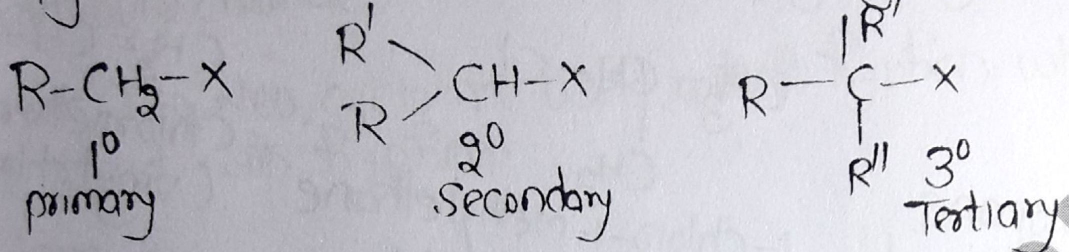
Haloalkanes & Haloarenes

These are the halogen derivatives of aliphatic & aromatic hydrocarbons.

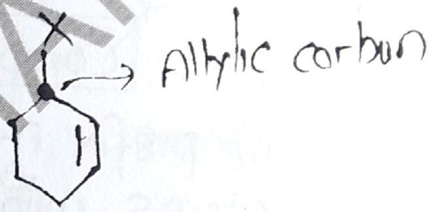
① Haloalkanes or Aryl halides:-

Halogen atom is bonded to an alkyl group (R).



⑪ Allyl halide:-

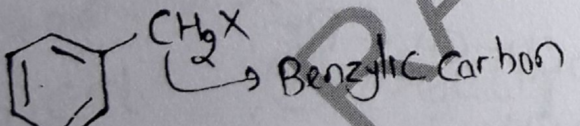
Halogen atom is bonded to an sp^3 hybridised carbon atom next to carbon-carbon double bond (C=C).



$CH_2=CH-CH_2-X$ → Allylic carbon

⑪ Benzylic halide:-

Halogen atom is bonded to an sp^3 hybridised carbon atom next to an aromatic ring (sp² hybridised carbon of Benzene ring).



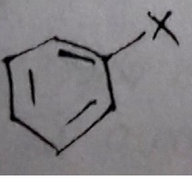
Ⓘ vinylic halide:-

Halogen atom is bonded to sp^2 hybridised carbon atom of carbon-carbon double bond (C=C)

$CH_2=CH-X$ → vinylic carbon

Ⓥ Aryl halides or Haloarenes:-

Halogen atom is bonded to sp^2 hybridised carbon atom of Benzene ring.



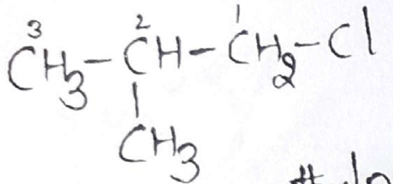
I. Haloalkanes R—X

Nomenclature :-

CH_3-Cl
Chloromethane
(Methyl chloride)

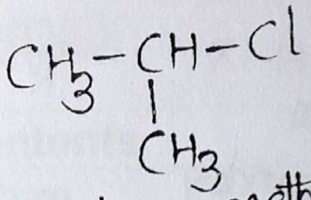
CH_3CH_2-Cl
Chloroethane
(Ethyl chloride)

$CH_3CH_2CH_2-Br$
1- Bromopropane
(n-propyl bromide)



$$\overset{3}{C}H_3-\overset{2}{C}H(CH_3)-\overset{1}{C}H_2-Cl$$

1-chloro-2-methylpropane
(Isobutyl chloride)



$$CH_3-CH(CH_3)-Cl$$

1-chloro-1-methylethane
(Isopropyl chloride)

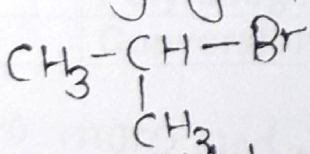
$CH_2=CH-Cl$
Chloroethene
(vinyl chloride)

Competition Boasters

(i) n- :- The prefix n- is used for alkyl groups having continous cha of carbon atoms with no branching.

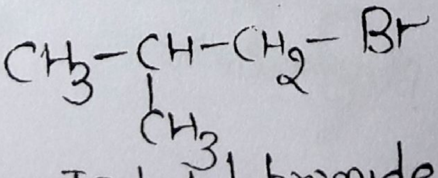
$CH_3CH_2CH_2CH_2-Cl$
n-Butylchloride

(ii) Iso :- The prefix Iso is used for alkyl groups which contains one methyl group on second or second last carbon.



$$CH_3-CH(CH_3)-Br$$

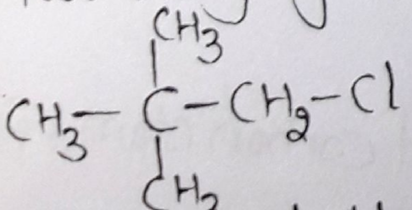
Isopropyl bromide



$$CH_3-CH(CH_3)-CH_2-Br$$

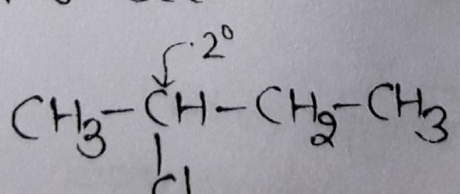
Isobutyl bromide

(iii) neo- :- The prefix neo is used for alkyl groups which Contai two methyl groups on second or second last carbon.



$$CH_3-C(CH_3)_2-CH_2-Cl$$

Neopentyl chloride

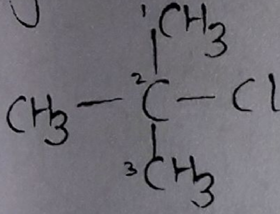


$$CH_3-\overset{2^\circ}{C}H(Cl)-CH_2-CH_3$$

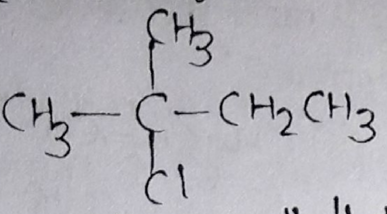
Sec- Butyl chloride

(iv) sec :- The prefix sec- is used for alkyl group in which halogen atom, functional group is attached to 2° Carbon atom

(v) **tert** :- The prefix tert- is used when halogen atom, functional group is bonded to 3° carbon atom.



2-chloro-2-methylpropane
(tert-butyl chloride)



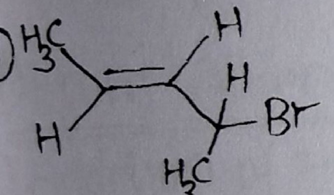
2-chloro-2-methylbutane
(tert-pentyl chloride)

- prefix Iso, Neo, Cyclo are used without hyphen while n-, sec-, tert- are used with hyphen.

problem

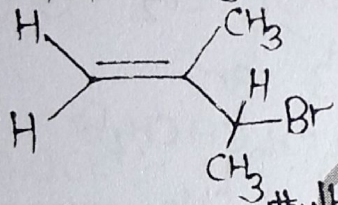
write IUPAC Names of following Compounds-

(i)



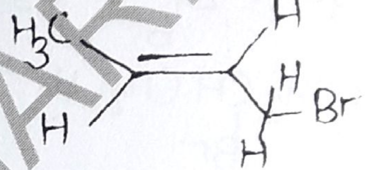
4-Bromopent-2-ene

(ii)



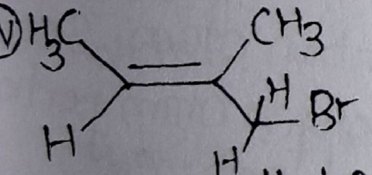
3-Bromo-2-methylbut-1-ene

(iii)



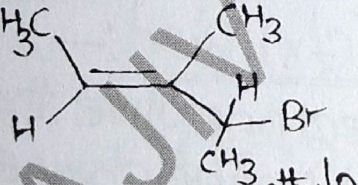
1-Bromobut-2-ene

(iv)



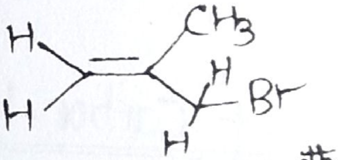
1-Bromo-2-methylbut-2-ene

(v)



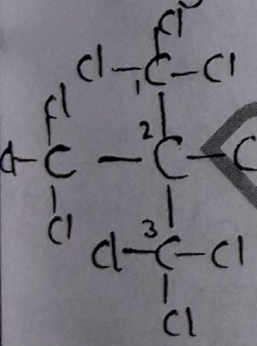
4-Bromo-3-methylpent-2-ene

(vi)



