

SBG STUDY

HALOALKANES AND HALOARENES

Haloalkanes

The halogen derivatives of alkanes are called haloalkanes.

Example:- CH_3Cl , CH_3Br , $\text{C}_2\text{H}_5\text{Cl}$ etc.

Common name of haloalkane is 'Alkyl halide'

Example:- Methyl Chloride (CH_3Cl)

Ethyl Chloride ($\text{C}_2\text{H}_5\text{Cl}$)

Mono-halogen Derivatives

These are also called alkyl halides. Their general formula is R-X where R is any alkyl halide group and X is any halogen atom, i.e. F, Cl, Br or I.

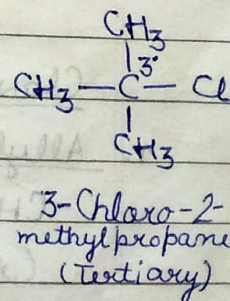
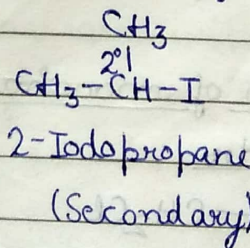
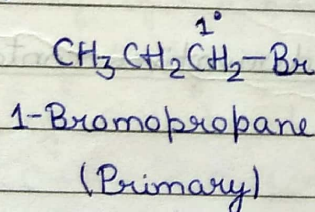
Example:- CH_3Cl (Methyl Chloride)

$\text{C}_2\text{H}_5\text{Br}$ (Ethyl Bromide)

Classification of alkyl halides

Alkyl halides are classified as primary (1°), secondary (2°) and tertiary (3°) according as the halogen atom is attached to primary, secondary, and tertiary carbon atom.

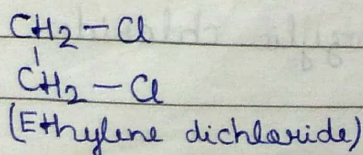
Example \Rightarrow



Dihalogen Derivatives

Example \Rightarrow CH_2Cl_2
(Methylene chloride)

$\text{CH}_2\text{-CH}_2\text{-Cl}_2$
(Ethylene dichloride)



(i) Geminal Dihalides or Alkylidene Dihalides

If two halogen atoms are attached to same carbon atoms are called geminal dihalides.

Example:- CH_3CHBr_2

(1,1-Dibromoethane)

(ii) Vicinal Dihalides or Alkylene Dihalides

If two halogen atoms are attached to two adjacent carbon atoms are called vicinal dihalides.

Example:- CH_2-Cl

CH_2-Cl

(1,2-Dichloroethane)

(iii) Tri halogen Derivatives

Example $\Rightarrow \text{CHCl}_3$

(Chloroform)

CHBr_3

(Bromoform)

CHI_3

(Iodoform)

Perhaloderivatives

Fully halogenated compounds are called perhaloderivatives.

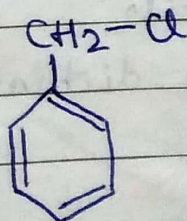
Example \Rightarrow Perchloromethane (CCl_4)

Per fluoro benzene (C_6F_6).

Classification of monohalogen derivatives containing Csp^3-X bond1. Allylic halides

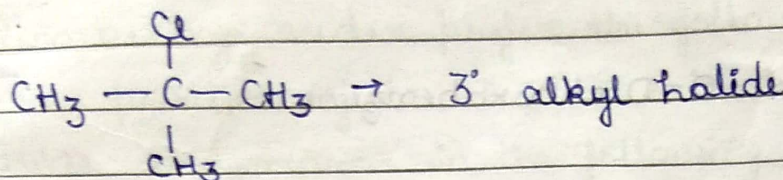
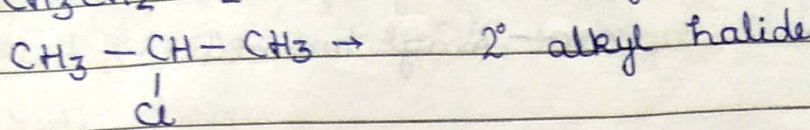
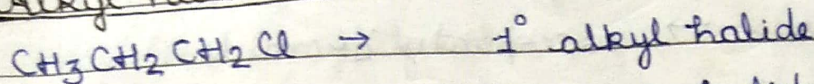
$\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}$

(Allyl chloride)

2. Benzylic halides

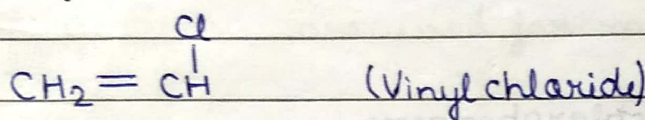
Benzylic chloride

3. Alkyl halides (R-X)

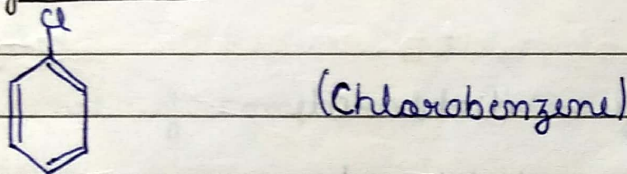


Classification of monohalogen derivative containing $\text{C}_{sp^2}\text{-X}$ bond

1. Vinyl halides



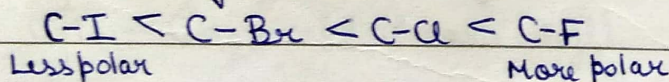
2. Aryl halides



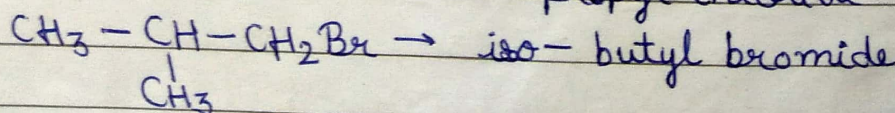
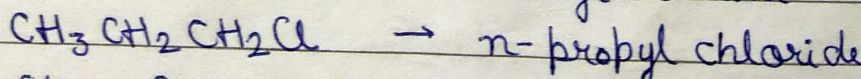
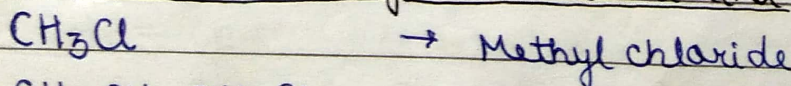
* Nature of C-X Bond

