CHAPTER – 1.

Haloalkane →

→ Haloalkanes are halogen derivatives of alkane which are obtained by replace one or more hydrogen atoms by halogens atoms.

→ Also called alkyl halides.

→ General formula : $C_nH_{2n+1}X$ (X = F, Cl, Br, I)

$$R-H \xrightarrow[+X]{-H} R-X$$

eg :- CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4 etc.

Classification:-

Haloalkanes

- monosubstituted
  - 1° – haloalkane
  - 2° – haloalkane
  - 3° – haloalkane
- disubstituted
  - vicinal dihalide
  - geminal dihalide
- Polysubstituted

DATE

(A) On the basis of nature of C-atoms:-

→ Depending on the nature of carbon-atoms attached (bond-ed) with halogens, haloalkane classified as:-

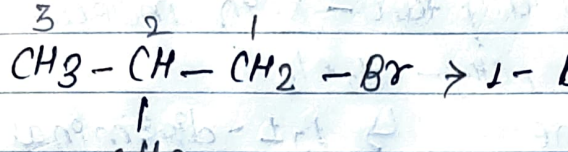
[1] Primary (1°) haloalkane (RCH_2X) →

→ These are the haloalkane in which halogen is bonded to primary carbon atoms.

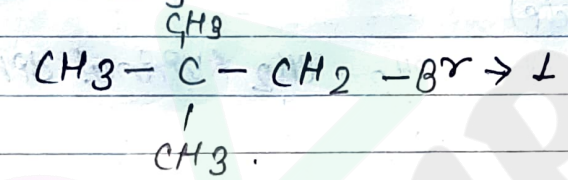
eg:-

$CH_3 - CH_2 - Cl$

$CH_3 - CH_2 - CH_2 - Br$



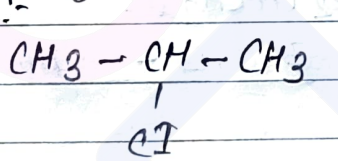
→ 1-bromo-2-methyl propane



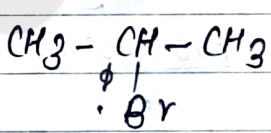
→ 1-bromo-2,2-demethyl propane

[2] Secondary (2°) haloalkanes [R_2CHX]

eg:-

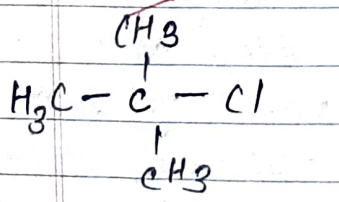


Isopropyl chloride

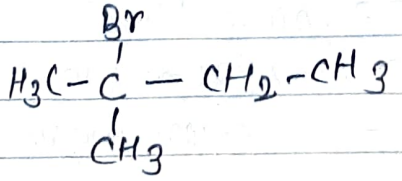


Isopropyl bromide.

[3] Tertiary (3°) haloalkane (R_3CX)



2-chloro-2-methyl propane



2-bromo-2-methyl butane

classmate

PAGE

B] On the basis of number of halogen atoms :-

1) Monosubsitutes 2) Disubstituted 3] poly substituted.

(1) Monosubstituted :- contain one -X in molecule.

eg :- CH_3Cl, CH_3CH_2-Br

Chloromethane

(Geminal halide)

(2] Disubstituted :- contain two -X in molecule.

eg :- CH_2Cl_2, $CH_3-CH_2Cl_2$

Dichloro methane ↳ 1,1 - digeminal

(Germinal halide)

CH_2-CH_2 (Vicinal dihalide)

Cl Cl

(3] Polysubstituted :- contain 3 or more than 3 -X in molecule

eg :- $CHCl_3$, CCl_4, Cl_2CHCH_2Cl

chloroform Tetrachloro form 1,1,2 - trichloroethane

Nomenclature-

Haloalkane	IUPAC	Common name
CH_3Cl	→ chloro methane	• Methyl chloride
CH_3CH_2Cl	→ chloroethane	• ethyl chloride
$CH_3-CH_2-CH_2-Cl$	→ 1-chloro propane	• n-propyl chloride
$CH_3-CH(Cl)-CH_3$	→ 2-chloro propane	• iso propyl chloride
$CH_3-CH_2-CH_2-CH_2-Cl$	→ 1-chloro butane	• n butyl chloride
$CH_3-CH_2-CH(Cl)-CH_3$	→ 2-chrobutane	• sec-butyl chloride

DATE

$CH_3-CH(CH_3)-CH_2-Cl$ 1-chloro-2-methyl propane — Iso butyl chloride

$H_3C-C(CH_3)_2-Cl$ 2-methyl-2-chloro propane — tert-butyl chloride

$H_3C-C(CH_3)_2-CH_2-Cl$ 1-chloro-2,2-dimethyl propane — neopentyl chloride.

ISOMERISM

→ shows 2 types of isomerism :-

a) chain isomerism :- Isomer that differ only in chain length is known as chain isomerism.

e.g:-

$CH_3-CH(CH_3)-CH_2-Cl$ $\quad$ $CH_3-CH_2-CH_2-CH_2-Cl$

b) Position isomerism :-

Isomer that have same length but different in position of functional group is known as position isomerism

eg:-

$CH_3-CH_2-CH_2-Cl$ $\quad$ $CH_3-CH(Cl)-CH_3$

DATE

General methods of preparation →

(I) from alkanes (B) from alkenes (C) from alcohol

Addition :- a. from halide exchange method.
b. from silver carbonyate.

