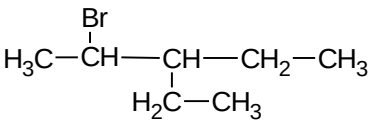
ORGANIC HALOGEN COMPOUNDS

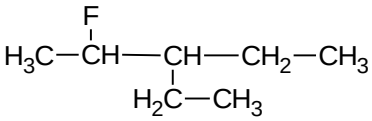
= derivatives of hydrocarbons, one or more hydrogen atoms are substituted by an atom or atoms of halogens.

Naming:

1. *Write the structures of all isomers of the molecular formula $C_4H_8Cl_2$ and name them. (9)*

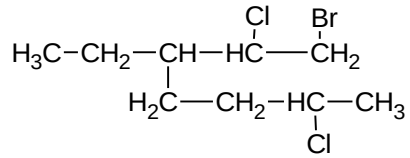
2. *Name these two compounds:*



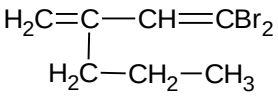


3. *Give the names or formulae for:*

a.



b.



c. CH_3Cl d. C_6H_5Cl e. $CH_3CH_2C(CH_3)BrCH_3$ f.$CHCl_3$

f. 1-bromo-3-iodocyclopentane g. 1,1,3-trichloro-2-iodo-2-methylbutane

h. perfluorocyclohexane i. ethyliodide j. *cis*-1,2-dichloroethene

k. 2-bromotoluene l. 2,4-dibromo- 3-chloro-1,3-difluoro-4-methyl-hex-1-ene

Classification of monosubstituted (one halogen atom) halogenoalkanes: R-X, X = ...

- Primary: a halogen atom bonded on a carbon which carries two hydrogen atoms, e.g CH_3CH_2Cl
- Secondary: a halogen atom bonded on a carbon which carries .....hydrogen atom, e.g $CH_3CHClCH_3$
- Tertiary: a halogen atom bonded on a carbon which carries ..... hydrogen atom, e.g

4. *Find in the questions 2 and 3 all monosubstituted halogenoalkanes and classify them as primary, secondary or tertiary.*

Physical properties

5. *Put CH_3F, CH_3Cl, CH_3Br, CH_3I in order with respect to increasing polarity of the molecules.*

6. *Put CH_3F, CH_3Cl, CH_3Br, CH_3I in order with respect to increasing van de Waals' forces.*

7. *Use the table of boiling points to state what has a bigger effect on boiling points of halogenoalkanes.*

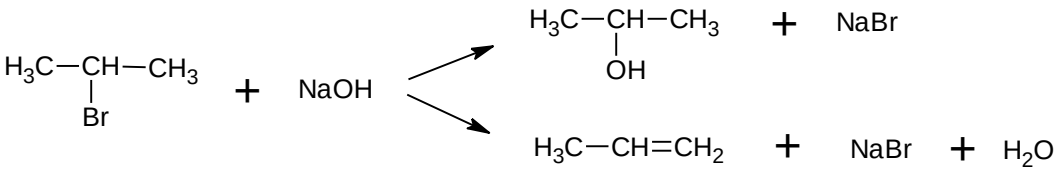
halogenoalkane	CH_3F	CH_3Cl	CH_3Br	CH_3I
boiling point /°C	−78.4	−24.2	4.5	42.2

However the bonds between carbon atom and halogens are ....., it doesn't affect the overall polarity of the molecule. That's why halogenoalkanes are mostly *soluble/insoluble* in water and they are *volatile/involatile.*

Chemical properties

8. *Put the bonds C−F, C−Cl, C−Br, C−I in order with respect to:*
   a. *increasing bond length*
   b. *increasing bond energy*
9. *Put C_2H_5F, C_2H_5Cl, C_2H_5Br and C_2H_5I in order with respect to increasing reactivity.*

