

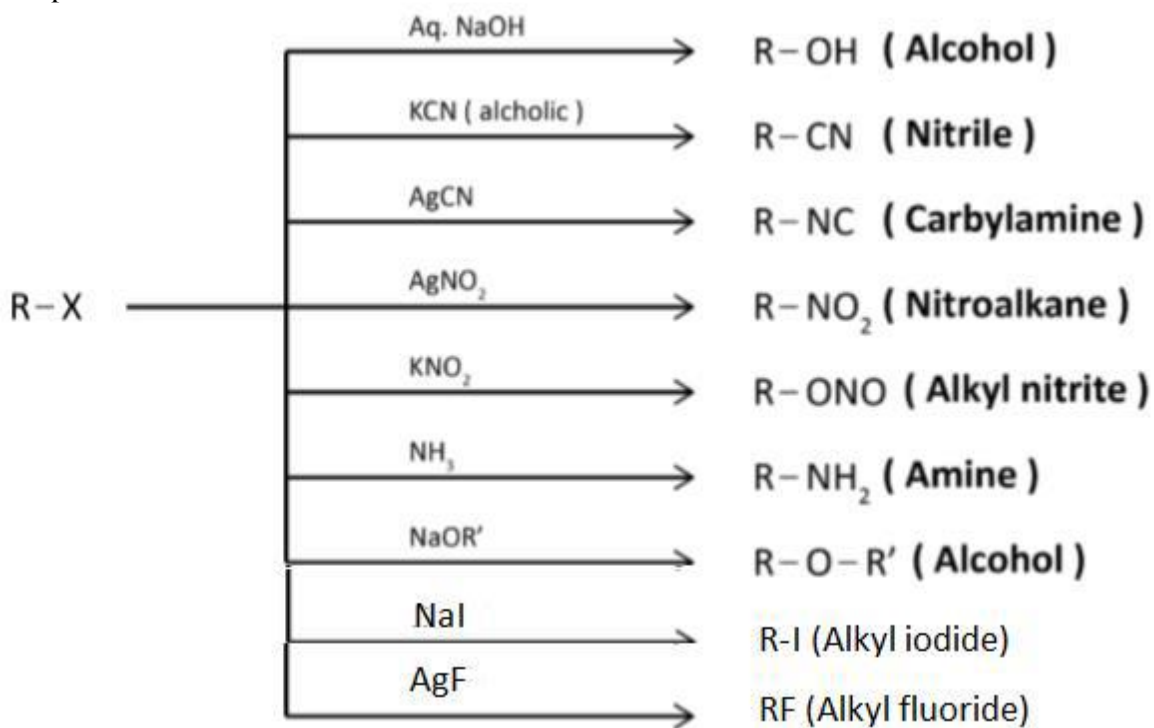
HALOALKANES AND HALOARENES

Reactions of Halo alkanes

a) Nucleophilic substitution reactions

Due to polar nature of C-X bond carbon atom gets a partial positive charge. As a result, a nucleophile can attack this carbon atom and causes the departure of the halogen atom as halide ion. This type of reaction in which a stronger nucleophile replaces weaker nucleophile is called nucleophilic substitution reaction.

Examples



Comparison between S_N^1 and S_N^2 reaction mechanisms

| Reaction Parameters | S_N^1 | S_N^2 |
|------------------------|--|---|
| Molecularity | It is unimolecular nucleophilic substitution reaction. | It is bimolecular nucleophilic substitution reaction. |
| Order | It is first ordered reaction Rate = k [Nu] | It is second ordered reaction. Rate = k [Nu][RX] |
| Alkyl halide structure | Tertiary > secondary >> primary > Methyl | Methyl > primary > secondary >> Tertiary |
| Nucleophile | Rate of reaction is independent of concentration of nucleophile. | Rate of reaction depends upon concentration of nucleophile. |
| | Attacks from both sides of carbonium ion | Attacks from backside of the substrate |
| Intermediate | The intermediate formed is carbocation | Five membered intermediate is formed |
| Mechanism | It is taking place in two step | It is a single step reaction |
| Stereochemistry | In this reaction racemisation takes place (Both retention and inversion) | In this reaction, 100% inversion takes place. |

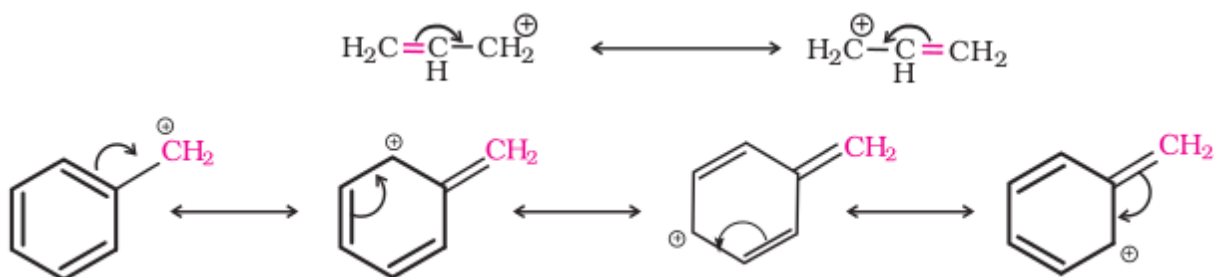
Q. 1. Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief product. Explain.

Ans. KCN is predominantly ionic and provides cyanide ions in solution. Both carbon and nitrogen atoms are in a position to donate electron pairs. The attack takes place mainly through carbon atom since C—C bond is more stable than C—N bond.

However, AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanides as the main product.

Q. 2 Allylic and benzylic halides show high reactivity towards the S_N1 reaction. Explain

Ans. The carbocation thus formed gets stabilised through resonance



Q. 3 Grignard reagents should be prepared under anhydrous conditions. Why?

Ans. Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons.

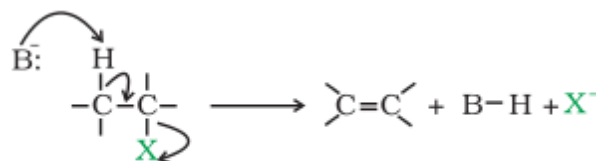
$\text{RMgX} + \text{H}_2\text{O} \rightarrow \text{RH} + \text{Mg}(\text{OH})\text{X}$ It is therefore necessary to avoid even traces of moisture from a Grignard reagent

Q. 4. What are elimination reactions?

Ans:

When a haloalkane with β -hydrogen atom is heated with alcoholic solution of potassium hydroxide, an alkene is formed as a product. There is elimination of hydrogen atom from β -carbon and a halogen atom from the α -carbon atom.

Since β -hydrogen atom is involved in elimination, it is often called β -elimination.



B=Base ; X=Leaving group

Q. 5 What are chiral and achiral molecules

Ans. The objects which are non-superimposable on their mirror image are said to be chiral and this property is known as chirality.

The objects, which are, superimposable on their mirror images are called achiral

Q. 6 What do you mean by racemic mixture and racemization?

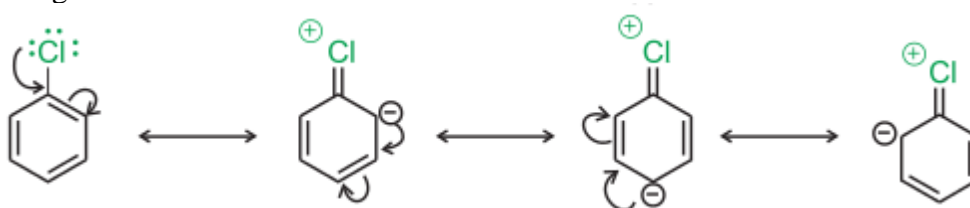
Ans. A mixture containing two enantiomers in equal proportions is known as racemic mixture. It will have zero optical rotation, as the rotation due to one isomer will be cancelled by the rotation due to the other isomer.

