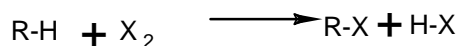
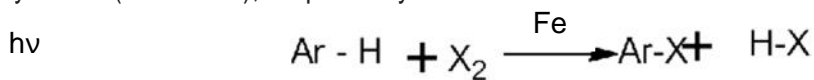


HALOALKANES AND HALOARENES (UNIT - 9)

The placement of hydrogen atom(s) in a hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkylhalide (haloalkane) and arylhalide (haloarene), respectively

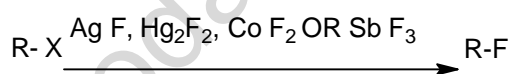


(A) IMPORTANT NAME REACTIONS

i) Finkelstein Reaction



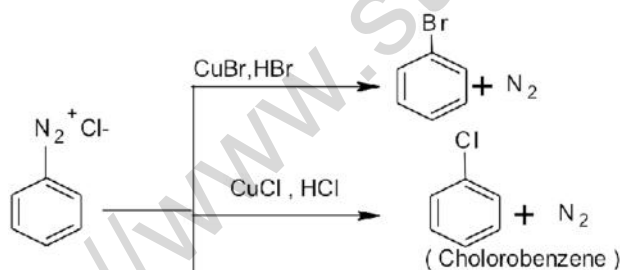
II) Swarts Reaction



1. Carbylamines reaction



2. Sandmeyer's reaction

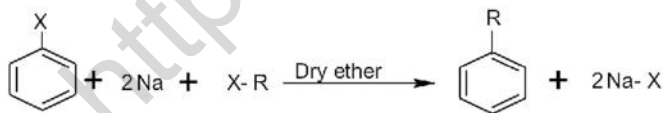


3. Wurtz Reaction

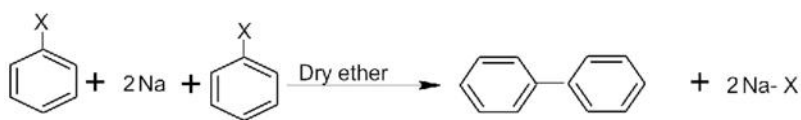


4. Wurtz Fittig reaction:-

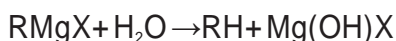
(in dry ether)



5. Fittig reaction



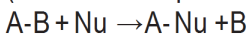
6. Grignard reagent:



(B) IMPORTANT MECHANISM

i) Nucleophilic Substitution ii) Elimination reaction iii) Electrophilic substitution

i) **Nucleophilic Substitution** :- it involves the replacement of an atom or group of atoms by a nucleophile (electron rich species)



It is of two types:-

a) Unimolecular nucleophilic substitution reaction (S_N1)

b) Bimolecular nucleophilic substitution reaction (S_N2)

a) Unimolecular substitution reaction (S_N1)

(i) it involves two steps

(ii) in this retention/Racemization of configuration take place.

(iii) unimolecular and all are first order.

Mechanism (step 1) formation of carbocation.



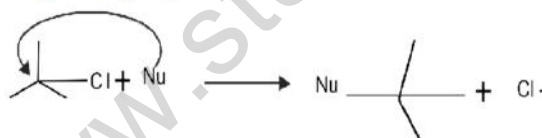
Step 2 Attack of nucleophile on carbocation

(front/rear end)



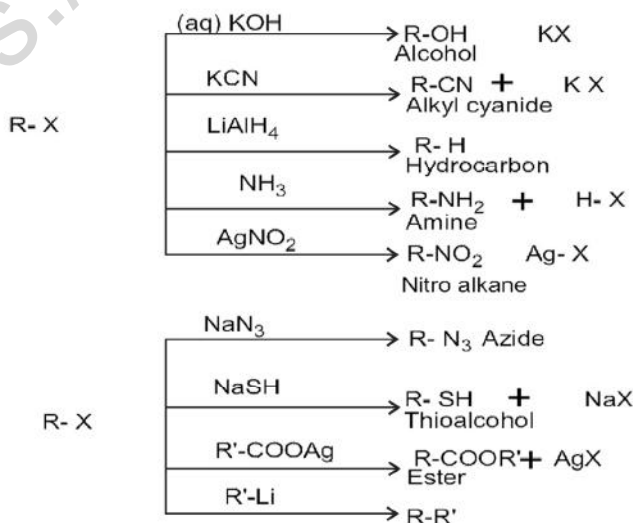
Order of reactivity: $3^\circ > 2^\circ > 1^\circ$ (Because 3° carbocation is more stable)

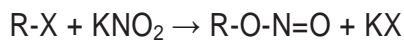
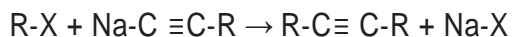
(b) **Bimolecular Nucleophilic Substitution S_N2** (i) it involves one step. (ii) in this inversion of configuration takes place. (iii) bimolecular mechanism: .in this nucleophile attacks from the backside Where halogen atom is attached. It facilitates the departure of leaving halide group.



