

## Chemistry for S5 students

Short notes & questions with answers & and other questions to help S5 Students to revise

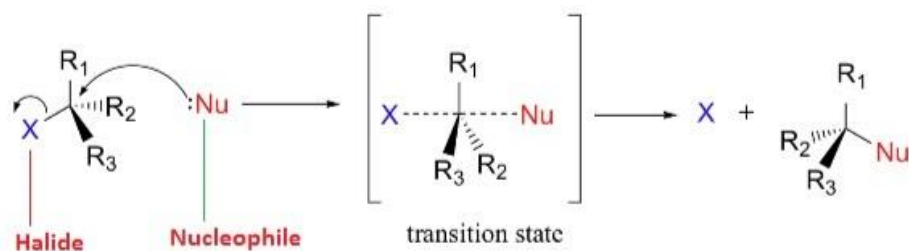
### Important Concepts:

#### Chemical Reactions of Alkyl Halides

The reaction can be broadly classified in two categories:

- (a) Nucleophilic substitution
- (b) Elimination reactions

**Nucleophilic substitution reactions:** In this reaction a nucleophile, which is rich in electrons, attacks partial positive charge on the carbon atom bonded to halogen to replace the leaving group.



#### Nucleophiles:

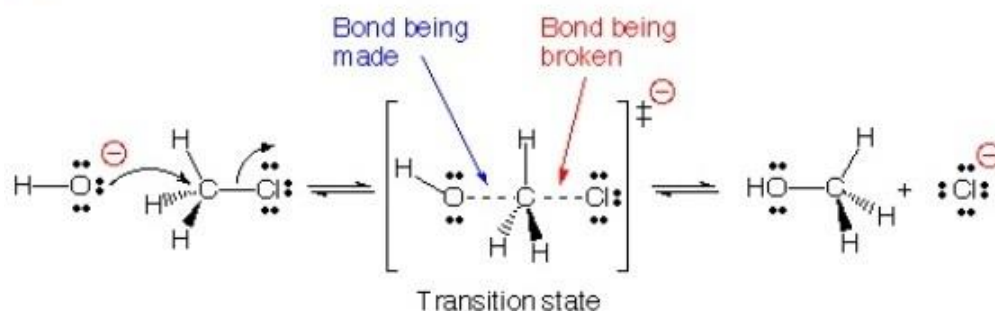
- These are electron rich species. All Lewis bases are nucleophiles.

Reagent	Nucleophile (Nu <sup>-</sup> )	Substitution product R-Nu	Class of main product
NaOH (KOH)	HO <sup>-</sup>	ROH	Alcohol
H <sub>2</sub> O	H <sub>2</sub> O	ROH	Alcohol
NaOR'	R'O <sup>-</sup>	ROR	Ether
NaI	I <sup>-</sup>	R-I	Alkyl iodide
NH <sub>3</sub>	NH <sub>3</sub>	RNH <sub>2</sub>	Primary amine
RNH <sub>2</sub>	RNH <sub>2</sub>	RNHR'	Sec. amine
RR'NH	RR'NH	RNR'R'	Tert. amine
KCN	C≡N <sup>-</sup>	RCN	Nitrile (cyanide)
AgCN	Ag-CN:	RNC (isocyanide)	Isonitrile
KNO <sub>2</sub>	O=N-O	R-O-N=O	Alkyl nitrite
AgNO <sub>2</sub>	Ag-O-N=O	R-NO <sub>2</sub>	Nitroalkane
R'COOAg	R'COO <sup>-</sup>	R'COOR	Ester
LiAlH <sub>4</sub>	H	RH	Hydrocarbon
R'-M <sup>+</sup>	R <sup>-</sup>	RR'	Alkane

Nucleophilic reactions proceed by two different mechanism:

- Substitution nucleophilic bimolecular (S<sub>N</sub>2)
- Substitution nucleophilic unimolecular (S<sub>N</sub>1)

**S<sub>N</sub>2:**



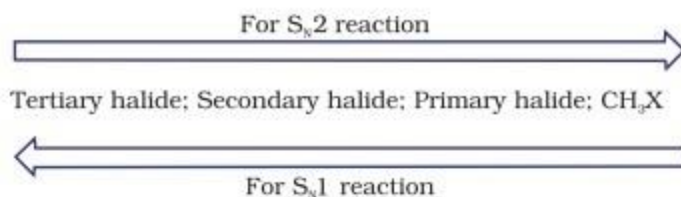
- The reaction follows second order kinetics
- No intermediate is formed.
- It usually requires a strong nucleophile.
- The order of reactivity followed as:

Primary halide > Secondary halide > Tertiary halide

### **S<sub>N</sub>1:**



- It is carried out in polar protic solvents (water, Alcohol, acetic acid etc.).
- These reactions occur in two steps as shown above
- The order of leaving ability is:  
 $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$
- The order of reactivity is as shown below:

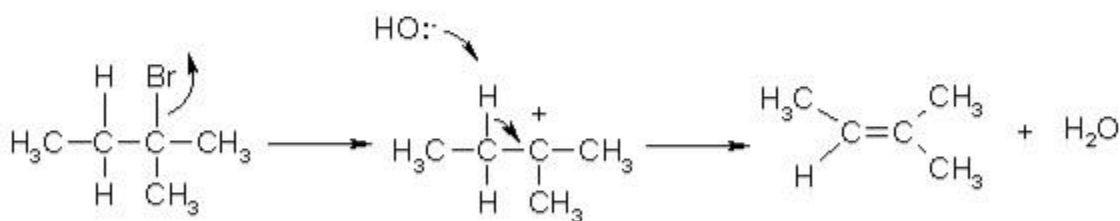


### Elimination reaction:

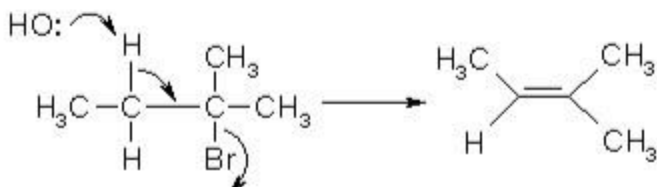
When a haloalkane with  $\beta$ -hydrogen atom is heated with alcoholic solution of potassium hydroxide, there is elimination of hydrogen.

Elimination reaction occur through two mechanism:

#### (a) E1



#### (2) E2



### Difference between E1 and E2 reaction mechanism:

Attributes	E1	E2
Rate law	Depend on the concentration of substrate	Depends on the concentration of both substrate and base
Barrier	Formation of carbocation $3^\circ > 2^\circ >> 1^\circ$	None
Base	Does not require strong base	Requires strong base

Stereochemistry	Does not require stereochemistry	Leaving group must be anti to hydrogen removed
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**Some solved questions are given below:**

**Question 1:** Which is the correct increasing order of boiling points of the following compounds?

1-bromoethane, 1-bromopropane, 1-bromobutane, Bromobenzene

- (a) Bromobenzene < 1-bromobutane < 1-bromopropane < 1-bromoethane
- (b) Bromobenzene < 1-bromoethane < 1-bromopropane < 1-bromobutane
- (c) 1-bromopropane < 1-bromobutane < 1-bromoethane < Bromobenzene
- (d) 1-bromoethane < 1-bromopropane < 1-bromobutane < Bromobenzene

**Solution 1:**

Boiling point increases with increase in size of hydrocarbon part for the same haloalkanes. All the given haloalkenes contain same halogen atom *i.e.*, bromine but the number of carbon atoms in hydrocarbon part of the molecule are increasing from ethane to benzene.

So the boiling point is minimum for 1-bromoethane and maximum for 1-bromobenzene.

Hence, the correct option is (d).

**Question 2:** Which C-X bond has the highest bond energy per mole?

- a) C-Br
- b) C-Cl
- c) C-F
- d) C-I

**Answer: c**

**Explanation:** Bond energies depend on many factors: electron affinities, sizes of atoms involved in the bond, differences in their electronegativity, and the overall structure of the molecule. There is a general trend in that the shorter the bond length, the higher the bond energy.

**Question 1:**

**Question 3:** Which alkyl halide has the highest reactivity for a particular alkyl group?

- a) R-F
- b) R-Cl

- c) R-I
- d) R-Br

**Answer: c**

**Explanation:** Reactivity order for the alkyl halides towards  $S_N2$  reaction is  $R-I > R-Br > R-Cl > R-F$ . This can be explained by which halogen atom is a better leaving group compared to the other.

