10. HALOALKANES AND HALOARENES



Chemistry Smart Booklet Theory + NCERT MCQs + Topic Wise Practice MCQs + NEET PYQs





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
- 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 numbress in thefingers and toes.

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Clum

- 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)



Uses:

- 1. Chemically, chloroform is used as a solvent for fats, alkaloids, iodine and other substances.
- 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 It was once used as a general anaesthetic in surgery but has been replaced by less toxic, saferanaesthetics such as ether.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.

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

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 Because of its objectionable smell, it has been replaced by other formulations containing iodine.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 CCl₄ 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



- 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 the effectiveness 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 of the world.

Preparation

Methods of Preparation of haloalkanes

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



By halogenations of alkenes with HX :





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.



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 (PX₅ or PX₃)

Thionyl chloride (SOCl₂)

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 ZnCl₂, which act as a catalyst in this reaction.

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

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.



Example of Preparation of Bromoethane from Ethanol

CH₃CH₂OH + NaBr + H₂SO₄ \longrightarrow CH₃CH₂Br + NaHSO₄ + H₂O 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 (PX₅ or PX₃)

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:

 $ROH + PCI_5 \rightarrow RCI + POCL_3 + HCI$

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.

 $ROH \xrightarrow{Red \ phosphorus/Br_2} R - Br$ Red Phosphorus/I2 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.

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

Example: Reaction of ethanol with PCl₃ for the formation of chloroethane

3CH₃CH₂OH + PCl₃ -----> 3CH₃CH₂Cl + H₃PO₃

Reaction of Ethanol with PCI₃

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 (SOCI2) 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.

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\mathsf{CH}_3\mathsf{CH}_2\mathsf{OH}+\mathsf{SOCI}_2 \rightarrow \mathbf{CH}_3\mathbf{CH}_2\mathbf{CI}+\mathsf{SO}_2 \uparrow +\mathsf{HCI} \uparrow
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Reaction of Ethanol with SOCI2

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.

 $CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2/h\nu} CH_3CH_2CH_2CH_2CH_2CH + CH_3CH_2CH(Cl)CH_3$

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



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.



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. HNO₃ or HIO₄ 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, HNO₂ is prepared within the reaction by reacting sodium nitrite and HX in the temperature of 273-278K.



Mechanism of the Sandmeyer's Reaction

In the first step

 $NaNO_2 + HCI \rightarrow HNO_2 + NaCI$

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 H₂O. In the second step, the diazonium salt reacts with cuprous halide to form the respective aryl halide



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



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.

CH₃CH=CH₂ + HBr

CH3-CH2-CH2-Br

Alliant Academy

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.



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 + Nal \rightleftharpoons R - I + NaX C₂H₅ - CI + Nal \rightleftharpoons C₂H₅ - 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/RCI. The reaction is carried out in the presence of metallic fluoride such as SbF₃, Hg₂F₂, AgF, CoF₂.

$CH_3Br + AgF \rightarrow CH_3F + AgBr$

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 (SOX₂) 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 byproducts are gaseous SO₂ 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.

 $ROH + SOCl_2 \qquad \frac{Pyridine}{Reflux} RCI + SO_2 + HCI$

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 AlCl₃, FeCl₃ etc. at low temperatures. It is



Sandmeyer reaction:

Diazonium salts are highly reactive compounds used to prepare arene derivatives. Treating diazonium salt with copper (I) chloride (Cu₂Cl₂) or copper (I) bromide (Cu₂Br₂) 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> RCI> 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.



- 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 metaisomers.
- 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

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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.

 $2\text{R-I} \rightarrow \text{R-R} + \text{I}_2$

lodoform 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



- (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.) $\operatorname{ClCH}_2(\operatorname{CH}_3)_2\operatorname{CH}_3$ (b.) $\operatorname{ClCH}_2\operatorname{CH}_2\operatorname{CH}_2\operatorname{CH}_3$ (c.) $\operatorname{ClCH}_2\operatorname{CH}(\operatorname{CH}_3)\operatorname{CH}_2\operatorname{CH}_3$ (d.) $\operatorname{CH}_3\operatorname{C}(\operatorname{Cl})(\operatorname{CH}_3)\operatorname{CH}_2\operatorname{CH}_3$
- (7.) Which of the following statement is incorrect? [Page: 291]

