Class 12 Haloalkanes and Haloarenes Important Questions with Answers

Short Answer Type Questions

Q1. Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts. But why does preparation of aryl iodides require the presence of an oxidising agent?

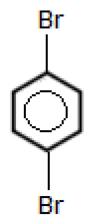
Answer:

In nature, iodination reactions are reversible. The HI produced during iodination is eliminated by oxidation in order to carry out the reaction in the forward direction. The oxidising agent HIO_4 is used. In nature, iodination reactions are reversible. The HI produced during iodination is eliminated by oxidation in order to carry out the reaction in the forward direction. The oxidising agent HIO_4 is used.

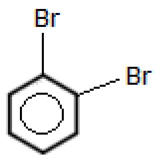
Q2. Out of o-and p-dibromobenzene which one has a higher melting point and why?

Answer:

The melting point of p-dibromobenzene is higher than that of the other two compounds. This is due to the symmetry of p-dibromobenzene, which allows the molecule to fit into the crystal lattice more easily. As a result, breaking the bonds between the molecules demands a higher temperature, resulting in a higher melting point.



p-Dibromobenzene



o-Dibromobenzene

Q3. Which of the compounds will react faster in S_N1 reaction with the "OH" ion?
CH_3-CH_2-C1 or $C_6H_5-CH_2-Cl$

Answer:

In the rate-determining phase of the S_N1 reaction, a carbocation intermediate is initially generated. The benzyl carbocation is resonance stabilised in benzyl chloride.

In the case of ethyl chloride or chloroethane, however, the $CH_3CH_2^+$ carbocation can only have a hyper-conjugation effect. It is less stable in comparison. As a result, in the S_N1 reaction, benzyl chloride reacts faster with the OH ion than ethyl chloride.

Q4. Why does iodoform have appreciable antiseptic properties?

Answer:

The antiseptic qualities of iodoform (CHI_3) are attributable to iodine, which is produced when the substance comes into contact with the skin. When Iodoform comes into touch with skin, it releases I_2. Iodine's antiseptic properties are attributable to the liberation of I_2, not iodoform itself.

Q5. Haloarenes are less reactive than haloalkanes and haloarenes. Explain.

Answer:

Polarity of the carbon-halogen bond- As we all know, the higher the polarity, the higher the reactivity. The dipole moment of the C-X bond in haloarenes is less than that of the haloalkane (for example, the dipole moment for C-X in haloalkane is 2.0-2.2D while the dipole moment for chlorobenzene is 1.7D), hence the higher the polarity of the haloalkane, the more reactive it is.

Haloarenes are in the sp^2 hybridization state, whereas haloalkanes are in the sp^3 hybridization state. Because the bond length in the sp^2 hybridisation is shorter than in the sp^3 hybridisation, the bond generated by the haloarenes is stronger than the haloalkane bond. so the haloarenes are less reactive.

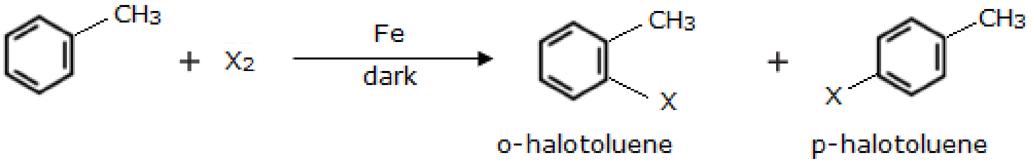
The electron of the benzene ring is in combination with the electron pair of the halogen in the haloarenes, resulting in resonance stabilisation. As a result of the resonance hybrid nature of haloarenes, the C-X bond possesses a partial double bond character, making the haloarene more stable and less reactive.

Q6. Discuss the role of Lewis acids in the preparation of aryl bromides and chlorides in the dark.

Answer:

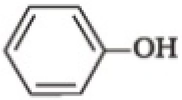
Lewis acids are species that lack electrons. They are the ones who cause halogen molecules to undergo heterolytic fission. Lewis acid's function is to form an electrophile. The electrophile produces aryl bromides and chlorides by attacking the electron-rich benzene ring. Lewis acid's function is to form an electrophile. The electrophile produces aryl bromides and chlorides by attacking the electron-rich benzene ring.

Aryl bromides and chlorides can be prepared in the presence of Lewis acid catalysts (iron or iron chloride) from the electrophilic substitution of arenas with bromine and chlorine respectively.



Q7. Which of the following compounds (a) and (b) will not react with a mixture of NaBr and H_2SO_4. Explain why?

