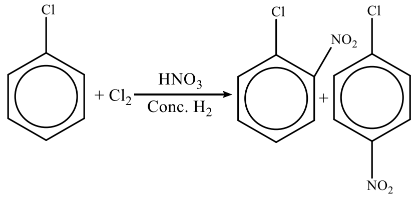
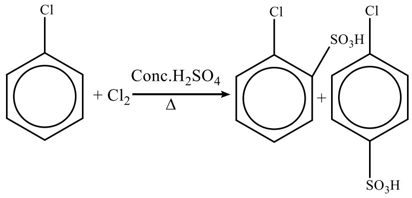
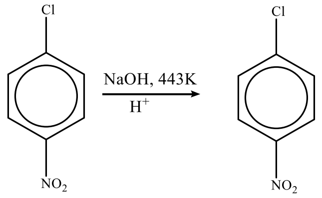
(a.) Both A and R are correct and R is correct explanation of A.
(b.) Both A and R are correct but R is not correct explanation of A.
(c.) A is correct but R is incorrect.
(d.) Both A and R are false.

(41.) Match the following. [Page: 315]

Column I (Reactant)	**Column II (Product)**
(A) 	(p) 
(B) 	(q) 
(C) 	(r) 
(D) 	(s) 

A B C D
(a.) r s q p
(b.) q r s p
(c.) q p r s
(d.) p q r s

(42.) Which of the following is not an electrophilic substitution reaction? [Page: 314]
Column I (Reactant)

 (a.)	 (b.)
 (c.)	 (d.)

(43.) Freons is manufactured from tetrachloromethane by [Page: 318]

(a.) Frankland reaction
(b.) Wurtz reaction
(c.) Swarts reaction
(d.) Sandmeyer reaction

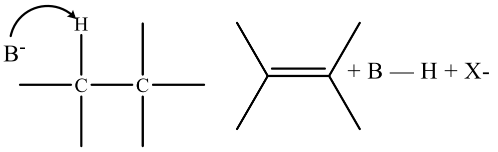
(44.) Assertion: Boiling point of alkyl halide increases with increase in molecular weight. Reason: Boiling point of alkyl halides is in the order $RI > RBr > RCl > RF$. [Page: 298]

(a.) Both A and R are correct and R is correct explanation of A.
(b.) Both A and R are correct but R is not correct explanation of A.
(c.) A is correct but R is incorrect.
(d.) Both A and R are false.

(45.) **Assertion**: p-dichlorobenzene has higher melting point than o-dichlorobenzene.
Reason: Stronger the van der Waal's forces of attraction, higher is the melting point. [Page: 298]

(a.) Both A and R are correct and R is correct explanation of A.
(b.) Both A and R are correct but R is not correct explanation of A.
(c.) A is correct but R is incorrect.
(d.) Both A and R are false.

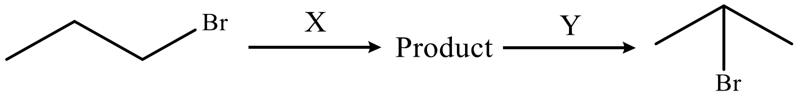
(46.) Consider the following reaction [Page: 309]



This reaction is called

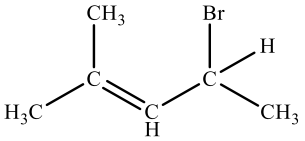
(a.) $\alpha-$elimination
(b.) $\beta-$elimination
(c.) substitution
(d.) free radical

(47.) Identify the set of reagents/reaction condition 'X' and 'Y' in the following set of transformations



(a.) X = dil. aqueous NaOH, 20°C Y = HBr/acetic acid 20°C
(b.) X = conc. alcoholic NaOH, 80°C Y = HBr/acetic acid 20°C
(c.) X = dil. aqueous NaOH, 20°C Y = $Br_2/CHCl_3$, 0°C
(d.) X = conc. alcoholic NaOH, 80°C Y= $Br_2/CHCl_3$, 0°C

(48.) The correct IUPAC name of the following structure is [Page: 293]



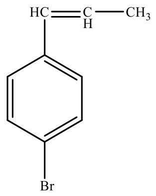
(a.) 4-bromopent-2-ene
(b.) 3-bromo-2-methylbutene
(c.) 1-bromobut-2-ene
(d.) 3-bromo-2-methylpropene

(49.) How much chloroform can cause dizziness for a short time? [Page: 317]

(a.) 100 parts per million
(b.) 200 parts per million
(c.) 900 parts per million
(d.) only 1 part per million

(50.) The reaction of $C_6H_5CH=CHCH_3$ with HBr produces [CBSE AIPMT-2015, Page: 296]

(a.) $C_6H_5CH(Br)CH_2CH_3$
(b.) $C_6H_5CH_2CH(Br)CH_3$
(c.) $C_6H_5CH_2CH_2CH_2Br$
(d.)



TOPIC WISE PRACTICE QUESTIONS

TOPIC 1: General Characteristics of Haloalkanes and Haloarenes

1. Read the following statements and choose the correct option.
(i) The general formula of alkyl halides is C*n*H2*n*+1 X
(ii) The general formula of aryl halides is C*n* H*n*–1 X
(iii) In alkyl halides halogen atom(s) is attached to *sp*2 hybridised carbon atom
(iv) In aryl halides halogen atom(s) is attached to *sp*2 hybridised carbon atom.
1) (i), (ii) and (iii) are correct 2) (i), (ii) and (iv) are correct
3) (ii), (iii) and (iv) are correct 4) (i), (ii), (iii) and (iv) are correct

2. Which one of the following is not an allylic halide?
1) 4-Bromopent-2-ene 2) 3-Bromo-2-methylbut-1-ene
3) 1-Bromobut-2-ene 4) 4-Bromobut-1-ene

3. The compound which contains all the four 1°, 2°, 3° and 4° carbon atoms is
1) 2, 3-dimethylpentane 2) 2, 3, 3-trimethylpentane 3) 2, 3, 4-trimethylpentane 4) 3,3-dimethylpentane

4. Benzene hexachloride is
1) 1, 2, 3, 4, 5, 6-hexachlorocyclohexane 2) 1, 1, 1, 6, 6, 6-hexachlorocyclohexane
3) 1, 6-phenyl-1, 6-chlorohexane 4) 1, 1-phenyl-6, 6-chlorohexane

5. In the following groups :
–OAc (I) –OMe (II)
– OSO2 Me (III) –OSO2CF3 (IV)
the order of leaving group ability is
1) I > II > III > IV 2) IV > III > I > II 3) III > II > I > IV 4) II > III > IV > I

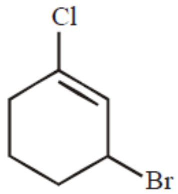
6. Phosgene is a common name for
1) phosphoryl chloride 2) thionyl chloride
3) carbon dioxide and phosphine 4) carbonyl chloride

7. Match the columns

Column - I	**Column - II**
1) CH2 = CH – CH2Cl	(p) *gem*-Dichloride
2) CH2 = CHX	(q) Vinylic halide
3) CH_3CHCl_2	(r) *vic*-Dichloride
4) $CH_2Cl\ CH_2Cl$	(s) Allylic halide

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

8. The IUPAC name of the compound shown below is



1) 2-bromo-6-chlorocyclohex-1-ene 2) 6-bromo-2-chlorocyclohexene
3) 3-bromo-1-chlorocyclohexene 4) 1-bromo-3-chlorocyclohexene

9. A compound is formed by substitution of two chlorine for two hydrogens in propane. The number of possible isomeric compounds is
1) 4 2) 3 3) 5 4) 2

10. Arrange the following halides in the decreasing order of S_N1 reactivity :
$\underset{(I)}{CH_3CH_2CH_2Cl}$, $\underset{(II)}{CH_2 = CHCH(Cl)CH_3}$,

$\underset{(III)}{CH_3CH_2CH(Cl)CH_3}$

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

TOPIC 2 : Preparation and Properties of Haloalkanes

11. Which of the following will give vinyl chloride ?

(a) $CH_2=CH_2+Cl_2 \xrightarrow{600°C}$

(b) $ClCH_2-CH_2Cl \xrightarrow[\text{ethanol}]{\text{KOH}}$

(c) $CH\equiv CH+HCl \xrightarrow{Hg^{2+}}$

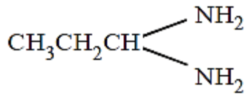
(d) All of these

12. Comment on the following reactions
(i) CH_3OH + NaCl → (ii) CH_3OH + HCl →
1) Both reactions take place easily. 2) Only reaction (ii) takes place.
3) Reaction (ii) takes places faster than (i) . 4) None of the two reactions in possible.

