CHEMISTRY STUDY MATERIALS FOR CLASS 12

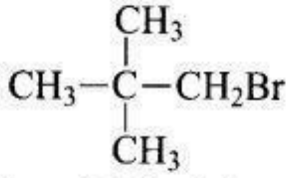
(NCERT Exemplar Problems of Chapter - 10)

GANESH KUMAR **DATE:- 13/09/2021**

Haloalkanes and Haloarenes

Question 59. Write down the structure and IUPAC name for neo-pentylbromide.

Solution:



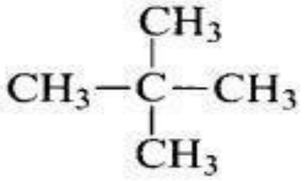
$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-CH_2Br$$

1–Bromo-2, 2-dimethylpropane

Question 60. A hydrocarbon of molecular mass 72 g mol^{-1} gives a single monochloro derivative and two dichloro derivatives on photo chlorination. Give the structure of the hydrocarbon.

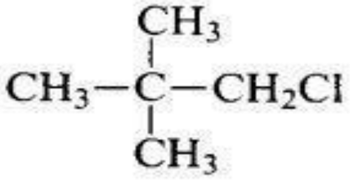
Solution: C_5H_{12}, pentane has molecular mass 72 g mol^{-1} i.e., isomer of pentane which yields single monochloro derivative should have all the 12 hydrogens equivalents.

The hydrocarbon is



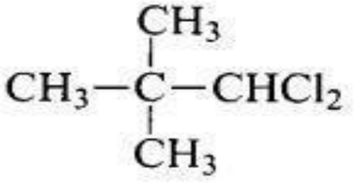
$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-CH_3$$

Monochloro derivative:



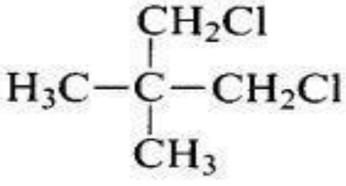
$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-CH_2Cl$$

Dichloro derivatives:



$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-CHCl_2$$

(i)

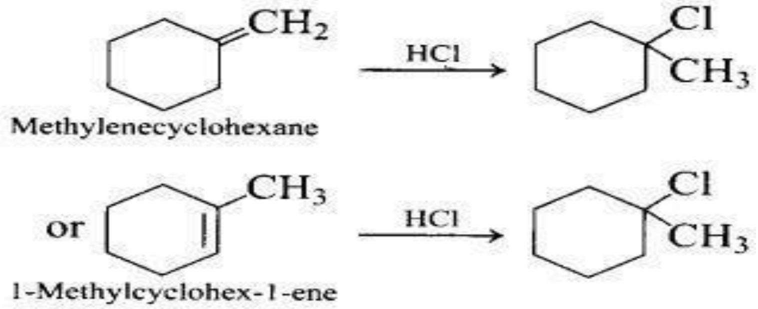


$$H_3C-\overset{\overset{\large CH_2Cl}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-CH_2Cl$$

(ii)

Question 61. Name the alkene which will yield 1-chloro-1-methylcyclohexane by its reaction with HCl. Write the reactions involved.

Solution: Two alkenes are possible. These are methylene cyclohexane and 1 - Methylcyclohex-1 –ene

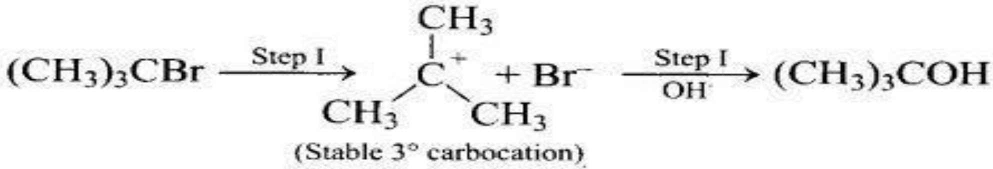


Question 62. Which of the following haloalkanes reacts with aqueous KOH most easily? Explain giving reason.