**Question 4:** When ethyl chloride reacts with nascent hydrogen, what is the formed product?

- a) Methane
- b) Propane
- c) Butane
- d) Ethane

**Answer: d**

**Explanation:** When an alkyl halide is treated with zinc and hydrochloric acid, it is reduced to the respective alkane. The nascent hydrogen formed by the reaction between zinc and HCl acid reduces ethyl chloride to ethane.

**Question 5:** Which alkyl halide out of the following may follow both  $S_N1$  and  $S_N2$  mechanism?

- a)  $CH_3-X$
- b)  $(CH_3)_2CH-X$
- c)  $(CH_3)_3C-X$
- d)  $(CH_3)_3C-CH_2-X$

**Answer: b**

**Explanation:**  $(CH_3)_2CH-X$  follows both  $S_N1$  and  $S_N2$  mechanism because the second  $CH_3$  of  $(CH_3)_2CH-X$  further blocks a nucleophile (such as:  $OH^-$ ) in backside  $S_N2$  attack, but it increases the stability of the carbocation resulting from  $S_N1$  ionization. As a result,  $S_N1$  and  $S_N2$  mechanisms are sometimes competitive for  $(CH_3)_2CH-X$ .

**Question 6:** When two moles of ethyl chloride react with two moles of sodium in the presence of ether what will be formed?

- a) 2 moles of ethane
- b) 1 moles of ethane
- c) 2 moles of butane
- d) 1 moles of butane

**Answer: d**

**Explanation:** Wurtz reaction is method of preparation of higher alkanes from lower alkyl halides. This is coupling reaction. In this reaction alkyl halides are reacted with sodium metal in presence of dry ether and higher alkanes with even number of carbon atoms only are formed, by this method.

**Question 7:** Which of the following halide can give best  $S_N2$  reaction?

- a) Primary alkyl halide
- b) Tertiary alkyl halide
- c) Secondary alkyl halide
- d) All can give  $S_N2$  reaction at same rate

**Answer: a**

**Explanation:** A 1° alkyl halide has only one alkyl group, so it is relatively unstable. It is unlikely to form a 1° carbocation in an S<sub>N</sub>1 reaction. Instead, it will take the lower-energy S<sub>N</sub>2 path as 1° alkyl is sterically unhindered. More the steric hinderance the substrate becomes less susceptible to SN2 attack.

**Question 8:** Why alkyl halides are considered to be very reactive compounds towards nucleophile?

- a) they have an electrophilic carbon & a bad leaving group
- b) they have a nucleophilic carbon & a good leaving group
- c) they have an electrophilic carbon
- d) they have an electrophilic carbon & a good leaving group

**Answer: d**

**Explanation:** Alkyl halides are considered to be very reactive compounds towards nucleophile because they have an electrophilic carbon & a good leaving group as we go down the periodic table, halides that are larger in size will also be able to distribute their charge over a larger volume, making them less reactive (less basic). This is why fluoride is a much poorer leaving group than any of the other halides. So, alkyl halides are good for nucleophilic substitution reactions.

**Question 9:** In primary alkyl halides, carbon attached to the halogen atom is further attached to how many carbon atoms?

- a) 1
- b) 2
- c) 3
- d) 4

**Answer: a**

**Explanation:** As we can see below, carbon attached to the halogen atom is further attached to one carbon atom.

Example: CH<sub>3</sub>-X → Methyl halide

CH<sub>3</sub>-CH<sub>2</sub>-X → Ethyl halide

CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-X → n-Propyl halide.

**Question 10:** Which of the following is not the method of preparation of alkyl halide?

- a) Addition of HX on alcohol
- b) Halogenation of alkene
- c) Addition of HX on alkenes
- d) Hydration of alkene

**Answer: d**

**Explanation:** Hydration of alkene is electrophilic addition of H<sub>2</sub>O to alkenes which forms alcohol not alkyl halides.

**Question 11:** Which of the following reactant gives the best method of preparation of alkyl halides when reacts with alcohol?