(I) From alkanes (halogenation) → when alkenes are treated with halogen (Cl_2 or Br_2) in the presence of sunlight or heat, haloalkane is formed.

→ Free radical substitution (FRS) reaction :-

$$R-H + X_2 \xrightarrow{UV \text{ or sunlight} / \Delta} R-X + HX.$$

Eg :-

$$CH_4 + Cl_2 \xrightarrow[\text{(limited)}]{\text{Sunlight}} CH_3-Cl + HCl.$$

$$CH_3-CH_3 + Cl_2 \xrightarrow{UV, 25^\circ C / 400^\circ C} CH_3CH_2-Cl + HCl$$

$$CH_3-CH_3 + Br_2 \xrightarrow{UV, 127^\circ C} CH_3CH_2-Br + HBr$$

But Iodination is reversible process because HI is strong reducing agent. Therefore it is carried out in the presence of oxidising agent HIO_3, HNO_3 etc. It converts HI back into I_2 and shift the equilibrium in forward direction.

$$CH_4 + I_2 \underset{}{\overset{O.A}{\rightleftharpoons}} CH_3-I + HI$$

$$HNO_3 + HI \xrightarrow[\text{conc.}]{} NO_2 + H_2O + I_2$$

$$HIO_3 + HI \longrightarrow I_2 + H_2O$$

→ Reactivity of halogens towards halogenation.

$$F_2 > Cl_2 > Br_2 > I_2$$

→ Reactivity of hydrogen towards halogenation.

$$3^\circ H > 2^\circ H > 1^\circ H > CH_4$$

* Addition →

Generally not good method for the lab preparation of haloalkanes due to:-

a) Excess X_2 (Cl_2 or Br_2) leads to formation of mixture of poly halides.

$$CH_4 + Cl_2 \xrightarrow[-HCl]{U.V} CH_3Cl \longrightarrow CH_2Cl \xrightarrow[-HCl]{UV} CHCl_3 \xrightarrow[-HCl]{UV} CCl_4$$

(excess)

(b) Higher alkane give a mixture of all possible isomeric halo alkane which are difficult to separate.

$$CH_3-CH_2-CH_3 \xrightarrow[25^\circ C]{Cl_2.UV} CH_3CH_2-CH_2-Cl + CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3 \text{ (major)}$$

$$CH_3-CH_2-CH_3 + Br_2 \xrightarrow[127^\circ C]{UV} CH_3-CH_2-CH_2-Br + CH_3-\underset{\underset{Br}{|}}{CH}-CH_3 \text{ (major)}$$

DATE

g. Why halogenation of alkane is not a suitable method for laboratory preparation of haloalkane

Mechanism:-

→ Chain initiation step

$$X-X \xrightarrow[\text{homolysis}]{UV} \dot{X} + \dot{X}$$

II Chain propagation step

$$R-H + \dot{X} \longrightarrow \dot{R} + HX$$

$$\dot{R} + X_2 \longrightarrow R-X + \dot{X}$$

III Chain termination →

$$\dot{X} + \dot{X} \longrightarrow X_2$$

$$\text{or, } \dot{R} + \dot{R} \longrightarrow R-R$$

$$\dot{R} + \dot{X} \longrightarrow R-X$$

(2) From alkene → (Hydrohalogenation)

→ When alkenes are treated with halogen acids (HCl, HBr or HI) haloalkane is formed.

→ Electrophile addition reaction (EAR)

$$CH_2 = CH_2 + HCl \rightarrow CH_3-CH_2-Cl$$

Markovnikov's Rule:- (unsymmetrical alkene)

According to M.R,** when an unsymmetrical reagent is added to an unsymmetrical alkene, positive part of the reagent gets bonded to carbon which contain more number of hydrogen atoms."

$$CH_3-CH=CH_2 \xrightarrow{HBr} CH_3-\underset{Br}{CH}-CH_3$$

$$CH_3-\underset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow{HBr} CH_3-\underset{CH_3}{\overset{Br}{\overset{|}{C}}}-CH_3$$

Additional :- mechanism :- Electrophilic add^n :-

→ $HBr \longrightarrow H^+ + Br^-$

Step-I

$$CH_3-CH=CH_2 + H^{\oplus} \longrightarrow CH_3-\overset{\oplus}{C}H-CH_3$$

Step-II

$$CH_3-\overset{\oplus}{C}H-CH_3 + Br^{\ominus} \longrightarrow CH_3-\underset{Br}{CH}-CH_3$$

Anti – Markovikons rule / peroxide effect / Khorasch effect.

→ Alc $\xrightarrow{\Delta MR}$ +ve part of reagent adds to less number of hydrogen atoms.

$$CH_3-CH=CH_2 + HBr \xrightarrow{org.\ peroxides} CH_3-CH_2-CH_2Br$$

* Additional mechanism :- The free radical reaction

Step - I $RO-OR \rightarrow 2RO^{\cdot}$

$RO^{\cdot} + H-Br \rightarrow ROH + Br^{\cdot}$

Step - II $CH_3-CH=CH_2 + Br^{\cdot} \rightarrow \begin{cases} CH_3 \\ \end{cases}$

$CH_3-\dot{C}H-CH_2Br + HBr \longrightarrow CH_3-\underset{H}{CH}-CH_2-Br$

Step - III Chain termination step.

※ Note :- only HBr in the presence of org. peroxide follow anti markovnikov's rule, other reagent like HCl, HI donot follow this rule because;

a) H - Cl is highly polar doesnot homolysis easily.

b) H - I undergo homolysis to give iodine free radical — which instantly combine to give I_2.