Order of reactivity: $1^\circ > 2^\circ > 3^\circ$ (Because of less steric hindrance in 1° alkyl halide)

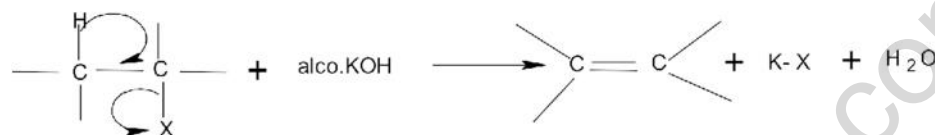
Nucleophilic substitution reaction of alkyl halides



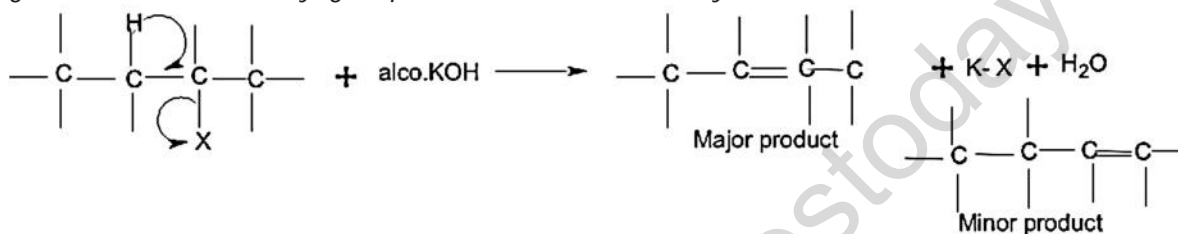


ii) **Elimination reaction** : Haloalkanes having hydrogen atom, when heated with alcoholic KOH, there is elimination of hydrogen atom from β -carbon and a halogen atom from the α - carbon atom & alkene is formed.

Saytzeff rule "in dehydrohalogenation reactions, the preferred product is that alkene which has the

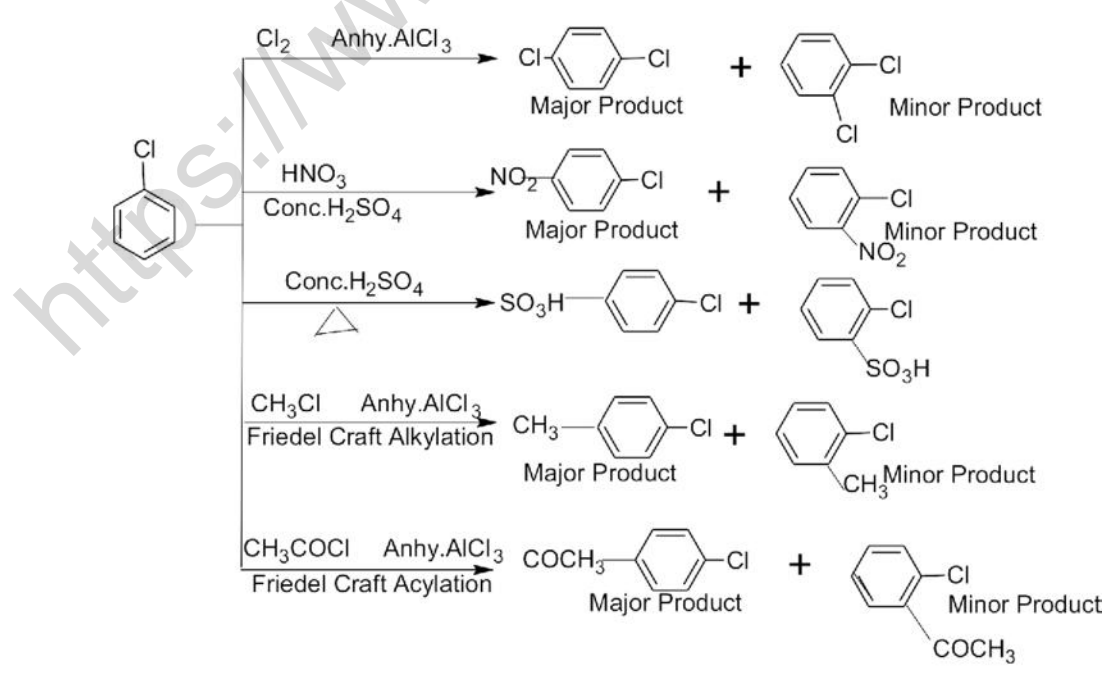
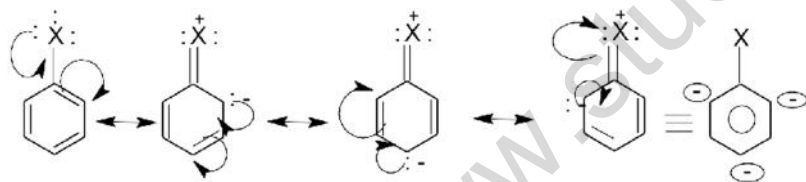