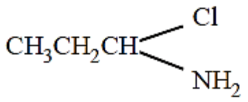
13. When chlorine is passed through propene at 400°C, which of the following is formed ?
1) PVC 2) Allyl chloride 3) Alkyl chloride 4) 1, 2-Dichloroethane

14. When $CH_3CH_2CHCl_2$ is treated with $NaNH_2$, the product formed is

(a) $CH_3-CH=CH_2$ (b) $CH_3-C\equiv CH$

(c) 

$CH_3CH_2CH(NH_2)_2$

(d) 

$CH_3CH_2CH(Cl)(NH_2)$

15. The reaction of tert-butyl bromide with sodium methoxide produces mainly –
1) iso-butane 2) iso-butylene 3) tert-butyl methyl ether 4) sodium tert butoxide

16. Ethylidene bromide on heating with metallic sodium in ether solution yields
1) ethene 2) ethyne 3) 2-butene 4) 1-butene

17. Vinyl chloride undergoes
1) only addition reactions 2) only elimination reactions
3) substitution reactions 4) both (1) and (2)

18. In the following sequence of reactions

$C_2H_5Br \xrightarrow{AgCN} X \xrightarrow{\text{Reduction}} Y$; Y is

1) *n*-propyl amine 2) isopropylamine 3) ethylamine 4) ethylmethyl amine

19. The number of structural and configurational isomers of a bromo compound, C_5H_9Br, formed by the addition of HBr to 2-pentyne respectively are
1) 1 and 2 2) 2 and 4 3) 4 and 2 4) 2 and 1

20. During debromination of *meso*-2,3-dibromobutane, the major compound formed is
1) *n*-butane 2) 1-butene 3) *cis*-2-butene 4) *trans*-2-butene

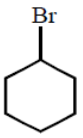
21. Halogenation of alkanes is
1) a reductive process 2) an oxidative process
3) an isothermal process 4) an endothermal process

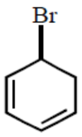
22. Which of the following reagent produces pure alkyl halides when heated with alcohols?
1) PCl_5 2) PCl_3 3) $SOCl_2$ 4) dry HCl

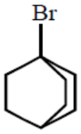
23. Which of following can be used as solvent for Grignard reagent ?
1) H_2O 2) C_2H_5OH 3) CH_3OH 4) $C_2H_5OC_2H_5$

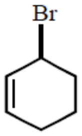
24. To prepare 3-ethylpentan-3-ol, the reagents needed are –
1) $CH_3CH_2MgBr + CH_3COCH_2CH_3$ 2) $CH_3MgBr + CH_3CH_2CH_2COCH_2CH_3$
3) $CH_3CH_2MgBr + CH_3CH_2COCH_2CH_3$ 4) $CH_3CH_2CH_2MgBr + CH_3COCH_2CH_3$

25. Rate of SN_2 will be negligible in :

(a)


(b)


(c)


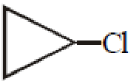
(d)


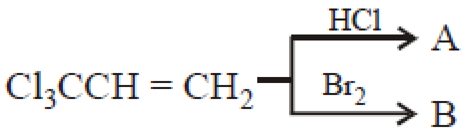
26. Identify Z in the following series

$C_2H_5I \xrightarrow{\text{Alc. KOH}} X \xrightarrow{Br_2} Y \xrightarrow{KCN} Z$

1) CH_3CH_2CN 2) $NCCH_2–CH_2CN$ 3) $BrCH_2–CH_2CN$ 4) $BrCH=CHCN$

27. The compound most reactive towards SN1 reaction is

1) Me_3COCH_2Cl 2) $MeOCH_2Cl$ 3) $C_6H_5CH_2CH_2Cl$ 4)


28.


Which of the following is correct?

1) A on reaction with aq. KOH gives $HOCH_2CH_2COOK$

2) B can be resolved into *d*– and *l* –forms

3) Both (1) and (2) 4) Neither (1) nor (2)

29. Which of the following order is not correct ?

1) $MeBr > Me_2CHBr > Me_3CBr > Et_3CBr(SN_2)$

2) $PhCH_2Br > PhCHBrMe > PhCBrMe_2 > PhCBrMePh(S_N1)$

3) $MeI > MeBr > MeCl > MeF\ (S_N2)$ 4) All the above are correct

30. Isopropyl chloride undergoes hydrolysis by

1) S_N1 mechanism 2) S_N2 mechanism

3) S_N1 and S_N2 mechanisms 4) Neither S_N1 nor S_N2 mechanism

31. Mg reacts with RBr best in

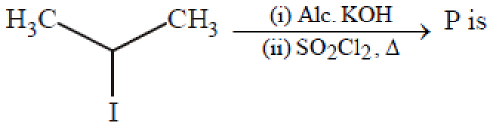
1) $C_2H_5OC_2H_5$ 2) $C_6H_5OCH_3$ 3) $C_6H_5N(CH_3)_2$ 4) Equally in all the three

32. Ethylene dichloride can be prepared by adding HCl to

1) ethane 2) ethylene 3) acetylene 4) ethylene glycol

33. $(CH_3)_3CCl \xrightarrow{NaCN} A \xrightarrow{dil.H_2SO_4} B$ compound B is

1) $(CH_3)_3CCOOH$ 2) $(CH_3)_3COH$ 3) $(CH_3)_3COC(CH_3)_3$ 4)all the three

34.


1) 3-Chloropropene 2) 2-Chloropropene 3) 1-Chloropropene 4) 1, 2-Dichloropropane

35. A solution of (+) –2–chloro–2–phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$, due to the formation of

1) carbanion 2) carbine 3) free-radical 4) carbocation

36. The best method for the conversion of an alcohol into an alkyl chloride is by treating the alcohol with

1) PCl_5 2) dry HCl in the presence of anhydrous $ZnCl_2$

3) $SOCl_2$ in presence of pyridine 4) none of these

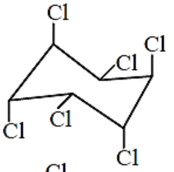
37. A Grignard reagent may be made by reacting magnesium with

1) Methyl amine 2) Diethyl ether 3) Ethyl iodide 4) Ethyl alcohol

38. Silver acetate $Br_2 \xrightarrow{CS_2}$. The main product of this reaction is
1) $CH_3 - Br$ 2) CH_3COH 3) CH_3COOH 4) None of these

39. Which of the following will have the maximum dipole moment?
1) CH_3F 2) CH_3Cl 3) CH_3Br 4) CH_3I

40. Dehydrohalogenation by strong base is slowest in

(a)


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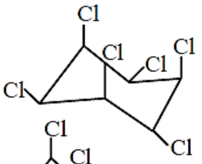

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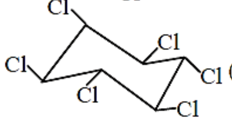

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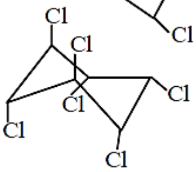

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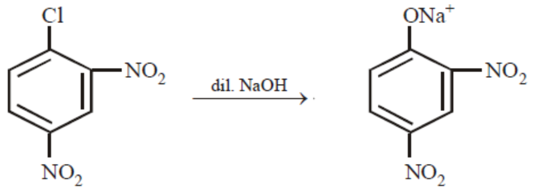


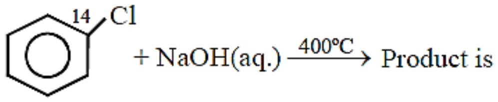
The above transformation proceeds through
1) electrophilic-addition 2) benzyne intermediate
3) activated nucleophilic substitution 4) S_N1

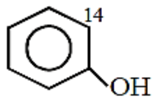
42. Which of the following is liquid at room temperature (b.p. is shown against it)?

1) CH_3I	42 °C
2) CH_3Br	3 °C
3) C_2H_5Cl	12 °C
4) CH_3F	–78 °C

43. The decreasing order of boiling points of alkyl halides is
1) RF > RCl > RBr > RI 2) RBr > RCl > RI > RF 3) RI > RBr > RCl > RF 4) RCl > RF > RI > RBr

44.



(a)


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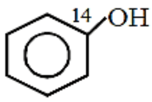


(c) Both (d) No reaction

45. C – Cl bond of chlorobenzene in comparison to C – Cl bond in methyl chloride is
1) Longer and weaker 2) Shorter and weaker
3) Shorter and stronger 4) Longer and stronger

TOPIC 3: Preparation and Properties of Haloarenes

46. Benzene reacts with *n*-propyl chloride in the presence of anhydrous $AlCl_3$ to give
1) 3 – Propyl – 1 – chlorobenzene 2) *n*-Propylbenzene
3) Isopropylbenzene 4) No reaction occurs

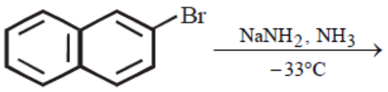
47. Aryl halides cannot be prepared by the reaction of aryl alcohols with PCl_3, PCl_5 or $SOCl_2$ because
1) Phenols are highly stable compounds.
2) carbon-oxygen bond in phenols has a partial double bond character.
3) carbon-oxygen bond is highly polar 4) all of these

48. In the preparation of chlorobenzene from aniline, the most suitable reagent is
1) Chlorine in the presence of ultraviolet light
2) Chlorine in the presence of $AlCl_3$
3) Nitrous acid followed by heating with Cu_2Cl_2 4) hCl and Cu_2Cl_2

49. The correct kinetic rate equation for the addition- elimination mechanism of nucleophilic aromatic substitution

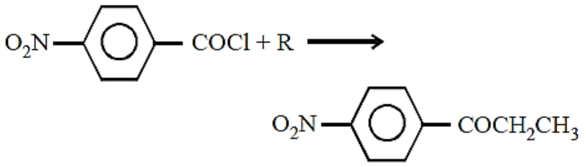
1) Rate = *k* [aryl halide] [nucleophile] 2) rate = *k* [aryl halide]
3) Rate = *k* [aryl halide] [nucleophile]2 4) rate = *k* [nucleophile]

50. How many isomeric naphthylamines are expected in the following reaction?



1) Two 2) only single product 3) four 4) three

51.