| (c.) For dihalogen derivatives, the prefixes o-, (d.) The dihaloalkanes having the same type of halogen atoms are named as alkylide. (8.) Consider the following reaction [Page: 295] $H \rightarrow H^{+}$ Br ₂ - CCH \rightarrow X ⁺ Here, X ⁻ is (a) Br CH ₂ - CH ₁ Br (b) CH ₂ - CH ₂ Br (c) br (c) br (c) br (c) br (c) haloalkane (c) (b) hydrocarbon (c) haloalkane (c) (b) hydrocarbon (c) haloalkane (c) (b) hydrocarbon (c) haloalkane (c) (b) hydrocarbon (c) haloalkane (c) (c) haloarene (d) haloarene (l) Match the organic compounds given in column I with their effects given in column II. [Page: 289] (Column I) (Column I) (p) treatment of malaria (l) Chloramphenicol (p) treatment of malaria (l) Chloraquine (r) lodine containing hormone (IV) Halothane (s) Anaesthetic Codes I II III IV (a) r q p s (c) P s (d) p q s r (c) q r p s (d) p q s r (1) Consider the following reaction [Page: 300] $\Re_{V} + \frac{\sqrt{s} - \frac{s}{v}}{\sqrt{s} - \frac{s}{v} - s$ | (a.) | The common name of alkyl halides as derived by naming the alkyl group followed by the name of halide. | re (b.) | For monohalogen substituted derivativ of benzene, common and IUPAC names are used. | res S |
|--|---|--|--|--|----------|
| (8) Consider the following reaction [Page: 295] $ \begin{array}{c} $ | (c.) | For dihalogen derivatives, the prefixe mand p- are used in IUPAC system. | es o-, (d.) | The dihaloalkanes having the same typ of halogen atoms are named as alkylide | e |
| (a) Br CH ₂ - CH ₂ Br (b) CH ₃ - CH ₃ Br (c) Br (c) Br (c) Br (c) Br (c) balaster (c) balaster (c) haloalkane (c) haloalkane (c | (8.) | Consider the following reaction [Page: $H \rightarrow H + Br_2 \rightarrow X'$ $H \rightarrow H + Br_2 \rightarrow X'$ | : 295] X' is | | |
| (c) Br (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 [Page: 289] (Column I) (Column I) Organic compounds (p) treatment of malaria (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 (1) Consider the following reaction [Page: 300] $\Re_{N} + \int_{C}^{X} \xrightarrow{X} \longrightarrow (C - N_{N} + \overset{O}{X}$ | (a.) | Br CH ₂ – CH ₂ Br $H_{3}C$ — CH | (b.) (d.) | CH ₃ - CH ₂ Br 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 (1) Consider the following reaction [Page: 300] $\bigotimes_{Nu} + \frac{\delta^{-}}{C} = \frac{\delta^{-}}{X} \longrightarrow C - Nu + \overset{\Theta}{X}$ | (c.) | Br | | | |
| (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] $\stackrel{\circ}{\mathbb{N}_{U}} + \underbrace{\delta^{*} \delta^{*}}_{\mathbb{N}_{U}} + \underbrace{\delta^{*} \delta^{*}}_{N$ | (9.) | Carbon compounds containing more 317] | than o <mark>ne ha</mark> | logen atom are usually referred to as [Pa | age: |
| (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] $\Re_{Nu} + \int_{C}^{S} \int_{-X}^{S} \longrightarrow (-Nu + X)$ | (a.) | polyhalogen compounds | (b.) | hydrocarbon | |
| (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] $\Re_{Nu} + \int_{C}^{\delta^{+}} \frac{\delta^{-}}{-X} \longrightarrow X_{Nu} + \frac{\Theta}{X}$ | (c.) | haloalkane | (d.) | haloarene | |