- a) Zn/HCl

- b)  $\text{PCl}_5$   
 c)  $\text{SOCl}_2$ / Pyridine  
 d)  $\text{PCl}_3$

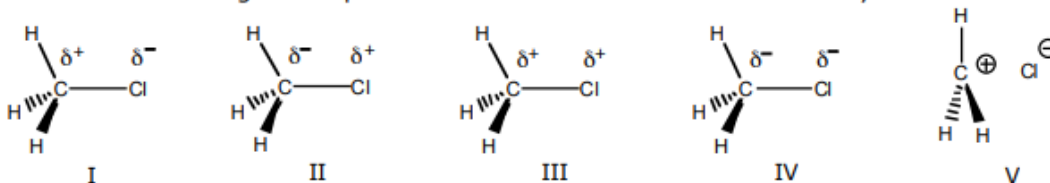
**Answer: c**

**Explanation:** The best method of preparation of alkyl halides is a reaction of alcohol with  $\text{SOCl}_2$ / Pyridine because by-products formed in the reaction are  $\text{SO}_2$  and  $\text{HCl}$  which are in gaseous form and escape into the atmosphere leaving behind pure alkyl chlorides.

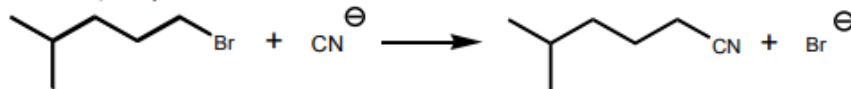


**ORGANIC CHEMISTRY I – PRACTICE EXERCISE**  
 **$\text{S}_\text{N}1$  and  $\text{S}_\text{N}2$  Reactions**

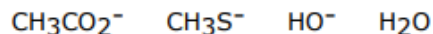
- 1) Which of the following best represents the carbon-chlorine bond of methyl chloride?



- 2) Provide a detailed, stepwise mechanism for the reaction below.



- 3) Rank the species below in order of increasing nucleophilicity in hydroxylic solvents:



- 4) Give a stereochemical structure of the product from the reaction between (*S*)-2-iodopentane and  $\text{KCN}$  in DMF (dimethyl formamide, a good polar solvent for ionic reagents).

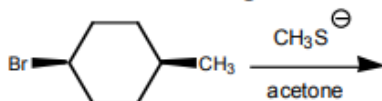
- 5) Consider the reaction of  $(\text{CH}_3)_3\text{CO}^-$  with iodomethane. Will the reaction rate increase, decrease, or remain the same if the concentration of iodomethane is increased? Explain.



6) Which of the following compounds will undergo an  $S_N2$  reaction most readily?

- A)  $(CH_3)_3CCH_2I$
- B)  $(CH_3)_3CCl$
- C)  $(CH_3)_2CHI$
- D)  $(CH_3)_2CHCH_2CH_2CH_2I$
- E)  $(CH_3)_2CHCH_2CH_2CH_2Cl$

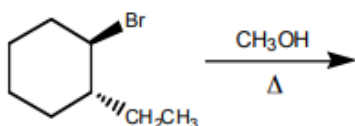
7) What is the major organic product in the following reaction?



8) Would 2-chloropropane or 1-chloro-2,2-dimethylpropane undergo substitution faster with  $Na^+ ^-CCH_3$ ? Give the structure of the substitution product.

9) *t*-butyl chloride undergoes solvolysis in 70% water/30% acetone at a rate slower than in 80% water/20% acetone. Explain.

10) Provide the major organic product of the reaction below and a detailed, stepwise mechanism which accounts for its formation.



11)  $S_N2$  reactions involving chiral electrophiles usually proceed with:

- A) inversion of configuration
- B) slightly more inversion than retention.
- C) slightly more retention than inversion.
- D) retention of configuration.
- E) equal amounts of inversion and retention of configuration.

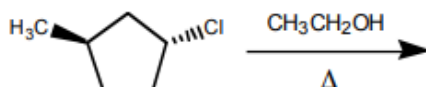
12) Which compound undergoes solvolysis in aqueous ethanol most rapidly and why? Remember: solvolysis refers to ionization of the molecule aided by the solvent.

cyclohexyl bromide   isopropyl chloride   methyl iodide

3-chloropentane   3-iodo-3-methylpentane

13) Why does  $CH_2=CHCHBrCH_3$  undergo solvolysis much more rapidly than 2-bromobutane?

14) Provide the structure of the major organic products which result in the reaction below.



15) What combination of reactants would be best to prepare  $CH_3OCH(CH_3)_2$  by an  $S_N2$  reaction?