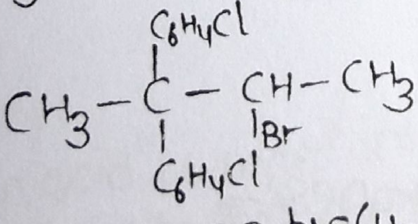
3-Bromo-2-methylpropene

(vii) $(CCl_3)_3CCl$



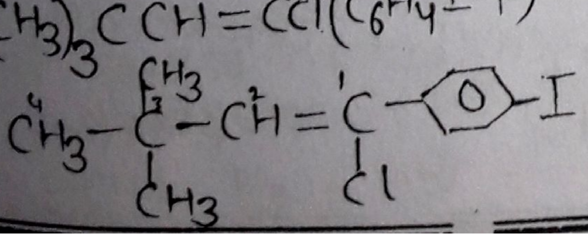
2-(trichloromethyl)-1,1,1,2,3,3,3-heptachloropropane

(viii) $CH_3C(p\text{-}ClC_6H_4)_2CH(Br)CH_3$



2-Bromo-3,3-bis(4-chlorophenyl)butane

(ix) $(CH_3)_3CCH=CCl(C_6H_4I\text{-}p)$



1-Chloro-1-(4-Iodophenyl)-3,3-dimethylbut-1-ene

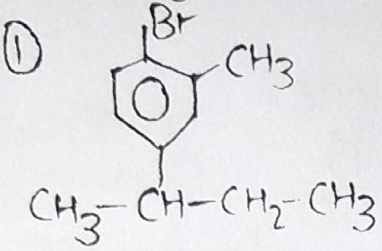
Problem

Write structures of given Compounds-

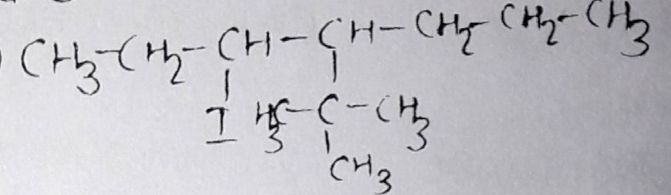
(i) 1-Bromo-4-sec-butyl-2-methylbenzene (iii) 1-chloro-4-ethylcyclohexan

(ii) 4-tert-Butyl-3-Iodoheptone

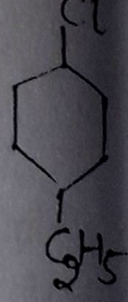
Soln:- (i)



(ii)


$CH_3-CH_2-\underset{I}{CH}-\underset{H_3C-\underset{CH_3}{C}-CH_3}{CH}-CH_2-CH_2-CH_3$

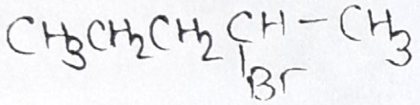
(iii)

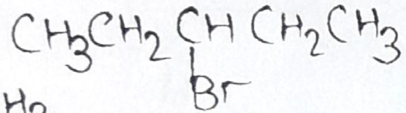


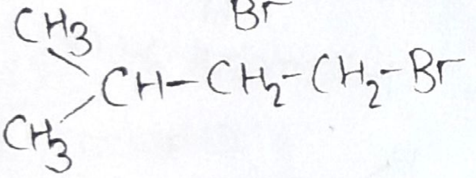
Problem

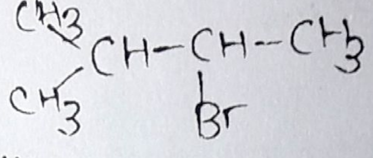
Draw all structural isomers of formula $C_5H_{11}Br$.

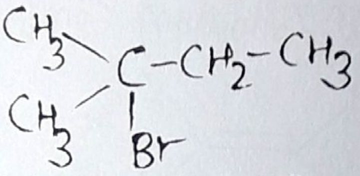
Soln:- $CH_3CH_2CH_2CH_2CH_2-Br$

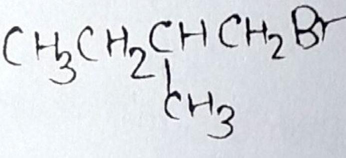

$CH_3CH_2CH_2\underset{Br}{CH}-CH_3$

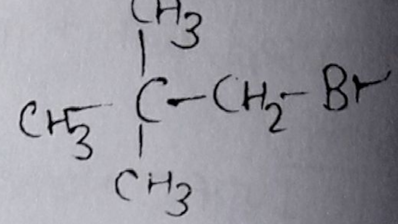

$CH_3CH_2\underset{Br}{CH}CH_2CH_3$





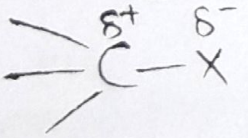



$CH_3CH_2\underset{CH_3}{CH}CH_2Br$



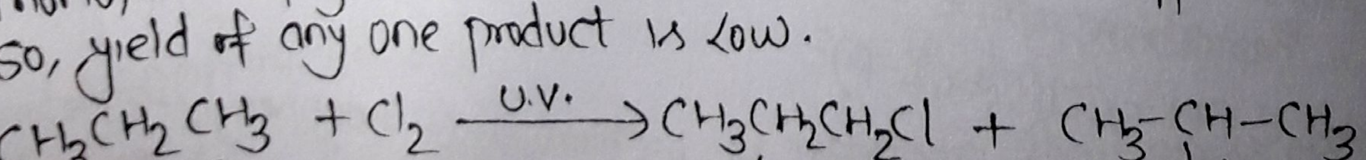
Nature of Carbon-halogen (C-X) Bond:-

Halogen atom is more electronegative than carbon atom, so carbon atom bears partial positive charge & halogen atom partial negative charge. So, C-X bond is polar in nature.



preparation of Haloalkanes:-

① From Alkanes:- These can be prepared by free radical chlorination or bromination of alkanes. But, this method produces mixture of mono, di or poly substituted haloalkanes which are difficult to separate so, yield of any one product is low.


$$\underset{\text{propane}}{CH_3CH_2CH_3} + Cl_2 \xrightarrow{U.V.} \underset{(45\%)}{CH_3CH_2CH_2Cl} + \underset{(55\%)}{CH_3-\underset{Cl}{CH}-CH_3}$$

$$CH_4 \xrightarrow[-HCl]{h\nu, Cl_2} CH_3-Cl \xrightarrow[-HCl]{h\nu, Cl_2} CH_2Cl_2 \xrightarrow[-HCl]{Cl_2, h\nu} CHCl_3 \xrightarrow[-HCl]{Cl_2, h\nu} CCl_4$$

Methane Chloromethane Dichloromethane Trichloromethane (Chloroform) Tetrachloromethane

- Fluorination of alkane is highly exothermic & violent rxn. Further, it produces poly substituted compounds so should not be used in Laboratory.
- Iodination is reversible rxn, so it occurs in presence of oxidising agents like HIO_3 (Iodic acid), Nitric acid.

$$CH_4 + I_2 \xrightarrow{HIO_3} CH_3I + HI$$

$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

- Reactivity of Hydrogen atoms in free radical halogenation -
  3° hydrogen > 2° hydrogen > 1° hydrogen

② From Alkenes:-

① Addition of Halogen acid:-

$$>C=C< + HX \longrightarrow >\underset{H}{\underset{|}{C}}-\underset{X}{\underset{|}{C}}<$$

alkene

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

Symt. alkene

$$CH_3-CH=CH_2 + HCl \xrightarrow{Mark. Add^n} CH_3-\underset{Cl}{\underset{|}{CH}}-CH_3$$

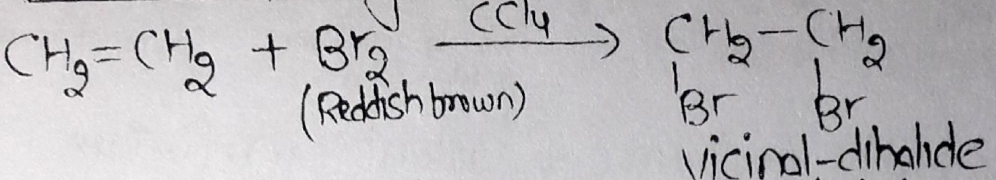
Alkene (unsymt)

Markonikov's Addition Rule!- when Halogen acid is added into unsymmetrical alkene, the negative (Halogen) part goes to that carbon of double bond which contain less no. of hydrogen atoms (more substituted carbon).