(i) 1-Bromobutane **(ii) 2-Bromobutane**

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

Solution: (iii) 2-Bromo-2-methylpropane will react the aqueous KOH most easily because the corbocation formed during hte reaction is tertiary and most stable.



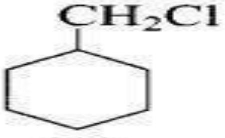
$$(CH_3)_3CBr \xrightarrow{\text{Step I}} (CH_3)_3C^+ + Br^- \xrightarrow[OH^-]{\text{Step I}} (CH_3)_3COH$$

(Stable 3° carbocation)

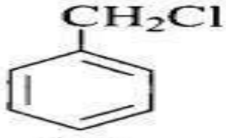
Question 63. Why can aryl halides not be prepared by reaction of phenol with HCl in the presence of $ZnCl_2$?

Solution: Phenol does not react with HCl and $ZnCl_2$ to give aryl halides due to partial double bond character between benzene ring and O which arises by resonance of benzene ring and OH group.

Question 64. Which of the following compounds would undergo SN1 reaction faster and why?

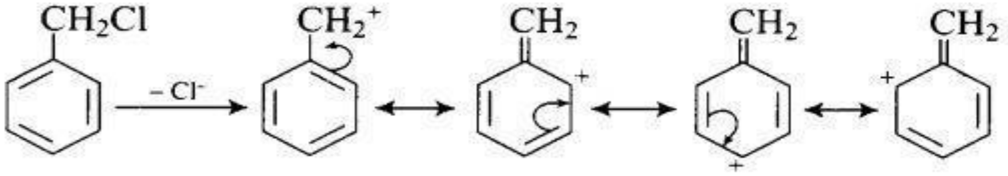


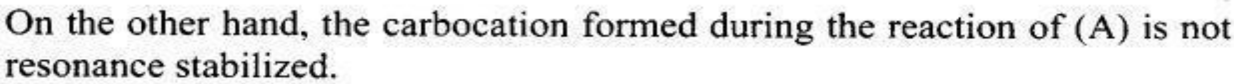
(A)



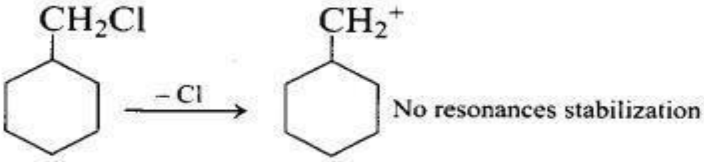
(B)

Solution: (B) undergoes S_N1 reaction faster because the carbocation formed after the loss of Cl stabilized by resonance



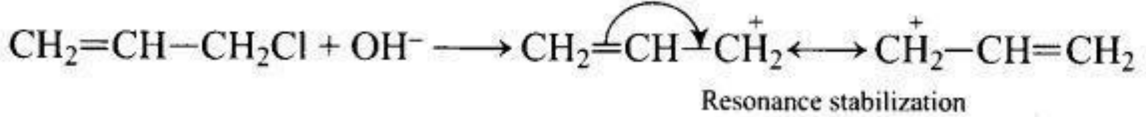


On the other hand, the carbocation formed during the reaction of (A) is not resonance stabilized.



Question 65. Allyl chloride is hydrolysed more readily than n-propyl chloride. Why?

Solution: Allyl chloride shows high reactivity because the carbocation formed by hydrolysis is stabilised by resonance while no such stabilisation of carbocation exists in the case of n-propyl chloride.



$$CH_2=CH-CH_2Cl + OH^- \longrightarrow CH_2=CH-\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2-CH=CH_2$$

Resonance stabilization

Question 66. Why is it necessary to avoid even traces of moisture during the use of a Grignard reagent?

Solution: Grignard reagents are highly reactive and react with even traces of water to give corresponding hydrocarbons.

