CHEMISTRY STUDY MATERIALS FOR CLASS 12

(NCERT Exemplar Problems of Chapter - 10)

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Haloalkanes and Haloarenes

Assertion and Reason Type Questions

In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question:

(a) Assertion and Reason both are correct and Reason is the correct explanation of Assertion.

(b) Assertion and Reason both are wrong.

(c) Assertion is correct but Reason is wrong.

(d) Assertion is wrong but Reason is correct.

(e) Assertion and Reason both are correct statements but Reason is not the correct explanation of Assertion.

Question 01.Assertion (A): Phosphorus chlorides (tri and penta) are preferred over thionyl chloride for the preparation of alkyl chlorides from alcohols.

Reason (R): Phosphorus chlorides give pure alkyl halides.

Solution: (b) Thionyl chloride is best halogen carrier to convert alcohol to alkyl halide because it gives byproducts in gaseous state. Thus, we get pure alkyl halide in this reaction.

Question 02.Assertion (A): The boiling points of alkyl halides decrease in the order: RI > RBr > RCl > RF

Reason (R): The boiling points of alkyl chlorides, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecular mass.

Solution: (e) The given sequence of boiling point is correct:

RI > RBr > RCl > RF

Halides are polar molecules hence they have greater boiling point than hydrocarbons.

Question 03. Assertion (A): KCN reacts with methyl chloride to give methyl isocyanide Reason (R): CN^{-} is an ambident nucleophile.

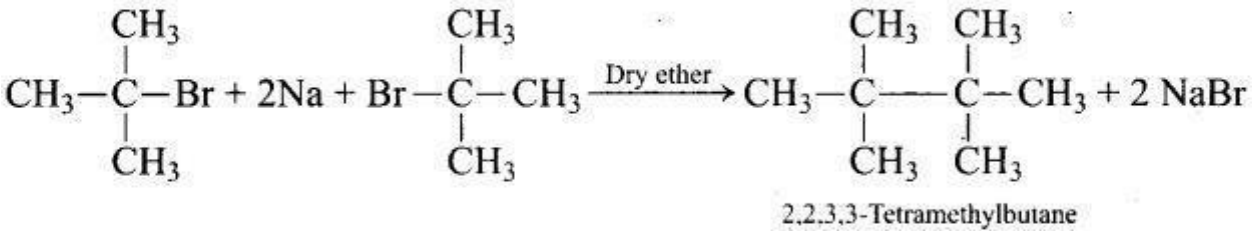
Solution: (d) R—Cl + KCN –> R-CN + KCL

Alkylcyanide isocyanide is not obtained in this reaction. CN^- is an ambident nucleophile.

Question 04. Assertion (A): tert-Butyl bromide undergoes Wurtz reaction to give 2, 2, 3, 3-tetramethylbutane.

Reason (R): In Wurtz reaction, alkyl halides react with sodium in dry ether to give hydrocarbon containing double the number of carbon atoms present in the halide.

Solution: (a)



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br + 2Na + Br-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow{\text{Dry ether}} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 + 2\,NaBr$$

2,2,3,3-Tetramethylbutane

Question 05. Assertion (A): Presence of a nitro group at ortho or para position increases

Reason (R): Nitro gjoup, being an electron withdrawing group decreases the electron density over the benzene ring.

Solution: (a) Nitro group being electron withdrawing group, decreases the electron density of ring hence increase the reactivity of haloarenes towards nucleophilic substitution.

Question 06. Assertion (A): In monohaloarenes, further electrophilic substitution occurs at ortho and para positions.

Reason (R): Halogen atom is a ring deactivator.

Solution: (e) Halogens are ortho-para directing due to (+M) or (+R) effect. Moreover, they are deactivating due to high electronegativity.

Question 07. Assertion (A): Aryl iodides can be prepared by reaction of arenas with iodine in the presence of an oxidizing agent.

Reason (R): Oxidising agent oxidizes I2 into HI.

Solution: (c) Oxidising agent like (HIO_3) converts HI to I_2, otherwise HI may reduce aryl halide to arenas. $5HI + HIO_3 \rightarrow 3H_2O + 3I_2$

Question 08. Assertion (A): It is difficult to replace chlorine by -OH in chlorobenzene in comparison to that in chloroethane.

Reason (R): Chlorine-carbon (C – Cl) bond in chlorobenzene has a partial double bond character due to resonance.

Solution: (a) Due to resonance, there is double bond character between benzene ring and halogen hence, nucleophilic substitution of aryl halide is difficult as compared to alkyl halide.