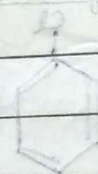
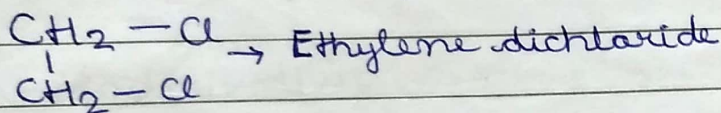
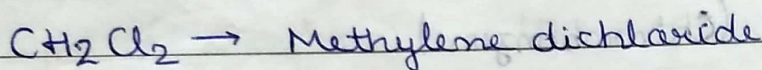
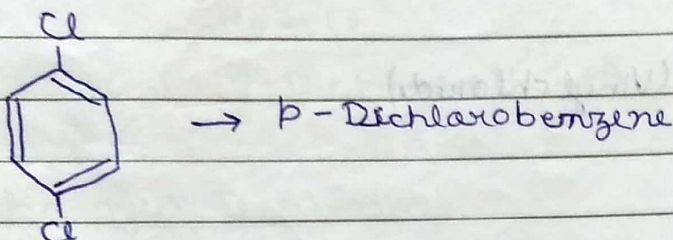
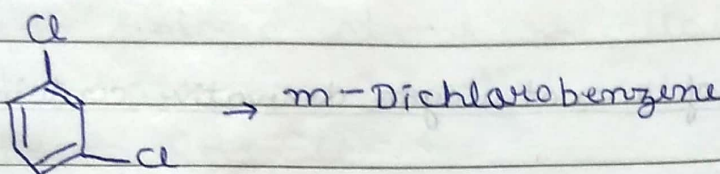
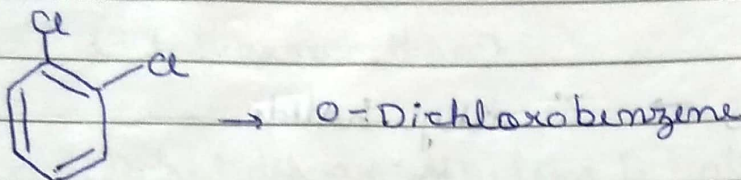
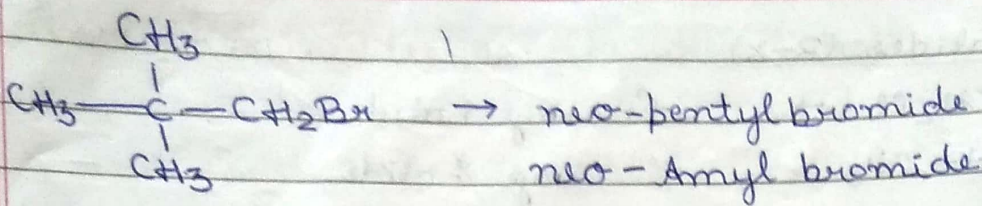
Due to greater electronegativity of halogen atom than carbon C-X bond is polar bond.

The polarity of C-X bond increase with increase in electronegativity of hydrogen atom. Therefore, the increasing order of C-X bond is



Common name of haloalkane and haloarenes





$\text{C-I} < \text{C-Br} < \text{C-Cl} < \text{C-F}$

more polar

less polar

IUPAC nomenclature of haloalkanes or haloarenes

1. Select the longest chain of carbon atom with multiple bond (double or triple), halogen atom (X) and maximum side chain.
2. Numbering order prefer the following sequence:
Near position of (= or \equiv) > X (halogen) > side chain.
3. Write the name in the following sequence:
Side chain with position and alphabetically + No. of carbon atom in selected chain + Types of bond between carbon atom.

Di and tri are used for multiple bond.

- * Neo and iso word include in alphabetical order.
- * Tertiary, secondary, di, tri, tetra etc not include in alphabetical order.
- * In case of complex side chain first letter involve in alphabetical order.
- * In case of side chain we use bis and tris in place of di and tri.

Naming of side chain

$\text{CH}_3 \rightarrow$ Methyl

$\text{Cl} \rightarrow$ Chloro

$\text{Br} \rightarrow$ Bromo

$\text{I} \rightarrow$ Iodo

$\text{F} \rightarrow$ Fluoro

$\text{CH}_2\text{Cl} \rightarrow$ Chloromethyl

$\text{CHCl}_2 \rightarrow$ Dichloromethyl

$\text{CH}_3\text{CH}_2 \rightarrow$ Ethyl

$\text{CCl}_3 \rightarrow$ Trichloromethyl

$\text{CH}_2=\text{CH}-$ (Ethenyl)

$\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \\ | \\ \text{Cl} \end{array} \rightarrow$ (2-chloro ethyl)

$\text{CH}_3-\text{CH}=\text{}$ (Ethylidene)

$\text{CH}_2=\text{}$ (Methylidene)

$\text{CH}_3\text{CH}_2\text{CH}=\text{}$ (Propylidene)

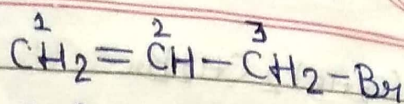
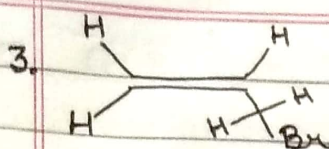
$\text{CH}_2=\text{}$ (Methylidene)

$\text{CH}_3-\text{CH}_2-\text{CH}_2-$ Propyl

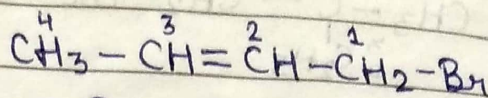
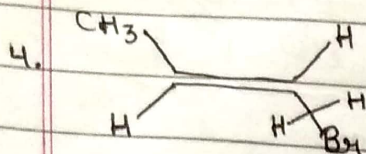
$\text{CH}_3-\text{CH}-$

1-Methylethyl

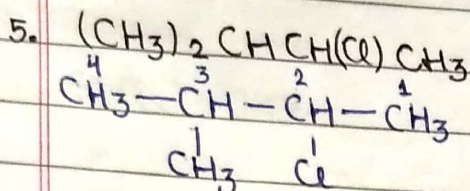
$\begin{array}{c} | \\ \text{CH}_3 \end{array}$



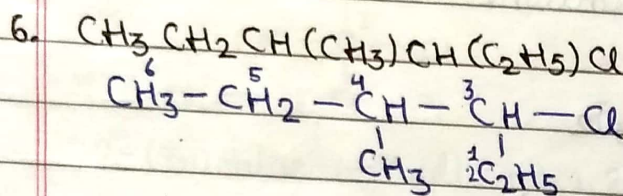
3-Bromo prop-1-ene



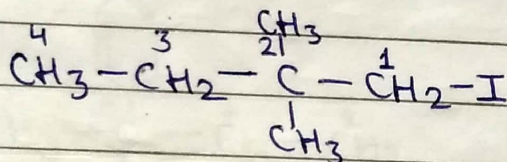
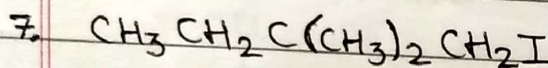
1-Bromo-but-2-ene



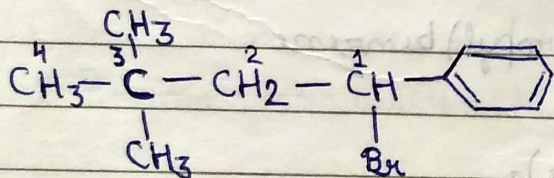
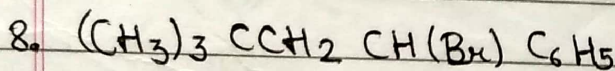
2-Chloro-3-methyl butane



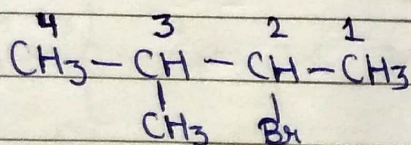
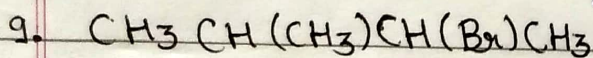
3-chloro-4-methyl Hexane



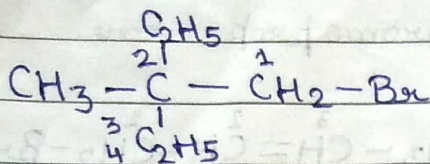
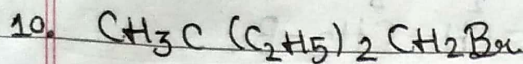
1-Iodo-2,2-dimethyl butane



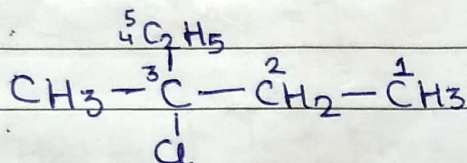
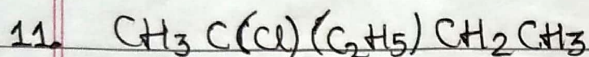
1-(1-Bromo-3,3-dimethyl butyl) benzene