1. Reactions of halogenoalkanes with OH^-



10. *State the reaction mechanisms of the above reactions.*

The ratio between the amount of alcohol and an alkene made depends on:

- The type of halogenoalkane: primary → alcohol, tertiary → alkene
- The conditions: NaOH(aq) → alcohol, NaOH(EtOH) → alkene, higher *t* → alkene, high concentration of hydroxide → alkene

2. Other substitution reactions:

11. *Identify the nucleophiles in the following reactions and write the formulae of the organic products:*
    a. With water: $C_2H_5Br + H_2O \rightarrow$
    b. With ammonia: $CH_3CH_2CH_2Cl + NH_3 \rightarrow$
    c. With cyanides: $(CH_3)_2CH{-}I + KCN \rightarrow$
    d. With alkoxides: $CH_3CH(CH_3)CH_2Br + CH_3ONa \rightarrow$
    e. With salts of carboxylic acids: $CH_3CH_2I + CH_3COOK \rightarrow$

<u>Reactivity of halogenoalkenes and halogenoarenes</u>

Due to a conjugation, i.e. an interaction of lone electron pairs of a halogen atom with the π-electrons of either alkenes or arenes, the carbon – halogen bond gets *shorter/longer → higher/lower* bond energy needed to break the bond → halogenoalkenes and halogenoarenes are *more/less* reactive than halogenoalkanes.

E.g. conversion of chlorobenzene to phenol takes place at extreme conditions only: t = 300-350°C, p = 15-20 MPa.

12. *Write down an equation of this reaction.*

13. *A byproduct of this reaction is a substance made by a reaction between chlorobenzene and sodium phenoxide (C_6H_5ONa). Write its formula.*

Manufacture and preparation

1. From alkanes:

$CH_4 + Cl_2 \rightarrow$

14. *What is the reaction mechanism, necessary condition and the steps of halogenation of alkanes?*

2. From alkenes

a. $CH_2{=}CH_2 + Br_2 \rightarrow$
b. $CH_2{=}CH_2 + HBr \rightarrow$

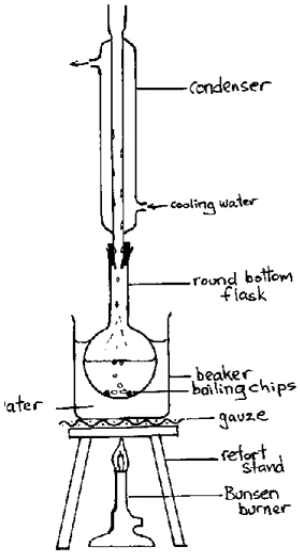
15. Write down an equation for the reaction between but-1-ene and hydrogen chloride.

3. From alcohols

a. + hydrogen halides: $C_3H_7OH + HCl(g) \xrightarrow{\text{reflux}}$

b. + PX_3 or PX_5 (Cl: PCl_3 or PC_5, Br: Br_2 + red P, I: I_2 + red P)

$C_2H_5OH + PCl_5 \xrightarrow{\text{reflux}}$



16. Write down the structures and names of alcohols that may be used for the preparation of :

a. 2-chloropropane

b. 1-bromobutane

4. From arenes

17. What are the reagents and catalysts for making chlorobenzene and bromobenzene?

18. Finish equations, name the products and state the reaction mechanisms:

a. $CH_3CH_2C(CH_3)=CHCH_3 + HCl \rightarrow$

b. $CH_3OH + Br_2 + P \rightarrow$

c. $CH_3CH=CHC_2H_5 + I_2 \rightarrow$

Uses of organic halogen compounds

19. Prepare presentations:

1. Anaesthetics – chloroform, halothane = 2-bromo-2-chloro-1,1,1-trifluoroethane

2. Plastics- PVC, Teflon

3. Solvents (*polar/nonpolar*)

4. Freons

5. Pesticides – DDT

6. PCB = polychlorinated biphenyls