AntiMarkonikov's Addition Rule (peroxide effect) :- only for (HBr + peroxide)
when HBr is added into unsymmetrical alkene in presence of peroxide the Br⁻ goes to that carbon of double bond which contain greater no. of hydrogen atoms (less substituted carbon).

$$CH_3-CH=CH_2 + HBr \xrightarrow{peroxide} CH_3-CH_2-CH_2Br$$

(ii) Addition of Halogen:-



$$CH_2=CH_2 + \underset{(Reddish\ brown)}{Br_2} \xrightarrow{CCl_4} \underset{Br}{CH_2}-\underset{Br}{CH_2}$$

Vicinal-dihalide

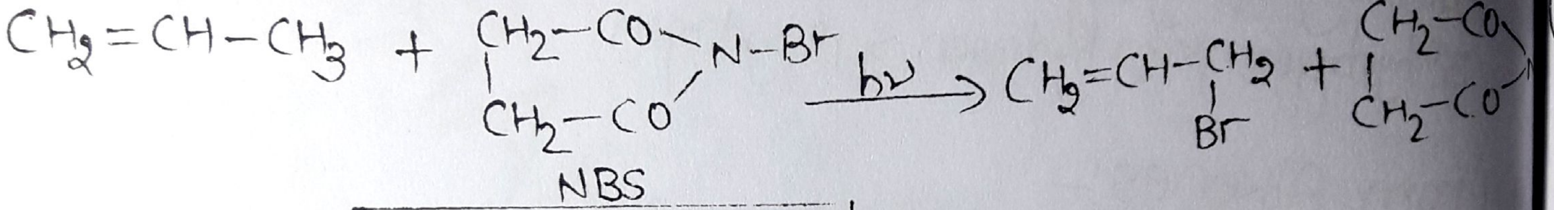
when Br_2 is added into alkene reddish brown Colour of Bromine is discharged, this is used as test for unsaturation

(iii) Allylic Halogenation:- High Temp', peroxides or sunlight (U.V.)

$$CH_2=CH-CH_3 + Cl_2/Br_2 \xrightarrow{773K} CH_2=CH-CH_2Cl + HCl$$

$$CH_2=CH-CH_3 + SO_2Cl_2 \xrightarrow{peroxide} CH_2=CH-CH_2Cl + SO_2 + HCl$$

Sulphuryl chloride



Competition Boosters

*1 Markonikov's Addition rxn occurs by electrophilic addition Mechanis

*2 Antimarkonikov's rxn occurs by free radical addition mechanis

*3 HF & HCl do not produce free radicals due to strong bond. HI produce free radicals Ḣ & İ but it changes to I_2 immediately so Antimarkonik Addition occurs only in HBr.

(3) From Alcohols:-

(i) Rxn with Halogen acids:-

$$\underset{alcohol}{R-OH} + HX \xrightarrow{Anhyd\ ZnCl_2} R-X + H_2O$$

e.g. $CH_3CH_2-OH + HCl \xrightarrow{Anhyd\ ZnCl_2} CH_3CH_2-Cl + H_2O$ (Groove's Rxn)

➔ The rxn of 1° & 2° alcohols require presence of anhyd. $ZnCl_2$ which helps in cleavage of C-O bond. But 3° alcohols are very reactive they reacts with conc. HCl even in absence of Anhyd. $ZnCl_2$.

(ii) Rxn with thionyl chloride:-

$$R-OH + \underset{Thionyl\ chloride}{SOCl_2} \xrightarrow{pyridine} \underset{Haloalkane}{R-Cl} + SO_2\uparrow + HCl\uparrow$$ (Darzen metho

e.g. $CH_3CH_2-OH + SOCl_2 \xrightarrow{pyridine} CH_3CH_2-Cl + SO_2\uparrow + HCl\uparrow$

This method is preferred over other methods because side products are gases so product can be purified easily.

(iii) $R-OH + NaBr + H_2SO_4 \longrightarrow R-Br + NaHSO_4 + H_2O$

(iv) $R-OH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$

(v) $3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3$
$(X = Cl, Br)$

(vi) $R-OH + X_2 \xrightarrow{Red\ P} R-X$
$(X = Br, I)$

④ Hunsdiecker Reaction:– (Free radical mechanism)

$CH_3COOAg + Br_2 \xrightarrow{CCl_4} CH_3-Br + CO_2\uparrow + AgBr$
silver acetate

⑤ Halide exchange Reaction:–

(i) Finkelstein Rxn:–

$R-X + NaI \xrightarrow[Reflux]{Acetone} R-I + NaX$
$(X = Cl, Br)$

e.g. $CH_3CH_2-Br + NaI \xrightarrow[Reflux]{Acetone} CH_3CH_2-I + NaBr$

(ii) Swart Rxn:– (Hg_2F_2, AgF, CoF_3, SbF_3)

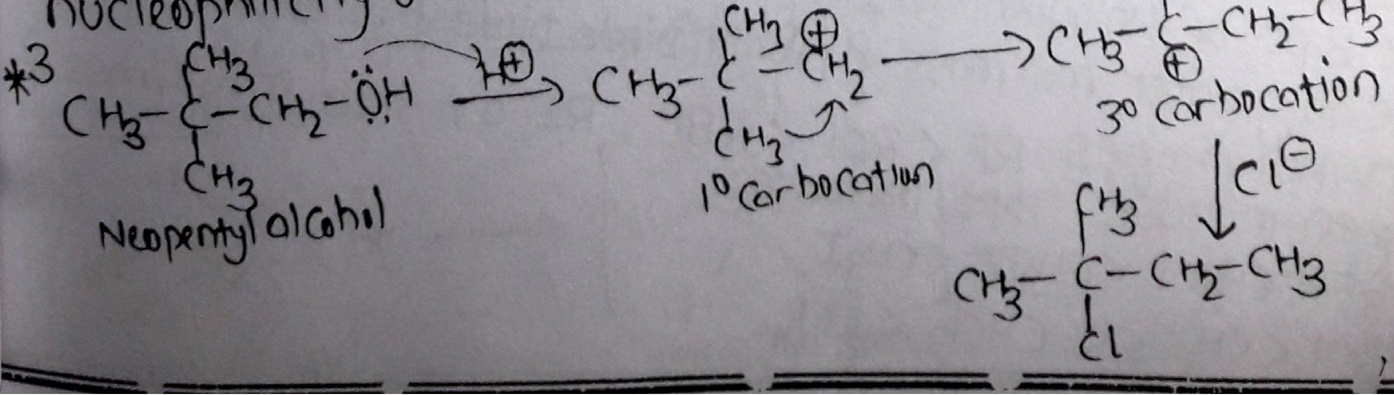
$2R-X + Hg_2F_2 \longrightarrow 2R-F + Hg_2X_2$
$(X = Cl, Br)$

Competition Boosters

*1 Reactivity of alcohols is $3° > 2° > 1°$ as stability of carbocations is $1° < 2° < 3°$.

*2 Reactivity of Halogen acids is $HCl < HBr < HI$, as nucleophilicity order = $Cl^- < Br^- < I^-$

*3



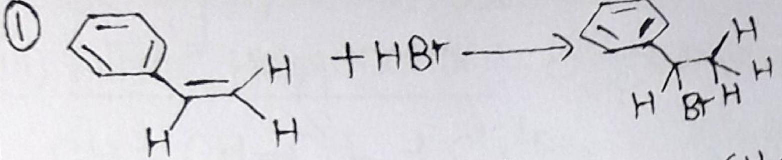
problem

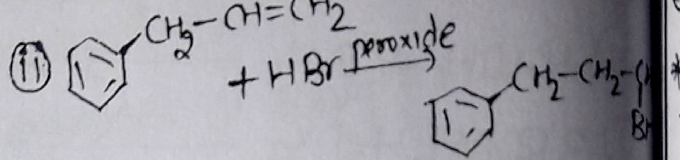
why sulphuric acid is not used during reaction of alcohols with KI?

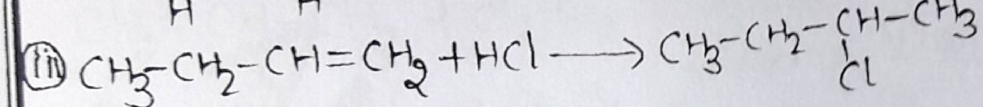
Soln:- Sulphuric acid is oxidising agent. It converts KI into I_2 So prevent rxn with alcohol. So, Non oxidising acid H_3PO_4 is used

problem

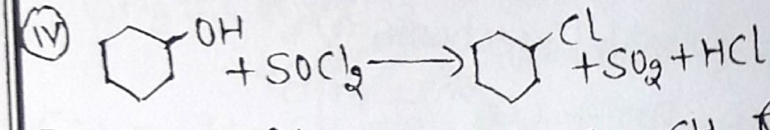
complete the rxns -

① 

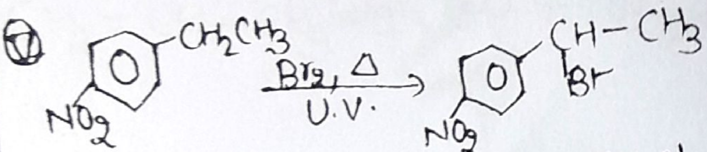
(ii) 

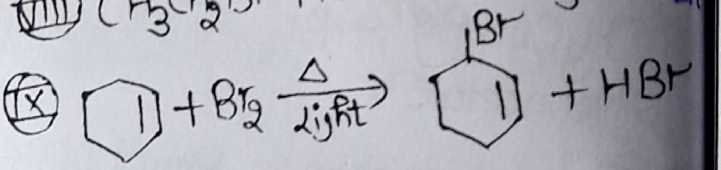
(iii) 

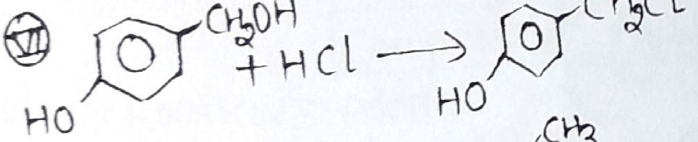
$CH_3-CH_2-CH=CH_2 + HCl \longrightarrow CH_3-CH_2-\underset{Cl}{CH}-CH_3$