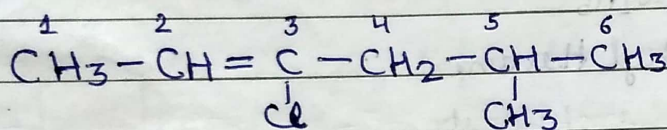
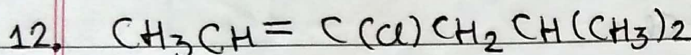
2-Bromo-3-methyl butane



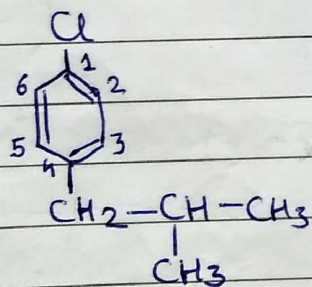
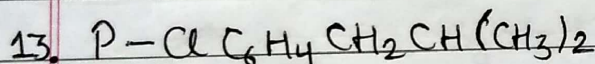
1-bromo-2-methyl-2-methyl butane



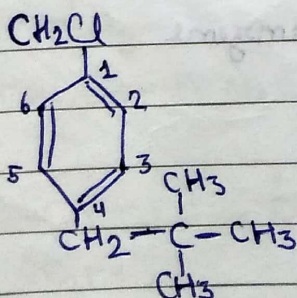
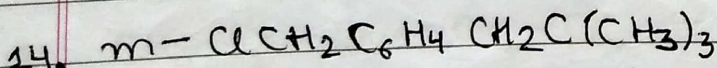
3-chloro-3-methyl pentane



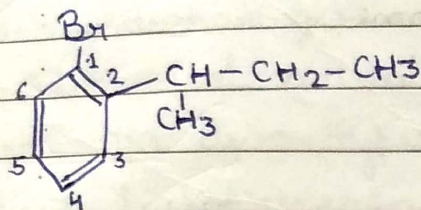
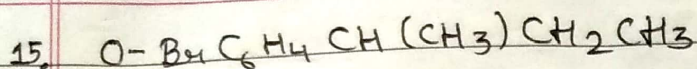
3-chloro-5-methyl hexa-2-ene



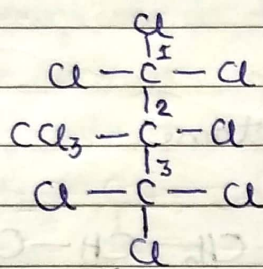
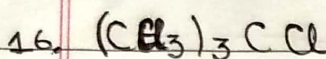
1-chloro-4-(2-methylpropyl) benzene



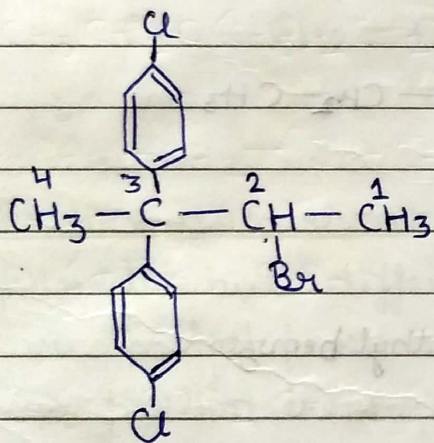
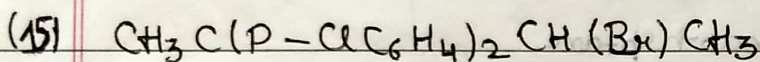
1-chloromethyl-3-(2,2-dimethylpropyl) benzene



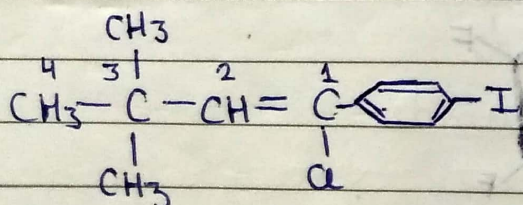
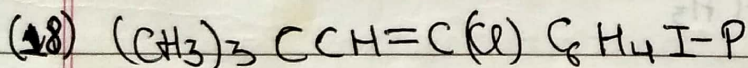
1-Bromo-2-(1-Methyl propyl) benzene



2-(Trichloromethyl)-1,1,1,2,2,2,3,3,3-hepta chloro propane



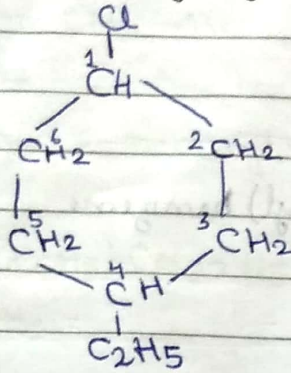
2-Bromo-3,3-bis(4-chlorophenyl) butane



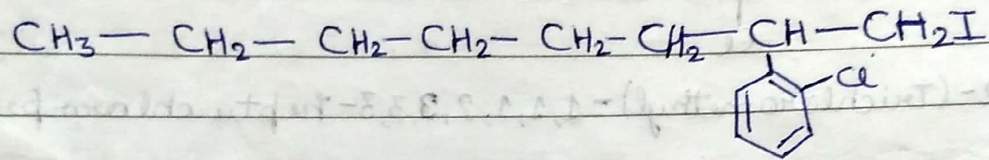
1-chloro-1-(4-iodophenyl)-3,3-dimethyl but-1-ene

Structure

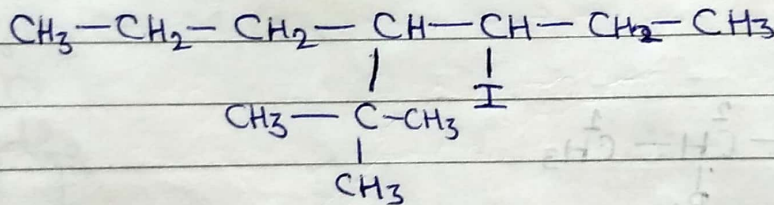
1. 1-chloro-4-ethylcyclohexane



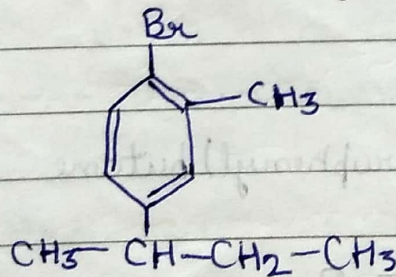
2. 2-(2-Chlorophenyl)-1-iodooctane



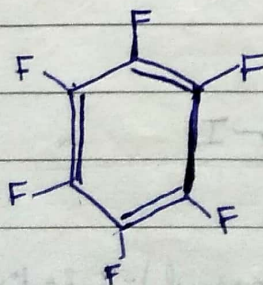
3. 4-tertiary butyl-3-iodoheptane



4. 1-Bromo-4-sec-butyl-2-methyl benzene



5. Perfluorobenzene



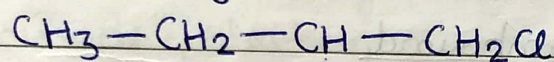
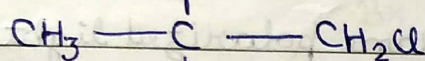
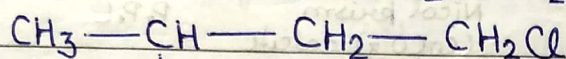
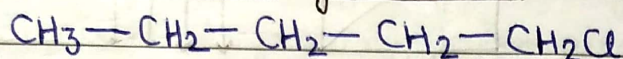
Isomerism

Compounds having same molecular formula but different chemical and physical are called Isomer and the phenomena is Isomerism.