The process of conversion of enantiomers into a racemic mixture is known as racemisation

Q. 7 Aryl halides are extremely less reactive towards nucleophilic substitution reactions. Why?

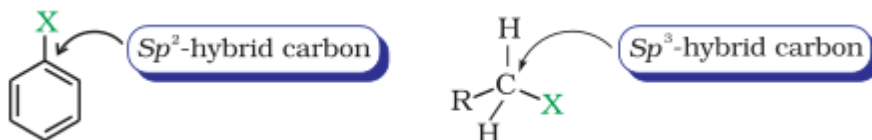
i) Resonance effect

In haloarenes, the electron pairs on halogen atom are in conjugation with π -electrons of the ring. C—Cl bond acquires a partial double bond character due to resonance and the bond cleavage in haloarene is difficult.



ii) Difference in hybridisation of carbon atom in C—X bond

In case of haloarene the sp^2 hybridized carbon with a greater s-character is more electronegative and can hold the electron pair of C—X bond more tightly than sp^3 -hybridised carbon in haloalkane with less s-character. Since it is difficult to break a shorter bond than a longer bond, haloarene are less reactive than haloalkane towards nucleophilic substitution reaction.



(iii) Instability of phenyl cation: In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilized by resonance and therefore, SN_1 mechanism is ruled out.

(iv) Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.

Q. 8. Electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene. Why?

Ans. • Due to resonance, the electron density increases more at ortho- and para-positions than at meta-positions.

• Further, the halogen atom because of its $-I$ effect has some tendency to withdraw electrons from the benzene ring.

As a result, the ring gets somewhat deactivated as compared to benzene

Q. 9 Cl is an electron withdrawing group but it is ortho, para- directing in electrophilic aromatic substitution reactions. Why?

Ans. • Chlorine withdraws electrons through inductive effect and releases electrons through resonance.

• Through inductive effect, chlorine destabilizes the intermediate carbocation and through resonance, halogen tends to stabilize the carbocation and the effect is more pronounced at ortho- and para- positions.

• The resonance effect tends to oppose the inductive effect for the attack at ortho- and para-positions and hence makes the deactivation less for ortho- and para- attack.

• Reactivity is thus controlled by the stronger inductive effect and orientation is controlled by resonance effect.

Q. 10 Give chemical tests to distinguish between

(a) Benzyl chloride & chloro benzene

(b) Vinyl iodide and ethyl iodide

Ans:

(a) On adding NaOH solution & aqueous $AgNO_3$, Benzyl chloride gives white precipitate of $AgCl$, while chlorobenzene does not react at room temperature.

(b) On adding NaOH solution & aqueous $AgNO_3$, ethyl iodide gives yellow precipitate of AgI , while vinyl iodide does not react

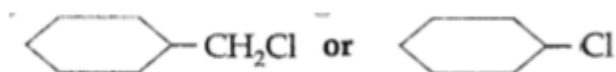
Q. 11 What do you mean by retention of configuration and inversion of configuration?

Ans: **Retention of configuration** is the preservation of integrity of the spatial arrangement of bonds to an asymmetric centre during a chemical reaction or transformation. Here the optical rotation of the reactant and product are the same

Inversion of configuration is the inversion of the spatial arrangement of bonds to an asymmetric centre during a chemical reaction or transformation. Here the optical rotation of the reactant and product are different

Q. 12. Which one of the two compounds reacts faster by SN_2 reaction?

(a)

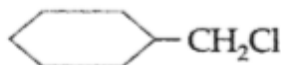


(b)



Ans.

(a)



(b)



Q. 13 Among the isomeric alkyl halides of molecular formula C_4H_9Cl , identify

(a) The optically active isomer

(b) The most reactive halide towards SN_1

(c) The isomer with lowest boiling point

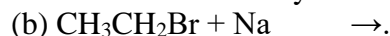
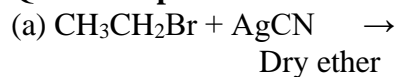
Ans: draw the structure and find out the isomer

(a) sec- Butyl chloride $CH_3CH(Cl)CH_2CH_3$

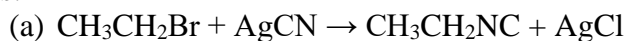
(b) tert- Butyl chloride $(CH_3)_3C-Cl$

(c) n- Butyl chloride $CH_3CH_2CH_2CH_2-Cl$

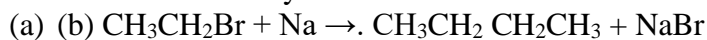
Q.14. Complete the reactions:



Ans:



Dry ether



Q15 Write short notes on a) Finkelstein reaction b) Swarts reactions c) Fittig reaction

Ans:

a) Finkelstein reaction:

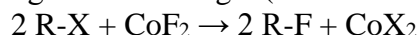
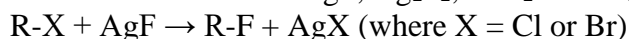
Alkyl chlorides or bromides when treated with NaI in dry acetone, alkyl iodides are formed. This reaction is known as Finkelstein reaction.

Dry acetone



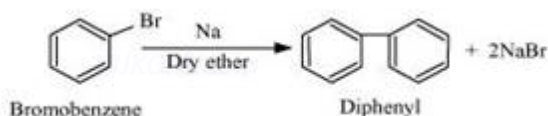
b) Swarts reaction:

This method is used for the preparation of alkyl fluorides. Here alkyl chloride or bromide is treated with a metallic fluoride like AgF , Hg_2F_2 , CoF_2 or SbF_3 , to get alkyl fluoride.



c) Fittig reaction

Aryl halide on treatment with sodium metal in presence of ether gives diphenyl and is called Fittig reaction

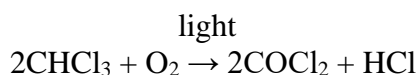


Q. 16 Give reasons

- a) Chloroform is stored in amber coloured bottle.
- b) Wurtz reaction cannot be used to prepare alkanes containing odd the number of carbon atom.
- c) Sulphuric acid not used during the reaction of alcohols with KI

Ans:

a) Chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas, carbonyl chloride (COCl₂), also known as phosgene.



b) Wurtz reaction not preferred for the preparation of alkane containing an odd number of carbon atoms **due to the formation of a number of products**. When two different types of alkyl halides are taken, a mixture of three alkanes with odd and even numbers of carbon atoms are obtained.

c) In the presence of sulphuric acid(H₂SO₄), KI produces HI



Since H₂SO₄ is an oxidizing agent, it oxidizes HI produced in the reaction to I₂)



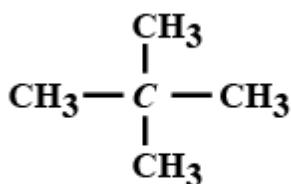
Hence it will not produce alkyl iodides

Q. 17 A hydrocarbon alkane (A), having molecular mass 72g/mol gives only one mono-chlorination product. Identify the hydrocarbon. and write the mono chlorinated product

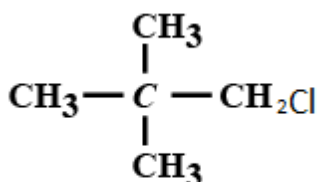
Ans: Since it is an alkane, its formula is