greater number of alkyl groups attached to the doubly bonded carbon atoms."



iii) **Electrophilic substitution:-** substitution occurs at *ortho*- and *para*- positions with respect to the halogen atom.

substitution occurs at *ortho*- and *para*- positions with respect to the halogen atom.



Q.1 What are ambident nucleophiles? (1 Mark)

Ans. Nucleophiles which can attack through two different sites are called ambident nucleophiles.

Example: -Cyanide ion: CN^- & $\text{C}=\text{N}^-$

Q.2 Which is a better nucleophile, a bromide ion or iodide ion? (1 Mark) Ans.

Iodide ion because it has lower electronegativity and larger size.

Q.3 Arrange the compounds of each set in order of reactivity towards $\text{S}_{\text{N}}2$ displacement:

2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane. (1 Mark)

Ans. The reactivity in $\text{S}_{\text{N}}2$ reactions depend upon steric hindrance; more the steric hindrance slower the reaction. The order of reactivity in $\text{S}_{\text{N}}2$ reactions follows the order: $1^\circ > 2^\circ > 3^\circ$. 1-Bromopentane > 2-Bromopentane > 2-Bromo-2-methylbutane.

Q.4 Arrange the following in increasing order of boiling point.

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$, $(\text{CH}_3)_3\text{CBr}$, $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$. (1 Mark)

Ans. The boiling point increases as the branching decreases, so the increasing order of boiling point is: $(\text{CH}_3)_3\text{CBr} < (\text{CH}_3)_2\text{CHCH}_2\text{Br} < \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$

Q.5 Define optical activity? (1 Mark)

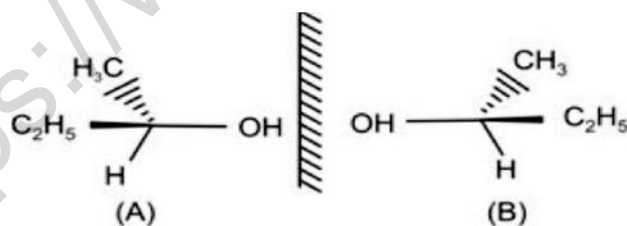
Ans. The compounds which rotate the plane of polarized light when it is passed through their solutions are called optically active compounds and this property is known as optical activity.

Q.6 What is racemic mixture or racemic modification? (1 Mark) Ans.

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

Q. 7 What are enantiomers? (1 Mark)

Ans. The stereo isomers related to each other as non-superimposable mirror images are called enantiomers.



ASSERTION -REASON TYPE

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

- Both assertion and reason are true and reason is the correct explanation of assertion.
- Both assertion and reason are true but reason is not the correct explanation of assertion.
- Assertion is true but reason is false.
- Both assertion and reason are false.

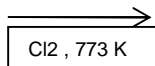
1. Assertion : S_N2 reactions do not proceed with retention of configuration.

Reason : S_N2 reactions proceed in a single step. (Ans - b)

2. Assertion : Chloroform is generally stored in dark coloured bottles filled to the brim.

Reason : Chloroform reacts with glass in the presence of sun light. (Ans - c)

3. Assertion : $CH_3-CH=CH_2 \xrightarrow{Cl_2, 773 K} Cl-CH_2-CH=CH_2 + HCl$



Reason : At high temperature, Cl_2 dissociates into chlorine free radicals which bring about allylic substitution. (Ans - a)

4. Assertion : Nucleophilic substitution reaction in an optically active alkyl halide gives a mixture of enantiomers.

Reason : Reaction occurs by S_N1 mechanism. (Ans - a)

5. Assertion : Primary allylic halides show higher reactivity in S_N1 reactions than other primary alkyl halides.

Reason : Intermediate carbocation is stabilised by resonance. (Ans - a)

One - word answer

1. Name the poisonous compound obtained when chloroform is exposed to air, in presence of sunlight. (Ans - Phosgene)

2. Name the compound formed when Grignard' s reagent is exposed to moisture. (Ans - Alkane)

Q.8 Haloalkanes react with aq. KOH to form alcohols but react with alc. KOH to form alkenes. Why? (2 Marks)

Ans. KOH is a strong base, so it completely ionizes in aqueous solution. OH^- ions are strong nucleophile, so it replaces the halogen atoms and form alcohols. In contrast, an alcoholic solution of KOH contains alkoxide ($R-O^-$) ions which being a much stronger base than (OH^-) ions preferentially eliminates a molecule of HCl from an alkylchloride to form an alkene.