There are two types of isomerism are found in haloalkane and haloarenes:

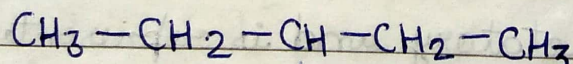
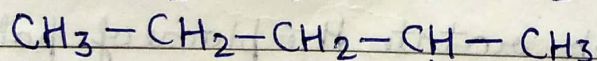
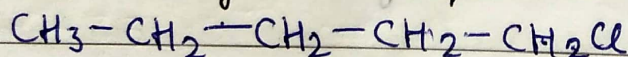
1. Chain Isomerism:- Compounds having the same molecular formula but different arrangement of carbon chain within the molecule are called chain isomer and the phenomena is known as chain isomerism.

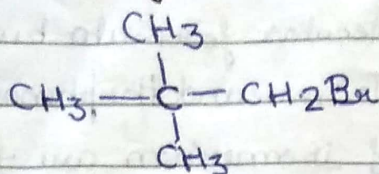
Chain isomer of $C_5H_{11}Cl$



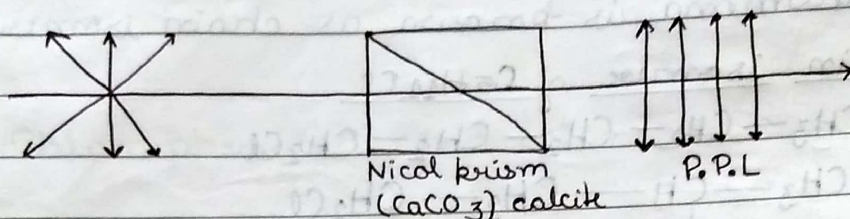
2. Position Isomerism:- Compounds having the same molecular formula but different position of ($=$ or \equiv) or F, Br, or halogen are called position isomer and the phenomena is known as position isomerism.

(a) Position Isomer of 1-chloropentane



(b) Position Isomers of neo-pentyl bromide

There will be no position isomers of neo-pentyl bromide.

Optical IsomerismPlane Polarized Light (P.P.L)

A beam of light which have vibration only in one plane is called plane polarized light.

Optically active Compound

Compounds which can rotate the plane of polarized light are called optically active compound and and this property is called optical active.

Compound which rotate the plane of polarized light towards right (in the clockwise direction) is called dextrorotatory and is represented by d or $(+)$.

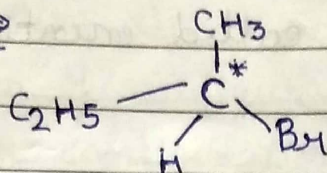
Compound which rotate the plane of polarized light towards left (in the anti-clockwise direction) is called laevorotatory and is represented by l or $(-)$.

Optically inactive compounds

Compounds which cannot rotate the plane of polarized light are called optically inactive compound.

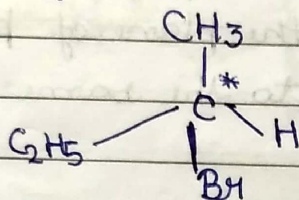
Asymmetric carbon or stereocentre or chiral carbon

If all the atoms or groups attached to a carbon atom are different such a carbon is called asymmetric carbon. Example ⇒



Asymmetric molecule

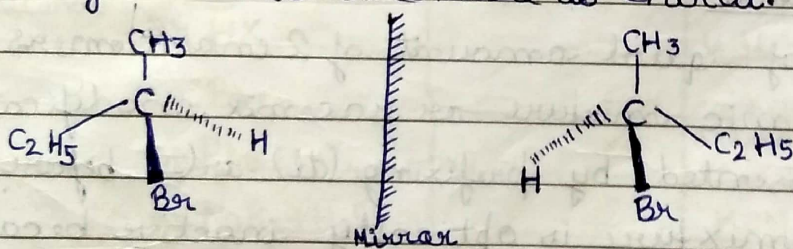
A molecule which contains asymmetric carbon, lacks a plane of symmetry is called an asymmetric molecule. An asymmetric molecule is optically active.



Chiral and Chirality

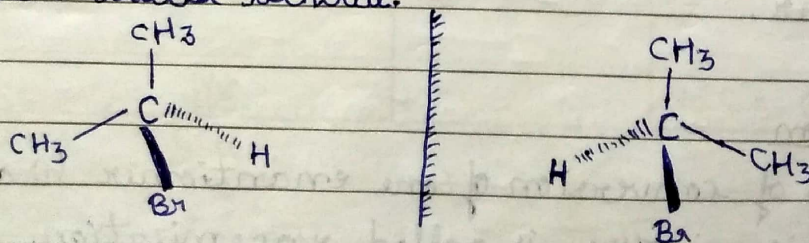
Compounds which are non-superimposable on their mirror image are called chiral and this property is called chirality.

An asymmetric molecule is chiral.



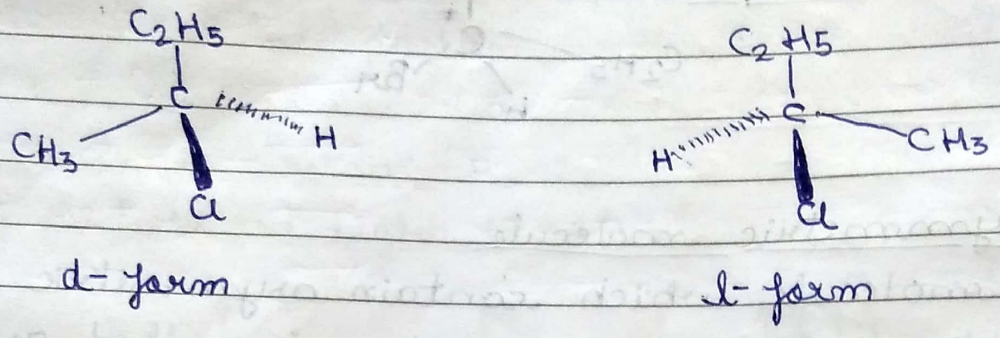
Achiral

Compounds which are superimposable on their mirror image are called achiral.



Enantiomers

Optical isomers which are non-super imposable mirror image of each other are called enantiomers and the phenomena is called enantiomers.



Enantiomers have identical physical and chemical properties but rotate the plane of polarized light in opposite direction but to the same extent.

Optical Isomers

(+) and (-) isomers of optical active compound are called optical isomers and the phenomena is called optical isomerism

Racemic mixture

A mixture of equal amount of 2 enantiomers is called racemic mixture or racemix modification. It is represented by prefixing (dl) or (±) before the name. A racemic mixture is optically inactive because the rotation caused by the molecules of 1 enantiomer is exactly cancelled by equal and opposite rotation caused by the same no. of molecule of the other enantiomer.

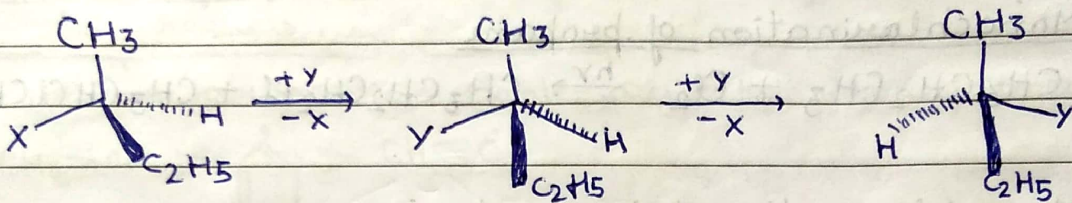
Racemization

The process of conversion of one enantiomer (+) or (-) into racemic mixture is called racemization.