Question 09. Assertion (A): Hydrolysis of (-)-2-bromooctane proceeds with inversion of configuration.

Reason (R): This reaction proceeds through the formation of a carbocation.

Solution: (c) Hydrolysis of 2-bromooctane follows S_N2 mechanism hence inversion in configuration takes place. This reaction does not involve the formation of carbocation intermediate.

Question 10. Assertion (A): Nitration of chlorobenzene leads to the formation of m- nitrochlorobenzene.

Reason (R): N02 group is a w-directing group.

Solution: (d) Nitration of chlorobenzene gives ortho and para nitro chlorobenzene. However, nitro group is meta directing in nature.

Long Answer Type Questions

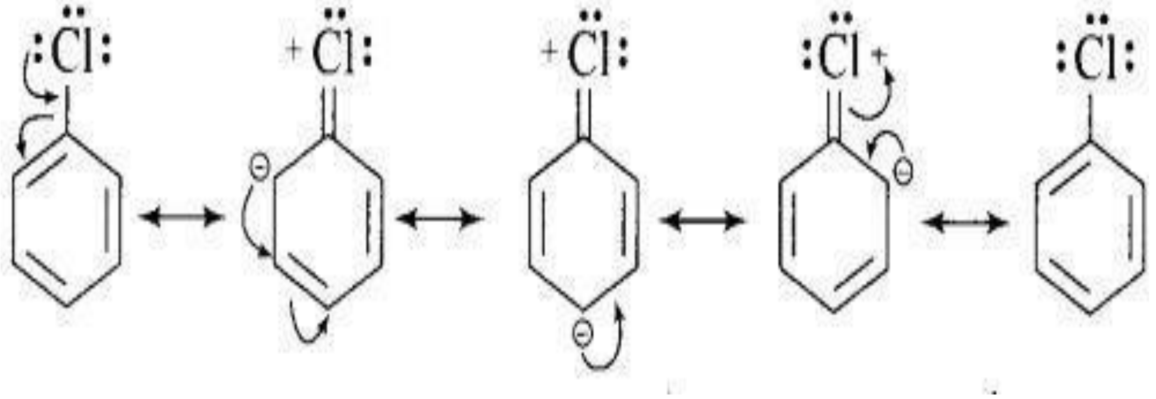
Question 01. Why are aryl halides less reactive towards nucleophilic substitution reactions than alkyl halides? How can we enhance the reactivity of aryl halides?

Solution: Aryl halides are less reactive towards nucleophilic substitution reaction due to the following reasons.

(i) In haloarenes, the lone pair of electron on halogen is in resonance with benzene ring.

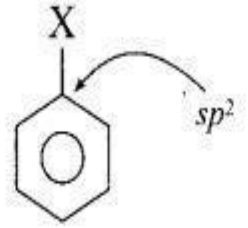
So, C – Cl bond acquires partial double bond character which strengthen C – Cl bond and difficult to be substituted by nucleophile.

Therefore, they are less reactive towards nucleophilic substitution reaction.

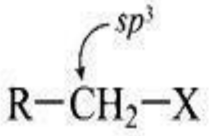


(ii) In haloarenes, the carbon atom attached to halogen is sp^2 hybridised. The sp2 hybridised carbon is more electronegative than sp^3 hybridised carbon.

This sp^2- hybridised carbon in haloarenes can hold the electron pair of C – X bond more tightly and make this C – Cl bond shorter than C Cl bond of haloalkanes.



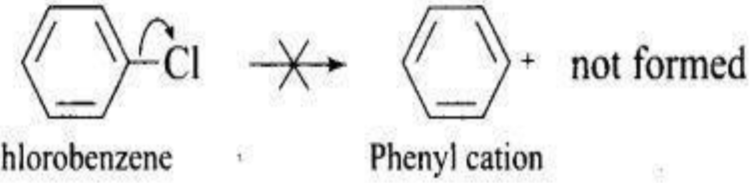
C involves sp^2 hybridisation



C involves sp^3 hybridisation

Since, it is difficult to break a shorter bond than a longer bond, therefore, haloarenes are less reactive than haloalkanes.