C_nH_{2n+2} ∴ 12n+2n+2=72 n = 5 (A) has the molecular formula C₅H₁₂

The isomer of pentane which yield single monochloro derivative should have all the 12 hydrogen's equivalent. Neopentane (2,2 - dimethyl propane) is the only possibility. The monochlorinated product is neopentyl chloride (1-chloro-2,,2-dimethyl propane)



Neopentane



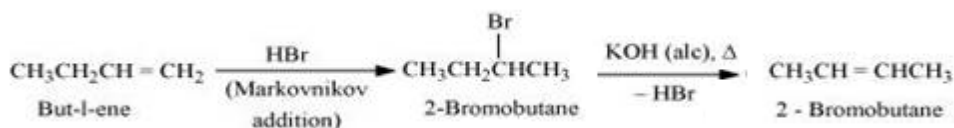
neopentyl chloride

Q. 18. How will you bring about the following conversion?

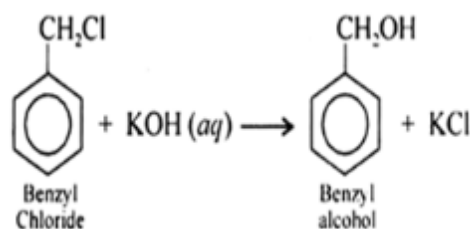
- i) . But-1-ene to but-2-ene
- ii) Benzyl chloride to benzyl alcohol

- iii) Aniline to bromobenzene
- iv) Benzene to 4-bromonitrobenzene

i.



ii)



iii)



iv)



Q 19.) Give reasons for the following:

- (i) Benzyl chloride is highly reactive towards the S_N1 reaction.
- (ii) 2-bromobutane is optically active but 1-bromobutane is optically inactive.
- (iii) Electrophilic reactions in haloarenes occur slowly.
- (iv) Dextro- and laevorotatory isomers of Butan-2-ol difficult to separate by fractional distillation
- (v) (±) 2-Butanol is optically inactive.

(i) Benzyl carbonium ion is stabilized by resonance.

(ii) 2-Bromobutane is chiral, therefore, optically active, whereas 1-chlorobutane is not chiral, therefore optically inactive.

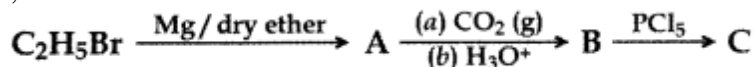
(iii) It is due to -I effect of halogens, it deactivates benzene ring towards electrophilic substitution reactions.

(iv) Dextro- and laevorotatory isomers of butan-2-ol are enantiomers of each other and both have the same boiling point. Hence, these cannot be separated by fractional distillation

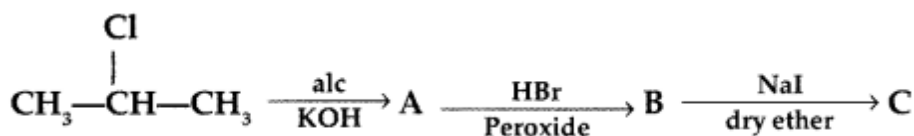
(v) (\pm) 2-Butanol represents a racemic mixture of (+) 2-butanol and (-) 2-butanol which rotate the plane polarized light in different directions but to an equal extent. Therefore, the (\pm) compound is optically inactive

Q 20. Write structures of compounds A, B and C in each of the following reactions:

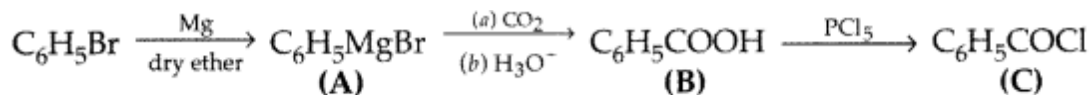
1,



2.



Ans. 1.

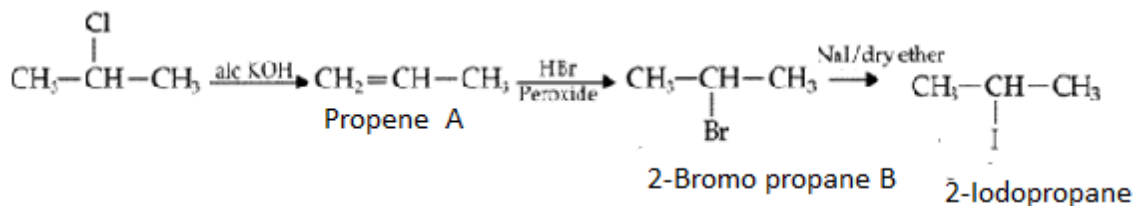


A = Phenylmagnesium bromide

B = Benzoic acid

C = Benzoyl chloride

2.



Q.21. What happens when

I) Ethyl chloride is treated with Sodium Iodide (NaI)

II) Chlorobenzene is treated with Sodium metal in presence of dry ether.

III) Methyl Chloride is treated with KNO_3

IV) n-butyl chloride is treated with alcoholic KOH.

V) 2,4,6-trinitrochlorobenzene is subjected to hydrolysis.

VI) Methyl chloride is treated with AgCN.

VII) Chlorobenzene is treated with $\text{Cl}_2/\text{FeCl}_3$

VIII) Ethyl Chloride is treated with AgNO_2

IX) 2-bromopentane is treated with alcoholic KOH.

X) Ethyl Chloride is treated with aqueous KOH

XI) Chlorobenzene is treated with CH_3COCl in presence of anhydrous AlCl_3

XII) Methyl chloride is treated with AgNO_2 .

XIII) Bromobenzene is treated with CH_3Cl in presence of anhydrous AlCl_3

XIV) Ethyl chloride is treated with alcoholic KOH

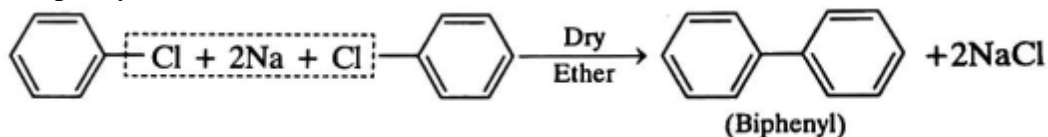
XV) Chlorobenzene is treated with CH_3Cl in the presence of anhydrous AlCl_3

ANSWERS

I) Ethyl Iodide is formed.



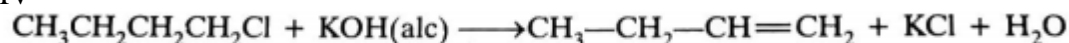
II- Biphenyl will be formed.



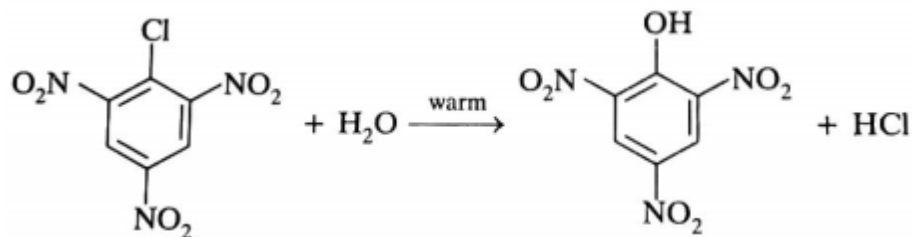
III- Methyl nitrite is formed.