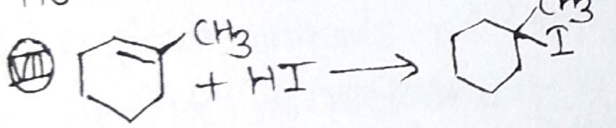
(iv) 

(viii) $CH_3CH_2Br + NaI \xrightarrow{\text{Dry acetone}} CH_3CH_2I + NaBr$

(v) 

(ix) 

(vi) 

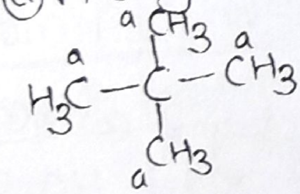
(vii) 

problem

write isomers of mol. formula C_5H_{12} which on chlorination produces -

ⓐ A single monochloride ⓑ Three isomeric monochlorides

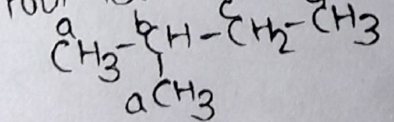
Soln:- ⓐ A single monochloride



ⓑ Three isomeric monochlorides

$\overset{a}{C}H_3-\overset{b}{C}H_2-\overset{c}{C}H_2-\overset{b}{C}H_2-\overset{a}{C}H_3$

ⓒ Four isomeric monochlorides -



$\overset{a}{C}H_3-\underset{{}^aCH_3}{\overset{b}{C}H}-\overset{c}{C}H_2-\overset{d}{C}H_3$

Physical properties :-

① Boiling point :-

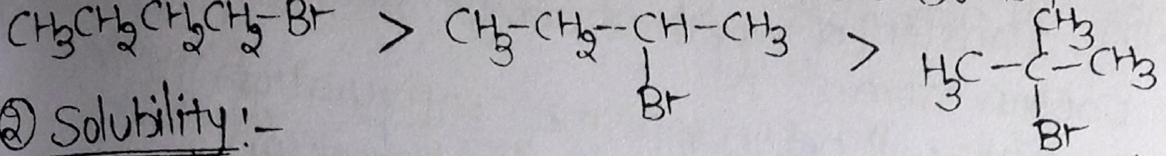
*¹ The B.pt. of Haloalkanes are greater than corresponding hydrocarbon due to greater mol. mass & polarity (Dipole-Dipole & vanderwaal's forces).

*² In Haloalkanes RF < RCl < RBr < RI as size & mol. mass of halogen increases B.pt increases.

e.g. $CH_3F < CH_3Cl < CH_3Br < CH_3I$

$CH_3Cl < CH_2Cl_2 < CHCl_3 < CCl_4$

*3 Among Isomeric haloalkanes, As branching increases surface area decreases so vanderwaal's forces decreases so B.pt. decreases.



$CH_3CH_2CH_2CH_2-Br > CH_3-CH_2-\underset{Br}{CH}-CH_3 > H_3C-\overset{CH_3}{\underset{Br}{C}}-CH_3$

② Solubility:-

*1 Haloalkanes are polar still very less soluble in water because the intermolecular forces between haloalkanes & water molecules are weaker than intermolecular forces between pure haloalkane molecules & between water molecules.

*2 Haloalkanes are more soluble in organic solvents as forces are of same strength as between pure solute & solvent molecules.

Problem.

Arrange in increasing order of B.pt -

① Bromomethane, Bromoform, chloromethane, Dibromomethane

⑪ 1-chloropropane, Isopropyl chloride, 1-chlorobutane

soln:- ① chloromethane < Bromomethane < Dibromomethane < Bromoform

⑪ Isopropyl chloride < 1-chloropropane < 1-chlorobutane

Chemical properties:-

① Nucleophilic Substitution Rxn:-

In this rxn, a nucleophile reacts with haloalkane & substitute it's halide ion. It occurs by two mechanisms-

ⓐ SN^2 (Nucleophilic substitution Bimolecular):-

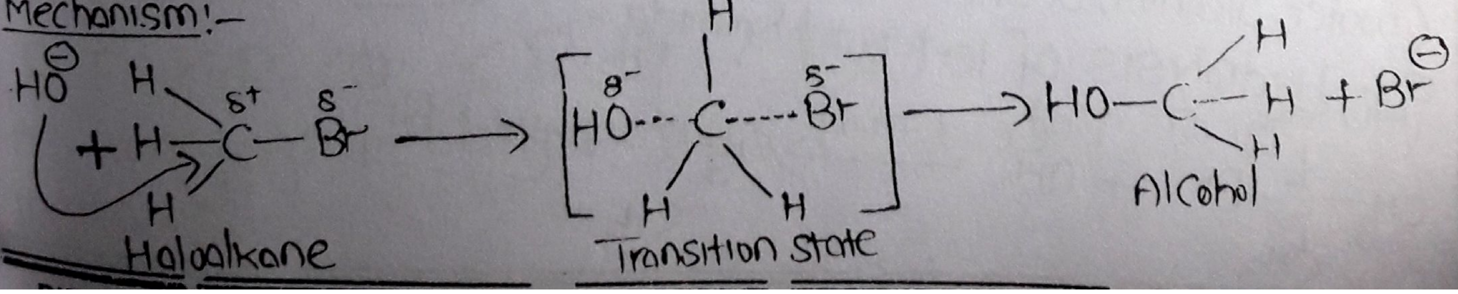
It is the nucleophilic substitution rxn in which rate depends upon Concent of both substrate & Nucleophile. occurs in polar aprotic solvents.

$$\text{Rate} \propto [\text{Substrate}][\text{Nucleophile}]$$

e.g. Hydrolysis of Bromoethane -

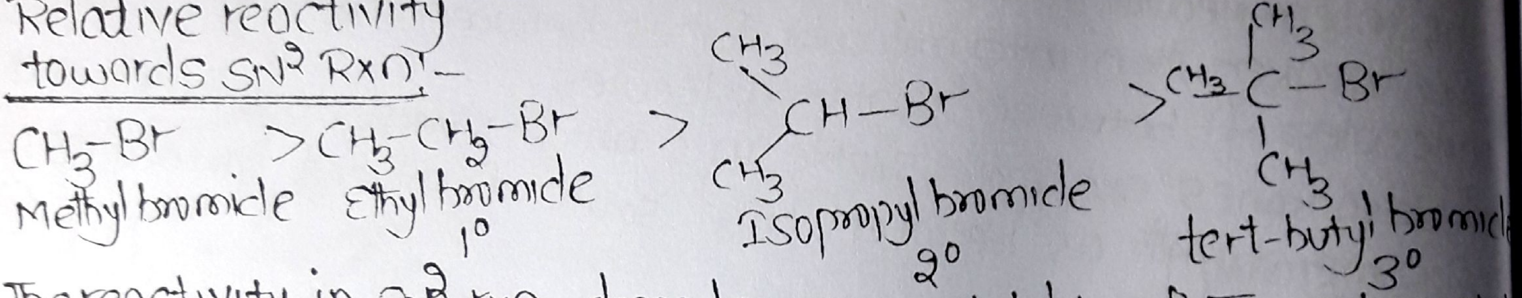
$$CH_3-Br + OH^{\ominus} \longrightarrow CH_3-OH + Br^{\ominus}$$

Mechanism:-



- This Rxn (reaction) is concerted one step rxn. The nucleophile attack from back side due to repulsion of $Br^{\ominus}$ group. A transition state will be produced. Now, transfer of Negative charge occurs from $OH^{\ominus}$ to $Br^{\ominus}$ via carbon atom.
- In this rxn, product will be in opposite configuration to the substrate. This is walden or umbrella inversion.

Relative reactivity towards SN^2 Rxn:-



$CH_3-Br > CH_3-CH_2-Br > (CH_3)_2CH-Br > (CH_3)_3C-Br$

Methyl bromide, Ethyl bromide 1°, Isopropyl bromide 2°, tert-butyl bromide 3°

The reactivity in SN^2 rxn depends upon stability of Transition state. Greater the stability of transition state greater will be the reactivity of haloalkane producing it. on moving from methyl halide to 3° alkyl halides stability of transition state decreases due to increase of steric hinderance, so their reactivity in SN^2 decrease.

$R-F < R-Cl < R-Br < R-I$

As, leaving group ability increases from F^- to I^- so, reactivity also increases.