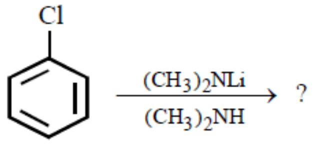


The reagent R may be

CH_3CH_2MgBr I
CH_3CH_2Li II
$(CH_3CH_2)_2Cd$ III
$(CH_3CH_2)_2CuLi$ IV

(a) I or II (b) I or II or III
(c) III or IV (d) Any of the four

52. What is the product of the following reaction?



1) N, N-dimethyl aniline 2) phenyl-lithium (C6H5Li)
3) *para*-chloro-N, N-dimethyl aniline 4) *meta*-chloro-N, N-dimethyl aniline

TOPIC 4: Some Important Polyhalogen Compounds

53. Which of the following is responsible for depletion of the ozone layer in the upper strata of the atmosphere?

1) Polyhalogens 2) Ferrocene 3) Fullerenes 4) Freons

54. Freon-12 is commonly used as

1) insecticide 2) refrigerant 3) a solvent 4) a fire extinguisher

55. Which of the following is used in fire extinguishers

1) CH_4 2) $CHCl_3$ 3) CH_2Cl_2 4) CCl_4

56. If chloroform is left open in air in the presence of sunlight, it gives

1) carbon tetrachloride 2) carbonyl chloride 3) mustard gas 4) lewisite

57. The product formed by heating iodoform with KOH is :

1) HCHO 2) HCOOK 3) CH_3COOK 4) CH_3CHO

58. Ethyl alcohol is used as a preservative for chloroform because it :

1) Prevents aerial oxidation of chloroform
2) Prevents decomposition of chloroform
3) Decomposes phosgene to CO and Cl_2
4) Removes phosgene by converting it to ethyl carbonate

59. Uses of dichloromethane is

1) paint remover 2) solvent in drugs manufacturing
3) metal cleansing and finishing solvent 4) All of the above

60. On warming with silver powder, chloroform is converted into

1) acetylene 2) hexachloroethane
3) 1,1,2,2-tetrachloroethane 4) ethylene

61. $AgNO_3$ does not give precipitate with chloroform because :

1) $CHCl_3$ does not ionise in water 2) $CHCl_3$ is insoluble in water

3) $AgNO_3$ is insoluble in $CHCl_3$ 4) $CHCl_3$ is an organic compound

62. $CHCl_3$ and KOH on heating with a compound forms a bad smelling product (X), X is
1) C_2H_5CN 2) C_2H_5NC 3) C_2H_5OH 4) $C_2H_5NH_2$

63. The compound which forms acetaldehyde when heated with dilute NaOH, is
1) 1, 1-dichloroethane 2) 1, 1, 1-trichloroethane 3) 1-chloroethane 4) 1, 2-dichloroethane

64. Which one of the following has antiseptic property?
1) Dichloromethane 2) Trifluoromethane 3) Triiodomethane 4) Tetrachloromethane

65. The major product formed when 1, 1, 1-trichloro-propane is treated with aqueous potassium hydroxide is:
1) Propyne 2) 1-Propanol 3) 2-Propanol 4) Propionic acid

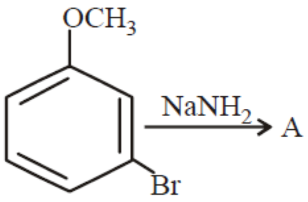
NEET PREVIOUS YEARS QUESTIONS

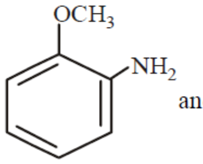
1. The compound C7H8 undergoes the following reactions:

$C_7H_8 \xrightarrow{3Cl_2/\Delta} A \xrightarrow{Br_2/Fe} B \xrightarrow{Zn/HCl} C$ The product 'C' is **[2018]**

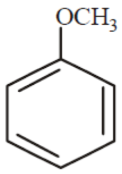
1) m-bromotoluene 2) o-bromotoluene
3) p-bromotoluene 4) 3-bromo-2,4,6-trichlorotoluene

2. Identify A and predict the type of reaction **[2017]**

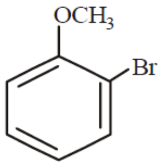


(a)


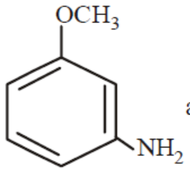
and elimination addition reaction

(c)


and cine substitution reaction

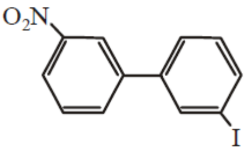
(b)


and cine substitution reaction

(d)


and substitution reaction

3. Which of the following biphenyls is optically active? **[2016]**

(a)


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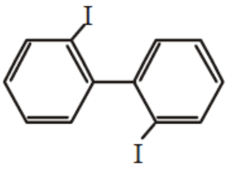

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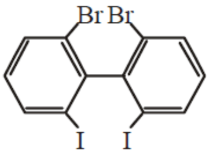
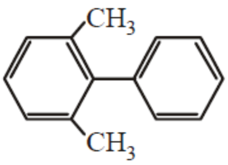
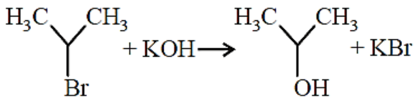
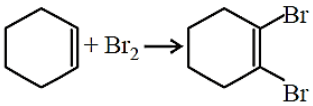


(d)


4. For the following reactions :-

(1) $CH_3CH_2CH_2Br + KOH \rightarrow$
$CH_3CH{=}CH_2 + KBr + H_2O$

(2) 

(3) 

Which of the following statements is correct? **[2016]**

1) (1) and (2) are elimination reaction and (3) is addition reaction
2) (1) is elimination, (2) is substitution and (3) is addition reaction
3) (1) is elimination, (2) and (3) are substitution reactions
4) (1) is substitution, (2) and (3) are addition reaction

5. Which of the following reaction (s) can be used for the preparation of alkyl halides? **[2015]**

(I) $CH_3CH_2OH + HCl \xrightarrow{anh.ZnCl_2}$

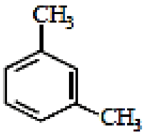
(II) $CH_3CH_2OH + HCl \longrightarrow$

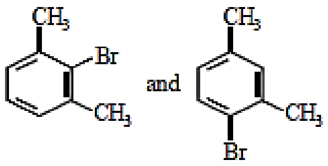
(III) $(CH_3)_3COH + HCl \longrightarrow$

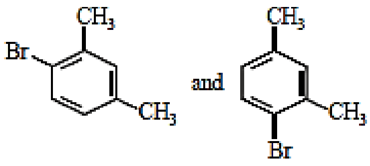
(IV) $(CH_3)_2CHOH + HCl \xrightarrow{anh.ZnCl_2}$

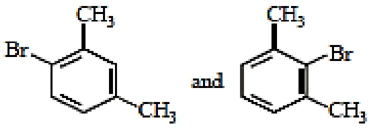
1) (I), (III) and (IV) only 2) (I) and (II) only 3) (IV) only 4) (III) and (IV) only

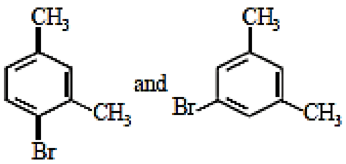
6. What products are formed when the following compounds is treated with Br2 in the presence of FeBr3? **[2014]**



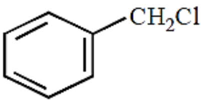
(a) 

(c) 

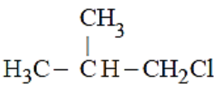
(b) 

(d) 

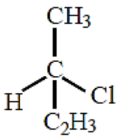
7. Which of the following compounds will undergo racemisation when solution of KOH hydrolyses? **[2014]**

(i) 

(ii) $CH_3CH_2CH_2Cl$

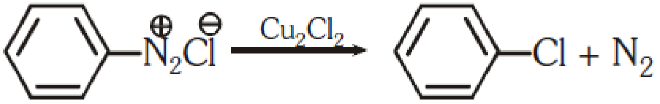
(iii) 

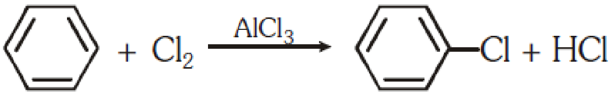
$H_3C-\overset{\displaystyle CH_3}{\overset{|}{C}}H-CH_2Cl$

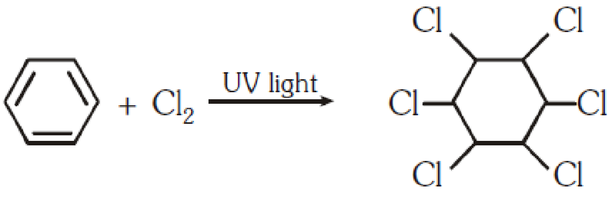
(iv) 

1) (i) and (ii) 2) (ii) and (iv) 3) (iii) and (iv) 4) (iv)

8. Among the following, the reaction that proceeds through an electrophilic substitution is : **[2019]**


(1)

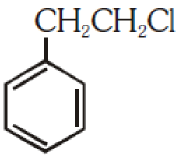

(2)

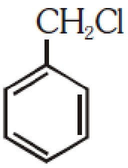

(3)


(4)

9. Which of the following will NOT undergo SN1 reaction with $\overline{O}H$? **[2020-COVID-19]**

(1) $CH_2=CH-CH_2Cl$ (2) $(CH_3)_3CCl$


(3)


(4)

10. The major product formed in dehydrohalogenation reaction of 2-Bromo pentane is Pent-2-ene. This product formation is based on? **[NEET-2021]**

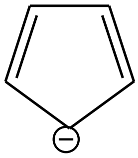
1) Hund's Rule 2) Hofmann Rule 3) Huckel's Rule 4) Saytzeff's Rule