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

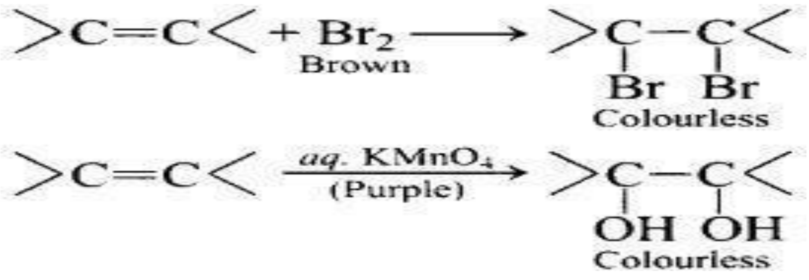
Question 67. How do polar solvents help in the first step in SN1 mechanism?

Solution: The SN1 mechanism proceeds through the formation of carbocation. It involves breaking of C-halogen bond for which energy is obtained through

the salvation of halide ion with the proton of the protic solvent. Thus, polar solvents help in ionisations step by stabilizing the ions by solvation.

Question 68. Write a test to detect the presence of double bond in a molecule.

Solution: Presence of a double bond in a molecule can be detected by bromine water test and Baeyer’s test. The molecules with a double bond decolourise bromine water and aqueous $KMnO_4$.



$$>C=C< + \underset{\text{Brown}}{Br_2} \longrightarrow \underset{\text{Colourless}}{>\underset{Br}{C}-\underset{Br}{C}<}$$

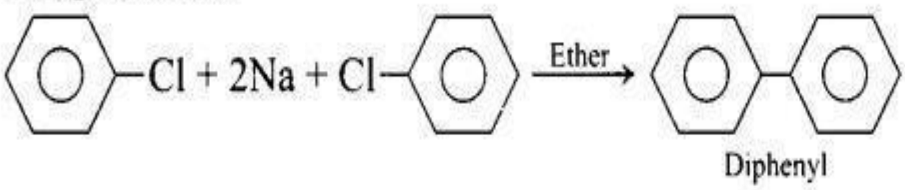
$$>C=C< \xrightarrow[\text{(Purple)}]{aq.\ KMnO_4} \underset{\text{Colourless}}{>\underset{OH}{C}-\underset{OH}{C}<}$$

Question 69. Diphenyls are potential threat to the environment. How are these produced from arylhalides?

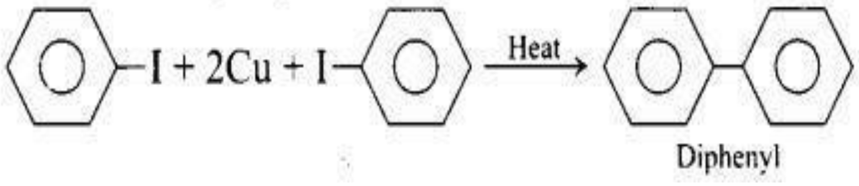
Solution: Diphenyls such as p,p ‘-dichlorodiphenyl trichloroethane (DDT) are posing serious environment problems because of its chemical stability and its fat solubility. Its residue accumulates in environment and its long-term effects could be highly dangerous.

Diphenyls can be prepared from aryl halides by the following two methods:

(i) Fittig reaction



(ii) Ullmann biaryl synthesis



Question 70. Elimination reactions (especially Beta-elimination) are as common as the nucleophilic substitution reaction in case of alkyl halides. Specify the reagents used in both cases.

Solution: Alkyl halides undergo nucleophilic substitution as well as elimination (Beta- elimination) reaction.

However, by proper choice of reagents and reaction conditions, a particular product can be obtained. Usually strong and bulky bases and high temperature favour elimination reactions while weaker and smaller bases and lower temperature favour substitution reactions. For example, ethyl bromide on heating with alcoholic KOH (which contain stronger base,C_2H_5O ion) at about 473-523 K undergoes elimination to give ethene. But with aqueous KOH at about 373 K, it gives ethanol.