Leaving GP. ability $= F^- < Cl^- < Br^- < I^-$

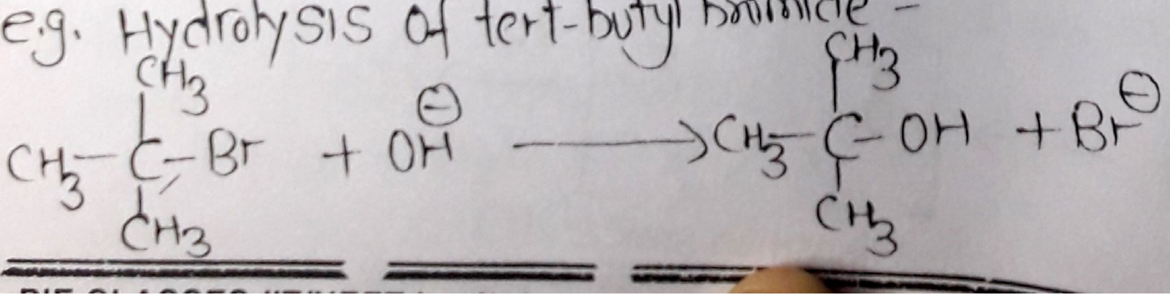
ⓑ SN' (Nucleophilic substitution unimolecular):-

It is the nucleophilic substitution rxn in which rate depends upon concentration of substrate only.

$$Rate \propto [Substrate]$$

These rxns generally occurs in presence of polar protic solvents (water, alcohols, acetic acid).

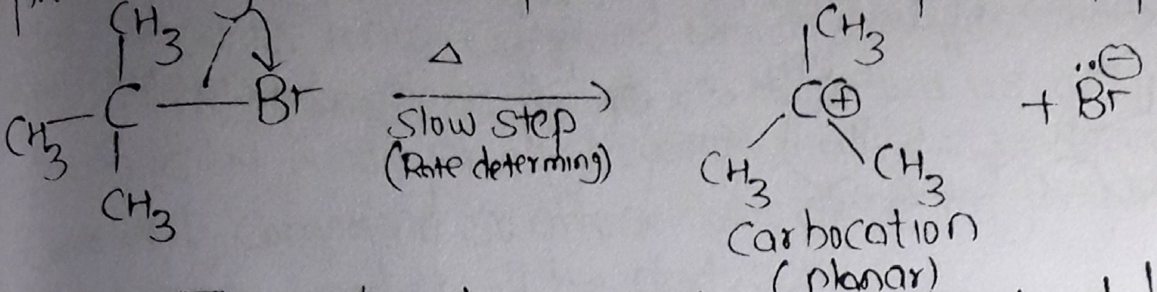
e.g. Hydrolysis of tert-butyl bromide -



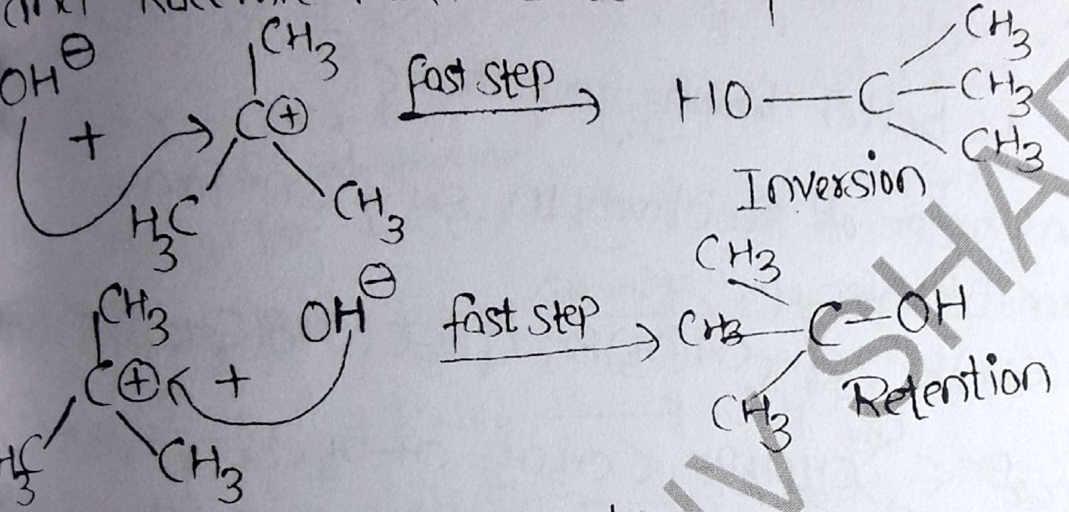
$$(CH_3)_3C-Br + OH^{\ominus} \longrightarrow (CH_3)_3C-OH + Br^{\ominus}$$

Mechanism:-

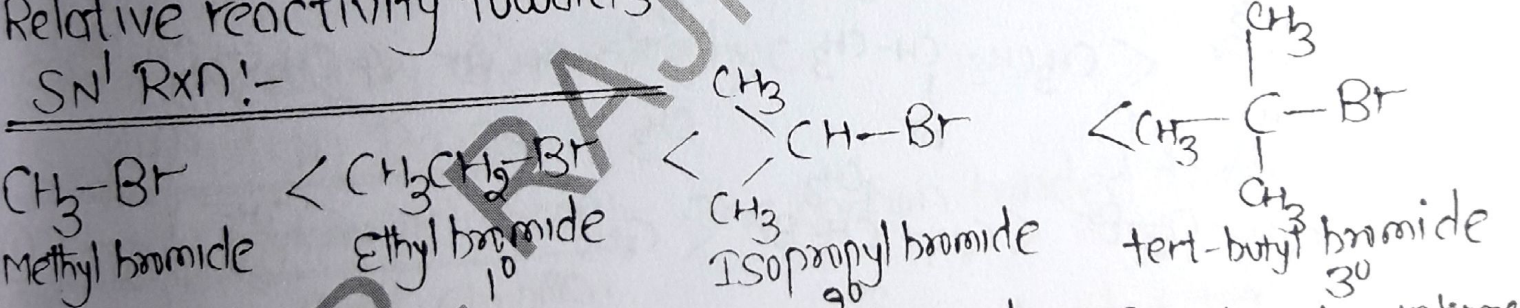
Step1:- In first step, breaking of C-X bond occurs. The energy is provided by solvation of halide ion with proton of protic solvents.



Step2:- The carbocation is planar, so nucleophile can attack both from front & back side. So both Retention & inversion occurs and Racemic mixture will be produced.



Relative reactivity towards SN¹ Rxn:-

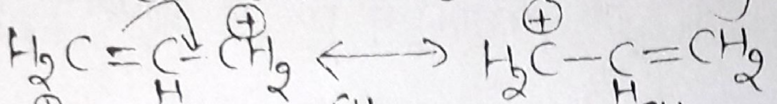


In SN¹ rxn, reactivity depends upon stability of carbocation intermediate. Greater the stability of carbocation, greater will be the reactivity of Haloalkane producing it. on moving from methyl halide to 3° alkyl halide, stability of carbocation increases so, their reactivity increases. stability:- 1° carbocation < 2° carbocation < 3° carbocation

R-F < R-Cl < R-Br < R-I

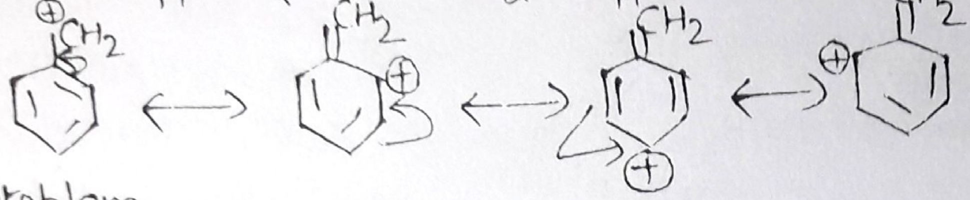
AS, leaving group ability increases from F^- to I^- so reactivity increases.

* Allyl halide & Benzyl halides have high reactivity in SN¹ Rxn as their carbocation is stabilized by Resonance.



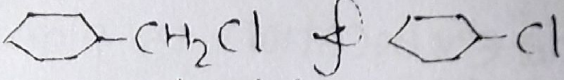
$H_2C=\underset{H}{C}-\overset{\oplus}{C}H_2 \longleftrightarrow H_2\overset{\oplus}{C}-\underset{H}{C}=CH_2$

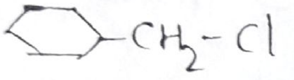
Allyl carbocation



Benzyl carbocation.

Problem

which undergo SN^2 rxn faster – ① 

Soln!-  because it is 1° alkyl halide.

(ii) 

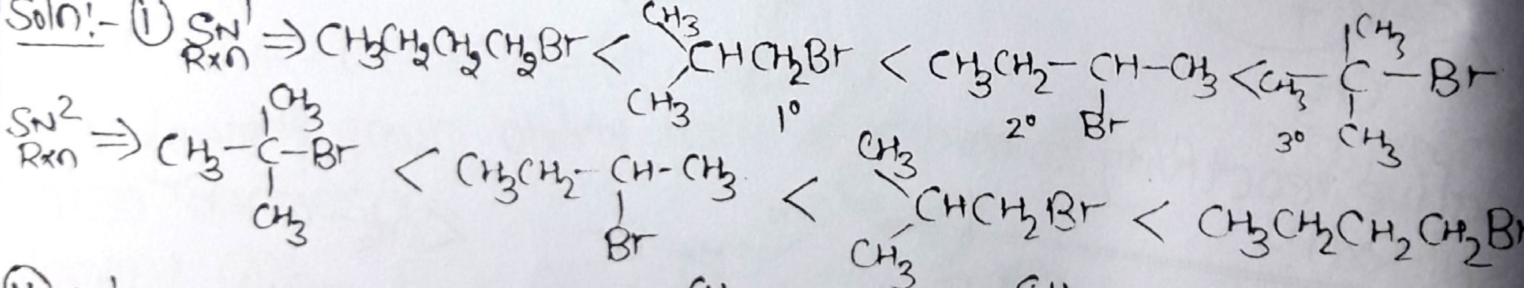
Soln!-  as I^- is better leaving group than $Cl^\ominus$.