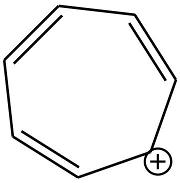
11. The correct sequence of bond enthalpy of 'C-X' bond is **[NEET-2021]**

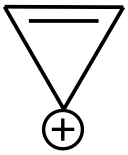
1) $CH_3-F > CH_3-Cl > CH_3-Br > CH_3-I$ 2) $CH_3-F < CH_3-Cl > CH_3-Br > CH_3-I$

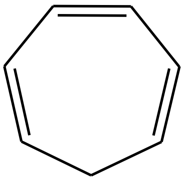
3) $CH_3-Cl > CH_3-F > CH_3-Br > CH_3-I$ 4) $CH_3-F < CH_3-Cl < CH_3-Br < CH_3-I$

12. Which compound amongst the following is not and aromatic compound? **[NEET-2022]**


1)

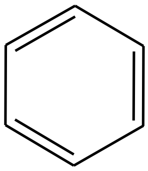

2)

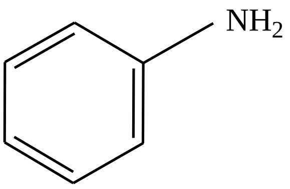

3)


4)

13. Which of the following sequence of reactions is suitable to synthesize chlorobenzene? **[NEET-2022]**

1) Benzene, Cl_2, anhydrous $FeCl_3$ 2) Phenol, $NaNO_2, HCl, CuCl$


3) , HCI


4) , HCI, Heating

14. The incorrect statement regarding chirality is **[NEET-2022]**

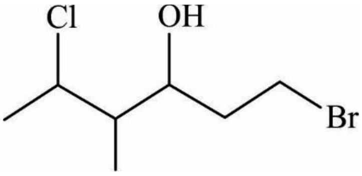
1) S_N1 reaction yields 1: 1 mixture of both enantiomers

2)The product obtained by S_N2 reaction of haloalkane having chirality at the reactive site shows inversion of configuration

3)Enantiomers are superiomposable mirror images on each other

4)A racemic mixture shows zero optical rotation

15. The correct IUPAC name of the following compound is: **[NEET-2022]**



1) 1-bromo-5-chloro-4-methylhexan-3-ol

2) 6-bromo-2-chloro-4-methylhexan-4-ol

3) 1-bromo-4-methyl-5-chlorohexan -3-ol

4) 6-bromo-4-methyl-2-chorohexan-4-ol

16. $CH_3CH_2COO^-Na^+ \overset{NaO+?}{\underset{Heat}{\rightarrow}}$

$CH_3CH_3 + Na_2CO_3$

Consider the above reaction and identify the missing reagent/chemical.

(a) B_2H_6 (b) Red phosphorus

(c) CaO (d) DIBAL-H

17. The compound C_7H_8 undergoes the following reactions :

$C_7H_8 \overset{3Cl_2/\Delta}{\rightarrow} A \overset{Br/Fe}{\rightarrow} B \overset{Zn/HCl}{\rightarrow} C$

The product ' C is

(a) 3-bromo-2, 4, 6-trichlorotoluene

(b) o-bromotoluene

(c) m-bromotoluene

(d) p-bromotoluene

NCERT LINE BY LINE QUESTIONS – ANSWERS

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

(41.)	b	**(42.)**	d	**(43.)**	c	**(44.)**	b	**(45.)**	b
(46.)	b	**(47.)**	b	**(48.)**	a	**(49.)**	c	**(50.)**	b

TOPIC WISE PRACTICE QUESTIONS - ANSWERS

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

NEET PREVIOUS YEARS QUESTIONS-ANSWERS

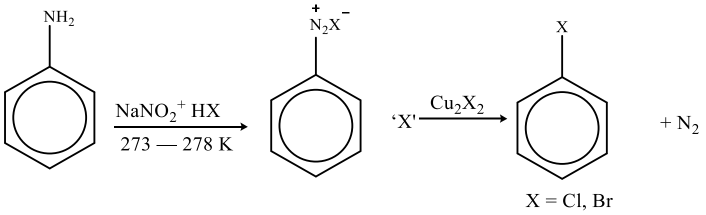
1) 1	**2)** 4	**3)** 2	**4)** 2	**5)** 1	**6)** 3	**7)** 4	**8)** 2	**9)** 3	**10)** 4
11) 1	**12)** 4	**13)** 1	**14)** 3	**15)** 1	16)c	17)c			

NCERT LINE BY LINE QUESTIONS – SOLUTIONS

(1.) **(a)** Product 'A+B' is racemic mixture and process involved is racemisation Here, 50:50 mixture of A and B is obtained.

(2.) **(a)** Solubility of haloalkanes in water is low. In order to dissolve, energy is required to overcome the attractions between haloalkane molecules and break the hydrogen bonds between water molecules. However, it tends to dissolve in organic solvents.

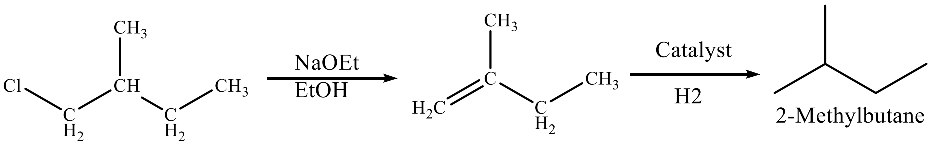
(3.) **(c)** Reaction **(c)** is Sandmeyer's reaction



(4.) **(a)** The reaction between CH_3Cl and hydroxide ion to yield methanol and chloride ion follows a second order kinetics, i.e. the rate depends upon the concentration of both reactants.

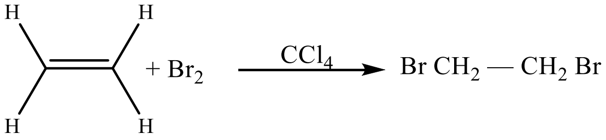
(5.) **(b)** Boiling point of isomeric haloalkanes decreases with increase in branching as with increase in branching surface area decrease which leads to decrease in intermolecular forces.

(6.) (c)



(7.) **(c)** Statement **(c)** is incorrect.
For dihalogen derivatives, the prefixes o-, m- and p- are used in common system but in IUPAC system, the numerals 1,2; 1,3 and 1,4 are used.

(8.) **(a)** The product 'X' is $BrCH_2-CH_2Br$. The reaction is as follows:



(9.) **(a)** Carbon compounds containing more than one halogen atom are usually referred to as polyhalogen compounds.

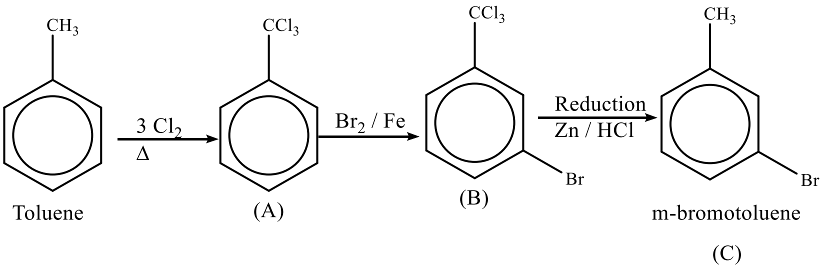
(10.) **(c)** I → q, II → r, III → p, IV → s

- Chloramphenicol is an antibiotic produced by microorganisms used in treatment of typhoid fever.
- Iodine containing hormone is thyroxine.
- Chloroquine is used for the treatment of malaria.
- Halothane is used as an anaesthetic during surgery.

(11.) **(a)** The given reaction is nucleophilic substitution reaction. In this reaction, a nucleophile replaces already existing nucleophile in a molecule.

(12.) **(d)** I → q, II → r, III → p

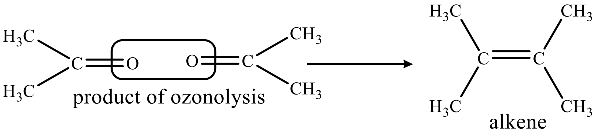
(13.) (d)



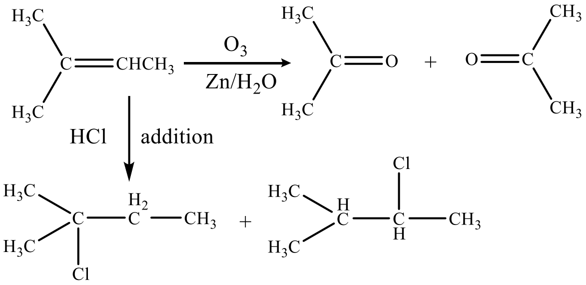
(14.) **(d)** Arylhalides are extremely less reactive towards nucleophilic substitution reactions due to following reasons

- Resonance effect
- Difference in hybridisation of carbon atom in C−X bond
- Instability of phenyl cation

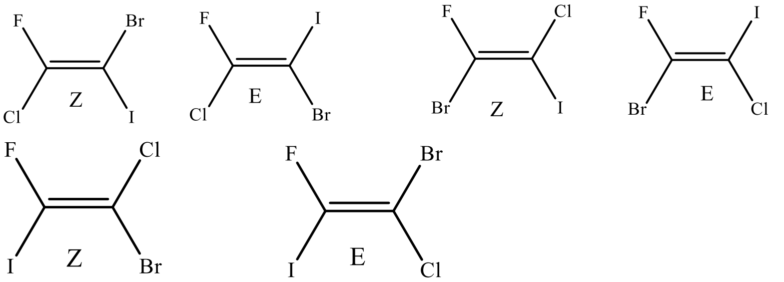
(15.) **(b)** The product of ozonolysis can give an idea about probable alkene. These are represented as follows



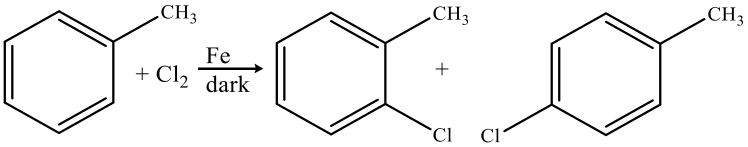
Complete reaction is as follows



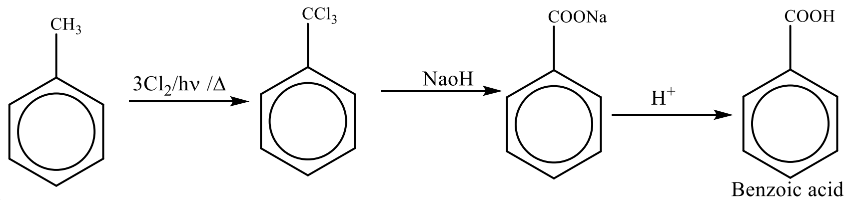
(16.) **(d)** Six isomers are possible.