Retention and Inversion

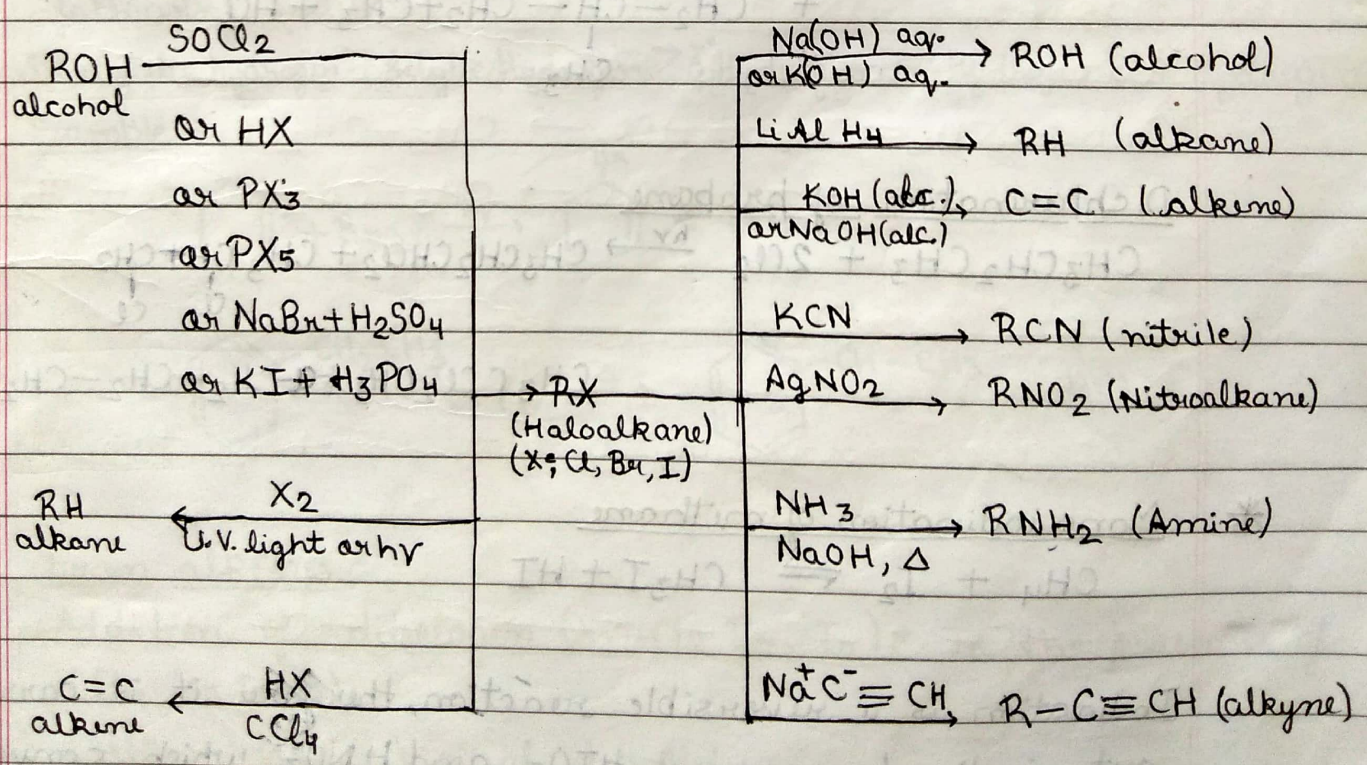
If the relative configuration of the atoms or groups around a chiral centre remains the same, before and after the reaction, the reaction is said to be proceed with retention of configuration.

If the relative configuration of the atoms or groups around a chiral centre in the product is opposite to that in the reactant, the reaction is said to proceed with inversion of configuration.



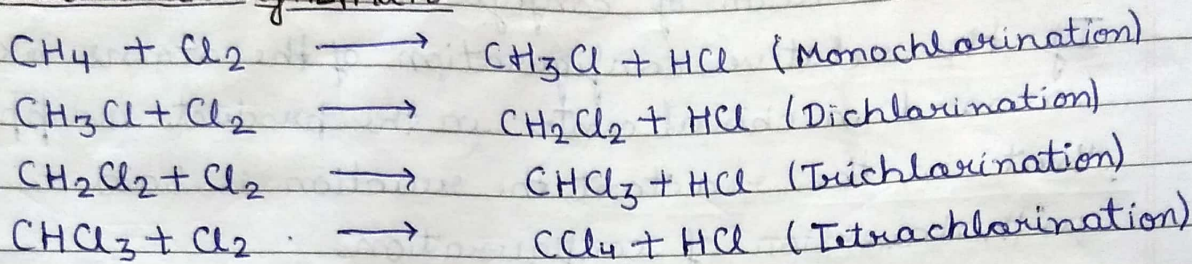
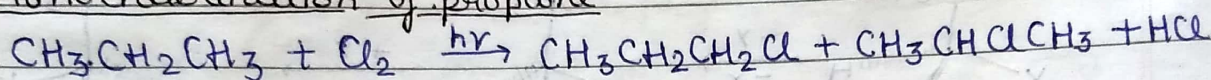
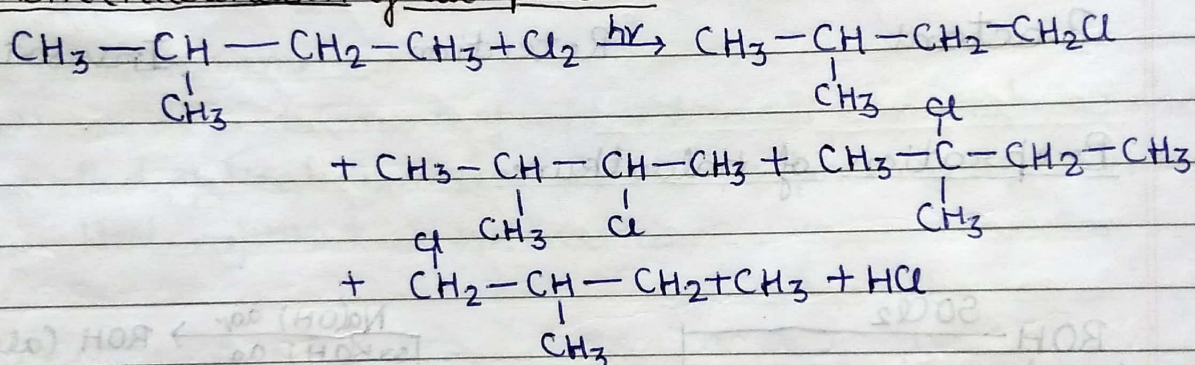
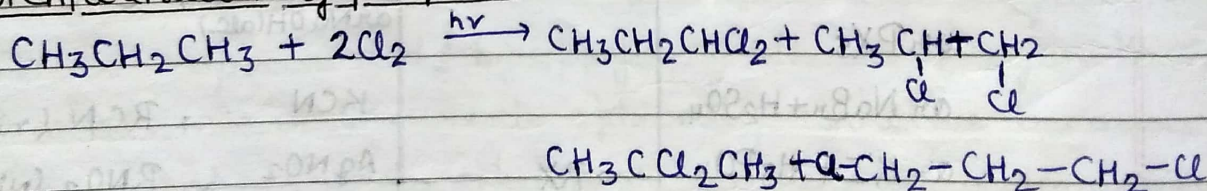
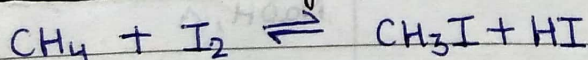
Reactant Retention Inversion

Preparation of Haloalkane

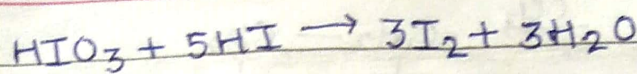


Exom alkanes

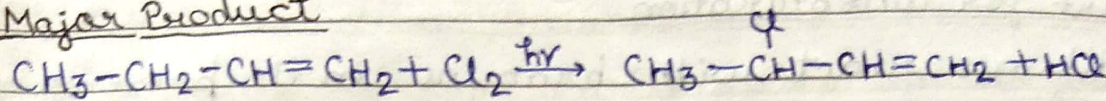
Alkanes react with dihalogen in the presence of bright sunlight or UV light or heat to give haloalkanes.