Problem

Arrange in Increasing order of Reactivity in SN^1 & SN^2 Rxn –

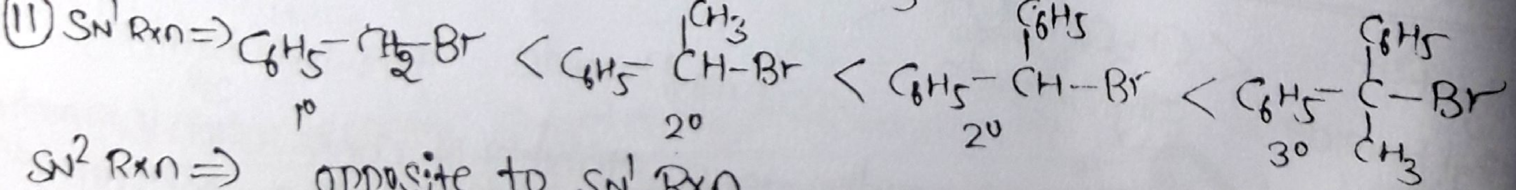
① Four Isomeric bromobutanes

(ii) $C_6H_5CH_2Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$, $C_6H_5C(CH_3)(C_6H_5)Br$

Soln!- ① 

SN^1 Rxn $\Rightarrow CH_3CH_2CH_2CH_2Br < \underset{1^\circ}{(CH_3)_2CHCH_2Br} < \underset{2^\circ}{CH_3CH_2-\underset{Br}{CH}-CH_3} < \underset{3^\circ}{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br}$

SN^2 Rxn $\Rightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br < CH_3CH_2-\underset{Br}{CH}-CH_3 < (CH_3)_2CHCH_2Br < CH_3CH_2CH_2CH_2Br$

(ii) 

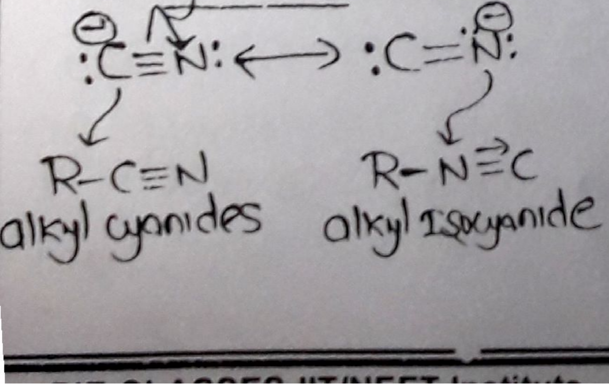
SN^1 Rxn $\Rightarrow \underset{1^\circ}{C_6H_5-CH_2-Br} < \underset{2^\circ}{C_6H_5-\overset{CH_3}{CH}-Br} < \underset{2^\circ}{C_6H_5-\overset{C_6H_5}{CH}-Br} < \underset{3^\circ}{C_6H_5-\overset{C_6H_5}{\underset{CH_3}{C}}-Br}$

SN^2 Rxn $\Rightarrow$ opposite to SN^1 Rxn

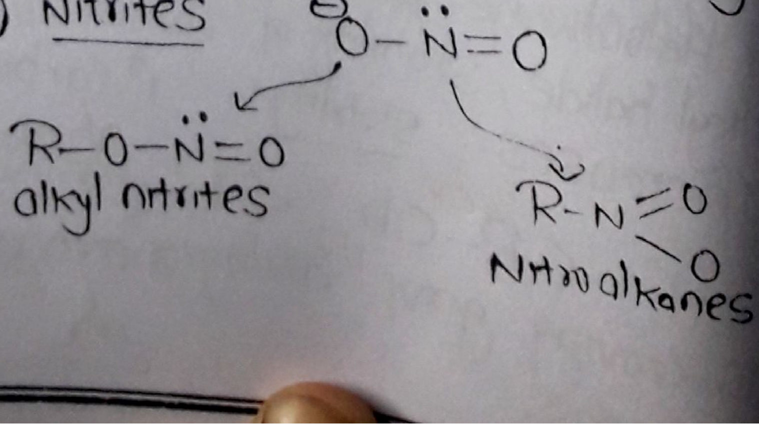
Ambidentate (Ambident) Nucleophile!-

These are the nucleophiles which have two nucleophilic sites e.g.

e.g. ① cyanides



(ii) Nitrites



problem

Haloalkanes reacts with KCN to form alkyl cyanides while with AgCN form Isocyanides. Explain.

soln!- KCN is ionic compound which provides $CN^\ominus$ ion in solution. The attack take place through carbon atom as C-C bond is more stable than C-N bond. So alkyl cyanide will be produced. But AgCN is covalent compound so attack take place through Nitrogen atom so alkyl Isocyanide will be produced.

Examples of Nucleophilic substitution rxns!-

(i) $CH_3CH_2-Br + \overset{aq.}{KOH} \longrightarrow CH_3CH_2-OH + KBr$

(ii) $\underset{}{R-X} + \underset{\text{Sod. alkoxide}}{Na-O-R'} \longrightarrow R-O-R' + NaX$ (williamson's synthesis)

(iii) $CH_3CH_2-Br + KCN \longrightarrow CH_3CH_2-CN + KBr$

(iv) $CH_3CH_2-Br + AgCN \xrightarrow{C_2H_5OH/H_2O} CH_3CH_2-N \overset{\rightarrow}{=} C + AgBr$

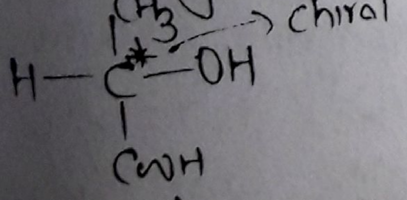
(v) $CH_3CH_2-Br + KNO_2 \longrightarrow CH_3CH_2-O-N=O + KBr$

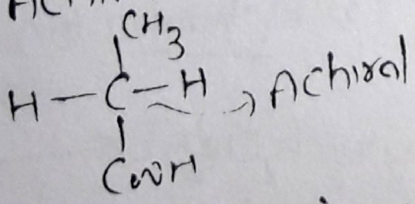
(vi) $CH_3CH_2-Br + AgNO_2 \longrightarrow CH_3CH_2-N\genfrac{}{}{0pt}{}{=O}{\to O} + AgBr$

Stereochemistry of Nucleophilic Substitution Rxns!-

(i) Chiral (Asymmetric) Carbon!- The carbon bonded to four different groups is chiral carbon.

(ii) Achiral (symmetric) Carbon!- The carbon bonded to two or more identical groups is Achiral carbon.


$H-\overset{CH_3}{\underset{COOH}{C^*}}-OH$


$H-\overset{CH_3}{\underset{COOH}{C}}-H$

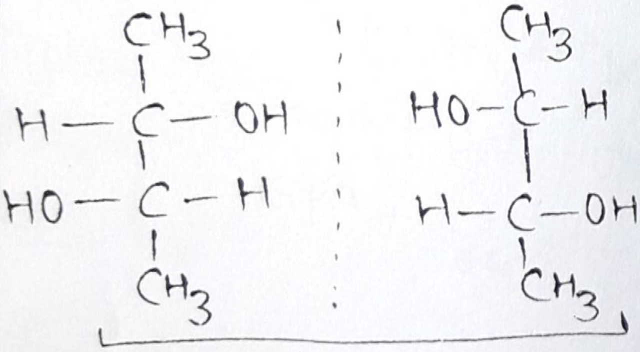
(iii) Inversion!- It is the process in which configuration of molecule changes from dextro to laevo or from laevo to dextro. e.g. SN^2

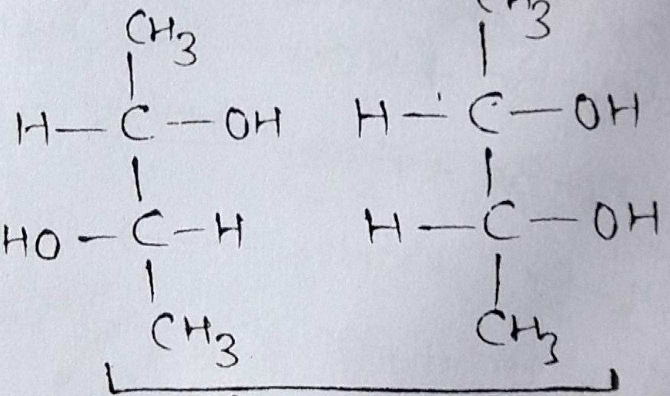
(iv) Retention!- It is the process in which configuration of moles does not changes.