| (Column I)(Column I)Organic compoundsEffects(I) Chloramphenicol(p) treatment of malaria(II) Thyroxine(q) antibiotic(III) Chloroquine(r) Iodine containing hormone(IV) Halothane(s) AnaestheticCodes(t) II III IV(a) r q p s(b.) p q r s(c.) q r p s(d.) p q s r(II.) Consider the following reaction [Page: 300] $\widehat{\mathbb{O}}_{Nu} + \int_{c}^{\delta^{+}} \frac{\delta^{-}}{X} \longrightarrow c_{-}^{Nu} + X = \sum_{c}^{O} \sum_{Nu}^{O} + X = \sum_{c}^{O} \sum$ | (10.) | Match the organic compounds given i 289] | in column I | with their effects given in column II. [Pa | age: |
| Organic compoundsEffects(I) Chloramphenicol(p) treatment of malaria(II) Thyroxine(q) antibiotic(III) Chloroquine(r) Iodine containing hormone(IV) Halothane(s) AnaestheticCodes(s) AnaestheticIIIIII(a.)rqps(b.)pq(c.)qrpg(d.)pq(II.)Consider the following reaction [Page: 300] $\bigotimes_{Nu} + \longrightarrow_{c-}^{\delta^{+}} \stackrel{\delta^{-}}{\longrightarrow_{u} + X} \longrightarrow_{c-}^{c-} Nu + X$ | | (Column I) | | (Column I) | |
| (1) Chloramphenicol(p) treatment of malaria(II) Thyroxine(q) antibiotic(III) Chloroquine(r) Iodine containing hormone(IV) Halothane(s) AnaestheticCodes(s) I II III IV(a.) r q p s(b.) p q r s(c.) q r p s(d.) p q s r(II) Consider the following reaction [Page: 300] $\bigotimes_{Nu} + \longrightarrow_{c}^{\delta^{+}} = \bigwedge_{x}^{\delta^{-}} \longrightarrow_{c}^{-} = Nu + \bigotimes_{x}^{\Theta}$ | | | | (Column I) | |
| (II) Thyroxine(q) antibiotic(III) Chloroquine(r) Iodine containing hormone(IV) Halothane(s) AnaestheticCodes(s) 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] $\bigotimes_{Nu} + \frac{\delta^+}{\sqrt{c^+ X^-}} \xrightarrow{\delta^-} \sqrt{c^- Nu + X^0}$ | | Organic compounds | | Effects | |
| (III) Chloroquine(r) Iodine containing hormone(IV) Halothane(s) AnaestheticCodes(s) 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] $\bigotimes_{Nu} + \longrightarrow_{C} \xrightarrow{\delta^{+}} \xrightarrow{\delta^{-}} \longrightarrow_{C} \xrightarrow{C} Nu + \stackrel{\odot}{X}$ | (I) (| Organic compounds Chloramphenicol | (p) treatn | Effects nent of malaria | |
| (IV) Halothane (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] $\bigotimes_{Nu} + \frac{1}{\sqrt{c}} \stackrel{\delta^+}{\xrightarrow{\Lambda^-}} \stackrel{\delta^-}{} \stackrel{\frown}{} \stackrel{\bullet}{} \bullet$ | (I) (II) | Organic compounds Chloramphenicol Thyroxine | (p) treatn (q) antibio | Effects nent of malaria otic | |
| 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] $ \begin{array}{c} \Theta \\ Nu + \end{array} \xrightarrow{\delta^{+}} \delta^{-} \\ \hline C \end{array} \xrightarrow{C \end{array} \xrightarrow{Nu + X}} \qquad \qquad$ | (I) (II) (III) | Organic compounds Chloramphenicol Thyroxine Chloroquine | (p) treatm (q) antibio (r) Iodine | Effects nent of malaria otic e containing hormone | |
| 24 | (I) ((II) (III) (IV) | Organic compounds Chloramphenicol Thyroxine Chloroquine Halothane | (p) treatm (q) antibio (r) Iodine (s) Anaes | Effects nent of malaria otic e containing hormone | |
| | (I) ((II) (III) (IV) Code I (a.) (c.) (11.) | Organic compounds Chloramphenicol Thyroxine Chloroquine Halothane es II III r q p q r p Q r p S Consider the following reaction [Page: $\bigotimes_{Nu}^{\delta^+}$ \bigotimes_{C^+} | (p) treatm (q) antibia (r) Iodine (s) Anaes (b.) (d.) (d.) : 300] $-Nu + \stackrel{\Theta}{X}$ | Effects nent of malaria otic containing hormone othetic p q r s p q s r | |