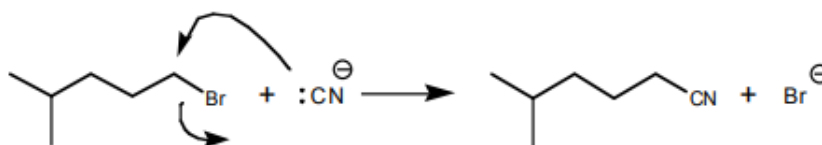
16) The reaction between 2-iodohexane and ethanol to give a substitution product most likely follows an \_\_\_\_\_ mechanism.

- 17) Which of the following alkyl halides is most likely to undergo rearrangement in an  $S_N1$  reaction?  
 A) 3-bromopentane  
 B) 2-chloro-3,3-dimethylpentane  
 C) 3-chloropentane  
 D) bromocyclohexane  
 E) 1-bromo-4-methylcyclohexane
- 18) Which compound is most nucleophilic? A)  $\text{CH}_3\text{SH}$  B)  $\text{CH}_3\text{OH}$  C)  $\text{H}_2\text{O}$  D)  $\text{CH}_3\text{CO}_2\text{H}$  E)  $\text{BF}_3$
- 19) Which halide has the smallest dipole moment?  
 A)  $\text{CH}_3\text{F}$  B)  $\text{CH}_3\text{Cl}$  C)  $\text{CH}_2\text{I}_2$  D)  $\text{CH}_2\text{Cl}_2$  E)  $\text{CF}_4$
- 20) When 2,2-dimethylbutane is subjected to free-radical chlorination, \_\_\_\_\_ distinct monochlorinated products are possible and \_\_\_\_\_ of these contain asymmetric carbon atoms.  
 A) 4, 2 B) 5, 0 C) 3, 0 D) 5, 2 E) 4, 0
- 21) Arrange the substrates in order of increasing  $S_N2$  reactivity with  $\text{NaCN}$ : Bromoethane, 1-chloro-3,3-dimethylpentane, 1-chloro-2,2-dimethylpentane, and 2-bromo-2-methylpentane.
- 22) Arrange the following compounds in order of increasing reactivity toward ethanol solvolysis: *t*-butyl bromide, *t*-butyl iodide, isopropyl chloride, and methyl iodide.

ANSWERS

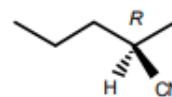
1) I

2)



3)  $\text{H}_2\text{O} < \text{CH}_3\text{CO}_2^- < \text{HO}^- < \text{CH}_3\text{S}^-$

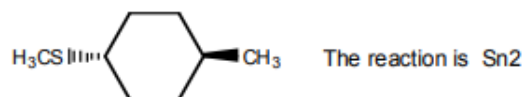
4)



5) This is an  $S_N2$  reaction.  $\text{Rate} = k[(\text{CH}_3)_3\text{CO}^-][\text{CH}_3\text{I}]$ . The rate increases as  $[\text{CH}_3\text{I}]$  increases.

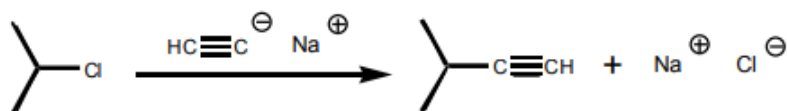
6) D

7)

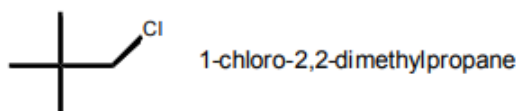


8)

2-Chloropropane. The reaction is  $S_N2$ , and even though 1-chloro-2,2-dimethylpropane is a primary chloride, it is more sterically hindered than 2-chloropropane, which is secondary.