(V) Racemic mixture. (Racemisation) : It is the mixture which contain equimolar Concn constant of both dextro & laevo isomers. (50% dextro + 50% laevo). The process of formation of Racemic mixture is Racemisation. This mixture is optically inactive. e.g. (±) Lactic acid (Racemic modification)

(VI) Enantiomers :- These are the optical isomers which are non-superimposable mirror image of each other. These have identical physical properties (except behaviour towards light), identical chemical properties but different biological properties.

(VII) Diasteriomers :- These are the optical isomers which have same mol. formula but are not mirror image of each other. These have same chemical properties but different physical properties, so can be easily separated from mixture.

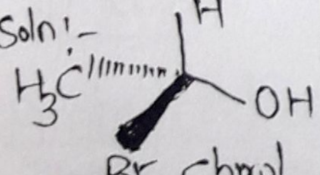

Enantiomers

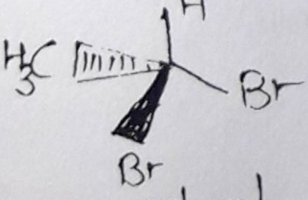

Diastereomers

* Chirality (Asymmetry) is responsible for optical activity.

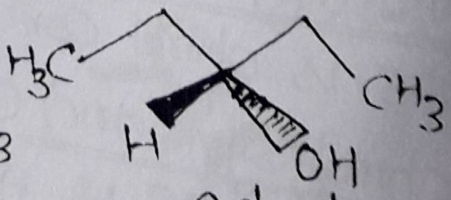
Problem
Identify chiral & achiral molecules -

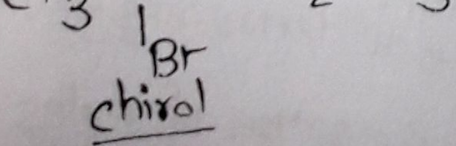
Soln :-


Chiral


Achiral


Chiral


Achiral


$CH_3-\underset{\underset{Br}{|}}{CH}-CH_2-CH_3$
chiral

$CH_3CH_2CH_2CH_2-Br$
Achiral

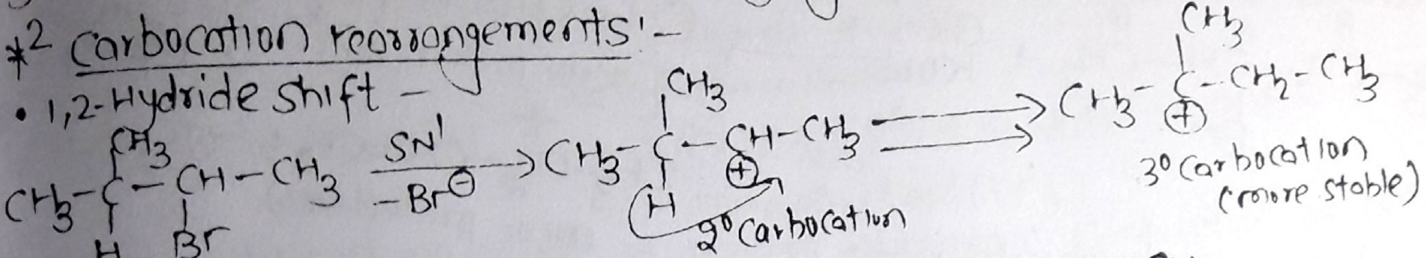
* Separation of dextro & laevo isomers from Racemic mixture is Racemic Resolution.

Competition Boosters

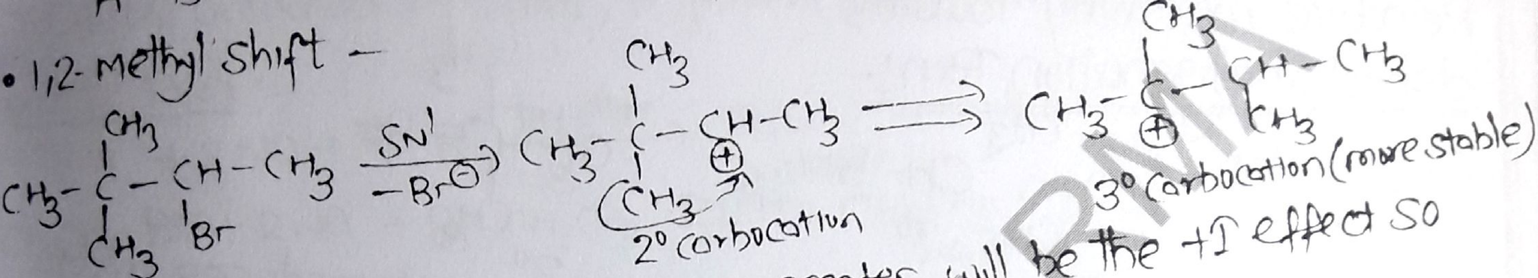
*1 Neopentyl chloride (1°) reacts slowly than Isopropyl chloride (2°) in S_N2 rxn as extremly bulky group attached to electrophilic carbon which has more steric hinderance than two small alkyl groups

*2 Carbocation rearrangements:–

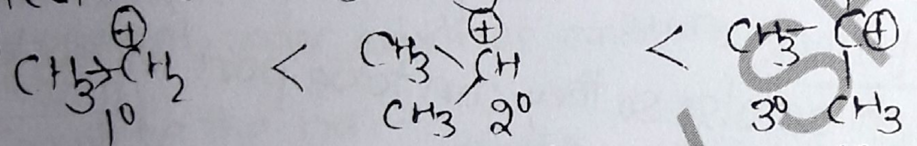
• 1,2-Hydride shift –



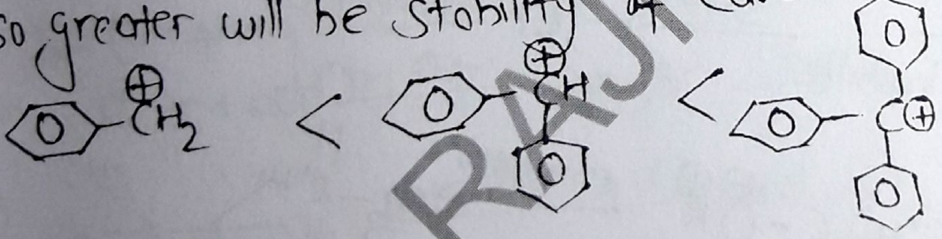
• 1,2-methyl shift –



*3 Greater the no of alkyl groups greater will be the +I effect so greater will be stability of carbocations –



*4 Greater the no. of phenyl groups greater will be the resonance effect so greater will be stability of carbocation –

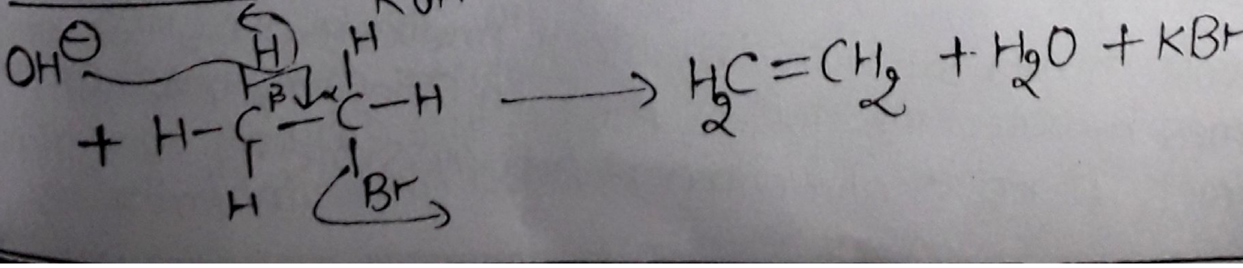


Elimination Rxn (Dehydrohalogenation Rxn):–

when alcoholic KOH is added into haloalkane formation of alkene occurs due to elimination of one hydrogen atom & one halogen atom. (β-elimination).