The type of reaction shown by the reaction is

- (a.) nucleophilic substitution
- (c.) addition reaction

- (b.) electrophilic substitution
- (d.) elimination reaction
- (12.) Match the following. [Page: 292]



| | $(+ Cl_2 \xrightarrow{`Y'} + Cl_2 \xrightarrow{`Y'} + (+ Cl_2 \xrightarrow{`Y'} + (+ Cl_2 \xrightarrow{`Y'} + Cl_2 \xrightarrow{`Y'} + (+ Cl_2 \xrightarrow{`Y'} + (+ Cl_2 \xrightarrow{`Y'} + Cl_2 \xrightarrow{`Y'} + (+ Cl_2 \xrightarrow{`Y'} + (+ Cl_2 \xrightarrow{`Y'} + Cl_2 \xrightarrow{`Y'} + (+ Cl_2 \xrightarrow{`Y'} + (+ Cl_2 \xrightarrow{`Y'} + (+ Cl_2 \xrightarrow{`Y'} + Cl_2 \xrightarrow{`Y'} + (+ Cl_2 \xrightarrow{`Y'} + ($ | CH ₃ | | | | | | |
|---------------------------|---|-----------------|---|--|--|--|--|--|
| (\mathbf{a}) | | | | | | | | |
| (a.) | Fe dark | | | | | | | |
| (0.) | FaCl | | | | | | | |
| (\mathbf{C},\mathbf{C}) | | | | | | | | |
| (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 <mark>hali</mark> de and POCl₃are formed | (d.) | alkyl halide and H_2O are formed | | | | | |
| (19.) | Chlorination of toluene in presence of light a acidification gives | ind hea | <mark>it follo</mark> wed by treatment with aq. NaOH and | | | | | |
| (a.) | o-cresol | (b.) | p-cresol | | | | | |
| (c.) | 2,4-dihydroxytoluene | (d.) | benzoic acid | | | | | |
| (20) | The alkane that gives only one mone chlow | o prod | uct on chloringtion with Cl. in presence of | | | | | |
| (20.) | diffused sunlight is | o piou | $[Odisha NFET_2019]$ | | | | | |
| (a) | 2.2-dimethylbutane | (\mathbf{h}) | neopentane | | | | | |
| (c.) | n-pentane | (d.) | isopentane | | | | | |
| (21.) | Name the polyhalogen compound which is e other substances. | employ | red as a solvent for fats, alkaloids, iodine and [Page: 317] | | | | | |
| (a.) | chloro <mark>for</mark> m | (b.) | methylene chloride | | | | | |
| (c.) | iodoform | (d.) | None of these | | | | | |
| (22.) | Consider the following statements | | [Page: 292] | | | | | |
| () | (I) The dihalo compounds is classified as gen | ninal h | alide. | | | | | |
| | (II) In common system, gem-dihalides are na | amed a | s alkylidene halides. | | | | | |
| | (III) Vic-dihalides are named as alkylene dihalides. | | | | | | | |
| | $(1V)$ for AC name of $\Pi_3 C$ – $CHCl_2$ is empirice Choose the correct option | the child | Shae. | | | | | |
| (a) | Land II | (h) | I and III | | | | | |
| (c.) | II, III and IV | (d.) | II and III | | | | | |
| () | · • | | | | | | | |
| (23.) | Which of the following has highest boiling p | oint? [| Page: 298] | | | | | |
| (a.) | CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ Br | | H_3C C CH_3 | | | | | |
| | | (b.) | Сн ₃ | | | | | |
| | | | | | | | | |
| | | | | | | | | |

| (c.) | $H_{3}C$ H_{2} H_{2} H_{2} H_{2} $H_{3}C$ H_{3} | (d.) | $H_{3}C$ |
|-------|---|--------------------|---|
| (24.) | When a compound rotates the plane of plane | e polar | ised light to the right, then it is called [Page: |
| (a.) | racemised | (b.) | leavorotatory |
| (c.) | dextrorotatory | (d.) | inverated |
| (25.) | The product of the following reaction [Page: H H H H H H H H | 297] | |
| (a.) | | | |
| (b.) | | | ademy |
| (c.) | B_r | | |
| (u.) | | _ | |
| (26.) | Which of the following is used as feedstock chemicals in pharmaceutical manufacturing | in the ? [Page | synthesis of chlorofluorocarbons and other : 317] |
| (a.) | CCl ₄ | (b.) | Iodoform |
| (c.) | Chloroform | (d.) | Methylene chloride |
| (27.) | The compound C_7H_8 undergoes the following The product 'C' is | ıg reac | tions: [NEET-2018, Page: 296] |
| (a.) | 3-bromo-2,4,6-trichlorotoluene | (b.) | o-bromotoluene |
| (c.) | m-bromotoluene | (d.) | p-bromotoluene |
| (28.) | Assertion : Vinyl chloride is less reactive that Reason : Stability of alkyl halide decreases as | n alkyl the sti | chloride. rength of C–Xbond 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. |
| | | | 27 |

| (c.) | A is correct but R is incorrect. | (d.) | Both A and R are false. |
|-------|---|------------------------------------|---|
| (29.) | Assertion: Chloral reacts with phenylchlorid Reason: It is an electophilic substitution react | e to fo tion. | rm DDT. [Page: 318] |
| (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 Reason : Alkyl iodides in general turn black of Both A and B are correct and B is correct. | colour on expo | less gases. osure to air and light. [Page: 297] Both A and B are correct but B is not |
| (a.) | explanation of A. | (0.) | 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: 30 (I) In S_N 1, the rate of reaction depends upon (II) S_N 1reaction occur in two steps. (III) The rate of reaction depends only of concentration of hydroxide ion. Read the given statements and then choose the | 3] the cor on the he corr | expression of only one reactant. concentration of $R-X$ and not on the rect 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 $-=^{CH_X}$ |
| (33.) | Assertion: CCL is a fire extinguisher | | |
| () | Reason: CCl_4 is insoluble in water. [Page: 317 | 7] | |
| (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 A and A a | ne slow | rest rate, among the following is |
| | | | |