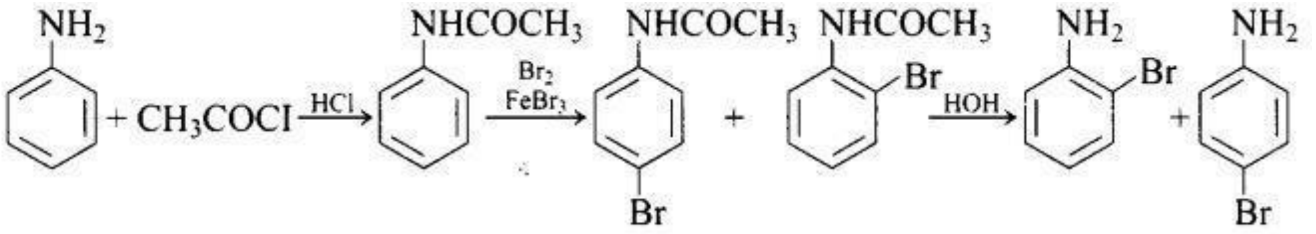
$$CH_3CH_2Br \xrightarrow[473\text{–}523\ K]{\text{alc. KOH}} CH_2{=}CH_2 \quad \text{(Elimination)}$$

$$CH_3CH_2Br \xrightarrow[373\ K]{\text{aq. KOH}} CH_3CH_2OH \quad \text{(Substitution)}$$

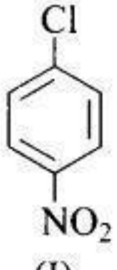
Nucleophilic substitution: Reagents used are nucleophiles like – $\bar{O}H$, NH_3, $\bar{C} \equiv N:$, AgCN:, O = N – O, $\bar{O}R'$ etc. Also, alc. KOH at lower temperature (373 K) undergoes substitution reaction.

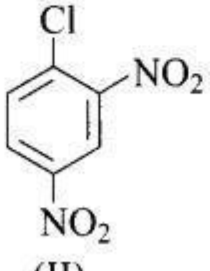
Question 71. How will you obtain monobromobenzene from aniline?

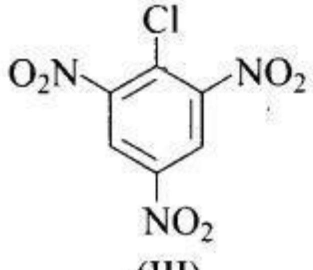
Solution:



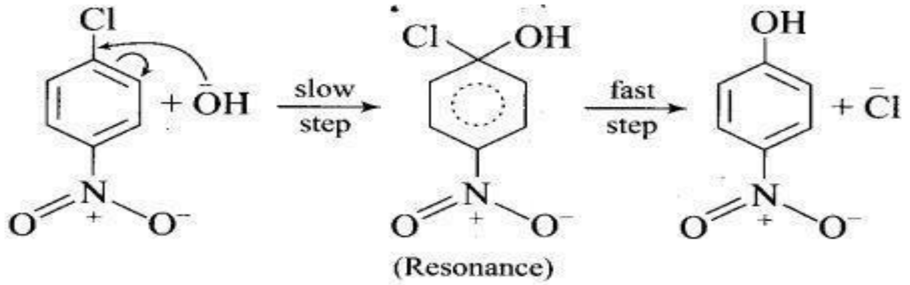
Question 72. Aryl halides are extremely less reactive towards nucleophilic substitution. Predict and explain the order of reactivity of the following compounds towards nucleophilic substitution:


(I)


(II)