Ans. Haloalkanes are more polar than haloarenes. As a result the carbon atom carrying the halogen in haloalkanes is more electron-deficient than that in haloarenes. So, haloalkanes undergo nucleophilic substitution more readily than haloarenes.

In contrast, haloarenes contain a benzene ring. Since the typical reactions of benzene are electrophilic substitutions, therefore, haloarenes undergo electrophilic substitution while haloalkanes which do not contain a benzene ring do not undergo electrophilic substitution.

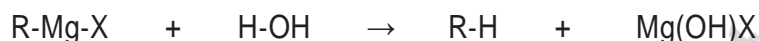
Q. 10 Explain why?

(a) Alkyl halides, though polar, are immiscible in water.

(b) Grignard reagents should be prepared under anhydrous conditions? (3Marks)

Ans. (a) Alkyl halides are polar in nature but it is insoluble in water because alkyl halide molecules are held together by dipole-dipole attraction and water molecules are held together by H-bonds. More energy is required to overcome these attractive forces between the haloalkanes. But less energy is released when haloalkanes and water molecules come together, so haloalkanes are not soluble in water.

(b) Grignard reagents are very reactive, so they react with moisture and form alkane.



Therefore, it must be prepared and stored under anhydrous conditions..

Q.9 Haloalkanes undergo nucleophilic substitution whereas haloarenes undergo electrophilic substitution. Why? (3Marks)

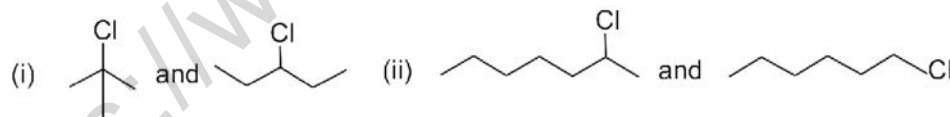
Assignment

Q1 In the following pairs of halogen compounds, which would undergo $\text{S}_{\text{N}}2$ reaction faster?



Q2 Although chlorine is an electron withdrawing group, yet it is *ortho*-, *para*- directing in electrophilic aromatic substitution reactions. Why?

Q3 In the following pairs of halogen compounds, which compound undergoes faster $\text{S}_{\text{N}}1$ reaction?



Q4 Why is sulphuric acid not used during the reaction of alcohols with KI?

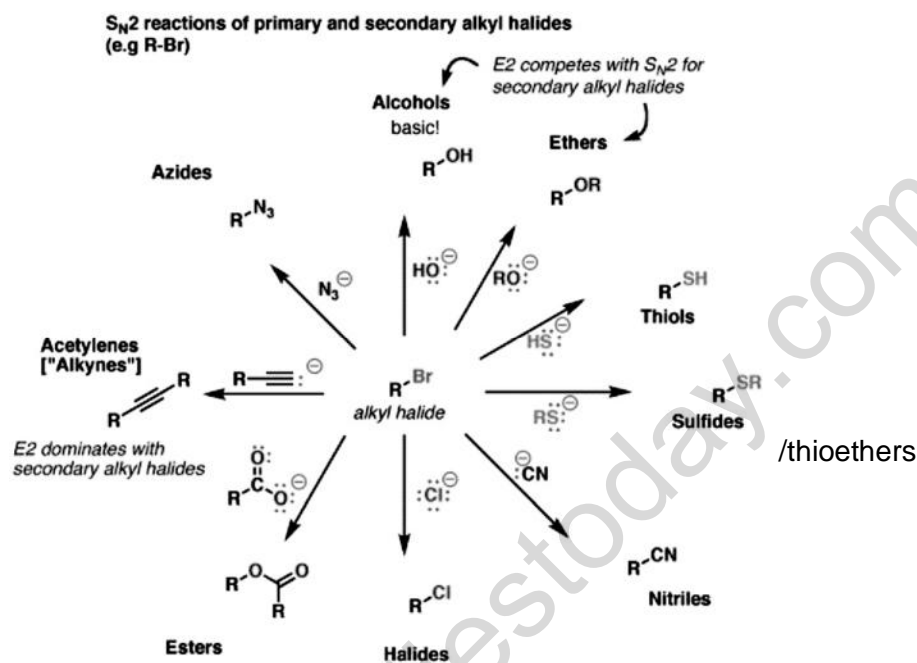
Q5 *p*-Dichlorobenzene has higher m.p. and solubility than those of *o*- and *m*-isomers. Discuss.