| | (b.) $H_3C - CH_2 - CI \xrightarrow{aq. NaOH} H_3C - CH_2 - OH$ | | | | | |
|-------|---|----------------------|--|--|--|--|
| | (c.) $H_2C = CH - CH_2 - Cl \xrightarrow{aq. NaOH} H_2C = CH - CH_2OH$ | | | | | |
| | (d.) $(H_2CI \xrightarrow{ad. NaOH} (H_2OH)$ | | | | | |
| (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 2,4-dinitrochlorobenzene is readily replaced | ve pheno ed becau | l requires drastic conditions but chlorine of se | | | |
| (a.) | NO ₂ makes the electron rich ring at ortho and para positions |) (b.) | NO ₂ withdraw electrons at metaposition | | | |
| (c.) | NO ₂ donates electrons at m-position | (d.) | NO ₂ withdraws electrons at ortho and para positions | | | |
| (37.) | Consider the following reaction [Page: 295 $CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2/UVLight}{or heat}$ 'X' and 'Y' Product 'X' and 'Y' are | <u>;]</u> | | | | |
| (a.) | a and a a a a a a a a a a a a a a a a a | (b.) | CH ₃ CH ₂ CH ₂ CH ₂ Cl and CH ₃ CH ₂ CHClCH ₃ | | | |
| (c.) | CH ₃ CH ₂ CHCl ₂ CH ₃ only | (d.) | CH ₃ CH ₂ CH ₂ CH ₂ Cl only | | | |
| (38.) | Which of the following is the correct ord ϵ | er of react | tivity of alkyl halides toward S_N^1 reaction? | | | |
| (a) | $3^{\circ} > 2^{\circ} > 1^{\circ} > CH.X$ | (h.) | 2° > 3° > 1° > CH X | | | |
| (c.) | $1^{\circ} > 2^{\circ} > 3^{\circ} > CH_{3}X$ | (d.) | $CH_{3}X > 1^{\circ} > 2^{\circ} > 3^{\circ}$ | | | |
| (39.) | The compound in which the halogen atom to $C = C$ double bond is | ı is bonde | ed to an sp ³ hybridised carbon atom adjacent | | | |
| (a.) | Benzylic halide | (b.) | Aryl halide | | | |
| (c.) | Allylic halide | (d.) | Vinylic halide | | | |
| (40.) | Assertion : Alkyl iodide can be prepare acetone. Reason : NaCl/NaBr are soluble i | d by tre | ating alkyl chloride/bromide with NaI in e 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) | | | |
| L | | | | | | |
| | | | | | | |
| | | | 29 | | | |





| 11 | TOPIC 2 : Preparation and Properties of Haloalkanes |
|------------|---|
| 11. | (a) $CH_2 = CH_2 + Cl_2 \xrightarrow{600^{\circ}C} \rightarrow$ |
| | (b) $ClCH_2 - CH_2Cl \xrightarrow{KOH}_{ethanol}$ |
| | (c) $CH \equiv CH + HC1 \xrightarrow{Hg^{2+}}$ |
| | (d) All of these |
| 12. | Comment on the following reactions (i) $CH_3OH + NaCl \rightarrow$ (ii) $CH_3OH + HCl \rightarrow$ 1) Both reactions take place easily. 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 ? |
| 14. | When $CH_3CH_2CHCl_2$ is treated with NaNH ₂ , the product formed is (a) $CH_3-CH=CH_2$ (b) $CH_3-C=CH$ |
| | (c) $CH_3CH_2CH < NH_2 MH_2$ (d) $CH_3CH_2CH < CI MH_2$ |
| 15. | The reaction of tert-butyl bromide with sodium methoxide produces mainly – |
| 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 undergoes1) only addition reactions2) only elimination reactions3) only elimination reactions4) heth (1) and (2) |
| 18. | S) substitution reactions 4) both (1) and (2) In the following sequence of reactions $C_{2}H_{5}Br \xrightarrow{AgCN} X \xrightarrow{Reduction} V : V is$ |
| | $C_{2115}BI \longrightarrow A \longrightarrow 1$, 1 is 1) <i>n</i> -propylamine 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 <i>meso</i> -2,3-dibromobutane, the major compound formed is |
| 21. | 1) <i>n</i> -butane 2) 1-butene 3) <i>cis-2</i> -butene 4) <i>trans-2</i> -butene Halogenation of alkanes is 1) a reductive process 2) an oxidative process |
| 22. | 3) an isothermal process4) an endothermal processWhich 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 ₂ O 2) C ₂ H ₅ OH 3) CH ₂ OH 4) C ₂ H ₅ OC ₂ H ₅ |
| 24. 25. | To prepare 3-ethylpentan-3-ol, the reagents needed are $-$ 1) CH ₃ CH ₂ MgBr + CH ₃ COCH ₂ CH ₃ 2) CH ₃ MgBr + CH ₃ CH ₂ CH ₂ COCH ₂ CH ₃ 3) CH ₃ CH ₂ MgBr + CH ₃ CH ₂ COCH ₂ CH ₃ 4) CH ₃ CH ₂ CH ₂ MgBr + CH ₃ COCH ₂ CH ₃ Rate of SN ₂ will be negligible in : |
| | |