(a) $CH_3CH_2CH_2OH$ (b)



Answer:

When we combine NaBr with H_2SO_4, we produce Br_2 gas. The product (b) will not react with Br_2 gas in this case. Because of resonance, it has already created a stable structure. The partial double bond feature of a bond increases the bond's strength while decreasing its stability. Because phenol is resonance stabilised, it will not react with a combination of NaBr and H_2SO_4. The double bond feature appears in the C bond of phenol due to resonance, making it more stable than alcohol.

Q8. Which of the products will be a major product in the reaction given below? Explain.

$$CH_3CH=CH_2 + HI \longrightarrow \underset{(A)}{CH_3CH_2CH_2I} + \underset{(B)}{CH_3CHICH_3}$$

Answer:

According to Markovnikov's Rule, (B) will be the major product. The electronegative part of the reagent is added to the carbon of the double bond with the least number of hydrogens.

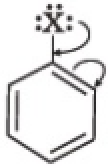
As a result of the reaction, compound B will be generated as a primary product. Also, according to the Markonikov rule, 2-Idopropane is the most important product. When an unsymmetrical reagent is added to an unsymmetrical alkene, the negative part of the reagent is connected to the unsaturated C atom with the least number of hydrogen atoms, according to Markonikoff's rule.

Q9. Why is the solubility of haloalkanes in water very low?

Answer:

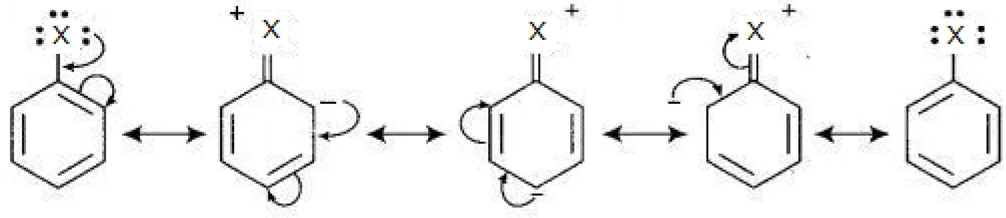
Because energy is required to overcome the attractions between the haloalkane molecules as well as to break the hydrogen bonds between water molecules in order to dissolve a haloalkane in water, haloalkane are only minimally soluble. New attractions between the haloalkane and the water molecules, on the other hand, release less energy since they are weaker than the initial hydrogen bonds in water.

Q10. Draw other resonance structures related to the following structure and find out whether the functional group present in the molecule is ortho, para directing or meta directing.



Answer:

Resonance in halobenzene.



Because electron density is higher at ortho and para locations, the functional groups contained in these compounds are ortho-para directed.

Q11. Classify the following compounds as primary, secondary and tertiary halides.
(i) 1-Bromobut-2-ene
(ii) 4-Bromopent-2-ene
(iiii) 2-Bromo-2-methylpropane

Answer:

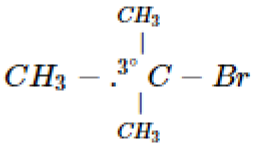
(i) Primary (ii) Secondary (iii) Tertiary

(i) $CH_3CH = CH - \overset{1°}{C}H_2Br$ = Primary halide

(1-Bromobut-2-ene)

(ii) $CH_3 - \overset{2°}{C}HBr - CH = CH - CH_3$ = Secondary halide

(4-Bromopent-2-ene)

(iii) 

$CH_3 - \overset{3°}{C}(CH_3)_2 - Br$ = Tertiary halide

(2-Bromo-2-methylpropane)

Q12. Compound 'A' with the molecular formula C_4H_9Br is treated with aq. KOH solution. The rate of this reaction depends upon the concentration of the compound 'A' only. When another optically active isomer 'B' of this compound was treated with aq.KOH solution, the rate of reaction was found to be dependent on concentration of compound and KOH 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?

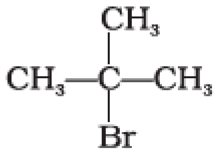
Answer:

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

$C_4H_9Br + KOH(aq) \rightarrow C_4H_9OH + KBr$

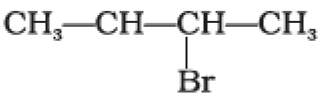
In the case of compound .A. rate of reaction depends upon the concentration of .A. only, the reaction proceeds through the SN mechanism. Since the SN mechanism is favoured by 3° alkyl halides.

A should be



$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large Br}{|}}{C}}-CH_3$$

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 KOH. Therefore, the reaction occurs by SN mechanism which is favoured by 1° and 2° alkyl halides.
The compound B is

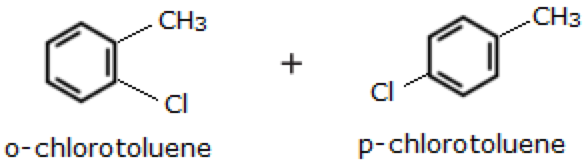


$$CH_3-CH-\underset{\underset{\large Br}{|}}{CH}-CH_3$$

Q13. Write the structures and names of the compounds formed when compound 'A' with the molecular formula C_7H_8 is treated with Cl_2 in the presence of $FeCl_3$.