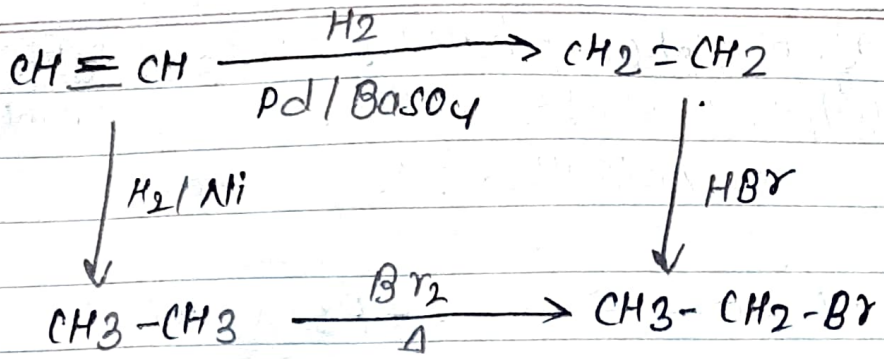
Q. Why HCl & HI donot give anti - Markonivous effect

$CH_3-CH=CH_2$ —

HBr →

HBr →

peroxide



(3) From alcohol →

→ Nucleophile substitution reaction

$$CH_3-CH_2-OH \xrightarrow[+X]{-OH} CH_3-CH_2-X$$

a) By the action of HX (haloacid) → when alcohol is treated with haloacid in presence of anhydrous $ZnCl_2$ (lucas reagent) haloalkane is formed.

$$R-\ddot{O}H + H-X \longrightarrow R-X + H_2O$$

eg:-

$$CH_3-CH_2-OH + H-Cl \xrightarrow[ZnCl_2]{Anhy} CH_3-CH_2-Cl + H_2O$$

V-slow

$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 + HCl \xrightarrow{anhy.\ ZnCl_2} CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3 + H_2O$$

flow

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH + HCl \xrightarrow[-H_2O]{anhy.\ ZnCl_2} H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl$$

fast

$$R-OH + H\ddot{I} \longrightarrow R-I + H_2O.$$

→ Reactivity of alcohol:- $3^0 > 2^0 > 1^0$

→ Reactivity of H-X:- HI > HBr > HCl.

(b) By the action of phosphorus halides (PCl_3 or PCl_5):-
When alcohol is refluxed with phosphorous halides (PCl_3 or PCl_5), haloalkane is formed.

For PCl_5:

G.R:- $R-OH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$
(phosphorous oxychloride)

E.g:-
$CH_3-CH_2-OH + PCl_5 \rightarrow CH_3CH_2-Cl + POCl_3 + HCl$.
(chloroethane)

For PCl_3,

G.R: $3R-OH + PCl_3 \longrightarrow 3R-Cl + H_3PO_3$.

E.g:-
$3CH_3-CH_2-OH + PCl_3 \rightarrow 3CH_3-CH_2-Cl + H_3PO_3$.
(chloroethane.)

Bromo and Iodo alkanes are obtained by the action of red P_4 on Br_2 or I_2 instead of PBr_3 or PI_3 because they are unstable in nature.

$P_4 + Br_2 \longrightarrow PBr_3$

$CH_3-CH_2-OH + PBr_3 \rightarrow CH_3-CH_2-Br + H_3PO_3$

$P_4 + I_2 \rightarrow PI_3$

$CH_3-CH_2-OH + PI_3 \rightarrow CH_3-CH_2I + H_3PO_3$.

Imp (c) By the action of thionyl chloride ($SOCl_2$):-
When alcohol is refluxed with thionyl chloride ($SOCl_2$) in the presence of pyridine (C_6H_5N), haloalkane is formed.

G.R) $R-OH + SOCl_2 \xrightarrow{\text{Pyridine}} R-Cl + SO_2\uparrow + HCl\uparrow$

E.g

$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3 + SO_2\uparrow + HCl\uparrow$

Here, HCl is absorbed by pyridine (C_6H_5N), while SO_2 gas escape out. Hence only chloroalkane is obtained in pure form. Therefore, this method is best method for preparing chloroalkane.

DATE

g. Why $SOCl_2$ is suitable for preparing chloroalkane from alcohol?

Note:

* $R-OH \xrightarrow[\text{(iii) } SOCl_2]{\text{(i) } HCl \text{ (ii) } PCl_3/PCl_5} R-Cl$

* $R-OH \xrightarrow[\text{ii) } P_4+Br_2 \text{ or } P_4+I_2]{\text{i) } HBr/HI} R-Br/R-I$

Note:- From silver salt of carboxylic acid → (Hunsdiecker or Borodine - Hundiecker reaction) →

$$RCOOAg + Cl_2 \xrightarrow[\text{(solvent)}]{CCl_4} R-Cl + CO_2 + AgCl \quad \text{(vapour)}$$

$$RCOOAg + Br_2 \xrightarrow{CCl_4} R-Br + CO_2 + AgBr$$

free radical reaction — alkyl bromide.