IV-



V-

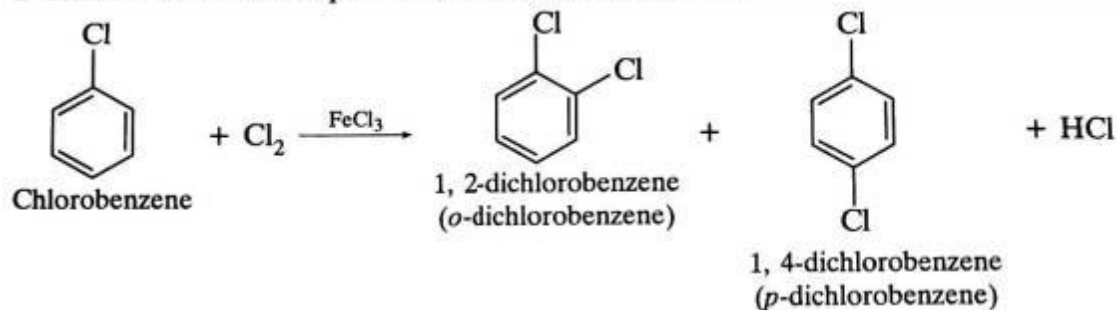


VI-



VII-

o-dichlorobenzene and *p*-dichlorobenzene are formed.

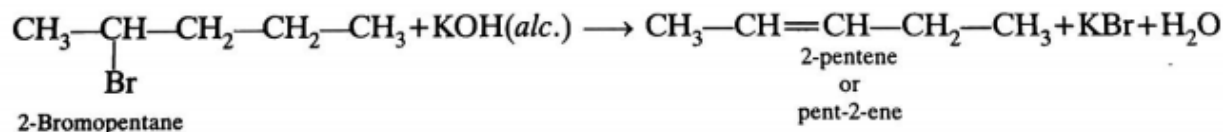


VIII-

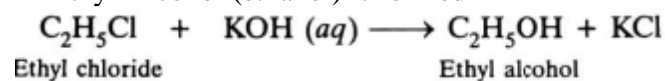
Nitroethane will be formed.



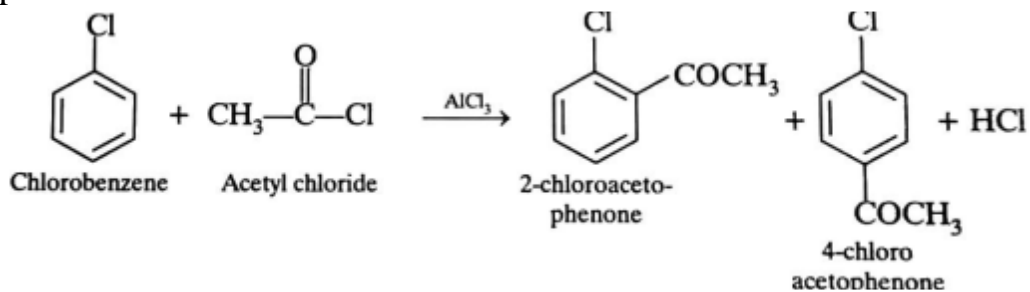
IX- 2-pentene will be formed as major product



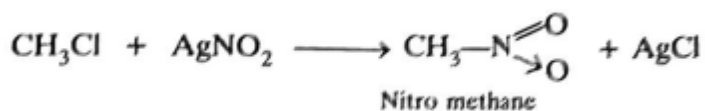
X- Ethyl Alcohol (ethanol) is formed



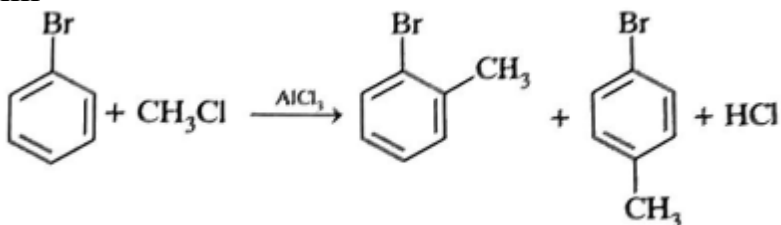
XI-



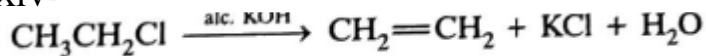
XII- Nitro methane is formed



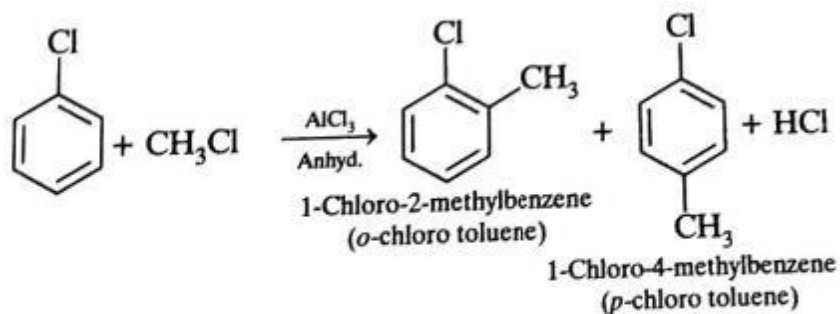
XIII-



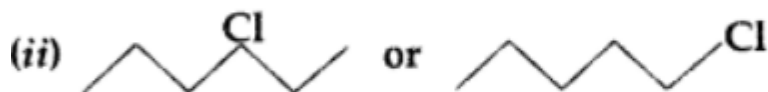
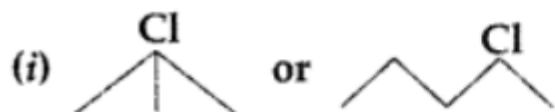
XIV-





XV-

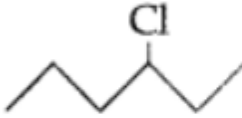



Q. 22 Which one in the following pairs undergoes SN1 substitution reaction faster and why?



Answer:

(i)  (3° alkyl halide) reacts faster than  (2° alkyl halide) due to greater stability of 3° carbocations over 2° carbocation.

(ii) As  is a secondary alkyl halide which reacts faster in S_N1 reaction than 1° alkyl halide  due to greater stability of 2° carbocations over 1° carbocations.

Q. 23. Which compound in each of the following pairs will react faster in S_N2 reaction with OH^- ?

(i) CH_3Br or CH_3I (ii) $(\text{CH}_3)_3\text{CCl}$ or CH_3Cl

Answer:

(i) CH_3I : Because Iodide is better leaving group than bromide.

(ii) CH_3Cl : Carbon atom leaving group is less hindered.

Q. 24. Account for the following:

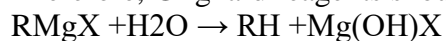
(i) The C – Cl bond length in chlorobenzene is shorter than that in CH_3Cl

(ii) Grignard reagent should be prepared under anhydrous conditions.

Answer:

(i) In haloalkanes, the halogen atom is attached to sp^3 -hybridized carbon while in haloarenes it is attached to sp^2 -hybridized carbon whose size is smaller than sp^3 orbital carbon. Therefore C – Cl bond in chloro-benzene is shorter than alkyl chloride.

(ii) Grignard reagents are very reactive. In the presence of moisture, they react to give alkanes. Therefore, Grignard reagents should be prepared under anhydrous conditions.



Q. 25 Give reason for the following:

a. During the electrophilic substitution reaction of haloarenes, para substituted derivative is the major product.

b. The product formed during S_N1 reaction is a racemic mixture.