Answer:

When compound 'A' with molecular formula, C_7H_8, is treated with Cl in the presence $FeCl_3$, o-chlorotoluene or p-chlorotoluene will be formed as the compound A with molecule formula C_7H_8, is toluene.



Q14. Identify the products A and B formed in the following reaction
(a) $CH_3\text{-}CH_2\text{-}CH=CH\text{-}CH_3 + HCl \rightarrow A + B$

Answer:

The products formed are 2-chloro-pentane and 3-chloro-pentane.

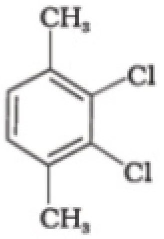
The addition of hydrogen and halide on both sides of the double bond occurs when an alkene reacts with hydrogen halide. Hydrohalogenation is the name for this reaction.

2-chloro-pentane and 3-chloro-pentane are the results of the process.

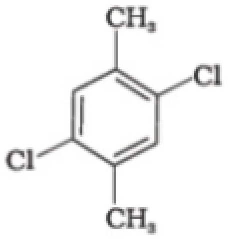
These products are created when the chlorine atom joins the second carbon atom and the hydrogen atom joins the third carbon atom in the first product. The chlorine atom is transferred to the third carbon atom, while hydrogen is transferred to the second carbon atom in the second product.

$$CH_3CH_2CH{=}CH{-}CH_3 + HCl \longrightarrow CH_3CH_2CH_2\underset{Cl}{C}HCH_3 + CH_3CH_2\underset{Cl}{C}HCH_2CH_3$$

Q15. Which of the following compounds will have the highest melting point and why?



(I)



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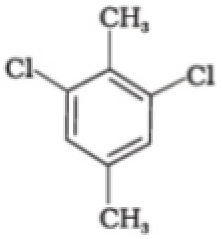


(III)

Answer:

Compound II is most symmetrical because it has both CH_3 groups and Cl atoms p− to each other. Therefore, it fits in the crystal lattice better than the other two isomers and hence it has a high melting point. Due to symmetry of para-positions; it fits into the crystal lattice better than other isomers.

Q16. Write down the structure and IUPAC name for neopentyl bromide.

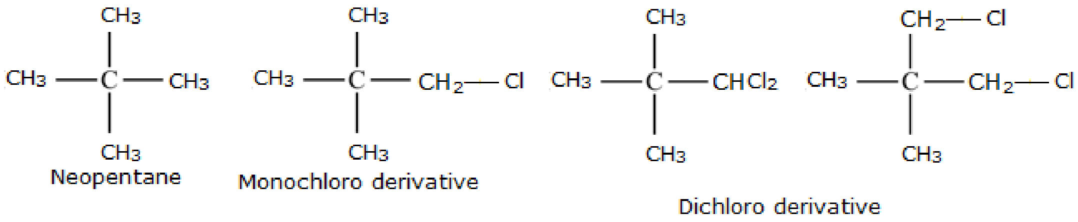
Answer:

IUPAC name ⇒ 1-bromo-2,2-dimethylpropane
Common name ⇒ neo-pentylbromide

Q17. A hydrocarbon of molecular mass 72 g mol/l gives a single monochloro derivative and two dichloro derivatives on photo chlorination. Give the structure of the hydrocarbon.

Answer:

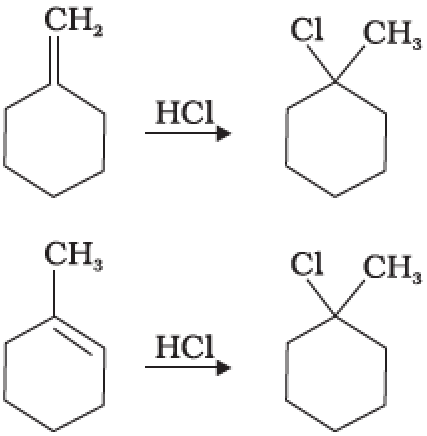
Molecular mass of hydrocarbon = 72
If it is a saturated hydrocarbon (alkane) then its molecular formula is C_nH_{2n+2}
Thus, the molecular formula of hydrocarbon is C_5H_{12}
Pentane has a molecular mass of 72g mol^{-1}, the isomer of pentane which yields a single monochloro derivative should have all the 12 hydrogens equivalent.
The structure of the alkane and the chloride derivatives are given as follows.



Q18. Name the alkene which will yield 1-chloro-1-methylcyclohexane by its reaction with HCl. Write the reactions involved.