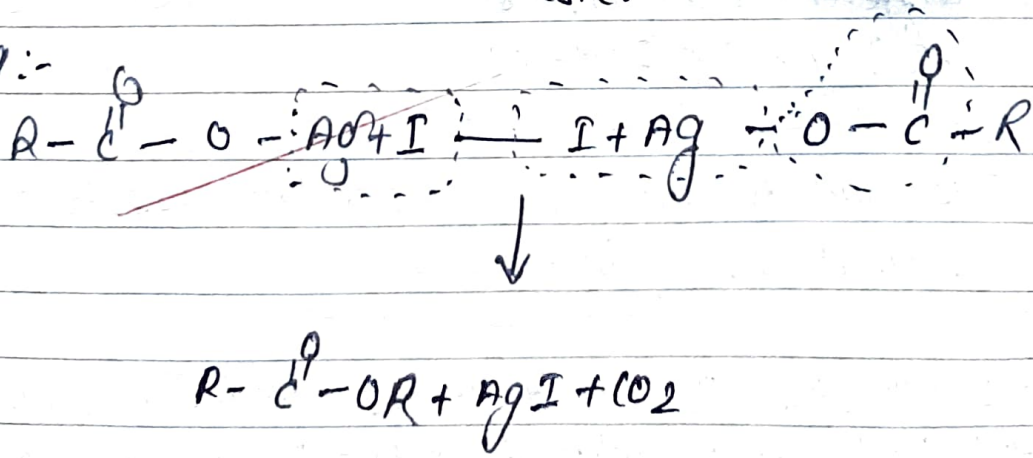
~~free radical reaction~~ or

Bimbaum - Simonini Reaction:-

$$R-COOAg + I_2 \longrightarrow R-COO-R + CO_2 + 2AgI$$

ester

eg:-



PHYSICAL PROPERTIES

1. State:-

lower member ⟶ gases.
Higher member ⟶ sweet smelling liquids (colourless lips)

2. Boiling point:-

(a) As carbon number increases, bpt of haloalkane also increase because 'vander waals' force is increased with increase in molecule size. As a result intermolecular force of attraction is increased.

eg:-

$CH_3-Cl < CH_3-CH_2-Cl < CH_3-CH_2-CH_2-Cl$

(b) Bpt. of haloalkane are higher than that of hydrocarbon. This is due to presence of polar C–X bond which increases intermolecular force of attraction.

$CH_4 < CH_3-Cl$.

(c) The order of boiling point of haloalkanes having same alkyl group but different haloген is

$R-I > R-Br > R-Cl$

(d) This is due to increase in molecular mass (vander waal's force of attraction increase).

(d) In isomeric alkylhalide, bpt decreases with increase in branching. this is because with branching, the shape of molecule tends to be spherical i.e surface area of molecule

decreases due to which intermolecular force of attraction (magnitude of Vander Waals force of attraction) decreases.

eg:- $CH_3-CH_2-CH_2-CH_2-Cl > CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-Cl > H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl$

3. Solubility →

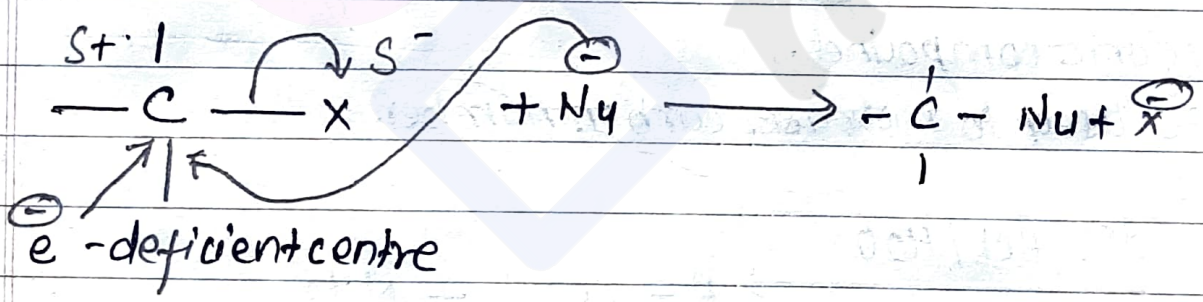
→ Insoluble in water because they cannot form intermolecular hydrogen bonding with water molecule. But they are soluble in organic solvent such as alcohol, ether etc.

CHEMICAL PROPERTIES.

[A] Nucleophilic substitution reaction → (NSR)

→ A substitution reaction initiated by nucleophile is called NSR

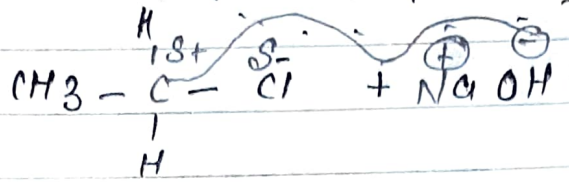
$$R-\overset{\delta+}{X}\ \overset{\delta-}{} + \overset{\ominus}{N}u \longrightarrow R-Nu + \overset{\ominus}{X}$$



→ Haloalkane are polar compounds. In haloalkanes C-X bond is polar because 'X' is more E.N than 'C'. therefore, nucleophile attack the carbon bearing halogen to give substitution reaction.

(1) Action of aq. NaOH →

$CH_3-CH_2-Cl + aq.NaOH \longrightarrow CH_3-CH_2-OH + NaCl$.



V.V.I NEB

(2) Action of alcoholic solution of KCN →

- Formation of alkane nitrile.

$CH_3-CH_2-Cl + KCN \longrightarrow CH_3-CH_2-CN + KCl$

(alc) propane nitrile (ethyl cyanide)

Note:-

Alkyl cyanide ($R-C\equiv N$) is useful synthetic reagent this chemical reagent can be used to synthesize different organic compound.

→ KCN is used to increase carbon number.