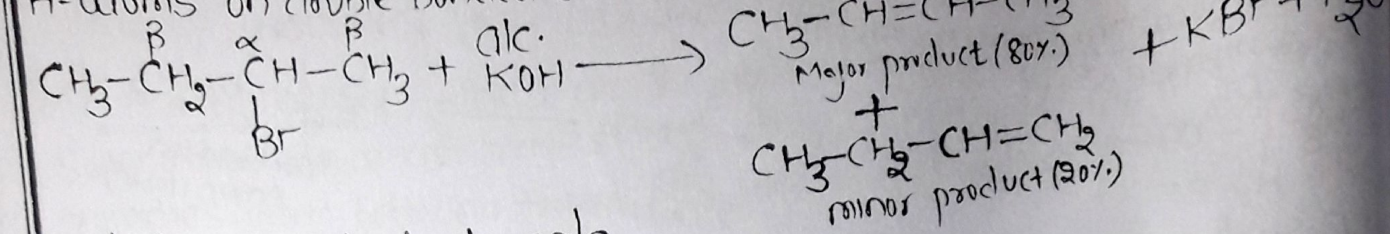
$$CH_3CH_2-Br + \underset{KOH}{alc.} \longrightarrow CH_2=CH_2 + H_2O + KBr$$

Mechanism:– $\underset{KOH}{alc.} \longrightarrow K^\oplus + OH^\ominus$



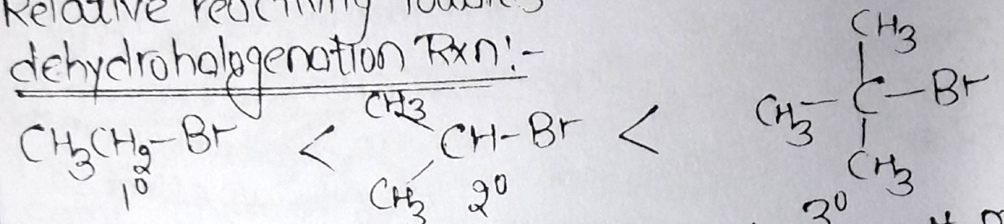
Saytzeff Rule:- (zaitsev)

when dehydrohalogenation rxn occurs in unsymmetrical haloalkanes, the more substituted product will be major product (containing less no. of H-atoms on double bonded carbon atoms).



$$CH_3-\overset{\beta}{C}H_2-\underset{Br}{\overset{\alpha}{C}H}-\overset{\beta}{C}H_3 + \overset{alc.}{KOH} \longrightarrow \underset{\text{Major product (80\%)}}{CH_3-CH=CH-CH_3} + KBr + H_2O$$
$$+ \underset{\text{minor product (20\%)}}{CH_3-CH_2-CH=CH_2}$$

Relative reactivity towards dehydrohalogenation Rxn:-

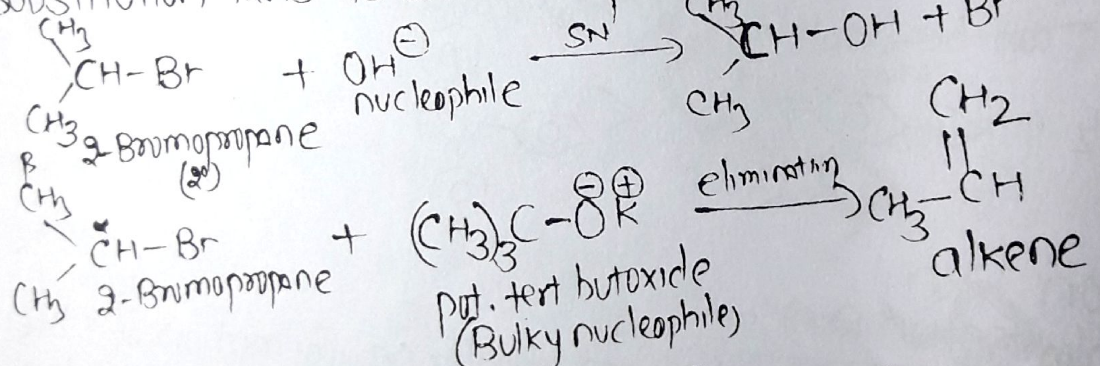


$$\underset{1^0}{CH_3CH_2-Br} < \underset{2^0}{(CH_3)_2CH-Br} < \underset{3^0}{(CH_3)_3C-Br}$$

3° alkyl halide will be most reactive because it produces most substituted product.

Elimination v/s Substitution:-

Most bases are nucleophiles also so they can take part in nucleophilic substitution rxns as well as elimination.



$$\underset{\text{2-Bromopropane }(2^0)}{(CH_3)_2CH-Br} + \underset{\text{nucleophile}}{OH^\ominus} \xrightarrow{SN^1} (CH_3)_2CH-OH + Br^\ominus$$

$$\underset{\text{2-Bromopropane}}{\overset{\beta}{C}H_3\overset{\alpha}{C}H(CH_3)-Br} + \underset{\text{(Bulky nucleophile)}}{\underset{\text{pot. tert butoxide}}{(CH_3)_3C-\overset{\ominus}{O}\overset{\oplus}{K}}} \xrightarrow{\text{elimination}} \underset{\text{alkene}}{CH_3-CH=CH_2}$$

*1 Elimination rxn require higher temp. than SN Rxns as greater no. of bonds are broken so greater activation energy is required.

*2 Elimination occurs when alkyl halide is Tertiary [or] → Sometimes SN^1
alkyl halide is secondary & nucleophile is bulky
alkyl halide is secondary & nucleophile is St. Base (Sod. alkoxide)

*3 Aqueous KOH causes SN Rxns because it produces $OH^\ominus$ ions which becomes hydrated in aqueous medium. These hydrated $OH^\ominus$ ion can not abstract H^+ ion so elimination is not possible.

③ Rxn with Metals:–

$CH_3CH_2-Br + Mg \longrightarrow CH_3CH_2-Mg-Br$
Ethyl magnesium bromide
(Grignard Reagent)

$CH_3CH_2-Br + 2Li \longrightarrow CH_3CH_2-Li + LiBr$
ethyl Lithium Complex

$4CH_3CH_2-Br + 4Na/Pb \longrightarrow (CH_3CH_2)_4Pb + 4NaBr + 3Pb$
Tetraethyl Lead (TEL)

T.E.L is antiknocking agent, it prevent automatic Combustion of petrol.

Wurtz Rxn:–

$R-X + 2Na + X-R \xrightarrow{\text{Dry ether}} R-R + 2NaX$
alkane

$CH_3CH_2-Br + 2Na + Br-CH_2CH_3 \xrightarrow{\text{Dry ether}} CH_3CH_2-CH_2CH_3 + 2NaBr$
Butane

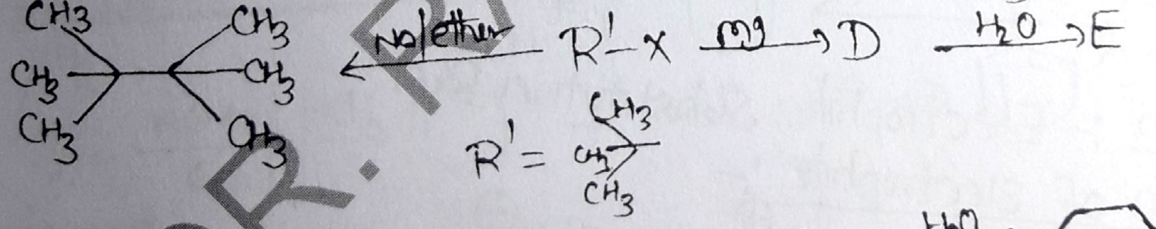
imp
* Grignard Reagent should be avoided from moisture as it reacts with water $R-MgX + H_2O \longrightarrow R-H + Mg\langle^{X}_{OH}$
alkane
So, prepared under anhydrous condition.

Problem
Complete the rxn –

① $n-BuBr + KCN \xrightarrow{EtOH, H_2O} CH_3CH_2CH_2CH_2-CN + KBr$

(II) $R-Br + Mg \xrightarrow{\text{Dry ether}} C \xrightarrow{D_2O} CH_3-\underset{D}{CH}-CH_3$

Soln:– $R-Br + Mg \xrightarrow{\text{Dry ether}} RMgBr \xrightarrow{D_2O} CH_3-\underset{D}{CH}-CH_3$

(III)


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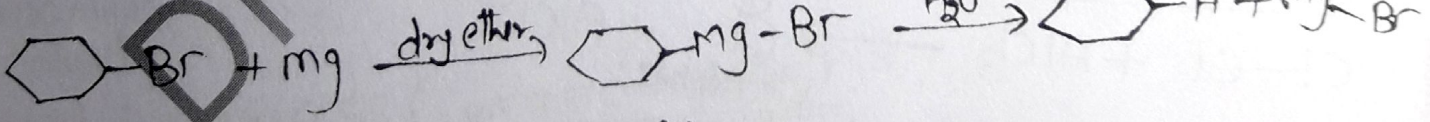

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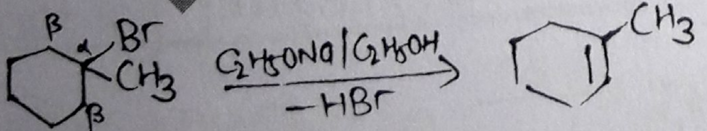

Problem
$\text{Alcohols} \xleftarrow{\text{Aq. KOH}} \text{Alkyl halide} \xrightarrow{\text{Alc. KOH}} \text{Alkene}$

Soln:– ✓Aq. KOH produces OH⁻ which acts as strong nucleophile because it becomes hydrated which decreases it basic character So, SN Rxn occurs.

✓Alc. KOH produces OH⁻ which becomes more basic as it is not hydrated So Elimination rxn occurs.