Answer:

There are two compounds which can yield 1-chloro-1-methylcyclohexane, methylenecyclohexane and 1-methylcyclohex-1-ene.

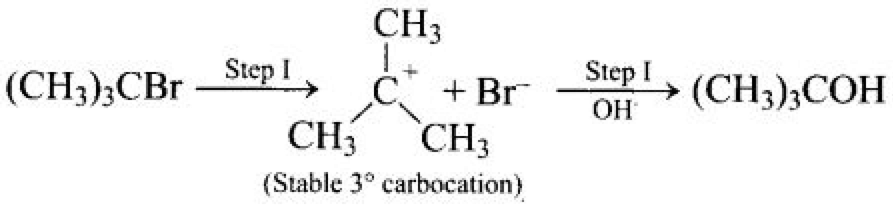


Q19. Which of the following haloalkanes reacts with aqueous KOH most easily? Explain why.
(i) 1-Bromobutane
(ii) 2-Bromobutane

(iii) 2-Bromo-2-methylpropane
(iv) 2-Chlorobutane

Answer:

The correct answer is 2-Bromo-2-methylpropane. The tertiary carbocation formed in the reaction is stable in 2-Bromo-2-methylpropane. So these haloalkanes react with aqueous KOH most easily.

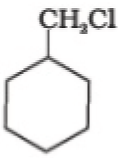


Q20. Why can aryl halides not be prepared by reaction of phenol with HCl in the presence of $ZnCl_2$?

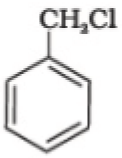
Answer:

When an alkyl halide is formed, a carbocation is formed, which then interacts with HCl to generate an alkyl halide.
However, in order for aryl halide to react with HCl in the presence of $ZnCl_2$, phenyl carbocation formation must occur, which is impossible because it is a highly unstable structure that never occurs in its free state. As a result, no aryl halide is generated.

Q21. Which of the following compounds would undergo S_N1 reaction faster and why?



(A)



(B)

Answer:

Compound (B) Undergoes S_N1 reaction faster than (A) because in case of (B), the carbocation formed after the loss of Cl^- is stabilised by resonance, whereas, no such stabilisation is possible in the carbocation obtained from (A).

Q22. Allyl chloride is hydrolysed more readily than n-propyl chloride. Why?

Answer:

Allyl chloride has a high reactivity because the carbocation generated by hydrolysis is stabilised by resonance, whereas n-propyl chloride has no such stabilisation.
Because n-propyl chloride does not undergo ionisation to form n-propyl carbocation, allyl chloride is more easily hydrolyzed than n-propyl chloride.

Q23. Why is it necessary to avoid even traces of moisture during the use of a Grignard reagent?

Answer:

Grignard reagents are highly reactive substances. They react with any source of proton to form hydrocarbons. Even water is sufficiently acidic to convert it into the corresponding hydrocarbon. So it is necessary to avoid even traces of moisture with the Grignard reagent as they arc highly reactive. Grignard reagents are highly reactive and react with water to give corresponding hydrocarbons.

$RMgX + H_2O \rightarrow RH + Mg(OH)X$.

Q24. How do polar solvents help in the first step in the S_N1 mechanism?

Answer:

Because polar solvents have the following features, they favour the S_N1 mechanism:

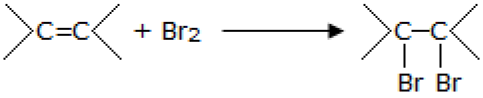
It stabilises the intermediate carbocation. Polar solvents, such as methanol, have a persistent dipole, which indicates that the carbocation will be stabilised via dipole-dipole interactions with the partial negative charge on the molecule.

It lowers the nucleophile's reactivity. The nucleophile and the polar solvent might interact electrostatically. This lowers the nucleophile's reactivity and speeds up the S_N1 reaction.

Q25. Write a test to detect the presence of a double bond in a molecule.

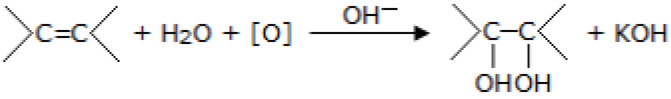
Answer:

Presence of double bond in a molecule is detected by the following two methods:
(i) Br_2 in the CCl4 test: when Br_2/CCl_4 is added to an unsaturated compound then the orange colour of bromine disappears and a dibromo derivative is formed. (colourless).



(ii) Bayer's test: when an alkaline solution of $KMnO_4$ is added to the solution of an unsaturated compound then its pink colour disappears due to the formation of a dihydroxy derivative.