ExampleChlorination of MethaneMonochlorination of propaneMonochlorination of iso-pentaneDichlorination of propane* Monoiodination of methane

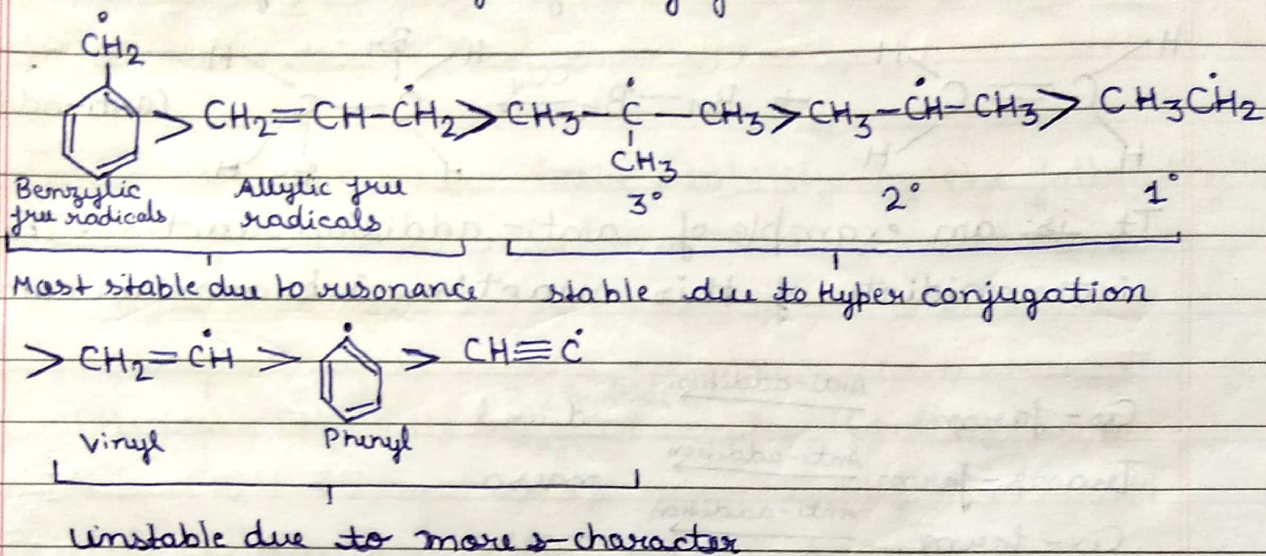
Iodination is a reversible reaction, therefore it is carried out in the presence of HIO_3 and HNO_3 which convert HI into I and reaction takes place in forward direction.



Major Product



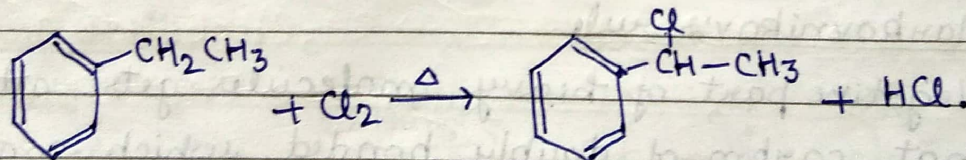
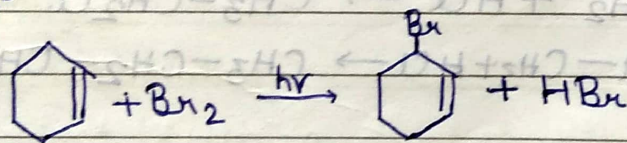
* Halogenation is an example of free radicals substitution reaction. The stability order of free radicals are as follows:-



In case of major product, replace hydrogen atom in the following order:-

Benzylic hydrogen > Allylic Hydrogen > 3° Hydrogen > 2° Hydrogen > 1° Hydrogen

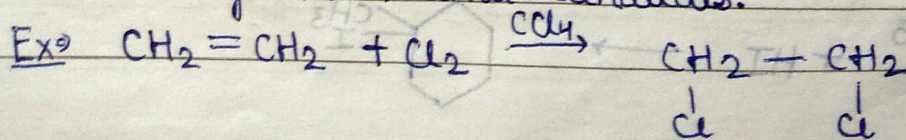
Example:-

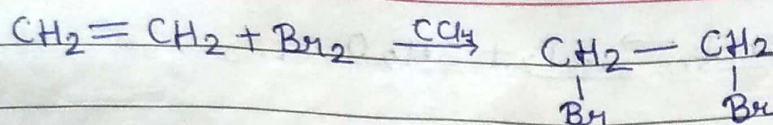


From alkenes

(A) Addition of dihalogen ($\text{X}_2 = \text{Cl}_2, \text{Br}_2, \text{I}_2$) In the presence of CCl_4 (or Dark).

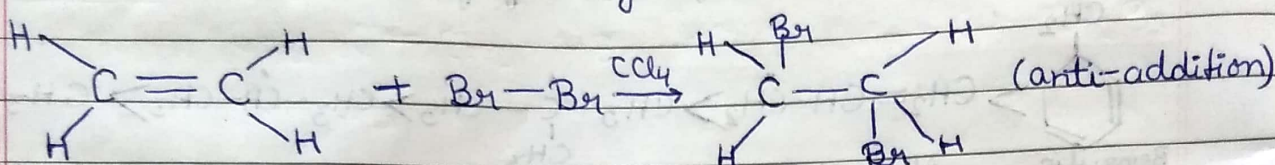
Alkene form Vicinal dihalides.



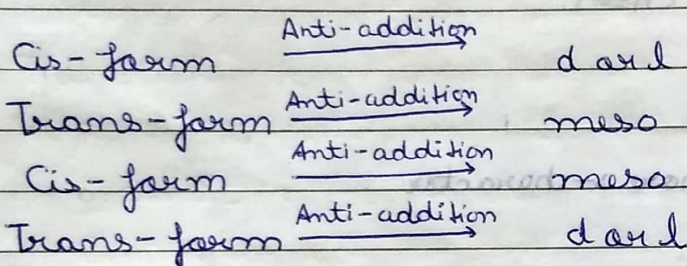


* Test for unsaturation

Alkenes react with bromine in the presence of CCl_4 , the reddish brown colour of bromine is discharged due to the formation of a colourless vic-dibromide. This reaction is used for the test of unsaturation.

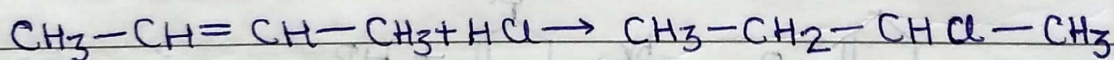
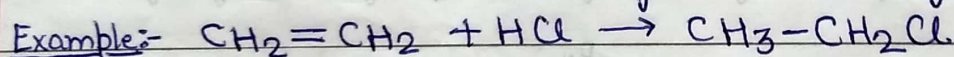


It is an example of anti-addition reaction. The intermediate of this reaction is bromonium complex.