(17.) **(a)** Arylchloride can be easily prepared by electrophilic substitution of arenes with chlorine in the presence of Lewis acid catalyst like iron or iron (III) chloride



(18.) **(b)** Thionyl chloride is preferred because in this reaction alkyl halide is formed along with gases SO$_2$ and HCl. The two gaseous products are escapable



(19.) (d)

(20.) **(a)** An alkene is connected to corresponding alkyl halide by reaction with hydrogen chloride. The reaction proceed via addition of hydrogen halides.

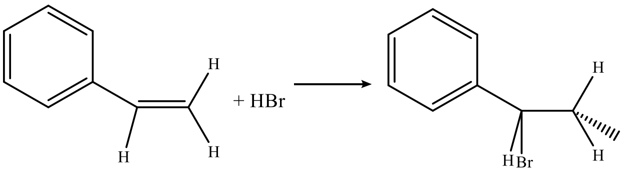
(21.) **(a)** Chloroform is the polyhalogen compound which is employed as a solvent for fats, alkaloids, iodine and other substances.

(22.) **(c)** Statements II, III and IV are correct while statement I is incorrect. The dihalo compounds having both the halogen atoms are further classified as geminal halides or gem-dihalides and vic-dihalides.

(23.) **(a)** The boiling points of isomeric haloalkanes decrease with increase in branching.

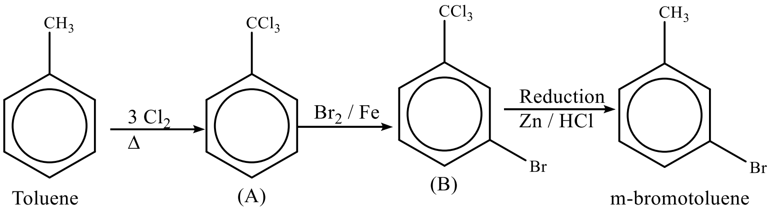
(24.) **(c)** When the compound rotates the plane of plane polarised light to the right i.e. clockwise direction,it is called dextrorotatory or the d-form and is indicated by placing a positive sign before the degree of rotation.

(25.) (a)

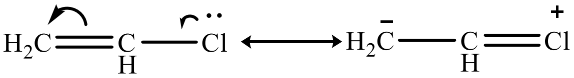


(26.) **(a)** CCl_4 (tetrachloromethane) is used as feedstock in the synthesis of chlorofluorocarbons and other chemicals, pharmaceutical manufacturing.

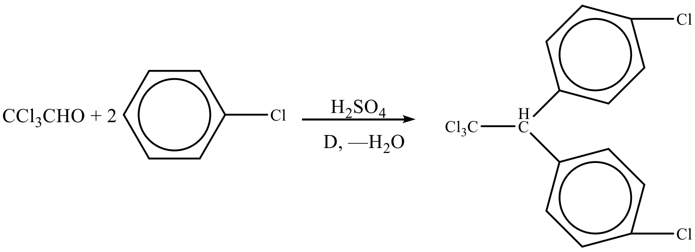
(27.) **(c)** The reaction is as follows:



(28.) **(b)** Vinyl chloride itself shows resonance structure and thus stabilised. As vinyl chloride has partial double bond character thus breaking of C−Cl bond is difficult which makes vinyl chloride less reactive than alkyl chloride.



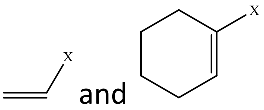
(29.) **(c)**When chlorobenzene is heated with chloral in the presence of conc. H_2SO_4, a powerful insecticide, DDT is formed with the elimination of H_2O molecule.



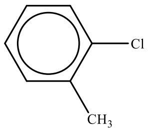
(30.) **(c)** Alkyl iodides in general turn brown due to liberation of I_2 on decomposition by the action of air and light.

(31.) **(d)** All given statements are correct

(32.) **(d)** Option **(d)** does not show a correct match. Vinyl halide are the compounds in which a halogen atom is bonded to a sp2 hybridised carbon atom of a carbon–carbon double bond $\left(C = C\right)$



(33.) **(b)** CCl_4 is used as a fire extinguisher. The dense, non-combustible vapours cover the burning substance and prevents the availability of oxygen around burning material.



(34.) **(a)** is a benzylic halide. There is a partial double bond character between sp^3hybridised C atom next to an aromatic ring and Cl. It is most difficult to break this bond .Hence, it undergoes hydrolysis with slowest rate.

(35.) **(c)** Molecules of organic halogen compounds are generally polar. Due to greater polarity as well as higher molecular mass as compared to the parent hydrocarbon, the bimolecular forces of attraction are stronger in the halogen derivatives. That is why the boiling points of chlorides are higher than those of the hydrocarbons of comparable molecular mass.

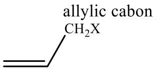
(36.) **(d)** NO_2 groups withdraw electrons at orthoand para-position and then deactivate the ring. This deactivation of ring stabilises the negatively charged intermediates formed during the reaction and therefore, increases the reactivity towards replacement.

(37.) **(b)** The products obtained are $CH_3CH_2CH_2CH_2Cl$ and $CH_3CH_2CHClCH_3$. The reaction proceed in a free radical chlorination of alkanes. Complete reaction is as follows:

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{Cl_2\ /\ \text{UV Light}} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

(38.) **(a)** S_N1 reaction depends on the stability of carbocation, greater will be its ease of formation from alkyl halide and faster will be the rate of reaction. In case of alkyl halides 3°alkyl halide undergo S_N1 reaction very fast because of high stability of 3°carbocations.

(39.) **(c)** Allylic halide are the compounds in which the halogen atom is bonded to an sp^3 hybridised carbon atom adjacent to $C-C$ double bond ($C-C$) i.e. to an allylic carbon.



(40.) **(c)** Given reaction is known as a Finkelstein reaction. NaI is soluble in acetone and NaCl, NaBr are not, the equilibrium is shifted by the precipitation of insoluble salt

$$R-X \xrightarrow[\text{Ma}]{MX'} R-X'$$

(41.) (b)

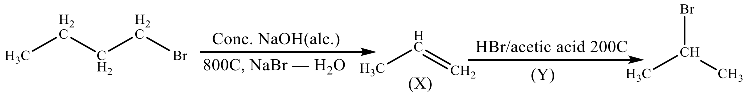
(42.) **(d)** Reaction **(d)** is nucleophilic substitution while others are electrophilic substitution.

(43.) **(c)**

(44.) **(b)** Greater the molecular mass, stronger the van der Waal's forces of attraction and hence, higher is the melting point or boiling point.

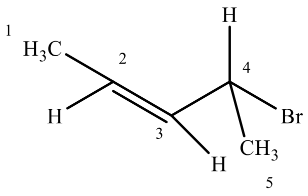
(45.) **(b)** Among dichlorobenzenes, the p-isomer being symmetrical packs closely in the crystal lattice and hence, has much higher melting point than o- and m-isomers.

(46.) **(b)** In the given reaction, the haloalkane on reaction with hydrogen atom is heated with alc. solution of KOH. There is elimination of hydrogen atom from -carbon and a halogen atom -carbon atom.



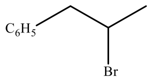
(47.) (b)

(48.) **(a)** The correct name of the given compound is



4-bromopent-2-ene

(49.) **(c)** Breathing about 900 parts of chloroform per million parts of air (900 parts per million) for a short time can cause dizziness, fatigue and headache.

(50.) **(b)** The reaction of $C_6H_5CH\ CHCH_3$ with HBr produces 

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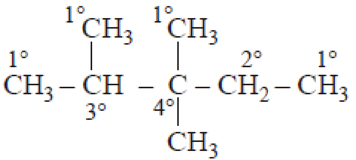
TOPIC WISE PRACTICE QUESTIONS - SOLUTIONS

1. (2) In alkyl halides halogen atom(s) is attached to sp^3 hybridised carbon atom.
2. (4) 4-Bromobut-l-ene is not an allylic halide

$$\underset{\text{4-Bromobut-1-ene}}{BrH_2C-CH_2-CH=CH_2}$$

3. 2)



$$\begin{array}{c} \quad\quad\ {}^{1°}CH_3 \quad {}^{1°}CH_3 \\ \overset{1°}{CH_3}-\underset{3°}{CH}-\underset{4°}{C}-\overset{2°}{CH_2}-\overset{1°}{CH_3} \\ \quad\quad\quad CH_3 \end{array}$$

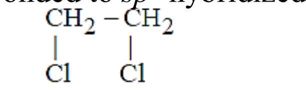
2,3,3-trimethylpentane

4. 1)
5. 2) Weaker the base, better the leaving group. Hence

$$\xrightarrow{\text{Decreasing order of basicity}}$$
$$\underset{(II)}{OMe}\quad \underset{(I)}{OAc}\quad \underset{(III)}{OSO_2Me}\quad \underset{(IV)}{OSO_2CF_3}$$
$$\xleftarrow[\text{Decreasing order of leaving group}]{}$$

6. 4)
7. 3) In allylic halides hydrogen atom is bonded to sp^3hybridized carbon atom. Whereas in vinylic halide, hydrogen atom is bonded to sp^2 hybridized carbon atom.