$R-CN$ —

① dil HCl / H_2O → complete hydrolysis → $R-COOH + NH_3$ (acid)

② conc. HCl / alk. H_2O_2 → Partial hydrolysis → $R-\overset{O}{\overset{\|}{C}}-NH_2$ (amide)

③ a) $SnCl_2$ / HCl
b) $H_3O^+ / H^\oplus$ → $R-CHO$ (aldehyde)

④ H_2/Ni or C_2H_5OH/Na or dil AlH_4 → $CH_3-CH_2-NH_2$ (amine)

(Mendius reduction)

DATE

3. Action with alc. $AgCN \rightarrow$ Isocyanide (Isonitrile) is obtained

$$CH_3-CH_2-Cl + AgCN\,(alc) \longrightarrow CH_3-CH_2-\overrightarrow{N}\equiv C + AgCl$$

$$CH_3-\overset{\delta+}{C}l + Ag^{\delta-}CN \longrightarrow CH_3-\overrightarrow{N}\equiv C + AgCl$$

Note:-

(1) An Isocyanide on complete reduction gives 2° - amine.

$$CH_3-CH_2-\overrightarrow{N}\equiv C + 4[H] \xrightarrow{Li\,AlH_4} CH_3-CH_2-NH-CH_3$$

N-methyl amine ethane.

$$CH_3-\overrightarrow{N}\equiv C + 4[H] \xrightarrow{Li\,AlH_4} CH_3-NH-CH_3$$

Dimethyl amine.

Additional

2) Formation of 1° amine (hydrolysis) :- Isonitrile on hydrolysis give 1° amine and formic acid.

$$R-N\rightleftharpoons C + 2H_2O \xrightarrow{H_2O/H^{\oplus}} R-NH_2 + HCOOH$$

$$CH_3-N\rightleftharpoons C + H_2O \xrightarrow{H_2O/H^{\oplus}} CH_3-NH_2 + HCOOH$$

(3) Formation of Nitrile (rearrangement) → when heated for long time

$$R-NC \xrightarrow{\Delta} R-CN$$

Alkyl isocyanide → alkylcyanide.

DATE

Mechanism:-

nucleophilic site

* $Ag - C \equiv N + CH_3 - \underset{H}{\overset{H}{C}} - Br \rightarrow CH_3CH_2NC + AgBr$

* covalent compound

$K^{\oplus}\overset{\ominus}{C} \equiv N + CH_3 - \underset{H}{\overset{H}{C}} - Br \rightarrow CH_3 - CH_2CN + KBr$

Ionic compound

nucleophilic site

* Action of alc. KNO_2:-

→ Alkyl nitrite is obtained

$CH_3 - CH_2 - Cl + K^{\oplus}O^{\ominus} - N = O \xrightarrow{\Delta} CH_3 - CH_2 - O - N = O + KCl$

ionic

ethyl nitrite

* Action with $AgNO_2$:-

→ Nitroalkane is obtained

$CH_3 - CH_2 - Cl + Ag - O - N = O \xrightarrow{\Delta} CH_3 - CH_2 - N(=O)=O + AgCl$

(covalent)

Nitroethane

DATE

Note:-

An atom with -ve charge is more nucleophile than the atom with lone pair of electron.

→ NaCN or KCN KNO_2 (alc) ⟶ Ionic

→ alc. AgCN $AgNO_2$ ÷ covalent

Ambident nucleophile

$\overset{\ominus}{C} \equiv \ddot{N}$ $\qquad$ $\overset{\ominus}{O} - \ddot{N} = O$

6) Action with ammonia ⟶ [Hofman's amonolysis]

→ When alkylhalide is heated with alc. solution of ammonia in a sealed tube of 100°C, it forms amine. This reaction is known Hofman's amonolysis.

$$\overset{\delta+}{R} - \overset{\delta-}{X} + \ddot{N}H_3 \xrightarrow{\Delta} R - NH_2 + HX$$

eg:-

$$CH_3 - CH_2 - Br + \ddot{N}H_3 \rightarrow CH_3 - CH_2 - NH_2 + HBr$$

equimolar ratio

→ If excess of haloalkane is used a mixture of 2°&3° and quartemary ammonium salts is obtained.

NH → amine
NH_2 →

DATE

$CH_3-CH_2-Br + \ddot{N}H_3 \longrightarrow CH_3-CH_2-NH_2 + HCl$
1°- amine

$CH_3-CH_2-\ddot{N}H_2 + CH_3-CH_2-Br \longrightarrow CH_3-CH_2-\underset{H}{\ddot{N}}-CH_2-CH_3$

$CH_3-CH_2-\ddot{N}H-CH_2-CH_3 + CH_3-CH_2-Br \longrightarrow (CH_3-CH_2)_3\ddot{N}H\ HBr$
(3°)

$(CH_3-CH_2)_3\ddot{N} + CH_3-CH_2-Br \longrightarrow (CH_3CH_2)_4\overset{\oplus}{N}\overset{\ominus}{Br}$
Tetramethyl ammonium bromide (4°)

6. Note :- the process of cleavage of C-X bond by ammonia molecules called ammonolysis.

7. Action of alc. KSH → (Potassium sulphide or hydro sulphide)

→ Alkyl thio alcohol (alkane thiol) is formed.

→ $CH_3-CH_2-Br + KSH \longrightarrow CH_3CH_2-SH + KBr$
ethyl thio alc
(ethan thiol)

8. Action of alc. silver salt of carbonylic acid (silver carbonate) :- An ester is obtained

ethyl ethanoate

→ $CH_3-CH_2-Br + CH_3-C(=O)-OAg \longrightarrow CH_3-CH_2-O-C(=O)-CH_3 + AgBr$
silver carbonate

B) ~~Action of alc. silver salt of carboxylic acid~~

NCERT V. Imp.