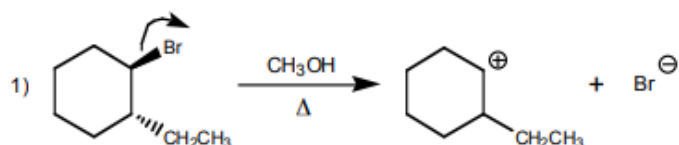


main organic product

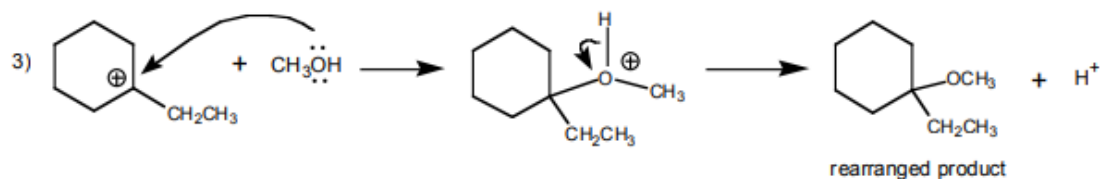
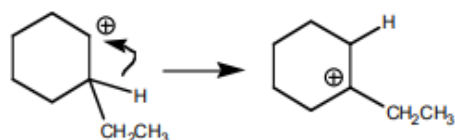


9) This is purely a solvent effect. The greater the percentage of water in this solvent mixture, the more polar the solvent. The more polar the solvent, the more easily solvated the developing carbocation and the more rapidly it is formed.

10)

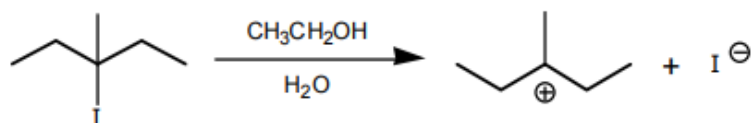


2) carbocation rearrangement from secondary to tertiary by means of a hydride shift



11) A

12) 3-Iodo-3-methylpentane. This molecule forms the most stable cation (tertiary).





**Other questions to solve are given below**

1. Name these compounds



2. Write developed formulas for the following compounds

a. 1,2-dibromo-3-chloropropane

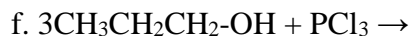
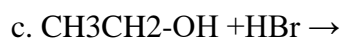
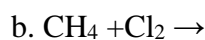
b. 1,1,2-trichloro-1,2,2-trifluoroethane.

c. 1,1,2-trichloropropane

d. 2-chloro-2-methylpropane

3. How many positional isomers are there of chlorobromopropane,  $\text{C}_3\text{H}_6\text{BrCl}$ ? How many of these

4. Complete the following chemical reactions :

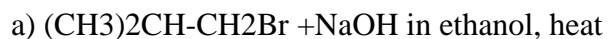


5. Write a chemical equation for the preparation of an halogenoalkanes from an aldehyde.

6. Give the reagents and conditions needed to make the following compounds from 1-bromopropane.

a) propan-1-ol,                      (b) propene,

7. . Give the structural formula of the main product of each of the following reactions:



b)  $\text{CH}_3\text{CH}_2\text{CHBrCH}_2\text{CH}_3 + \text{NaOH}(\text{aq})$

8. Halogenoalkanes undergo nucleophilic substitution reaction. Discuss this statement.

9. (a) What is a nucleophile? Give two examples.

(b) Why do nucleophiles attack halogenoalkanes?

(c) What two types of reaction are in competition when a halogenoalkane reacts with a nucleophile? Name two products which can be formed from 1-bromopropane by these reactions.

10. 2-Chloro-2-methylpropane reacts with aqueous sodium hydroxide to form 2-methyl Propan-2-ol

a) Draw what should be the energy diagram for the reaction.

b) Write the mechanism for the reaction.

11. Using suitable examples, define the terms:

a) Nucleophile

b) Substitution

12. 1-bromobutane is refluxed with aqueous potassium hydroxide to form an alcohol. Write a balanced equation for this reaction and name the alcohol formed.

13. Suggest the structural formulae of the possible alkenes produced when 2-chloro-2-methylbutane is treated with hot KOH in ethanol. Which of the possible product alkenes will be found in greatest yield?

14. Use of CFCs has been declining due to concern over the possible effects on the environment. It is thought that this damage is a result of a light catalysed radical process involving chlorine radicals.

a) State one possible type of damage caused by CFCs to the environment.

b) Explain what is meant by a radical.

c) Give an equation for the formation of a radical from the chlorofluorocarbon  $\text{CCl}_2\text{F}_2$

15. Which of the following is NOT an halogenoalkanes compounds:

a. Tribromobenzene

b. 3-iodohexane

c. 2-chloro-3-methylpentane

d. 2-bromopentane

16. Choose from a list of words and fill in the missing words in the text below

(Halogenoalkanes, iodine, alkyl halide, haloarene, thyroxine )

.....compound are compounds in which the halogen atoms like chlorine, bromine, ..... or fluorine are attached to a hydrocarbon chain or an aromatic ring. When the halogen atom is attached to a hydrocarbon chain the compound is called an ..... or .....