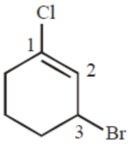
CH_3CHCl_2
Ethylidene chloride
(gem-dihalide)



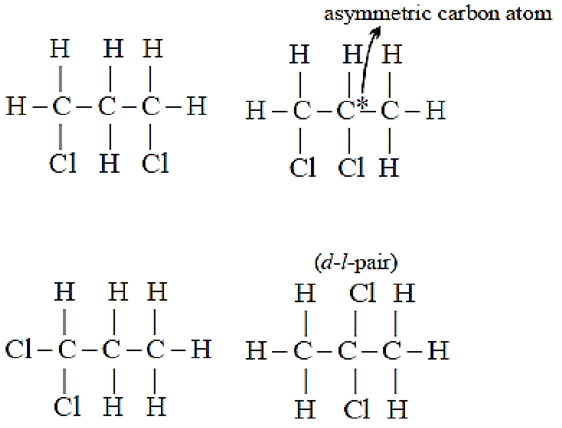
$$\underset{Cl}{CH_2}-\underset{Cl}{CH_2}$$

Ethylene dichloride (vic-dihalide)

8. 3)



9. 3) The compound is $C_3H_6Cl_2$ and the number of possible isomeric compounds is 5



$$\begin{array}{ccccccc} & H & & H & & H & \\ H- & C & - & C & - & C & -H \\ & Cl & & H & & Cl & \end{array} \qquad \begin{array}{ccccccc} & H & & H & & H & \\ H- & C & - & C^* & - & C & -H \\ & Cl & & Cl & & H & \end{array}$$

$$\begin{array}{ccccccc} & H & & H & & H & \\ Cl- & C & - & C & - & C & -H \\ & Cl & & H & & H & \end{array} \qquad \begin{array}{ccccccc} & H & & Cl & & H & \\ H- & C & - & C & - & C & -H \\ & H & & Cl & & H & \end{array}$$

10. 3) Stability of the three corresponding carbocations

$$\underset{\text{Allyl Carbocation}}{CH_2=CH\overset{+}{C}HCH_3} > \underset{\text{2° Carbocation}}{CH_3CH_2\overset{+}{C}HCH_3} > \underset{\text{1° Carbocation}}{CH_3CH_2\overset{+}{C}H_2}$$

11. 4) All given reactions give the vinyl chloride by substitution 1), by dehydrohalogenation 2) and by addition 3)

12. (2) Reaction (i) is not possible because OH^- is a stronger base than Cl^-; hence it can't be replaced by Cl^-. However, in reaction (ii) OH group is first protonated to form $R\overset{+}{O}H_2$ in which H_2O, being a very weak base, is easily replaced by Cl^-.

13. (2) At high temp. i.e., 400°C substitution occurs in preference to addition.

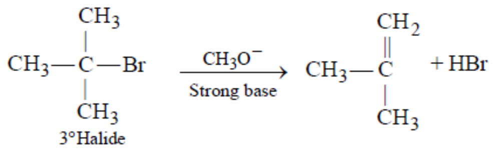
$$CH_3CH=CH_2 \xrightarrow[-HCl]{Cl_2,\,400°C} ClCH_2CH=CH_2$$

14. 2)

$$CH_3-CH_2-CHCl_2 \xrightarrow[\Delta]{NaNH_2}$$

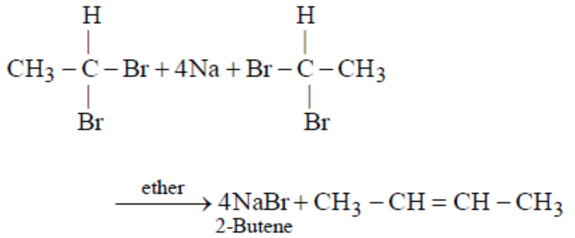
$$CH_3-CH=CHCl \xrightarrow[\Delta]{NaNH_2} \underset{\text{Final Product}}{CH_3-C\equiv CH}$$

15. 2) 3° alkyl halides on reaction with strong base (CH_3O^-) undergo elimination reaction and forms alkene as major product.



$$\underset{\text{3°Halide}}{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br} \xrightarrow[\text{Strong base}]{CH_3O^-} CH_3-\overset{CH_2}{\overset{\|}{\underset{CH_3}{C}}} + HBr$$

16. 3)



$$CH_3-\overset{H}{\underset{Br}{C}}-Br+4Na+Br-\overset{H}{\underset{Br}{C}}-CH_3$$

$$\xrightarrow{\text{ether}} 4NaBr+\underset{\text{2-Butene}}{CH_3-CH=CH-CH_3}$$

17. 4) $CH\equiv CH \xleftarrow{-HCl} CH_2=CHCl \xrightarrow{H_2} CH_3CH_2Cl$

18. 4)

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} \xrightarrow{AgCN} \underset{\text{Ethyl isocyanide}}{C_2H_5NC} \xrightarrow{\text{Reduction}}$$

$$\underset{\text{Ethylmethylamine}}{C_2H_5NHCH_3}$$

19. 2) Addition of HBr to 2-pentyne gives two structural isomers (I) and (II)

$$CH_3-C\equiv C-CH_2CH_3 \xrightarrow{HBr}$$

$$\underset{(I)}{CH_3C(Br)=CHCH_2CH_3}+\underset{(II)}{CH_3CH=C(Br)CH_2CH_3}$$

Each one of these will exist as a pair of geometrical isomers. Thus, there are two structural and four configurational isomers.

20. 4) Debromination is a *trans*-elimination reaction. *meso*- 2, 3-Dibromobutane on debromination gives *trans*-2-butene.

21. 2)

22. 3) Thionyl chloride is preferred because the other two products formed in the reaction are escapable gases. Hence the reaction gives pure alkyl halides

$$ROH+SOCl_2 \rightarrow R-Cl+SO_2\uparrow+HCl\uparrow$$

23. 4) Except 4) all contain abstractable proton

24. (3)

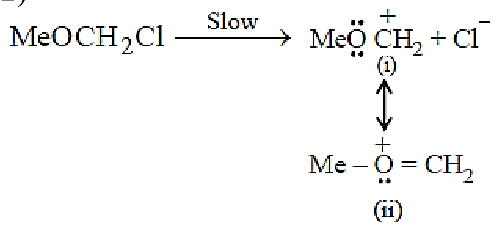
25. (3) At a bridge head position S_N1 and S_N2 do not takes place.

26. 2)

$$C_2H_5I \xrightarrow{\text{alc. KOH}} CH_2=CH_2 \xrightarrow{Br_2}$$

$$BrCH_2\text{-}CH_2Br \xrightarrow{KCN} CNCH_2CH_2CN$$

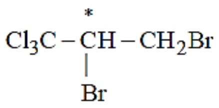
27. 2)



Though (ii) contains +ve charge on oxygen. Since octet around each atom is complete the structure II is more stable than I.

28. (3) The compound A is

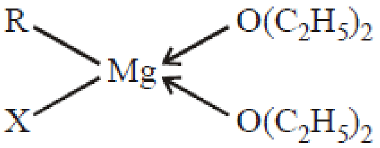
$$Cl_3CCH_2CH_2Cl \xrightarrow{aq.KOH} (OH)_3CCH_2CH_2OH \xrightarrow{-2H_2O} HOCH_2CH_2COOK$$

The compounds B is  $Cl_3C-\overset{*}{C}H(Br)-CH_2Br$ has chiral centre and can be resolved into *d* and *l* form.

29. 2) The more is the stability of intermediate carbonium ion, the more is the chance of SN1 mechanism. The intermediates obtained will be . $Ph\overset{+}{C}H_2$ (i) $Ph\overset{+}{C}H-Me$ (ii), $Ph\overset{+}{C}-Me_2$ (iii), $Ph\overset{+}{C}MePh$ (iv) .The stabilty is of the order iv > iii > ii > i.

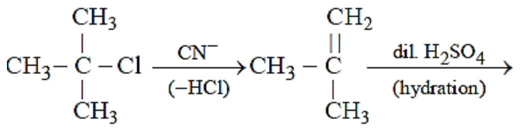
30. (3) Isopropyl chloride, being 2° alkyl halides, can undergo SN1 as well as SN2 mechanism.

31. (1) Although all the three compounds can be used for preparing Grignard reagents, diethyl ether is considered as the best because it provides electron pairs to Mg of the reagent fully for coordination, in case of $C_6H_5OCH_3$ and $C_6H_5N(CH_3)_2$ electron pair on O and N are partialy delocalised over the benzene and hence are less available for coordination with Mg.

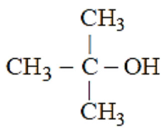


32. (4) Ethylene dichloride can be prepared by adding HCl to ethylene glycol (CH_2OH. CH_2OH).