9) Action of sodium or potassium alkoxide:- Etherification rxn

→ Ether is formed. This reaction is called 'Williamson's synthesis'

$$CH_3-CH_2-\bar{C}l + CH_3-CH_2-O^{\ominus}Na^{\oplus} \xrightarrow[\Delta]{\text{distillation}} CH_3-CH_2-O-CH_2-CH_3 + NaCl$$

* This chemical reaction is used to prepare both symmetrical and unsymmetrical ether.
* Sodium alkoxide is a salt of alcohol which is obtained by treating alcohol with Na-metal.

$$CH_3-CH_2-OH + Na \longrightarrow CH_3-CH_2-ONa + \frac{1}{2}H_2$$

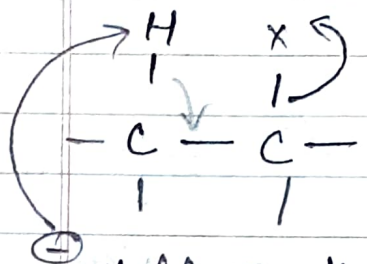
* Summary of reaction. (In short) (Nucleophilic substⁿ rxn)

R-X →
- aq. NaOH / aq. KOH → R-OH + NaX
- alc. KCN → R-CN + KX
- alc. AgCN → R-NC + AgX
- alc. KNO_2 → R-ONO + KX
- $AgNO_2$ → $R-NO_2$ + AgX
- alc. NH_3 → $R-NH_2$ + HX
- alc. KSH → R-SH + HX
- alc. $CH_3COO^{\ominus}Ag^{\oplus}$ → $R-O-\overset{O}{\overset{\|}{C}}-CH_3$ + AgX
- $R-O^{\ominus}Na^{\oplus}$ → R-O-R' + NaX
- alc. KOH → alkene (elimination / dehydrohalogenation)

{α, β-elimination / α, γ-elimination} Halogen grp attached - α
α-halide - β.

DATE

B. Elimination reaction → 1) (Dehydrohalogenation)
When a haloalkane is heated with an alcoholic solution of KOH, then alkene is obtained. This is an example of β-elimination reaction (β-elimination)



$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \xrightarrow[\Delta]{\text{alc.KOH}} -\overset{|}{C}=\overset{|}{C}- + KX + H_2O$

eg :-

$CH_3-CH_2-Cl + KOH\ (alc) \xrightarrow{\Delta} CH_2=CH_2 + KCl + H_2O$

$CH_3-CH_2-Cl \xrightarrow{\text{alc.KOH (base)},\ \Delta} CH_2=CH_2$

$CH_3-CH_2-Cl \xrightarrow{\text{aq.KOH}} CH_3-CH_2-OH.$

aq. KOH → $K^{\oplus} + OH^{\ominus}$ (nucleophile)
alc. KOH → $K^{\oplus} + OH^{\ominus}$ (base) → abstract $H^{\oplus}$

Saytzeff's Rule → During dehydrohalogenation of haloalkane if more than one products are formed then the major product is given by Saytzeff's rule.
this rule states that "During halogen atom of a haloalkane if more than one products are obtained then highly substituted alkene is the mayor product.
OR
A/c to it, "In dehydrohalogenation reaction, the prefe

med product is that alkene which has greater number of alkyl groups attached to doubly bonded carbon atoms.

$$CH_3-CH_2-\underset{Cl}{CH}-CH_3 \xrightarrow[\Delta]{alc.KOH} CH_3-CH_2-CH=CH_2$$
(minor product)

+

$CH_3-CH=CH-CH_3$
(major product).

[C] Reaction with metal:-

1. Reaction with Na:- [Wurtz reaction] when haloalkane is heated with Na metal in presence of dry ether, an alkane with double volume of 2 molecules of even number of C-atom is obtained. This reaction is called Wurtz-reaction.

Eg:-

$$CH_3-Cl + 2Na + Cl-CH_3 \xrightarrow[\Delta]{dry\ ether} \underset{Ethane}{CH_3-CH_3} + 2NaCl$$

Limitation:-

1. Methane cannot be prepared.
2. Cannot be used to prepare alkanes having odd number of carbon atoms as mixture of alkane is obtained.

$$CH_3-Cl + 2Na + Cl-CH_2-CH_3 \longrightarrow CH_3-CH_3 + CH_3-CH_2-CH_2-CH_3 + CH_3-CH_2-CH_2-CH_3 + 2NaCl$$

3. Tertiary alkyhalide do not undergo this reaction.

2. **Reaction with Mg metal (Grignard's reaction) ⇒**

When haloalkane is treated with magnesium metal in the presence of dry ether and inert atmosphere alkyl magnesium halide (Grignard reagent) is formed.

Rxn

$$R-X + Mg \xrightarrow[\text{inert atmosphere}]{\text{dry ether}} R-MgX$$

(Grignard agent)

Grignard reagent are highly reactive organometallic compound. They easily react with atm moisture CO_2 etc and form various other products.

The reaction of grignard reagent are carried out in an inert medium like dry ether, THF etc.

a) $RMgX + O_2 \longrightarrow R-O-OMgX$ (hydroproxide)

b) $CH_3CH_2-MgBr + H_2O \xrightarrow{H\text{ or }H} CH_3-CH_3 / Mg(OH)X$

~~c) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH + Mg(OH)Br$~~

d) $CH_3-CH_2-MgBr + C=O \longrightarrow CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O\,MgBr$

($\delta-$ on Mg, $\delta+$ on C)

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH + Mg(OH)Br \xleftarrow{H_2O/H^+}$$

NEB

DATE

[D] **Reduction Reaction** → When haloalkane is treated with reducing agent like $LiAlH_4$, Zn/HCl, H_2/Ni, Cu couple ethanol, Na/C_2H_5OH etc. alkane is formed/obtained.