17. Answer by true or false

- a. Chloroform is employed as a solvent as a paint remover.
- b. Iodoform was used earlier as an antiseptic.
- c. Methyl chloride, methyl bromide, ethyl chloride and some chlorofluoromethanes are gases at room temperature.
- d. The objects which are non-superimposable on their mirror image (like a pair of hands) are said to be chiral and this property is known as chirality. While the objects, which are superimposable on their mirror images are called achiral.
- e.  $\text{CHCl}_3$  (chloroform): is used as insecticide
- f. DDT: Dichloro diphenyl trichloroethane is used as anaesthesia
- g. Halogenoalkanes therefore, although they dissolve more than alkanes, are only slightly soluble in water.
- h. Halogenoalkanes undergo nucleophilic substitution reactions in which the halogen atom is replaced by a nucleophile.
- i. Elimination reaction is where a saturated organic compound loses an atom or groups attached to form unsaturated organic compound.

18. Name the following halides according to IUPAC system and classify them as primary, secondary or tertiary halogenoalkanes

- a)  $(\text{CH}_3)_2\text{CHCHClCH}_3$
- b)  $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{I}$
- c)  $(\text{CH}_3)_3\text{CH}_2\text{CH}_2\text{Br}$
- d)  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CHBrCH}_3$
- e)  $\text{CH}_3\text{CH}=\text{CHC}(\text{Br})(\text{CH}_3)_2$
- f)  $\text{CH}_3\text{CH}=\text{C}(\text{Cl})\text{CH}_2\text{CH}(\text{CH}_3)_2$

19. Write the structures of the following organic halogen compounds.

- a) 2-chloro-3-methylpentane
- b) 2-chloro-2-methylpropane
- c) 2,3-dichlorobutane
- d) 2-bromo-4-chloropentane
- e) 1,1,2-trichloropropane

20. Why do bromoalkanes react more readily than chloroalkanes?

21. Why does 1-bromopropane react with nucleophiles but propane does not?

22. Write the equations for the preparation of 1-iodobutane from

- (a) 1-butanol,                      (b) 1-chlorobutane,                      (c) but-1-ene

23. Write the structure of the major organic product in each of the following reactions:

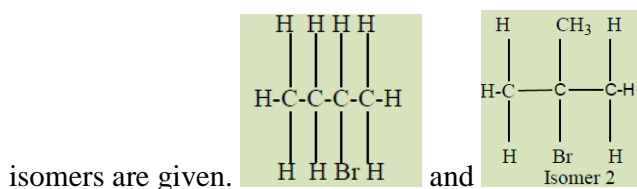
- a.  $(\text{CH}_3)_3\text{CBr} + \text{KOH}$  ethanol heat
- b.  $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_3 + \text{NaOH}$  water
- c.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{SOCl}_2$
- d.  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{HBr}$  peroxide

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

- a) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane
- b) 1-bromo-3-methylbutane, 2-Bromo-2-methylbutane, 3-Bromo-2-methylbutane

c) 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1-bromo-3-methylbutane.

25. a) There are four structural isomers of molecular formula  $C_4H_9Br$ . The formulae of two of these



Isomer 1 Isomer 2 respectively

i. Draw the remaining two structural isomers.

ii. Give the name of isomer 2

b) All four structural isomers of  $C_4H_9Br$  undergo similar reactions with ammonia

i. Give the name of the mechanism involved in these reactions.

ii. Draw the structural formula of the product formed by the reaction of isomer 2 with ammonia.

iii. Select the isomer of molecular formula  $C_4H_9Br$  that would be most reactive with ammonia. State the structural feature of your chosen isomer that makes it the most reactive of the four isomers.

d) The elimination of  $HBr$  from Isomer 1 produces two structural isomers, compounds A and B.

i. Give the reagents and conditions required for this elimination reaction.

ii. Give the structural formulae of the two isomers, A and B formed by elimination of  $HBr$  from isomer 1.

e) Ethene,  $C_2H_4$ , reacts with bromine to give 1,2-dibromoethane.

i. Give the name of the mechanism involved.

ii. Show the mechanism for this reaction.