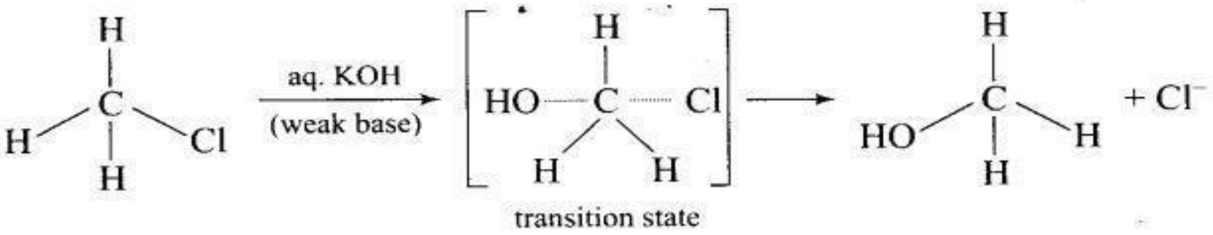
(iii) In haloarenes, the phenyl cation is not stabilised by resonance therefore S_N1 mechanism cannot be followed.



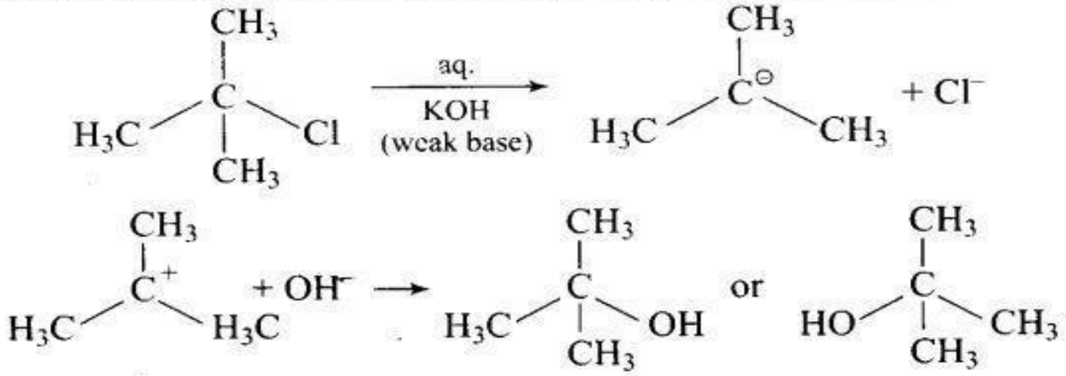
(iv) Because of the repulsion between the nucleophile and electron rich arenas, aryl halides are less reactive than alkyl halides.

Question 02. Some alkyl halides undergo substitution whereas some undergo elimination reaction on treatment with bases. Discuss the structural features of alkyl halides with the help of examples which are responsible for this difference.

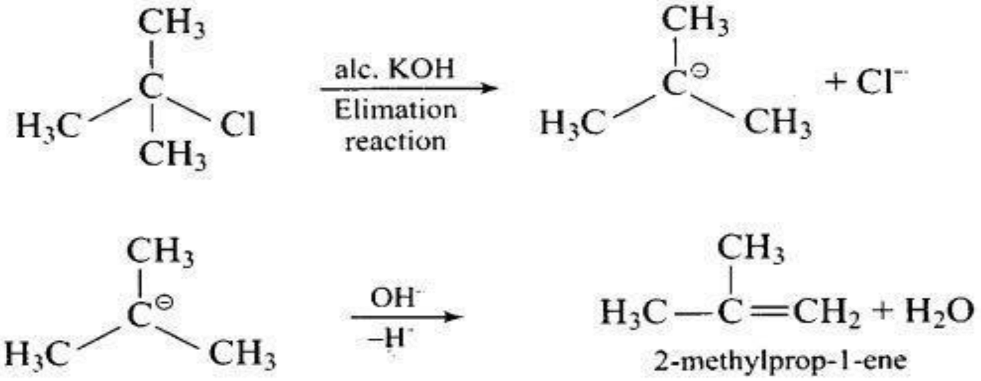
Solution: Case I: Primary alkyl halides follow S_N2 mechanism in which a nucleophile attacks from back to the halogen atom. A transition state is formed in which carbon is bonded to nucleophiles and finally halogen atom is pushed out. In S_N2 mechanism, substitution of nucleophile takes place as follows:



Case II: Tertiary alkyl halides follow S_N1 mechanism by forming 3° carbocations. Now, if the reagent used is a weak base then substitution occur while if it is a strong base then instead of substitution elimination occur.



Here, the reagent used is aq. KOH. It is a weak base so, substitution takes place.



As alc. KOH is a strong base, so elimination competes over substitution and alkene is formed.

Case III: Second alkyl halides can undergo substitution or elimination depending on type of solvent and temperature conditions.

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