Answers:

- a. At the ortho position, higher steric hindrance is there, hence para isomer is usually predominate and is obtained in the major amount.
- b. During the S_N1 mechanism, intermediate carbocation formed is sp^2 hybridized and planar in nature. This allows the attack of nucleophile from either side of the plane resulting in a racemic mixture. (1)

Q. 26. Identify the major product formed when 2-cyclohexylchloroethane undergoes a dehydrohalogenation reaction. Name the reagent which is used to carry out the reaction.

Answer:

The major product formed when 2-cyclohexylchloroethane undergoes dehydrohalogenation reaction is 1-cyclohexylethene. The reagent which is used to carry out the reaction is ethanolic KOH.

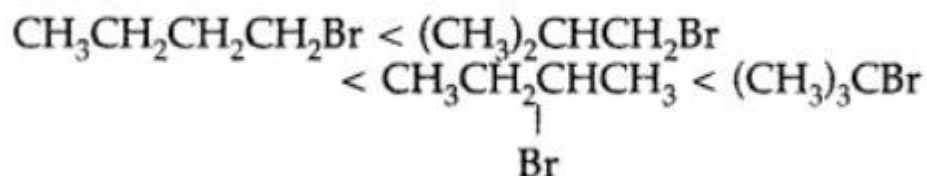
Q. 27. Predict the order of reactivity of the following compounds in S_N1 reaction :

$C_6H_5CH_2Br$, $C_6H_5C(CH_3)(C_6H_5)Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$

Answer: $C_6H_5C(CH_3)(C_6H_5)Br > C_6H_5CH(C_6H_5)Br > C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$

Q. 28. . (a) Predict the increase in order of reactivity of four isomeric bromobutanes in S_N1 reaction.

Answer:



(b) In the following pair of halogen compounds, which compound will react faster by S_N1 mechanism? $(CH_3)_3C-Cl$ and $CH_3CH_2CH(Cl)CH_3$

Ans: $(CH_3)_3C-Cl$

Q. 29. How are the following conversions carried out?

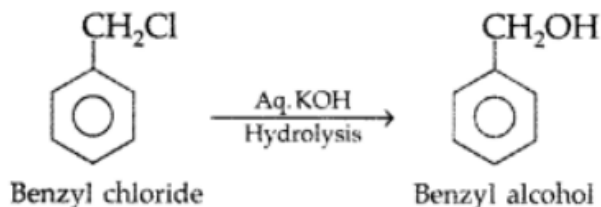
- (i) Benzyl chloride to benzyl alcohol,
(ii) Methyl magnesium bromide to 2-methyl- propan-2-ol.
(iii) Chlorobenzene to Toluene

OR

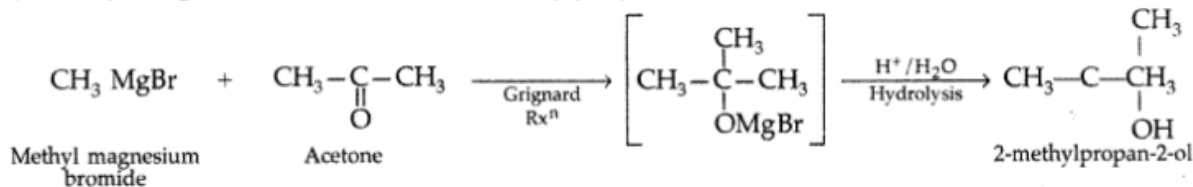
- (i) Aniline to bromobenzene
(ii) Chlorobenzene to 2-chloroacetophenone
(iii) Chloroethane to butane

Answer:

(i) Benzyl chloride to benzyl alcohol



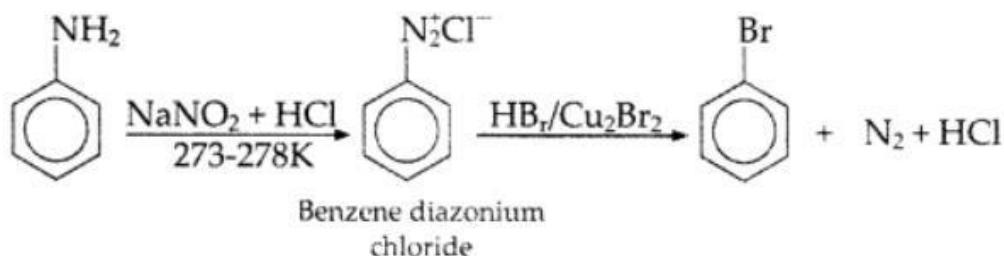
(ii) Methyl magnesium bromide to 2-methylpropan-2-ol



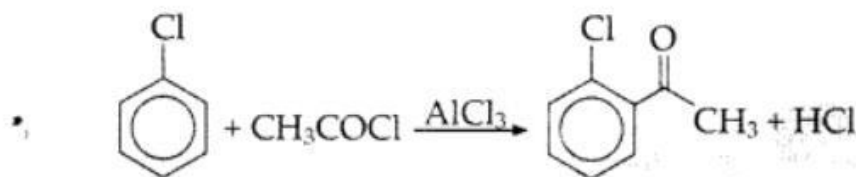
(iii) $C_6H_5Cl + 2Na + CH_3Cl \rightarrow$ (in presence of dry ether) $C_6H_5-CH_3$

OR

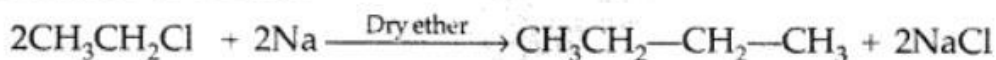
(I)



(ii) Chlorobenzene to 2-chloroacetophenone



(iii) Chloroethane to butane



Q. 30. Give reasons :

- n-Butyl bromide has higher boiling point than t-butyl bromide.
- Racemic mixture is optically inactive.
- The presence of nitro group (-NO₂) at o/p positions increases the reactivity of haloarenes towards nucleophilic substitution reactions.

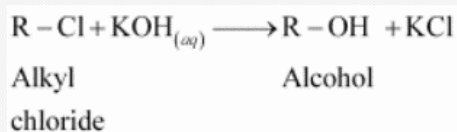
Answer:

- n-Butyl bromide has higher boiling point than t-butyl bromide because it has larger surface area hence have more Van der Waals' forces.
- Rotation due to one enantiomer is cancelled by another enantiomer.
- The presence of nitro group (-NO₂) at ortho and para positions withdraws the electron density' from benzene ring and thus facilitating the attack of nucleophile.

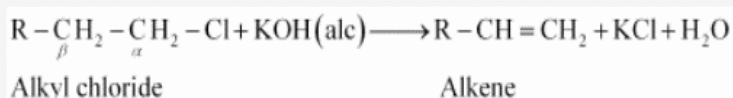
Q. 31. The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.

Answer:

In an aqueous solution, KOH almost completely ionizes to give OH^- ions. OH^- ion is a strong nucleophile, which leads the alkyl chloride to undergo a substitution reaction to form alcohol.



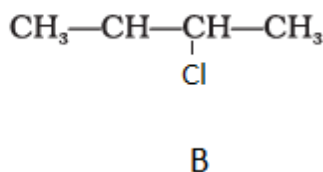
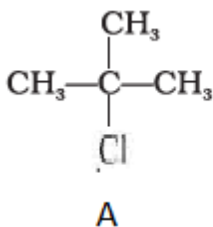
On the other hand, an alcoholic solution of KOH contains alkoxide (RO^-) ion, which is a strong base. Thus, it can abstract a hydrogen from the β -carbon of the alkyl chloride and form an alkene by eliminating a molecule of HCl.