3) Nitrous acid followed by heating with Cu₂Cl₂ 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] How many isomeric naphthylamines are expected in the following reaction? 50. NaNH₂, NH₃ -33°C 1) Two 2) only single product 3) four 4) three 51. COC1 + RCOCH₂CH₃ The reagent R may be CH₃CH₂MgBr CH, CH, Li Т TT (CH₂CH₂)₂Cd (CH2CH2)2CuLi \mathbf{III} 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? C1(CH₃)₂NLi 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 Freon-12 is commonly used as 54. 2) refrigerant 1) insecticide 3) a solvent 4) a fire extinguisher 55. Which of the following is used in fire extinguishers 1) CH₄ 2) CHCl₃ 3) CH_2Cl_2 4) CCl₄ If chloroform is left open in air in the presence of sunlight, it gives 56. 1) carbon tetrachloride 2) carbonyl chloride 3) mustard gas 4) lewisite The product formed by heating iodoform with KOH is : 57. 2) HCOOK 1) HCHO 3) CH₃COOK 4) CH₃CHO 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 Cl₂ 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) acetvlene 2) hexachloroethane 3) 1,1,2,2-tetrachloroethane 4) ethylene





Which of the following compounds will undergo racemisation when solution of KOH hydrolyses?

7.





| NCEPT LINE BY LINE OUESTIC | | | | | | . A NI | | | | | |
|--|--------------------|-----------------------------|----------------|-----------------|---------------|---------------|--------------|-------------|------------------------|--------------------------|---------------|
| | (1) | | | Р Я | | C | | - AN | | h | |
| | (1.) | u C | (2.) | u C | (3.) | 2 | (9) | а а | (10) | c | |
| | (0.) | е а | (12) | d | (13) | d | (1.1) | d d | (10.) | b | |
| | (16) | d d | (12.) | <u>ч</u> а | (18) | h | (14.) | d | (13.) | a | |
| | (10.) | а а | (17.) | u C | (10.) | 2 | (13.) | C | (25) | a | |
| | (26) | a a | (27) | C | (28) | a b | (29) | <u>с</u> | (20) | a | |
| | (20.) | d | (27.) | d | (22) | b | (29.) | 2 | (30.) | C | |
| | (31.) | d | (32.) | u h | (33.) | 0 | (34.) | a | (33.) | C | |
| | (30.) | u b | (37.) | 4 | (30.) | a | (39.) | h | (40.) | b C | |
| | (41.) | b | (42.) | u h | (43.) | | (44.) | 0 | (45.) | h | |
| | (40.) | | | | | | (49.) | | | | |
| | | OPIC | WIJE I | PKA | LICE | QUE2 | | - AI | NOVER | () | |
| 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 | | <u>38) 1</u> | 39) 2 | 40)3 |
| 41) 3 51) 2 | 42) 1 | 43) 3 | 44) 3 | 1 | 45)3 55)4 | 46) 3 | 47)2 | · | 48) 3 59) 4 | 49) 50) | 50) I |
| 51) 5 61) 1 | 52) 1 62) 2 | 53) 4 | 54) 2 64) 3 | | <u>55)4</u> | 50) 2 | 57)2 | , | 58)4 | 59)4 | <u>60)</u> I |
| 01)1 | | | | | | | | | | | |
| | | | KEVIC | 102 | TEARS | QUES | | S-Ar | | 3 | |
| 1) 1 11) 1 | 2) 4 | 3) 2 13) 1 | 4) 2 | | 5) I 15) 1 | 6) 3 | 7) 4 | | 8) 2 | 9) 3 | 10) 4 |
| 11)1 | 12)4 | | 14)3 | | | | | | | C | |
| | | NCER | | BIL | INE Q | DESIIC | JN2 – | 30 L | | 3 | |
| (1.) | (a) Product ' | A+B' is | racemic | mixtur | e and pro | ocess invo | olved is 1 | racemi | sation He | ere, 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. | | | | | | | | | | | |
| (a) | However, it t | ends to d | lissolve ir | n orgar | nic solven | its. | | | | | |
| (3.) | (c) Reaction | (c) is Sar | ndmeyer's | s react | ion | | | | | | |
| | | | | | | | | | | | |
| | | | | | | | | | | | |
| | | | | | | | | | | | |
| | | | | | | | | | | | |
| | | | | | | | | | | | |