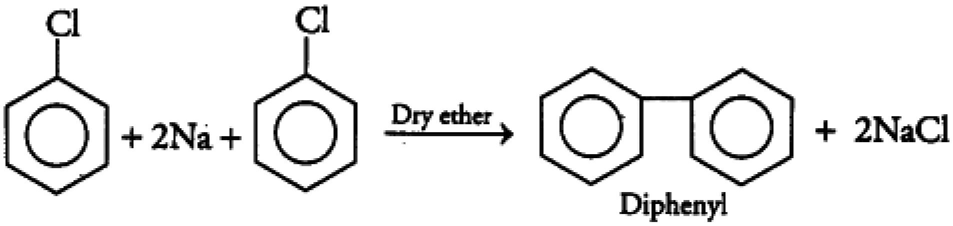
$$2KMnO_4 + H_2O \rightarrow 2KOH + 2MnO_2 + 3[O]$$



Q26. Diphenyls are a potential threat to the environment. How are these produced from aryl halides?

Answer:

Diphenyl is generated in the environment when mineral oil and coal are burned incompletely. It can be found in car exhaust gases as well as the exhaust air of home and industrial heating systems. Eye and skin irritation, as well as toxic effects on the liver, kidneys, and central/peripheral nervous system, have been documented after acute exposure to high doses of biphenyl. Ingestion of biphenyls affects the kidneys of animals as well. Diphenyl is formed when aryl halides are reacted with sodium in the presence of dry ether. Fitting reaction is the name for this reaction.



Q27. What are the IUPAC names of the insecticide DDT and benzene hexachloride? Why is their use banned in India and other countries?

Answer:

The IUPAC name of DDT is 2,2-bis (4-chloropheny)-1,1.1-trichloroethane and that of benzene hexachloride is 1,2,3,4,5,6-hexachlorocyclohexane.
Because they are not biodegradable, their usage has been outlawed in India and other countries. As a result, these insecticides penetrate the food chain of animals and accumulate in their fatty tissues over time, affecting their reproductive systems.

Q28. Elimination reactions (especially B-elimination) are as common as the nucleophilic substitution reaction in case of alkyl halides. Specify the reagents used in both cases.

Answer:

Nucleophilic substitution and elimination (beta-elimination) reactions are both possible with alkyl halides.

Although, with the correct reaction conditions and reagent selection, a specific product can be obtained. In most cases, the elimination reaction is best suited to strong and bigger bases, as well as high temperatures. The substitution reaction, on the other hand, is best for weaker and smaller bases at lower temperatures.

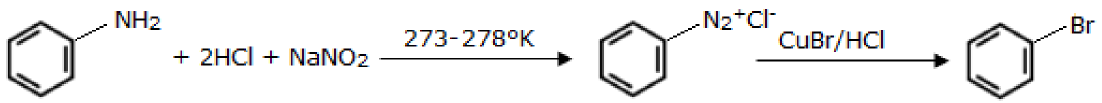
$$CH_3CH_2Br \xrightarrow[373K]{Aq.KOH} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

$$CH_3CH_2Br \xrightarrow[473-523K]{AlcKOH} \underset{\text{Ethene}}{CH_2=CH_2}$$

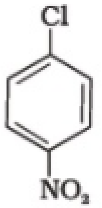
Q29. How will you obtain mono bromobenzene from aniline?

Answer:

Sandmeyer's reaction can be used to make mono bromobenzene from aniline ($C_6H_5NH_2$). A diazonium salt is generated when aniline suspended in cold mineral acid is treated with sodium nitrite. When the diazonium salt is combined with cuprous bromide, the diazonium ion is replaced by –Br, resulting in mono bromobenzene.



Q30. Aryl halides are extremely less reactive towards nucleophilic substitution. Predict and explain the order of reactivity of the following compounds towards nucleophilic substitution.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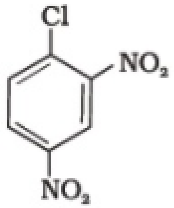
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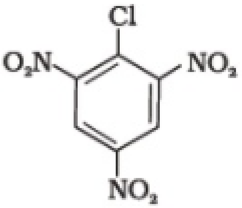

(III)

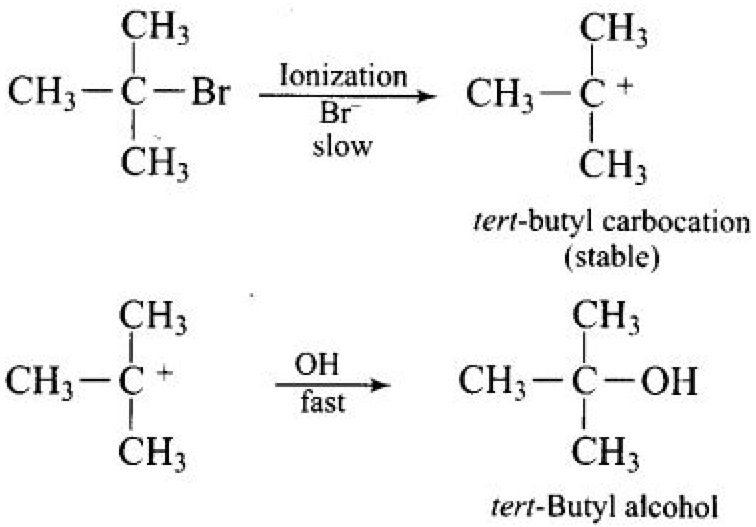
Answer:

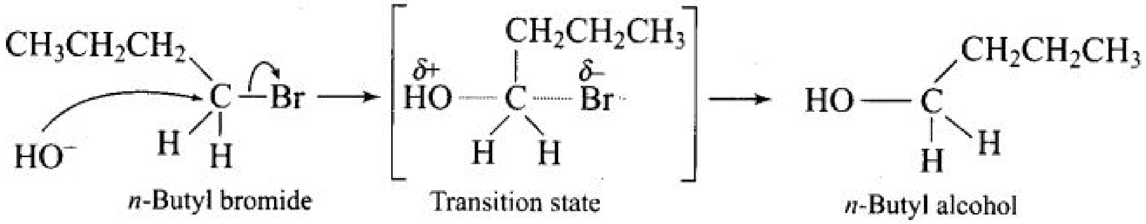
The nucleophilic substitution process is less reactive with aryl halides. The presence of an electron withdrawing group at the o- and p-positions improves the stability of intermediates and hence the reactivity of aryl halides in nucleophilic substitution reactions.
The reactivity of aryl halide will increase as the number of EWG at the o- and p-position increases. Compound (III) is the most reactive since it contains three EWG, whereas compound (I) contains just one EWG and is hence the least reactive. So, the order of reactivity is (I) < (II) < (III).

Q31. tert-Butyl Bromide reacts with aq. NaOH by S_N1 mechanism while n-butyl bromide reacts by S_N2 mechanism. Why?

Answer:

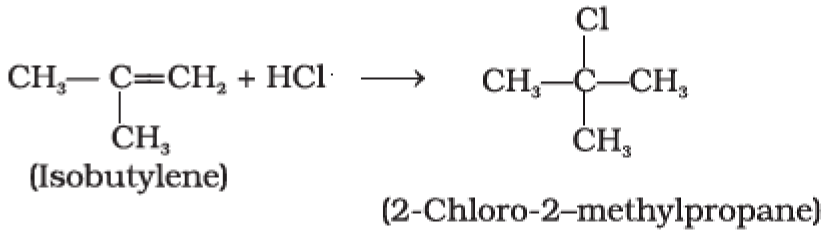
Because it can produce a stable carbocation in the first step after cleavage of the halide group, tert-butyl bromide is substituted using the S_N1 process. The nucleophile OH^- interacts with the carbocation next. The primary halide n-butylbromide, on the other hand, is unable to create a stable carbocation, therefore it undergoes the S_N2 process, which is a one-step substitution involving OH^- attack and concomitant X- leaving to form n-butyl alcohol.





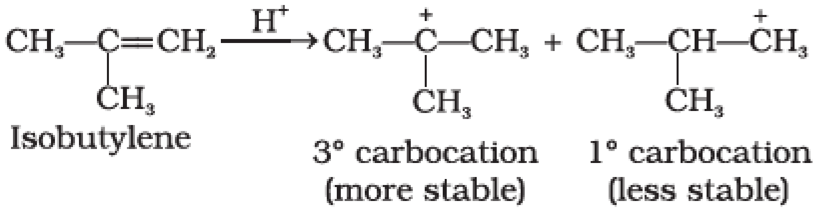
Q32. Predict the major product formed when HCl is added to isobutylene. Explain the mechanism involved.

Answer:



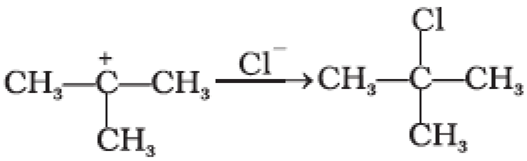
The mechanism involved in this reaction is given below.

Step I



$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 \xrightarrow{H^+} CH_3-\underset{\underset{CH_3}{|}}{\overset{+}{C}}-CH_3 + CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{+}{C}H_3$$

Step II



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{+}{C}}-CH_3 \xrightarrow{Cl^-} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_3$$

Q33. Discuss the nature of C-X bond in the haloarenes.

Answer:

The carbon of benzene is linked to the halogen in haloarenes. The electronegativity of halogen is higher than that of the benzene ring's sp2 hybridised carbon. As a result, the C- X bond is a polar bond. Aside from that, the halogen atom's lone pair of electrons are engaged in the benzene ring's resonance. As a result, this C- X bond now has a partial bond character.