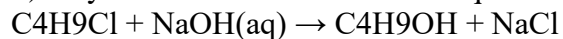
OH^- ion is a much weaker base than RO^- ion. Also, OH^- ion is highly solvated in an aqueous solution and as a result, the basic character of OH^- ion decreases. Therefore, it cannot abstract a hydrogen from the β -carbon.

Q. 32 Compound (A) with molecular formula $\text{C}_4\text{H}_9\text{Cl}$ is treated with aq. NaOH solution. The rate of this reaction depends upon the concentration of the compound 'A' only. When an optically active isomer 'B' of this compound was treated with aq. NaOH solution, the rate of reaction was found to be dependent on concentration of compound and NaOH both. (i) Write down the structural formula of both compounds 'A' and 'B'. (ii) Out of these two compounds, which one will be converted to the product with inverted configuration. (iii) which one will undergo racemisation on treatment with aq. NaOH.

Ans.

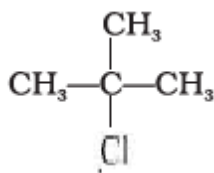


ii) Alkyl halides on treatment with aq. KOH gives alcohol as the major product.



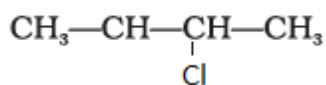
In the case of compound A, rate of reaction depends upon the concentration of A only, the reaction proceeds through the $\text{S}_{\text{N}}1$ mechanism as the alkyl halide is a tertiary alkyl halide.

A should be

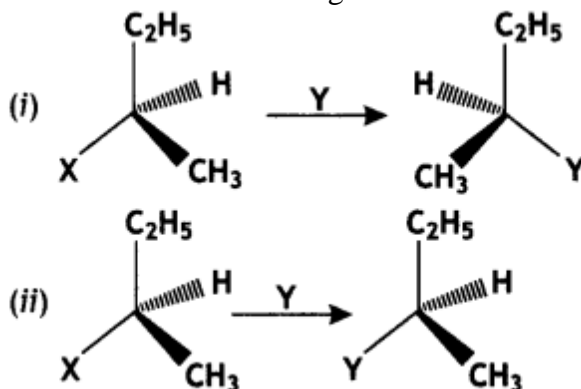


iii) In the case of compound .B. which is an optically active isomer of .A., rate of reaction depends upon the concentration of .B. as well as NaOH. Therefore, the reaction occurs by SN₂ mechanism which is favoured by 1^o and 2^o alkyl halides.

The compound B is



Q 33. Which of the following two reactions is SN₂ and why?



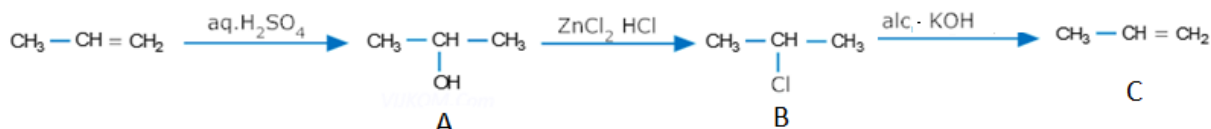
Ans. Reaction (i) is SN₂ because it proceeds by inversion of configuration

Q. 34 An organic compound 'A' having molecular formula C₃H₆ on treatment with aqueous sulphuric acid given 'B' which on treatment with Lucas reagent gives 'C'. The compound 'C' on treatment with ethanolic KOH gives back on compound 'A'. Identify A, B, & C.

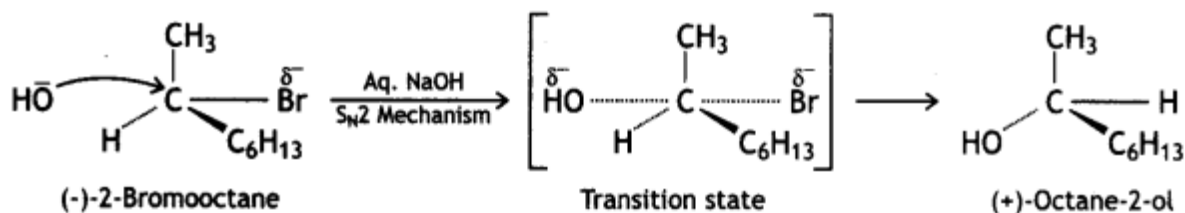
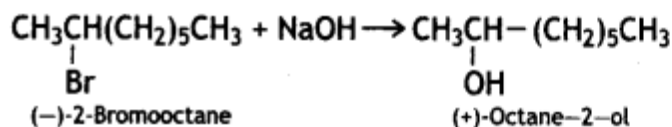
b) Propose the mechanism of the reaction taking place when (i) (-) - 2 - Bromooctane reacts with sodium hydroxide to form (+) - octane-2-ol.

Answer.

a)



b)



Q 35. Give reasons for the following:

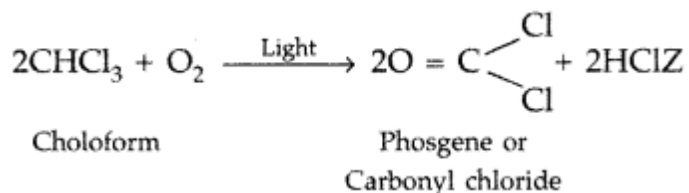
- (i) Benzyl chloride is highly reactive towards the $\text{S}_{\text{N}}1$ reaction.
- (ii) 2-bromobutane is optically active but 1-bromobutane is optically inactive.
- (iii) Electrophilic reactions in haloarenes occur slowly.
- (iv) Chloroform is stored in closed dark brown bottles.

Ans. (i) Benzyl carbonium ion is stabilized by resonance.

(ii) 2-Bromobutane is chiral, therefore, optically active, whereas 1-chlorobutane is not chiral, therefore optically inactive.

(iii) It is due to $-\text{I}$ effect of halogens, it deactivates benzene ring towards electrophilic substitution reactions.

(iv) (i) CHCl_3 is stored in dark coloured bottles to cut off light because CHCl_3 is slowly oxidised by air in presence of light to form an extremely poisonous gas, carbonyl chloride, popularly known as phosgene.



Q. 36. Which compound in each of the following pairs will react faster in $\text{S}_{\text{N}}2$ reaction with $-\text{OH}$? (i) CH_3Br or CH_3I (ii) $(\text{CH}_3)_3\text{CCl}$ or CH_3Cl

Answer: (i) CH_3I : Because Iodide is better leaving group than bromide. (ii) CH_3Cl : Carbon atom leaving group is less hindered.

CASE BASED QUESTIONS:- .

Case i) Read the following passage and answer the questions given below.

Alkyl halides are best prepared from alcohols, on treating with Hydrogen halides, phosphorus halides or thionyl chloride. Thionyl chloride is preferred because other two products are escapable gases. The reaction of primary secondary and tertiary alcohols with HCl need a catalyst ZnCl_2 . With tertiary alcohol the reaction is conducted by shaking with Con. HCl at room temperature. Tertiary alcohols are more reactive. The above methods are not applicable for the preparation of Aryl halides because the carbon oxygen bond in phenols has a partial double bond character and is difficult to break being stronger than a single bond

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below :

- (a) Both assertion and reason are true and reason is the correct explanation of assertion.
- (b) Both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) Assertion is true but reason is false.
- (d) Assertion is false but reason is true

- 1) **Assertion:** Thionyl chloride is the best reagent to convert alcohols to Alkyl chlorides
Reason: With Thionyl chloride alkyl chloride is the only product formed.
- 2) **Assertion:** Primary secondary and tertiary alcohols can be distinguished using Lucas test
Reason: Tertiary alcohols immediately form turbidity due to the formation of alkyl halides.
- 3) **Assertion:** Primary alcohols react fast with HCl and forms alkyl halide at room temperature.
Reason: Alkyl halides are insoluble in water.
- 4) **Assertion:** Aryl halides can be prepared by treating phenols with halogen acid
Reason: In phenol C-O bond is having partial double bond character.