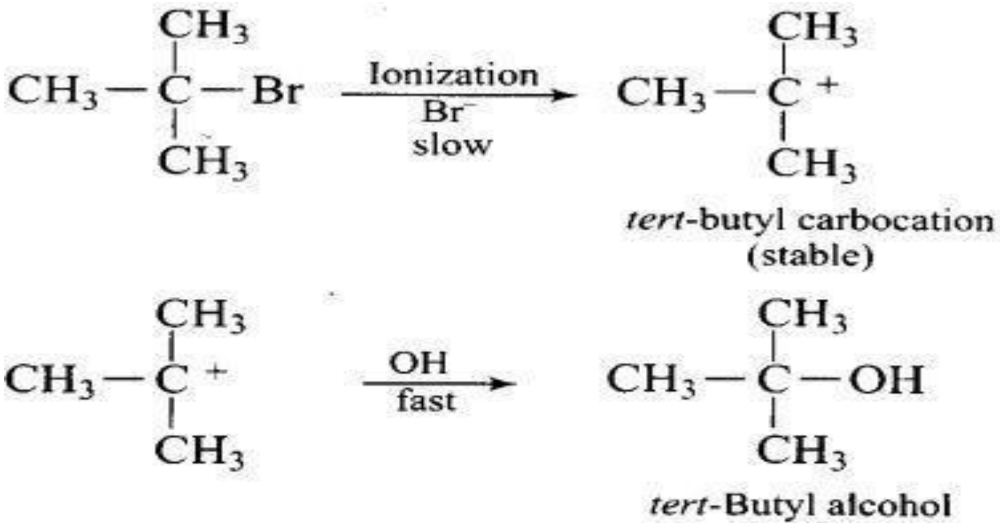

(III)

Solution: After the attachment of the nucleophile at the carbon carrying -Cl, the intermediate compound is stabilised due to resonance. Due to electron withdrawing nature of-NO_2, the nucleophile is easily attached to the benzene ring. Greater the number of -NO_2 groups in the molecule, greater will be the ease with which the nucleophile will be attached. Hence, the order of reactivity is III > II > I.

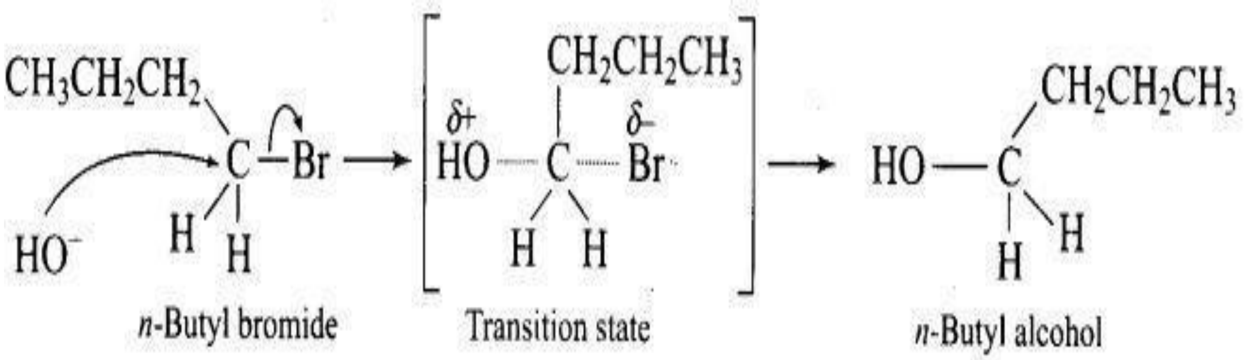


Question 73. tert-Butylbromide reacts with aq. NaOH by S_N^1 mechanism while n- butylbromide reacts by S_N^2mechanism. Why?

Solution: In general, the S_N1 reaction proceeds through the formation of carbocation. The tert-butylbromide readily loses Br ion to form stable 3° carbocation. Therefore, it reacts with aqueous KOH by S_N1 mechanism as:



On the other hand, n-Butyl bromide does not undergo ionization to form n-Butyl carbocation (1°) because it is not stable. Therefore, it prefers to undergo reaction by S_N2 mechanism, which occurs is one step through a transition state involving nucleophilic attack of OH^- ion from the back side with simultaneous expulsion of Br^- ion from the front side.