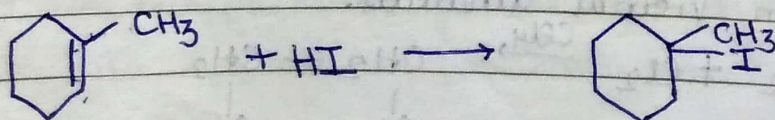
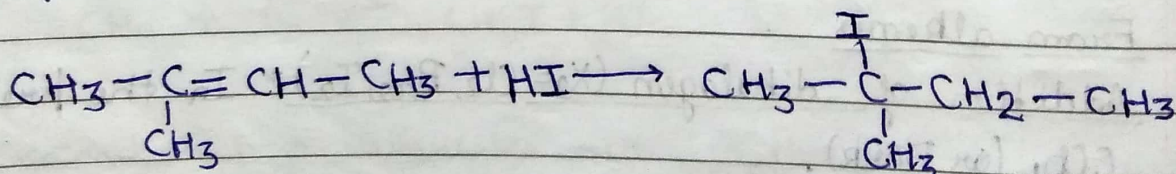
(B) Addition of HX (HCl, HBr, HI)

Alkene react with halogen acid to give haloalkane.



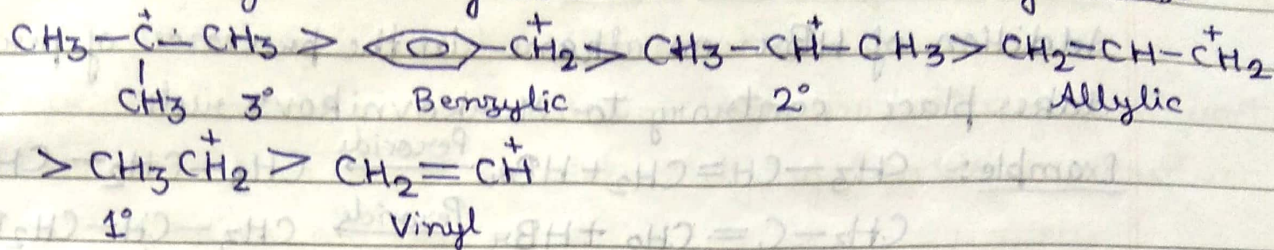
* Markovnikov's rule

Negative part of heavy molecules gets attached to that carbon of doubly bonded which contain less no. of hydrogen atom.



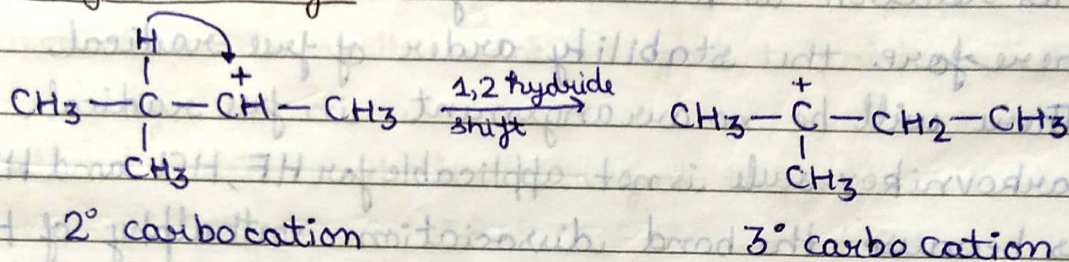
* 1. Addition of HX on alkene is an example of electrophilic addition reaction. The reaction intermediate of this reaction is carbo-cation.

2. The stability order of carbon cation are as follows:-

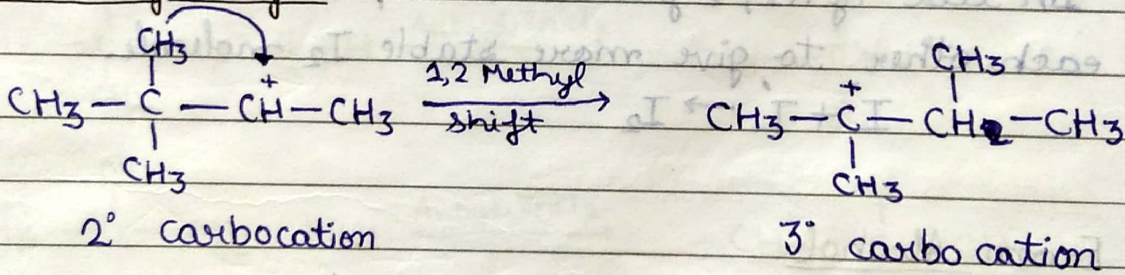


3. Carbocation increase their stability by the following rearrangements:-

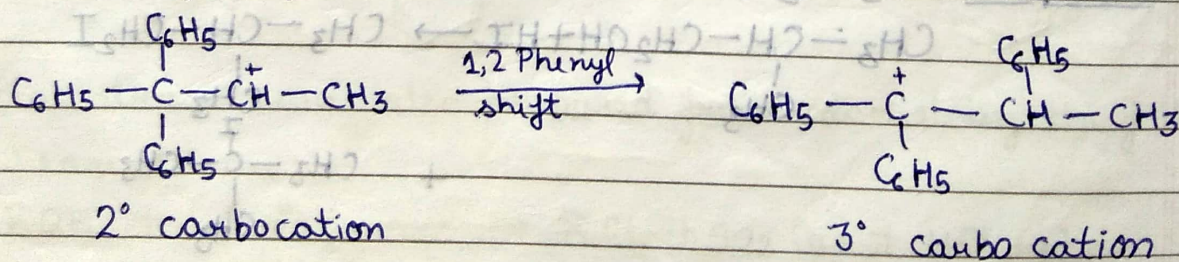
1,2 hydride shift



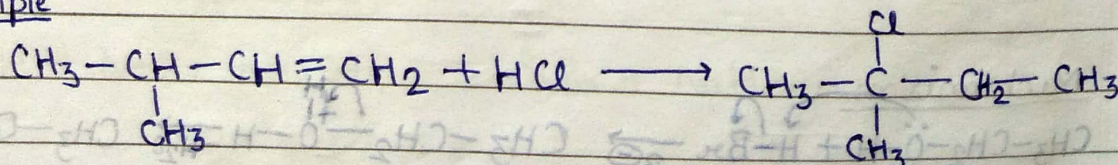
1,2 Methyl shift

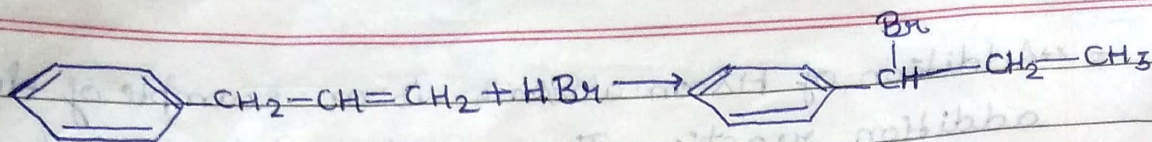


1,2 Phenyl shift



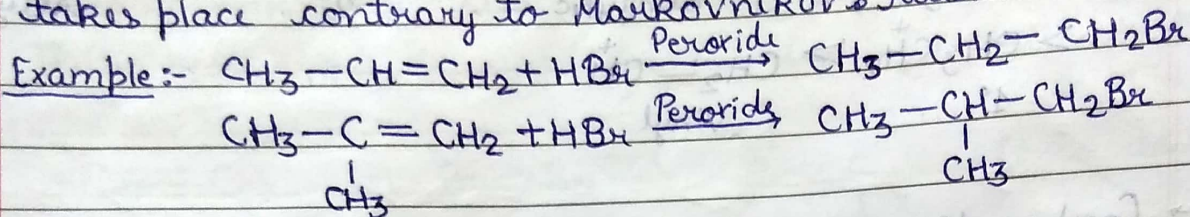
Example





* Anti-Markovnikov's rule

Addition of HBr on alkene in the presence of peroxide takes place contrary to Markovnikov's rule.