Case ii) Read the following passage and answer the questions given below.

SN₁ reactions are generally carried out in presence of protic solvents. Like acetic acid. The reaction between a tertiary alkyl halide and nucleophile follows the first order kinetics. The rate of reaction depends on the concentration of alkyl halide .it occurs in two steps. In first step C-X bond undergoes cleavage to form carbocation, it is then attacked by nucleophile in second step which is very fast. The energy needed for breaking C-X bond is obtained through solvation of halide ion with proton of protic solvent. Greater the stability of carbocation, Greater will be its ease of formation and faster will be its rate of reaction. In the case of optically active alkyl halide SN₁ reaction is accompanied by Racemisation. The carbocation formed in step one is sp² hybridised. Which is trigonal planar. The attack of nucleophile may be accomplished from either side to give a mixture of products.

- 5) **Assertion:** SN₂ reaction takes place in presence of protic solvent.
Reason: The energy is released by the solvation of halide ion with proton.
- 6) **Assertion.** The rate of SN₁ reaction depends only on the concentration of alkyl halide.
Reason: Formation of carbocation is slow step and slow step determines the rate of reaction.
- 7) **Assertion:** Tertiary alkyl halides reacts faster in SN₁ reaction
Reason. Tertiary carbocations are more stable and formed at faster rate.
- 8) **Assertion:** During SN₁ reaction of an optically active alkyl halide Racemisation takes place
Reason. Racemic mixture consists of equal amount of dextro and leavo isomer.
- 9) **Assertion:** Attack of nucleophile to carbon of carbocation takes place through either side forming two isomers with opposite configuration.
Reason: Carbocation is sp³ hybridised and have trigonal planar geometry
- 10) **Assertion:** - In SN₁ reaction second step is very fast and reversible.
Reason: - The carbocation formed is highly unstable and highly reactive.

Answer

1)c 2) b 3) d 4) d 5) d 6) a 7) a 8) b 9) c 10) d

Q. 3 Read the passage given below and answer the following questions:

Nucleophilic substitution reactions are of two types; substitution nucleophilic bimolecular (SN₂) and substitution nucleophilic unimolecular (SN₁) depending on molecules taking part in determining the rate of reaction. Reactivity of alkyl halide towards SN₁ and SN₂ reactions depends on various factors such as steric hindrance, stability of intermediate or transition state and polarity of solvent. SN₂ reaction mechanism is favoured mostly by primary alkyl halide or transition state and polarity of solvent, SN₂ reaction mechanism is favoured mostly by primary alkyl halide then secondary and then tertiary. This order is reversed in case of SN₁ reactions.

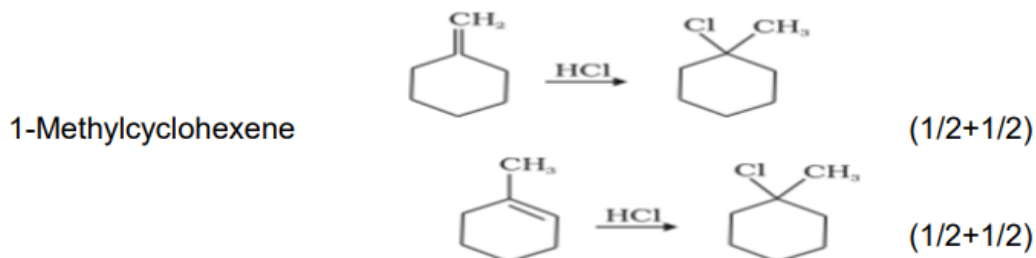
a. Name the possible alkenes which will yield 1-chloro-1-methylcyclohexane

on their reaction with HCl. Write the reactions involved. (1+1)

b. Allyl chloride is hydrolysed more readily than n-propyl chloride. Why? (1)

c. Why are haloalkanes more reactive towards nucleophilic substitution reactions than haloarenes and vinylic halides? (1)

a. Methylene cyclohexane



b. Allyl chloride shows high reactivity as the carbocation formed in the first step is stabilised by resonance while no such stabilisation of carbocation exists in the case of n-propyl chloride. (1)

c. Haloalkanes are more reactive than haloarenes and vinylic halides because of the presence of partial double bond character C-X bond in haloarenes and vinylic halides. Hence they do not undergo nucleophilic reactions easily. (1)

Q. 4. Read the passage given below and answer the following questions:

Nucleophilic substitution reaction of halo alkane can be conducted according to both SN 1 and SN 2 mechanisms. However, which mechanism it is based on is related to such factors as the structure of halo alkane, and properties of leaving group, nucleophilic reagent and solvent.

Influences of halogen: No matter which mechanism the nucleophilic substitution reaction is based on; the leaving group always leave the central carbon atom with electron pair. This is just the opposite of the situation that nucleophilic reagent attacks the central carbon atom with electron pair. Therefore, the weaker the alkalinity of leaving group is, the more stable the anion formed is and it will be more easier for the leaving group to leave the central carbon atom; that is to say, the reactant is more easier to be substituted. The alkalinity order of halogen ion is $I^- < Br^- < Cl^- < F^-$ and the order of their leaving tendency should be $I^- > Br^- > Cl^- > F^-$.

Therefore, in four halides with the same alkyl and different halogens, the order of substitution reaction rate is $RI > RBr > RCl > RF$. In addition, if the leaving group is very easy to leave, many carbocation intermediates are generated in the reaction and the reaction is based on SN 1 mechanism. If the leaving group is not easy to leave, the reaction is based on SN 2 mechanism.

Influences of solvent polarity: In SN 1 reaction, the polarity of the system increases from the reactant to the transition state, because polar solvent has a greater stabilizing effect on the transition state than the reactant, thereby reduce activation energy and accelerate the reaction. In SN 2 reaction, the polarity of the system generally does not change from the reactant to the transition state and only charge dispersion occurs. At this time, polar solvent has a great stabilizing effect on Nu than the transition state, thereby increasing activation energy and slow down the reaction rate. In a word, the level of solvent polarity has influence on both SN 1 and SN 2 reactions, but with different results. Generally speaking, weak polar solvent is favorable for SN 2 reaction, while strong polar solvent is favorable for SN 1 reaction, because only

under the action of polar solvent can halogenated hydrocarbon dissociate into carbocation and halogen ion and solvents with a strong polarity is favorable for solvation of carbocation, increasing its stability. Generally speaking, the substitution reaction of tertiary halo alkane is based on SN 1 mechanism in solvents with a strong polarity (for example, ethanol containing water).

The following questions are multiple choice questions. Choose the most appropriate answer:

Q. 1. SN1 mechanism is favored in which of the following solvents:

- (A) benzene (B) carbon tetrachloride (C) acetic acid (D) carbon disulphide

Ans. Option(C) is correct

Q. 2. Nucleophilic substitution will be fastest in case of:

- (A) 1-Chloro-2,2-dimethyl propane (B) 1-Iodo-2,2-dimethyl propane
(C) 1-Bromo-2,2-dimethyl propane (D) 1-Fluoro-2,2-dimethyl propane

Ans. Option (B) is correct.