Eg:-

$$CH_3-CH_2-Cl + 2[H] \xrightarrow{Sn/HCl} CH_3-CH_3 + HCl.$$

$$CH_3-Cl + [H] \xrightarrow[\Delta]{Ni} CH_4 + HCl.$$

Q1) Convert 1-chloropropane to 2-chloropropane and vice versa.

Ans

$$CH_3-CH_2-CH_2-Cl \xrightarrow{aq.KOH\ /\ anhy.NaOH} CH_3-CH_2-CH_2OH - H_2O$$

1-chloropropane

$$CH_3-CH_2-CH_2OH \xrightarrow{conc.H_2SO_4} CH_3-CH=CH_2$$

$$CH_3-CH=CH_2 \xrightarrow{HCl} CH_3-\underset{Cl}{CH}-CH_3$$

2-chloropropane

2) Convert propan-1-ol to propan-2-ol & viceversa.

→ Ans

$$CH_3-CH_2-CH_2OH \xrightarrow{conc.H_2SO_4} CH_3-CH=CH_2$$

1-propanol

$$CH_3-CH=CH_2 \xrightarrow{HCl} CH_3-\underset{Cl}{CH}-CH_3$$

$$CH_3-\underset{Cl}{CH}-CH_3 \xrightarrow{aq.KOH} CH_3-\underset{OH}{CH}-CH_3$$

2-propanal

(Haloalkane exercise)

DATE

Short questions:-

(1) Why is chloroform stored in a dark brown bottle?

Ans. Chloroform is kept in dark coloured bottle containing ethanol to protect $CHCl_3$ from sunlight and to convert phosgene gas produced (when exposed to sunlight and O_2) into non-poisonous gas by ethanol.

(2) Convert bromoethane to ethyne.

CH_3-CH_2-Br (Bromoethane) $\longrightarrow$ CH_3-CH_2-OH (ethanol) $\xrightarrow[\text{Iodoform}]{I_2/NaOH}$ CI_3-H (Iodoform) $\xrightarrow{Ag}$ $CH\equiv CH$ (Ethyne.)

(3) A primary haloalkane (X), is allowed to react with KCN yields a compound (Y), which on acidic hydrolysis give ~~propane~~ propanoic acid. Identify (X) and (Y)

Ans

CH_3-CH_2-X (Haloethane) $\xrightarrow{KCN}$ CH_3-CH_2-CN (propanenitrile) $\xrightarrow{H_2O/H^+}$ $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH + NH_3$ (propanic)

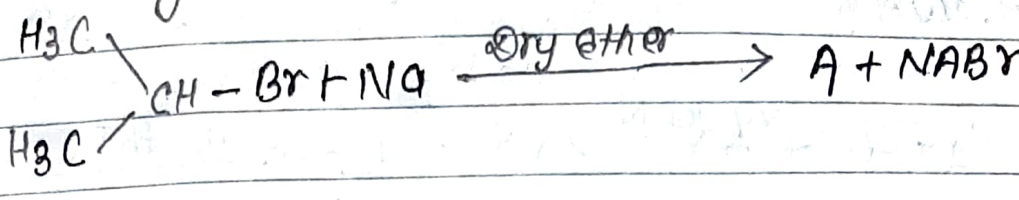
(4) Identify (X) and (Y) in the following reactions:

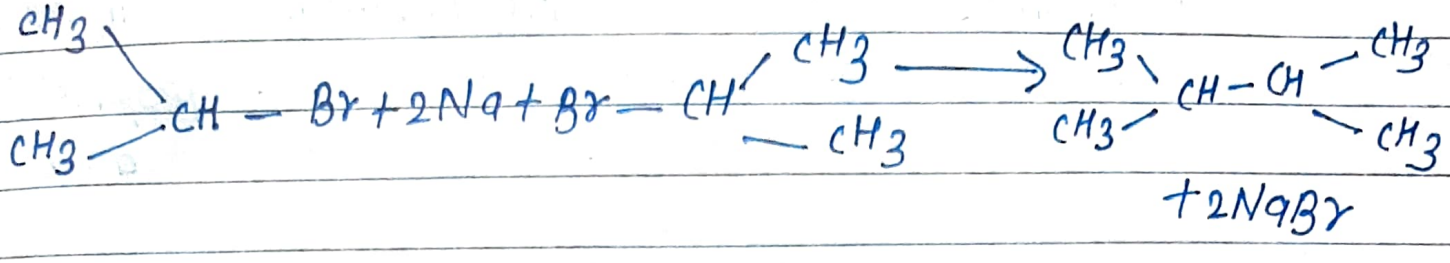
Ans

$X \xrightarrow{Mg/ether} Y \xrightarrow[(ii)\ H_2O/H^+]{(i)\ CO_2}$ Propanoic acid

$CH_3-CH_2-X \xrightarrow{Mg/ether} CH_3-CH_2-MgX \xrightarrow[(ii)\ H_2O+H^+]{(i)\ CO_2}$ propanoic acid

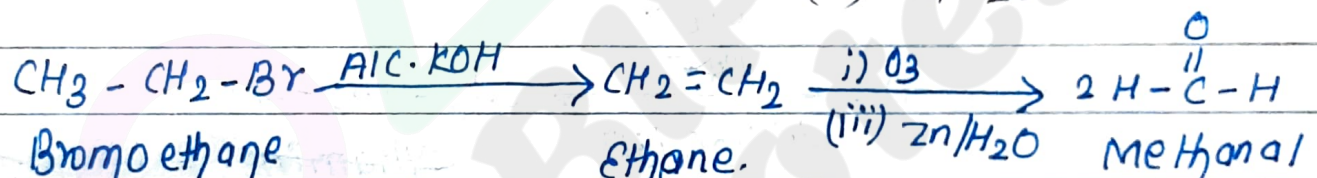
5. Identify A and write its IUPAC name in the following reaction.