Haloarenes' C-X bond is less polar than haloalkanes' C-X bond. The fact that the dipole moment of chlorobenzene (= 1.69 D) is slightly lower than that of CH_3Cl (= 1.83 D) supports this.

Q34. How can you obtain iodoethane from ethanol when no other iodine containing reagent except NaI is available in the laboratory?

Answer:

Ethanol is converted to chloroethane and -Cl can be replaced by iodine. Ethanol can be reacted with HCl to give chloroethane in the presence of $ZnCl_2$. Chloroethane when reacting with NaI gives iodoethane.

$$C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl \xrightarrow{NaI} C_2H_5I$$

Q35. Cyanide ion acts as an ambident nucleophile. From which end does it act as a stronger nucleophile in an aqueous medium? Give reason for your answer.

Answer:

It acts as a stronger nucleophile from the carbon end because it will lead to the formation of C-C bond which is more stable than C- N bond. Cyanide ion (C= N) is an ambident nucleophile because it can react either through nitrogen. Since, C-C bond is stronger than C-N bond so, cyanide ion carbon or will mainly attack through carbon to form alkyl cyanide.

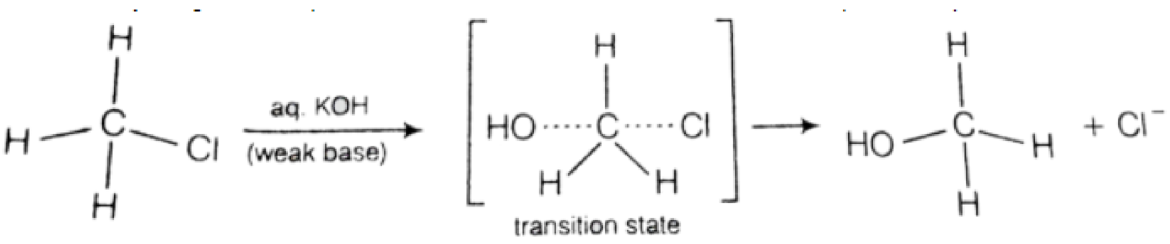
Long Answer Type Questions

Q1. Some alkyl halides undergo substitution whereas some undergo elimination reactions on treatment with bases. Discuss the structural features of alkyl halides with the help of examples which are responsible for this difference.

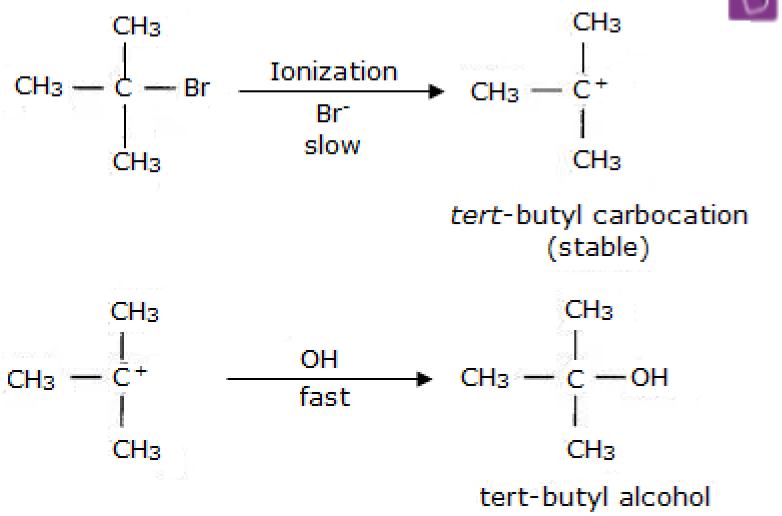
Answer:

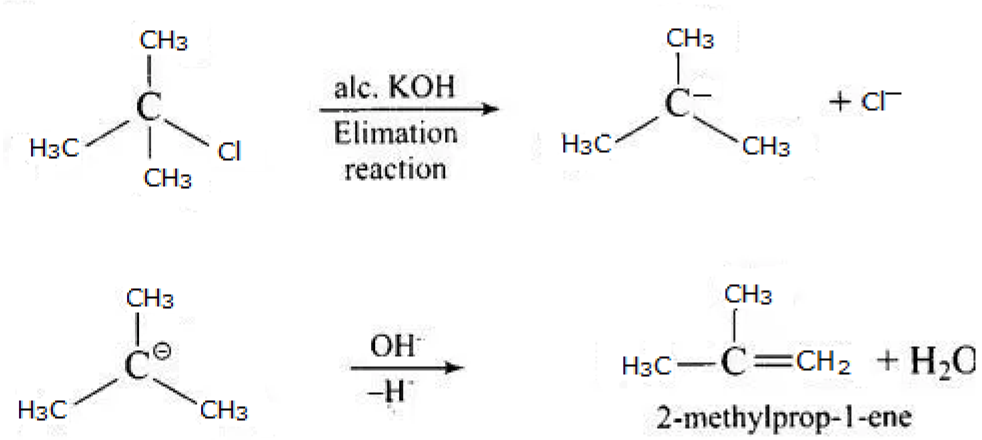
The structure of the alkyl halide as well as the chemicals used in the reaction dictate whether it undergoes substitution or elimination. The reactivity of alkyl halides to substitution mechanisms can be observed to better understand their structural properties. The S_N2 mechanism, which involves cleavage of the halide from the carbon atom and simultaneous attachment of the attacking nucleophile, is preferred by primary alkyl halides for substitution reactions. Tertiary halides, on the other hand, go through an elimination reaction due to the creation of stable carbocation. Tertiary halides also prefer to go through the S_N1 reaction, which is a two-step reaction including the production of a stable carbocation once the halide atom is cleaved.

The given reaction is for a primary alkyl halide to undergo S_N2 substitution.



The described reaction is for an S_N1 substitution of a tertiary alkyl halide. The strength of the base employed determines the mechanism. When using a weak base, such as aqueous KOH, the reaction is substitution, whereas when using a strong base, such as alcoholic base, the reaction is elimination.





Q2. Some halogen-containing compounds are useful in daily life. Some compounds of this class are responsible for exposure of flora and fauna to more and more of UV light which causes destruction to a great extent. Name the class of these halo compounds. In your opinion, what should be done to minimise harmful effects of these compounds.

Answer:

The following are some halogen-containing chemicals that are useful in daily life. Dichloromethane is used as a paint stripper, a propellant in aerosols, and a process solvent in the pharmaceutical industry. It's also utilised as a cleaning and finishing solution for metals. Trichloromethane It's used to dissolve lipids, alkaloids, iodine, and other compounds. Triiodomethane It's a type of antiseptic. Because of its unpleasant odour, it has now been substituted by alternative chemicals.

However, several compounds in this class are responsible for exposing flora and wildlife to increasing amounts of UV radiation, which causes significant damage.

(i) Tetrachloromethane

When CCl_3 is discharged into the atmosphere, it begins to deplete the ozone layer. As a result, UV radiation will easily reach the earth, causing harm to humans. This will result in skin cancer, functioning disorders, eye illnesses, and immune system harm. These UV rays not only harm humans, but also plants and other animals.

(ii) Freons

Freon-113 is released into the atmosphere and will rise to the top. It produces Cl atoms here in order to deplete the ozone layer. As a result of this ozone depletion, UV rays reach our atmosphere and do significant damage.

(iii) p – p' – Dichlorodiphenyltrichloroethane (DDT)

Because DDT is not totally biodegradable, it cannot be eliminated and removed from the atmosphere. It forms a chain when dissolved in lipids. When DDT enters a human's body, it has an effect on the reproductive system.

We should reduce the usage of the following compounds, namely freons, hydrofluorocarbons, and fluorocarbons, in order to eliminate their detrimental impacts.

Q3. Why are aryl halides less reactive towards nucleophilic substitution reactions than alkyl halides? How can we enhance the reactivity of aryl halides?

Answer:

Because of the following reasons, aryl halides are less reactive in nucleophilic substitution reactions.

- The lone pair of electrons on the halogen are in resonance with the benzene ring in haloarenes. As a result, the C-Cl bond gains a partial double bond character, which strengthens the bond. As a result, they have a lower reactivity to nucleophilic substitution reactions.
- The carbon atom linked to the halogen is sp^2 hybridised in haloarenes. Compared to sp^3 hybridised carbon, sp^2 hybridised carbon is more electronegative. In haloarenes, the sp^2-hybridised carbon can retain the electron pair of the C-X bond more tightly, making the C-Cl link shorter than the C-Cl bond in haloalkanes.
- Because a shorter bond is more difficult to break than a longer connection, haloarenes are less reactive than haloarenes.
- The phenyl cation will not be stabilised by resonance in haloarenes, hence the S_N1 mechanism is ruled out (iv) Because the nucleaphile and electron-rich arenes repel each other, aryl halides are less reactive than alkyl halides.

When an electron withdrawing group (NO_2) is present at the ortho and para positions, the reactivity of aryl halides can be increased. The presence of this electron withdrawing group at the above-mentioned location causes the benzene ring to lose electron density. As a result, the nucleophile will have an easier time attacking. Carbocation is produced as a result of resonance. The electron density is clearly higher at the ortho and para locations. As a result, the presence of EWG facilitates nucleophilic at ortho and para locations but not at meta.