Q. 3. SN 1 reaction will be fastest in which of the following solvents?

- (A) Acetone (dielectric constant 21) (B) Ethanol (dielectric constant 24)
(C) Methanol (dielectric constant 32) (D) Chloroform (dielectric constant 5)

Ans. Option (C) is correct.

Q. 4. Polar solvents make the reaction faster as they:

- (A) destabilize transition state and decrease the activation energy
(B) destabilize transition state and increase the activation energy
(C) stabilize transition state and increase the activation energy
(D) stabilize transition state and decrease the activation energy

Ans. Option (D) is correct.

Q. 5. SN1 reaction will be fastest in case of:

- (A) 1-Chloro-2-methyl propane (B) 1-Iodo-2-methyl propane
(C) 1-Chlorobutane (D) 1-Iodobutane

Ans. Option (B) is correct

Q. 5 Read the passage given below and answer the following questions:

The substitution reaction of alkyl halides occurs in SN1 or SN2 mechanism whatever mechanism alkyl halide follow for substitution reaction to occur; the polarity of the carbon-halogen bond is responsible for the substitution reaction. The rate of SN1 reactions is governed by the stability of carbocation where as for SN2 reactions steric factor is the deciding factor. If the starting material is a chiral compound, we may end up with an inverted product or racemic mixture depending upon the type of mechanism followed by alkyl halide. Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons: (i) In haloarenes, the electron pairs on halogen atom are in conjugation with δ -electrons of the ring. (ii) In haloalkane, the carbon atom attached to halogen is sp^3 hybridized while in case of haloarene, the carbon atom attached to halogen is sp^2 -hybridized. (iii) In case of haloarenes, the phenyl cation formed as a result of self-ionization will not be stabilized by resonance.

The following questions are Multiple Choice Questions. Choose the most appropriate answer:

Q. 1. A primary alkyl halide would prefer to undergo _____.

- (A) SN1 reaction (B) SN2 reaction (C) α -Elimination (D) Racemization

Ans. Option (B) is correct.

Q. 2. Which of the following alkyl halides will undergoes SN1 reaction most readily?

- (A) $(CH_3)_3C-F$ (B) $(CH_3)_3C-Cl$ (C) $(CH_3)_3C-Br$ (D) $(CH_3)_3C-I$

Ans. Option (D) is correct

Q. 3. Which of the following statements are correct about the reaction intermediate in SN1 reaction?

- (A) Intermediate is unstable because in this carbon is attached to 5 atoms.
- (B) Intermediate is unstable because carbon atom is sp^2 hybridized.
- (C) Intermediate is stable because carbon atom is sp^2 hybridized.
- (D) Intermediate is more stable than the reactant.

Ans. Option (C) is correct.

Q. 4. Reaction of $C_6H_5CH_2Br$ with aqueous sodium hydroxide follows_____.

- (A) SN1 mechanism
- (B) SN2 mechanism
- (C) Any of the above two depending upon the temperature of reaction
- (D) Saytzeff rule.

Ans. Option (A) is correct.

Q.5. Molecules whose mirror image is non-superimposable over them are known as chiral. Which of the following molecules is chiral in nature?

- (A) 2-Bromobutane
- (B) 1-Bromobutane
- (C) 2-Bromopropane
- (D) 2-Bromopropan-2-ol

Ans. Option (A) is correct

Q.6 .Read the given passage and answer the questions that follow:

Halo alkanes are colorless (when pure), sweet smelling liquids. CH_3Cl , CH_3Br and C_2H_5Cl and freons are gases. Boiling point increases with increase in molecular weight and increase in carbon chain and decreases with branching. They are insoluble in water due to inability to form H-bonds with water. Dipole moment increases with polarity, density increases with increase in molar mass. They are non-inflammable, therefore, CCl_4 is used as fire extinguisher under the name pyrene. p-dichloro benzene has zero dipole moment, higher melting point than o-dichloro benzene due to symmetry, fits into crystal lattice readily. Haloalkanes undergo nucleophilic substitution reaction by SN2 mechanism, $1^\circ > 2^\circ > 3^\circ$, SN1 if carbocation formed is stable. They also undergo nucleophilic elimination reactions with alcoholic KOH. Haloarenes are less reactive than halo alkanes towards nucleophilic substitution due to resonance. Haloarenes undergo electrophilic substitution reaction like nitration, sulphonation, Friedel Crafts alkylation, acylation. Chloroform is used as solvent, Freon is used as refrigerant, dichloromethane is used as paint remover. Iodoform is used as antiseptic. DDT is insecticide but non-biodegradable.

Q.1. Arrange R—F, R—Br, R—I, R—Cl in increasing order of boiling point.

- (A) R—F < R—Cl < R—Br < R—I
- (B) R—Cl < R—Br < R—I < R—F
- (C) R—Br < R—I < R—F < R—Cl
- (D) R—I < R—F < R—Cl < R—Br

Ans. A

Q.2. Name the chlorine containing drug used in treatment of coronavirus and malaria.

- (A) Chloroquin
- (B) Hydroxychloroquin
- (C) Pencillin
- (D) Pyrene

Ans. B

(OR)

Which of the following have highest boiling point?

- (A) CH_3CH_2Br
- (B) CH_3CH_2Cl
- (C) $CH_3CH_2CH_2I$
- (D) $CH_3CH_2CH_2F$

Ans: (C)

As the size of halogen atom increases the boiling points also increase due to more molar mass.

Q.3. Toluene reacts with a halogen in the presence of iron (III) chloride giving ortho and para halo compounds. The reaction is

- (A) Electrophilic elimination reaction (B) Electrophilic substitution reaction
(C) Free radical addition reaction (D) Nucleophilic substitution reaction

Ans. B

Q4. What is the stereochemistry of the product formed if (+) 2-bromopentane reacts with aqueous KOH by S_N2 mechanism.

- (A) (-) (+) 2-pentanol (B) (+) 2-pentanol (C) (-) 2-pentanol (D) None of the above.

Ans. C

Q5. Out of the following which one undergoes S_N1 mechanism faster?

- (A) $CH_2=CH-CH_2Cl$ (B) $CH_3CH_2CH_2Cl$
(C) $(CH_3)_2CHCl$ (D) $CH_3CH_2CH_2Cl$

Ans. (A) $CH_2=CH-CH_2Cl$ because $CH_2=CH-CH_2^+$ is more stable due to resonance

Q. 6 The polarity of carbon-halogen bond of alkyl halide is responsible for their nucleophilic substitution and elimination reaction. Nucleophilic substitution reactions are categorised into S_N1 and S_N2 . Chirality has a profound role in understanding the reaction mechanism of S_N1 and S_N2 reactions. S_N2 reactions of chiral alkyl halides are characterized by inversion of configuration while S_N1 reactions are categorised by racemization. Due to their tendency to undergo substitution by a large number of nucleophiles, they form a variety of products

a) Which will react faster in S_N2 reaction

- (1) 1-bromopentane (2) 2-bromopentane (3) Both of these (4) Non of these

b) Which will undergo S_N1 reaction faster

- (1) 2-chloro-2-methylpropane (2) 2-chlorobutane (3) None of these (4) Both of these

c) Which one is the correct statement

- (1) In S_N2 racemization occurs (2) S_N1 is a two-step reaction
(3) In S_N1 reaction inversion takes place (4) S_N2 is a two-step reaction

d) What happens when CH_3Br is treated with KCN

- (1) Racemization occurs (2) S_N1 reaction takes place
(3) S_N2 reaction takes place (4) More than one option correct

Answers 1) a - 1 b - 1 c - 2 d - 3