33. (2) CN– is a strong base and since the substrate is a *tert*halide, it mainly udnergoes elimination reaction forming alkene 1). In presence of dil. H_2SO_4, alkenes undergo hydration in Markovnikov's way.

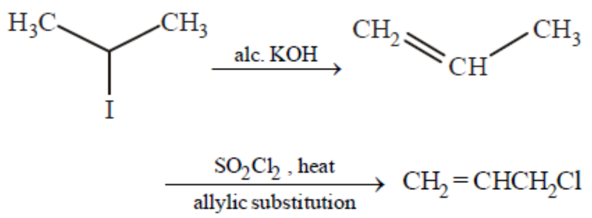


A

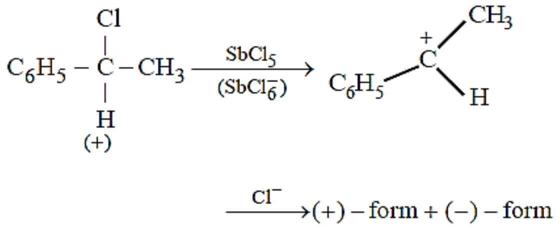


B

34. 1)



35. 4) Occurrence of racemization points towards the formation of carbocation as intermediate, which being planar can be attacked from either side.



36. 3) $R-OH + SOCl_2 \xrightarrow{\text{Pyridine}} RCl + SO_2\uparrow + HCl\uparrow$

SO2 and HCl being gases escape leaving behind pure alkyl halide.

37. 3) $CH_3CH_2I + Mg \xrightarrow[\text{ether}]{\text{Dry}} \underset{\text{Ethyl magnesium iodide}}{CH_3CH_2MgI}$

38. 1) $CH_3COOAg + Br_2 \xrightarrow{CS_2} CH_3Br + AgBr + CO_2$

39. 2) CH3Cl has higher dipole moment than CH3F due to much longer C–Cl bond length than the C–F bond. The much longer bond length of the C–Cl bond outweighs the effect produced by lower electronegativity of Cl than that of F.

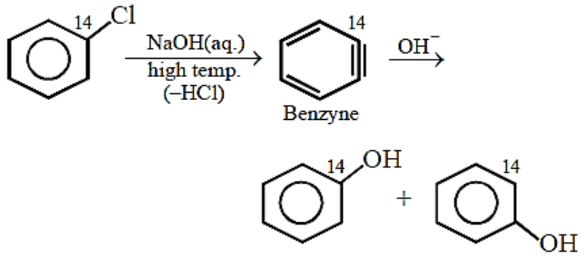
40. (3)

41. (3)

42. (1) Boiling point of CH3I is 42°C which indicates that it is liquid at room temperature. CH3I is larger molecule so it has stronger vander Waal's force of attraction than others.

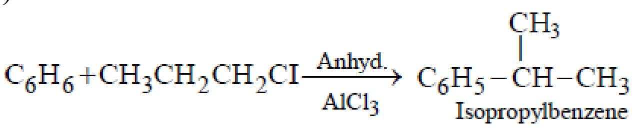
43. (3) For the same alkyl group, the boiling points of alkyl halides decrease in the order :
RI > RBr > RCl > RF This is because with the increase in size and mass of halogen atom, the magnitude of van der Waal's forces increases.

44. 3)



45. 3) Due to resonance in chlorobenzene

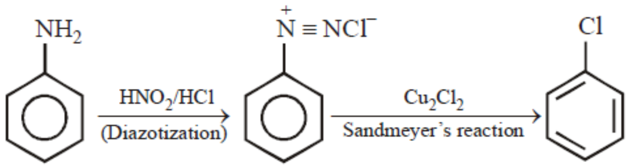
46. 3)



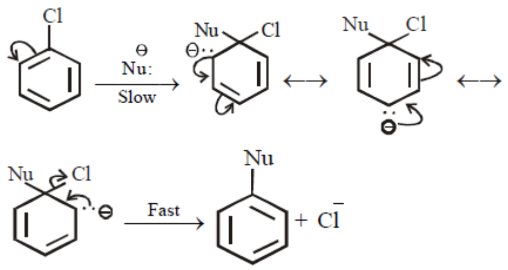
$$C_6H_6 + CH_3CH_2CH_2Cl \xrightarrow[AlCl_3]{\text{Anhyd.}} \underset{\text{Isopropylbenzene}}{C_6H_5-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_3}$$

47. 2) This method is not applicable for the preparation of aryl halides because the C–O bond in phenol has a partial double bond character and is difficult to break being stronger than a single bond.

48. 3)



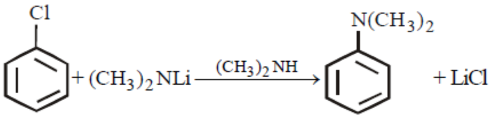
49. 1)



Rate ∝ $[C_6H_5Cl][\bar{Nu}:]$

50. 1)

51. 3) Organomagnesium and organolithium compounds can’t be prepared from the alkyl (or aryl) halide having $–NO_2$ group. On the other hand, organocopper and organocadmium compounds, do not react with the $–NO_2$ group.



52. 1)

53. 4) 54. 2)

55. 4) CCl_4 vapours are non-inflammable (*i.e.* do not catch fire). Hence used as fire extinguishers under the name pyrene.

$$CHCl_3 + \frac{1}{2}O_2 \xrightarrow{\text{Light}} COCl_2 + HCl$$

56. 2)

57. 2)

$$\begin{tikzcd}
\underset{\text{iodoform}}{CHI_3} + 3KOH \arrow[r] & CH(OH)_3 + 3KI \arrow[d] \\
HCOOK & HCOOH + H_2O \arrow[l, "KOH"']
\end{tikzcd}$$

58. 4) $CHCl_3$ on exposure to air forms phosgene which is poisonous gas and removed by converting it into diethyl carbonate (which is non-poisonous substance).

$$CHCl_3 \xrightarrow{O_2/\text{light}} \underset{\substack{\text{Phosgene} \\ \text{(Poisonous)}}}{COCl_2} + HCl$$

$$COCl_2 + 2C_2H_5OH \longrightarrow \underset{\substack{\text{Diethyl carbonate} \\ \text{(non-poisonous)}}}{(C_2H_5)_2CO_3} + 2HCl$$

59. (4) Dichloromethane is widely used as solvent as a paint remover, as a propellant in aerosols and as a process solvent in the manufacture of drugs. It is also used as a metal cleansing and finishing solvent.

60. 1) $HCCl_3 + 6Ag + HCCl_3 \xrightarrow{\Delta} HC \equiv CH + 6AgCl$

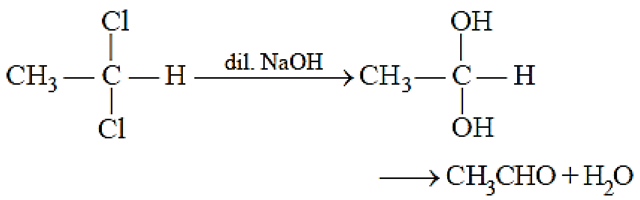
61. (1) Since $CHCl_3$ is covalent compound it does not produce Cl^- ion in H_2O, hence no white ppt is formed during reaction with $AgNO_3$

62. (2) This is carbylamine reaction which is used to detect presence of 1° amine in organic compounds. The bad smelling compound is isocyanide.

$$\underset{\text{Chloroform}}{CHCl_3} + 3KOH + \underset{\text{Ethyl amine}}{C_2H_5NH_2} \longrightarrow$$

$$\underset{\text{Ethylisocyanide}}{C_2H_5N \equiv C} + 3KCl + 3H_2O$$

63. 1) 1, 1-dichloroethane on heating with dil. NaOH gives acetaldehyde.

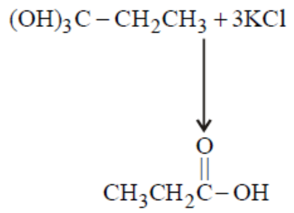


$$CH_3-CCl_2-H \xrightarrow{\text{dil. NaOH}} CH_3-C(OH)_2-H \longrightarrow CH_3CHO + H_2O$$

64. (3) Triiodomethane (CHI_3) when comes in contact with organic matter decomposes easily to free iodine which has antiseptic property.