→ 

A = 2,3 - dimethyl Butane.

(6) Identify A and B in the following reaction.

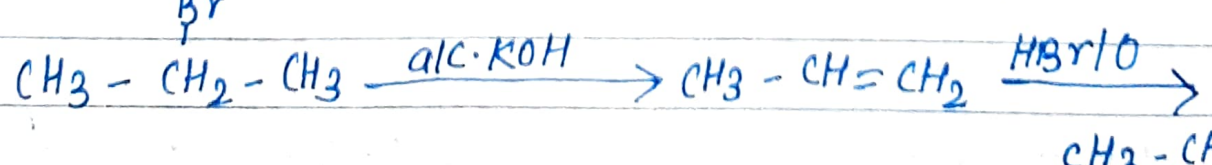


the compounds are:-

A = ethene

B = Methanol

(7) With the help of chemical equations, show how you will convert 2-bromopropane to 1-bromopropane in two steps.



1 - bromopropane

DATE

(8) Starting from ethane, how can you synthesize ethanol and propanoic acid?

$CH_3-CH_2-OH \xrightarrow{aq.KCN} CH_3-CH_2-CN \xrightarrow{H_2O/H^+} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH$

ethanol. Propane nitrile propanoic acid

(9) Complete the following reactions:

i. $H_3C-CH_2-CH_2-I \xrightarrow[\Delta]{alc.KOH} CH_3-CH=CH_2 \xrightarrow{HBr} CH_3-\underset{Br}{CH}-CH_3$

Iodopropane propene

ii) $CH_3-CH_2-OH \xrightarrow[(ii)\,H_2O/H^+]{i)\,KCN} CH_3-CH_2-CN$

~~Ethanamine~~. Ethane nitrile

(10) Give the reagent or reaction condition that cause the transformation listed below:-

i) $H_3C-CH_2-CH_2-Br \xrightarrow{alc.KOH} CH_3-CH=CH_2 \xrightarrow[Br]{HBr.} H_3C-\underset{Br}{CH}-CH_3$

ii) $H_3C-CH_2-OH \xrightarrow{HBr} H_3C-CH_2-Br \xrightarrow{Mg} H_3C-CH_2-MgBr$

11. How will you obtain?

(a) Iodoform from ethanol.

$CH_3 - CH_2OH$ = ethanol

$NaOH + I_2 \longrightarrow NaI + NaOI + H_2O$

$C_2H_5OH + NaOI \longrightarrow CH_3 - \overset{O}{\overset{\|}{C}} - H$

$CH_3 - \overset{O}{\overset{\|}{C}} - H + 3I_2 \longrightarrow CI_3 - \overset{O}{\overset{\|}{C}} - H$

$CI_3 - \overset{O}{\overset{\|}{C}} - H + NaOH \longrightarrow CHI_3 + HCOONa.$

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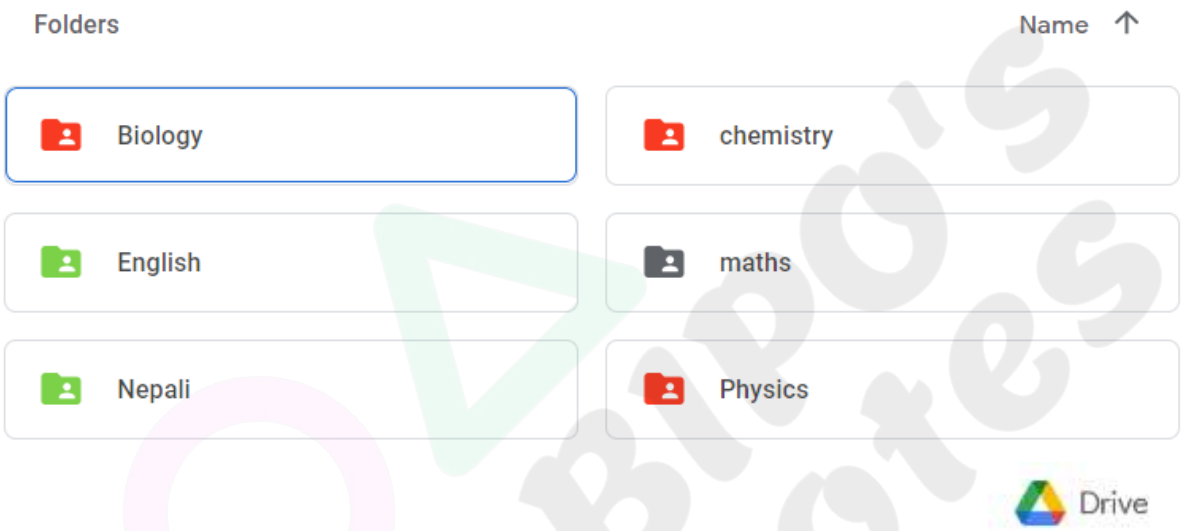
(Bipo)

Class 12 complete notes and paper collection.



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