(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.

$$H_2C \xrightarrow{c} C_1 \xrightarrow{c} H_2C \xrightarrow{c} C_1 \xrightarrow{c} H_2C$$

(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 I2 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 (C = C)

(33.) (b) CCl₄ 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 sp³hybridised 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) NO₂ 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 CH₃CH₂CH₂CH₂Cl and CH₃CH₂CHClCH₃. The reaction proceed in a free radical chlorination of alkanes. Complete reaction is as follows: $CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2 / UV \text{ Light}} CH_3CH_2CH_2CH_2CH_2CH + CH_3CH_2CHClCH_3$
- (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.

7. 3) In allylic halides hydrogen atom is bonded to sp^3 hybridized carbon atom. Whereas in vinylic halide, hydrogen atom is bonded to sp^2 hybridized carbon atom. CH₂CHCl₂ CH₂ - CH₂

C1

Ethylidene chloride Cl Cl (gem-dihalide) Ethylene dichloride (vic-dihalide)

3)

8.

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

| H H H H-C-C-C-H C1 H C1 | asymmetric carbon atom H H/H / H-C-C*C-H Cl Cl H |
|--|--|
| | |

10. 3) Stability of the three corresponding carbocations $CH_2 = CHCHCH_3 > CH_3CH_2CHCH_3 > CH_3CH_2CH_2$

- 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 ROH_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.

$$CH_3CH = CH_2 \xrightarrow{Cl_2, 400^{\circ}C} -HCl \rightarrow CICH_2CH = CH_2$$

14. 2)

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

$$CH_3 - CH = CHCl \xrightarrow{NaNH_2} CH_3 - C \equiv CH$$

Final Product

15. 2) 3° alkyl halides on reaction with strong base (CH₃O⁻) undergo elimination reaction and forms alkene as major product.

$$\begin{array}{c} CH_{3} \\ CH_{3} - C - Br \\ | \\ CH_{3} \\ CH_{3} \\ 3^{\circ} Halide \end{array} \xrightarrow{ CH_{3}O^{-} \\ Strong base } CH_{3} - \begin{array}{c} CH_{2} \\ | \\ CH_{3} \\ CH_{3} \\ CH_{3} \end{array} + HBr$$

H H H H

$$CH_3 = C - Br + 4Na + Br - C - CH_3$$

 Br Br
 $-\frac{e^{40}cr}{2.30000} + 4NaBr + CH_3 - CH = CH - CH_3$
 2.300000
17. 4) CH = CH = CH - e^{-CH} - CH_2 - CHC1 = H_2 + CH_2CH_2CI
18. 4)
CH_2H_2H_2 - ACCN + C_{H_2NC} - Reduction + Entry isosynate
Exploring/instrumentation is compared by the compared by

29. 2) The more is the stability of intermediate carbonium ion, the more is the chance of $S_N l$ 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.

- $30. \qquad (3) \ Isopropyl \ chloride, \ being \ 2^\circ \ alkyl \ halides, \ can \ undergo \ S_N1 \ as \ well \ as \ S_N2 \ mechanism.$
- 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 C₆H₅OCH₃ and C₆H₅N(CH₃)₂ electron pair on O and N are partially 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 (CH₂OH. CH₂OH).
- 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. H₂SO₄, alkenes undergo hydration in Markovnikov's way.

Ethyl magnesium iodide

1) $CH_3COOAg + Br_2 \xrightarrow{CS_2} CH_2Br + AgBr + CO_2$ 38.

- 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.

- 45. 3) Due to resonance in chlorobenzene 3)
- 46.

$$C_6H_6 + CH_3CH_2CH_2CI \xrightarrow{Anhyd.} C_6H_5 - CH - CH_3$$

Isopropylbenzene

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.