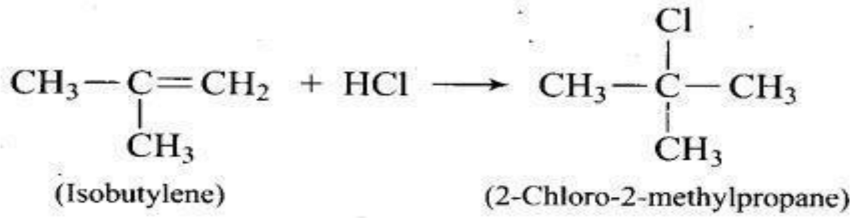


S_N1 mechanism follows the reactivity order as 3° > 2° > 1° while S_N2 mechanism follows the reactivity order as 1° > 2° > 3°

Therefore, tert-butylbromide (3°) reacts by S_N1 mechanism while *n*-Butylbromide (1°) reacts by S_N2 mechanism.

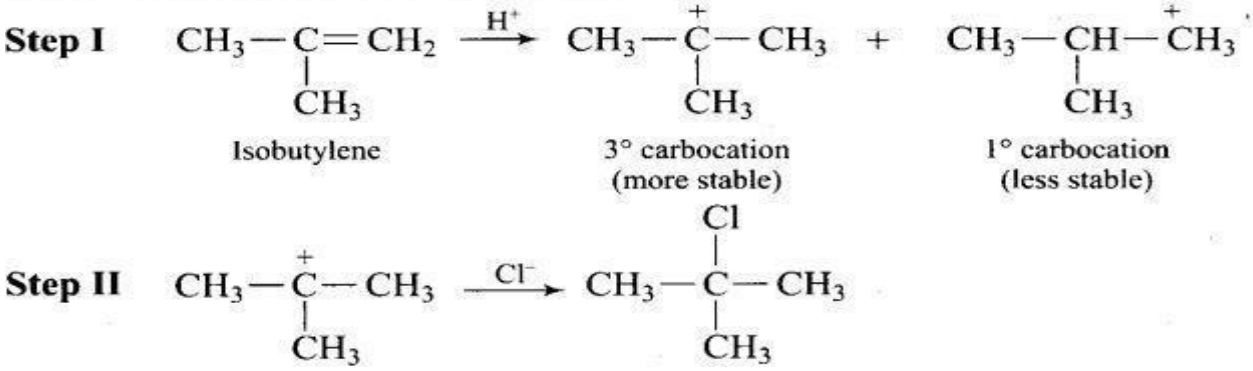
Question 75. Predict the major product formed when HCl is added to isobutylene. Explain the mechanism involved.

Solution: The major product is 2-chloro-2-methypropane



$$CH_3-\underset{CH_3}{C}=CH_2 + HCl \longrightarrow CH_3-\overset{Cl}{\underset{CH_3}{C}}-CH_3$$

The mechanism involved in this reaction is:



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

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

Question 76.Discuss the nature of C – X bond in the haloarenes. C – X bond in haloarenes is extremely less reactive towards nucleophilic

Solution: substitution reactions due to:

(i) Resonance effect: C – X bond acquires a partial double bond character and it becomes difficult to break C – X bond.

(ii) In C – X bond, C atom attached to halogen is sp^2 hybridised. The sp2 hybridised carbon with a greater s character is more electronegative and can hold the electron pair of C – X bond more tightly than sp3 hybridised carbon in haloalkane with less 5-character.

Question 77. How can you obtain iodoethane from ethanol when no other iodine containing reagent except NaI is available in the laboratory?

Solution: Ethanol is converted to chloroethane and Cl can be replaced by I.

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

Question 78. Cyanide ion acts as an ambident nucleophile. From which end it acts as a stronger nucleophile in aqueous medium?
Give reason for your answer.

Solution: 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 (bond between two similar atoms) than C – N bond.

****