Q6 Hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound $\text{C}_5\text{H}_9\text{Cl}$ in bright sunlight. Identify the hydrocarbon.

Q7. Chloroform is stored in dark coloured & sealed bottle. Why?

Q8 Aryl halides cannot be prepared by the action of sodium halide in the presence of H_2SO_4 . Why?

MIND MAP FOR CONVERSION



MULTIPLE CHOICE QUESTION (MCQs)

1). Identify the following compounds as primary halide:

- (i) 1-Bromobut-2-ene
- (ii) 4-Bromopent-2-ene
- (iii) 2-Bromo-2-methylpropane

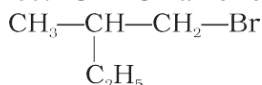
Ans : (i) 1-Bromobut-2-ene (1° alkyl halide)

2). Which of the following compounds are gem-dihalides ?

- (a) Ethylidene chloride (b) Ethylene dichloride
- (c) Methyl chloride (d) Benzyl chloride

Ans : Option (a) is correct . In gem-dihalides both the halogens are attached to the same carbon atom.

3). Which is the correct IUPAC name for



- i) 1-Bromo-2-ethylpropane ii) 1-Bromo-2-ethyl-2-methylethane
- iii) 1-Bromo-2-methylbutane iv) 2-Methyl-1-bromobutane

Ans. iii) 1-Bromo-2-methylbutane

4). What should be the correct IUPAC name for diethylbromomethane?

- i) 1-Bromo-1,1-diethylmethane ii) 3-Bromopentane
- iii) 1-Bromo-1-ethylpropane iv) 1-Bromopentane

Ans. ii). 3-Bromopentane

5). Which of the following is /are secondary bromide?

- (i) $\text{CH}_3\text{CH}_2\text{Br}$
- (ii) $(\text{CH}_3)_3\text{CCH}_2\text{Br}$
- (iii) $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_3$
- (iv) $(\text{CH}_3)_2\text{CBrCH}_2\text{CH}_3$

Ans. (iii) $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_3$

6.) Pure chloroform is obtained by treating

- (i) Ethanol with bleaching powder (ii) Acetone with bleaching powder
- (iii) Chloral with Sodium hydroxide (iv) CCl_4 with moist Iron

Ans : (iii) Chloral with Sodium hydroxide

7.) 1,1-Dichloropropane on hydrolysis gives

- a) Propanone
- b) Propanal
- c) Ethanal
- d) 1,1-Propanediol

Ans : b) Propanal

8.). Among the following , the molecule with the highest dipole moment is :

- a) CH_3Cl
- b) CH_2Cl_2

c) CHCl_3

d) CCl_4

Ans : a) CH_3Cl

9.) Which of the following represents Freon?

a) Ethylene dichloride

b) Ethylidene dichloride

c) Tetrafluoro ethylene

d) Dichlorodifluoromethane

Ans: d). Dichlorodifluoromethane

SHORT ANSWERED QUESTIONS (1-MARK)

1. Write the IUPAC name of $(\text{CH}_3)_3\text{CCH}_2\text{Cl}$

2. Which of the following under goes $\text{S}_{\text{N}}1$ faster: 2-chlorobutane or 1-chlorobutane

3. Arrange each set of compounds in order of increasing boiling points.

(i) Bromomethane, (ii) Bromoform, (iii) Chloromethane, (iv) Dibromomethane.

4. Write the product formed when toluene is chlorinated in presence of sunlight.

5. Write the product formed when n-butyl chloride is treated with alcoholic KOH ?

6. Which is a better nucleophile, a bromide ion or an iodide ion ?

7. Which has higher dipole moment, Chlorobenzene or Cyclohexyl chloride?

8. Draw the structure of DDT.

9. Expand BHC

10. How many centres of chirality are present in 3-Bromopent-1-ene.

ANSWERS

1. 1- chloro-2,2-dimethylpropane

2. 2-chlorobutane.

3. (iii) < (i) < (iv) < (ii)

4. Chloromethylbenzene

5. But-2-ene

6. Iodide ion

7. Cyclohexyl chloride

8. Correct structure(Dichloro diphenyl trichloroethane)

9. Benzenehexachloride

10. one