CH₃

48.

49.

Rate
$$\propto [C_6H_5C1][N\overline{u}:]$$

- 50. 1)
- 51. 3) Organomagnesium and organolithium compounds can't be prepared from the alkyl (or aryl) halide having -NO₂ group. On the other hand, organocopper and organocadmium compounds, do not react with the $-NO_2$ group.

55. 4) CCl₄ vapours are non-inflammable (*i.e.* do not catch fire). Hence used as fire extinguishers under the name pyrene.

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

57. 2)

2)

56.

 $\begin{array}{c} CHI_3 + 3KOH \longrightarrow CH(OH)_3 + 3KI \\ iodoform & \downarrow \\ HCOOK \xleftarrow{KOH} & HCOOH + H_2O \end{array}$

58. 4) CHCl₃ on exposure to air forms phosgene which is poisonous gas and removed by converting it into diethyl carbonate (which is non-poisonous substance).

$$\begin{array}{c} \text{CHCl}_3 \xrightarrow{O_2/\text{light}} \text{COCl}_2 + \text{HCl} \\ & \text{Phosgene} \\ & (\text{Poisonous}) \end{array}$$

$$\begin{array}{c} \text{COCl}_2 + 2\text{C}_2\text{H}_5\text{OH} \longrightarrow (\text{C}_2\text{H}_5)_2\text{CO}_3 + 2\text{HCl} \\ \text{Diethyl carbonate} \\ \text{(non-poisonous)} \end{array}$$

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)
$$HCCl_3 + 6Ag + HCCl_3 \longrightarrow HC \equiv CH + 6AgCl_3$$

- 61. (1) Since CHCl₃ is covalent compound it does not produce Cl⁻ ion in H₂O, hence no white ppt is formed during reaction with AgNO₃
- 62. (2) This is carbylamine reaction which is used to detect presence of 1° amine in organic compounds. The bad smelling compound is isocyanide.

$$CHCl_3 + 3KOH + C_2H_5NH_2 \longrightarrow$$

Chloroform Ethyl amine

$$C_2H_5N \Longrightarrow C + 3KCl + 3H_2O$$

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

$$\longrightarrow$$
 CH₃CHO + H₂O

- 64. (3) Triiodomethane (CHI₃) when comes in contact with organic matter decomposes easily to free iodine which has antiseptic property.
- 65. 4)

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

NEET PREVIOUS YEARS QUESTIONS-EXPLANATIONS

1. 1)

3.

4.

5.

b)

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 2)

is optically active due to absence of plane of symmetry and center of symmetry 2) a)

CH₃CH₂CH₂-Br+KOH

Br F

$$\rightarrow$$
 CH₂CH=CH₂ + KBr + H₂O

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

$$\begin{array}{c} H_{3}C \\ C \\ H_{3}C \\ H_{3}C \\ H_{3}C \\ H_{3}C \\ C \\ H_{3}C \\ H_{3}C$$

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

c) $+Br_2 \rightarrow \bigcup_{Br}^{Br}$

Above reaction involves addition of Br_2 across double bond. Thus it is called addition reaction a) $ZnCl_2$ is a lewis acid and interact with alcohol.

$$CH_{3} - CH_{2}OH + ZnCl_{2} \rightarrow R - \overset{+}{O} - ZnCl_{2}$$

$$(R = CH_{3} - CH_{2} -)$$

$$R - \overset{+}{O} - ZnCl_{2} \rightarrow R^{+} + [HOZnCl_{2}]^{-}$$

$$H$$

$$(I)$$

Carbocation is formed as intermediate in the S_N^1 mechanism which these reaction undergoes. In the absence of ZnCl₂ 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

$$CH_{3} \xrightarrow{P}{} CH_{3} \xrightarrow{C}{} CH_{3} \xrightarrow{C}{} CH_{3} \xrightarrow{+}{} CH_{3} \xrightarrow{+}{} CH_{3} \xrightarrow{+}{} H_{2}O$$

(iv) In the presence of ZnCl₂, 2° carbocation is formed

from
$$(CH_3)_2 - C - OH$$

....

6. 3) Methyl group is ortho para directing but due to steric hinderce effect, generated by two CH₃ groups substitution will not take place on position (I). Hence only two products are possible.

- 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 AlCl₃

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

$$CH_2-CH_2-Cl$$
 $CH_2-\overrightarrow{CH}_2+Cl^-$
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.

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 |
| CH₃ — CI | 351 |
| CH_{3} — Br | 293 |
| $CH_{_3} - I$ | 234 |

12. $(4n+2)\pi e^{-1}$ 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-