65. 4)

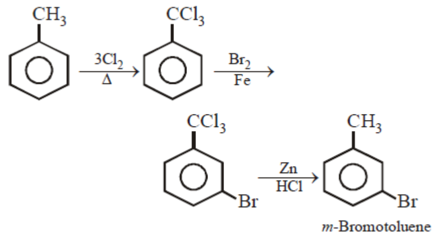
$$Cl_3C-CH_2CH_3 + KOH \xrightarrow{\text{heat}}$$



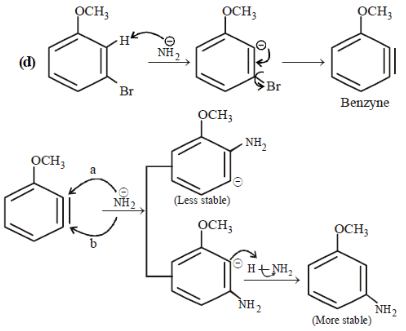
$$(OH)_3C-CH_2CH_3 + 3KCl \longrightarrow CH_3CH_2\overset{O}{\overset{\|}{C}}-OH$$

NEET PREVIOUS YEARS QUESTIONS-EXPLANATIONS

1. 1)

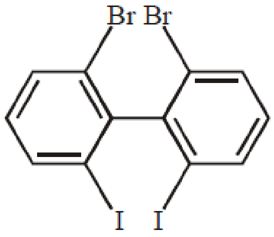


2. 4)



More stable as –ve charge is close to electron withdrawing group. Also, incoming nucleophile gets attached on same 'C' on which 'Br' (Leaving group) was present. ∴ not a cine substitution reaction

3. 2)

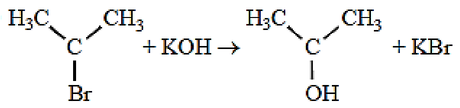


is optically active due to absence of plane of symmetry and center of symmetry

4. 2) a)

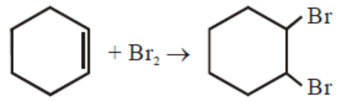
$$CH_3CH_2CH_2–Br+KOH$$
$$\rightarrow CH_3CH=CH_2 + KBr + H_2O$$

This is dehydrohalogenation reaction which is an example of elimination reaction.



b)

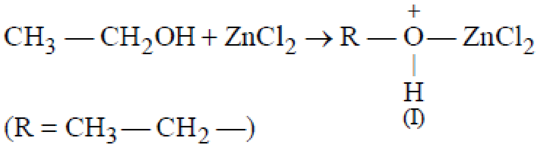
Replacement of Br^- by OH^- is substitution reaction thus it is a nucleophilic substitution reaction.



c)

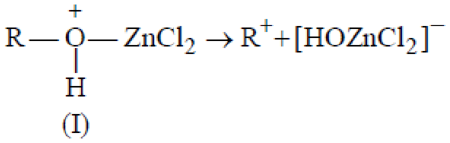
Above reaction involves addition of Br_2 across double bond. Thus it is called addition reaction

5. a) $ZnCl_2$ is a lewis acid and interact with alcohol.



$$CH_3-CH_2OH + ZnCl_2 \rightarrow R-\underset{\underset{(I)}{H}}{\overset{+}{\underset{|}{O}}}-ZnCl_2$$

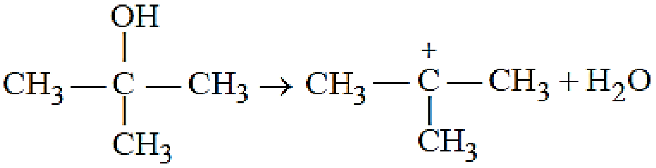
$$(R = CH_3-CH_2-)$$



$$R-\underset{\underset{(I)}{H}}{\overset{+}{\underset{|}{O}}}-ZnCl_2 \rightarrow R^+ + [HOZnCl_2]^-$$

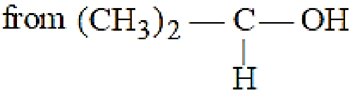
Carbocation is formed as intermediate in the S_N^1 mechanism which these reaction undergoes.

In the absence of $ZnCl_2$ formation of primary carbocation is difficult which is the case with (ii) while (i) undergoes reaction. (iii) Tertiary carbocation casily formed due to the stability

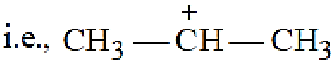


$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 \rightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{+}{C}}-CH_3 + H_2O$$

(iv) In the presence of $ZnCl_2$, 2° carbocation is formed

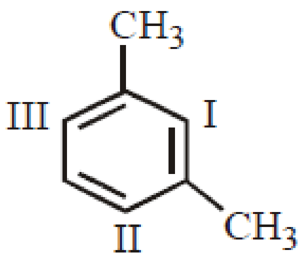


$$\text{from } (CH_3)_2-\underset{\underset{H}{|}}{C}-OH$$

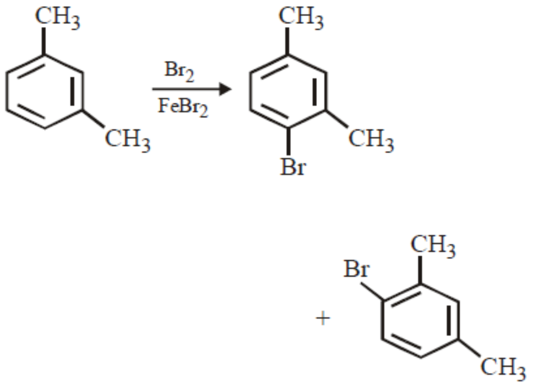


$$\text{i.e., } CH_3-\overset{+}{CH}-CH_3$$

6. 3) Methyl group is ortho para directing but due to steric hinderce effect, generated by two CH_3 groups substitution will not take place on position (I). Hence only two products are possible.



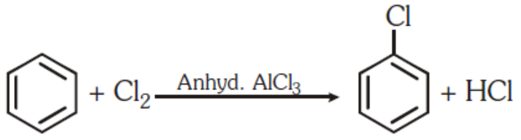
i.e.



7. (4) Out of the given four compounds only (iv) compound is chiral and hence only this compound will undergo racemisation.

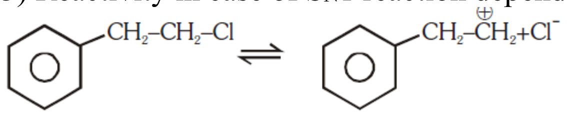
8. 2)Halogenation (Electrophilic substitution reactions) : Arenes react with halogens in the

presence of a Lewis acid like anhydrous $AlCl_3$



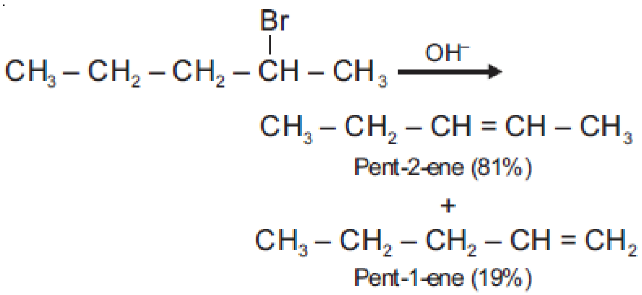
Chlorobenzene

9 3) Reactivity in case of S_N1 reaction depends upon formation of carbocation.



Primary carbocation
is less likely to be formed
(due to unstability)

10. 4)Major product formed in dehydrohalogenation reaction of 2-bromopentane is pent-2-ene because according to Saytzeff's rule, in dehydrohalogenation reactions, the preferred product is that alkene which has greater number of alkyl group(s) attached to the doubly bonded carbon atoms.



$$CH_3-CH_2-CH_2-\overset{\overset{\displaystyle Br}{|}}{C}H-CH_3 \xrightarrow{OH^-}$$

$$CH_3-CH_2-CH=CH-CH_3$$

Pent-2-ene (81%)

+

$$CH_3-CH_2-CH_2-CH=CH_2$$

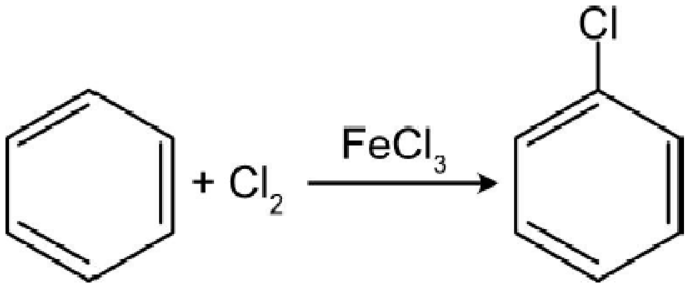
Pent-1-ene (19%)

11. 1)The size of halogen atom increases from F to I hence bond length from C – F to C – I increases Bond enthalpy from CH_3 – F to CH_3 – I decreases

C – X Bond	Bond dissociation enthalpies/kJ mol^{-1}
CH_3 — F	452
CH_3 — Cl	351
CH_3 — Br	293
CH_3 — I	234

12. $(4n+2)\pi\ e^-$ is not equal to 6

13.



The reaction is aromatic electrophilic substitution reaction

14. Enantiomers are not super imposable mirror images of each other

15. 1-bromo, 5 – chloro 4- methyl hexan – 3 ol
1+3+4+5-13/2+3+4+6-

16.Ans.(c)

In this reaction, removal of carbon dioxide takes place. So, this is a decarboxylation reaction. A decarboxylation reaction takes place with soda lime (NaOH + CaO) So, missing reagent is CaO

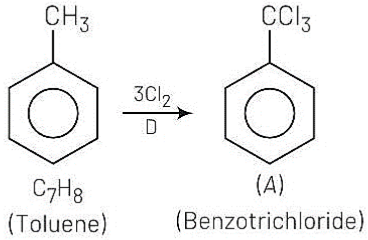
17.Ans. (c)

Given

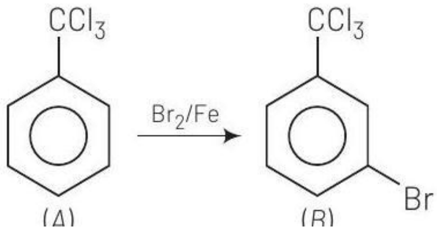
$$C_7H_8 \xrightarrow{3Cl_2/\Delta} A \xrightarrow{Br_2/Fe} B \xrightarrow{Zn/HCl} C$$

The reaction in the above road map can be explained by the following steps

Step I Toluene (A) undergoes side chain halogenation with excess of chlorine to give benzotrichloride(A)



Step II In compound (A), the substituent CCl_3 is an electron withdrawing group, so the electrophile will attack at m-position. Thus, benzotrichloride reacts with bromine in presence of Fe- catalyst to give m-bromobenzotrichloride (B).



m-bromobenzotrichloride

Step III m-bromobenzotrichloride undergoes reduction with Zn in presence of HCl to give m-bromotoluene (C).