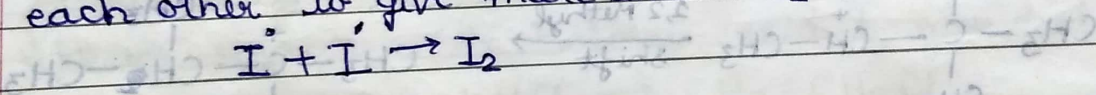
1 → Anti-Markovnikov's rule apply only for HBr with peroxide.

This reaction is known as free radicals addition reaction.

Therefore the stability order of free radical.

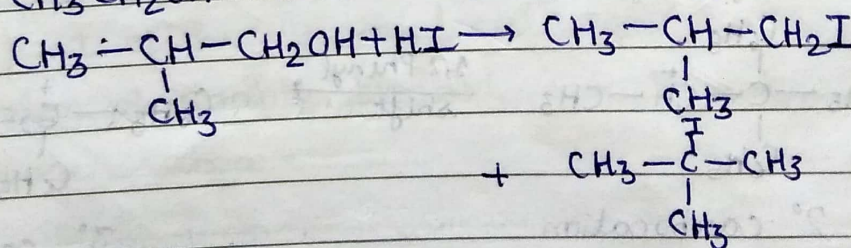
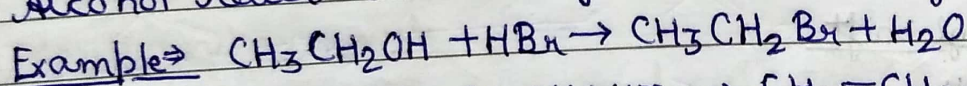
There will be no arrangement in free radical. Anti-Markovnikov rule is not applicable for HF, HCl and HI. This is because the bond dissociation enthalpy of H-F, and H-Cl are very high and does not produce free radicals.

In case of HI, I free radical produce which combine with each other to give more stable I₂ molecule.

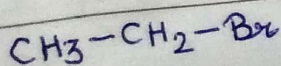
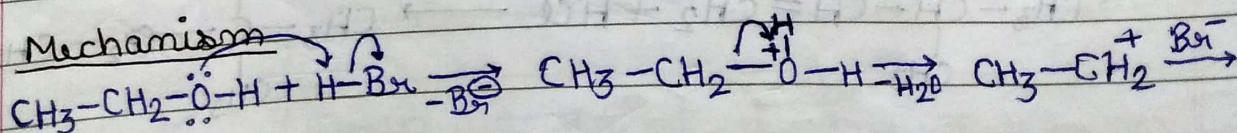


From Alcohol

Alcohol react with halogen acid (HX) to give haloalkane.



Mechanism



* The reactivity order of halogen acids are as follows:
 $\text{HCl} < \text{HBr} < \text{HI}$ (due to low bond dissociation enthalpy)

* Reactivity of alcohol increase in the following order:-
 $1^\circ \text{ alcohol} < 2^\circ \text{ alcohol} < 3^\circ \text{ alcohol}$

This is because the reaction intermediate of this reaction is carbocation and the stability of cation increases in the same order.

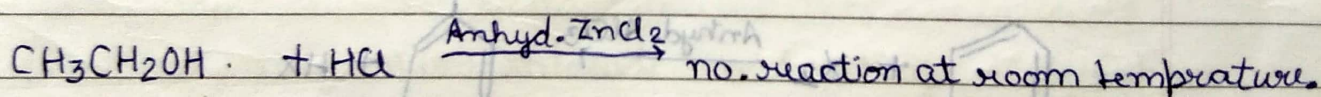
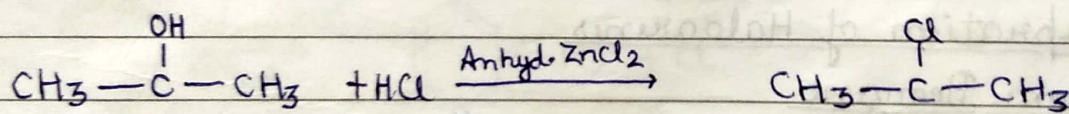
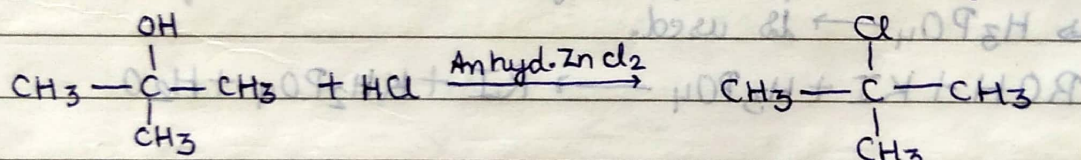
* Lucas Reagent

It is a mixture of conc. HCl and Anhyd. ZnCl_2 . It is used to difference among $1^\circ, 2^\circ, 3^\circ$ alcohol.

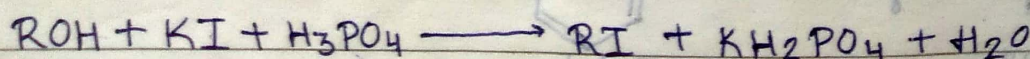
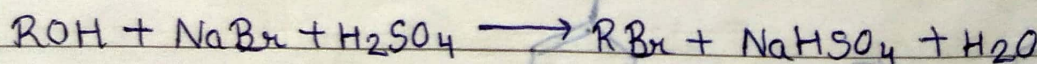
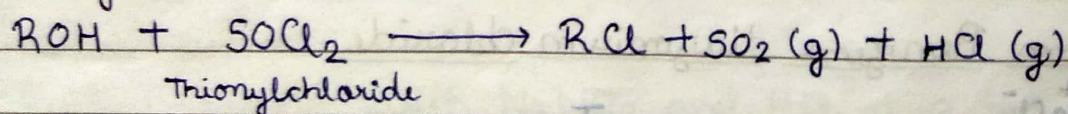
3° alcohol reacts with Lucas reagent to produce Turbidity immediately.

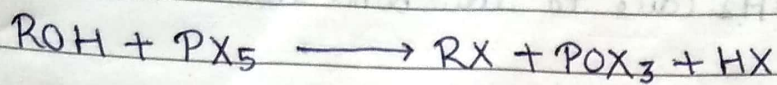
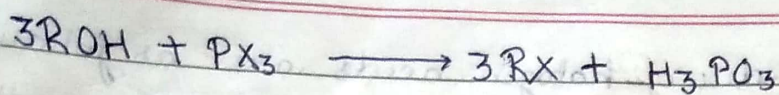
2° alcohol reacts with Lucas reagent to produce Turbidity after five minutes.

1° (Primary) alcohol does not react with Lucas reagent at room temp.



Haloalkane are also prepared from alcohol by the following reagent:-

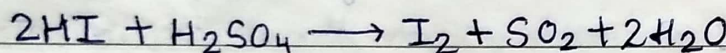
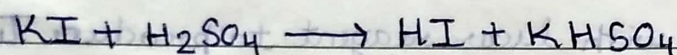




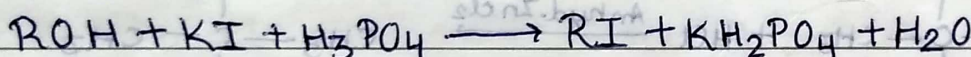
* Thionyl chloride method is preferred for the preparation of chloroalkane. Since its both by-product (SO_2 , HCl) are gases which can be easily removed and chloroalkane is obtained in pure state.

* Why is sulphuric acid not used during the reaction of alcohol with KI ?

H_2SO_4 is a strong oxidising agent. It oxidises HI produced during the reaction to I_2 and hinders the reaction between alcohol and HI .

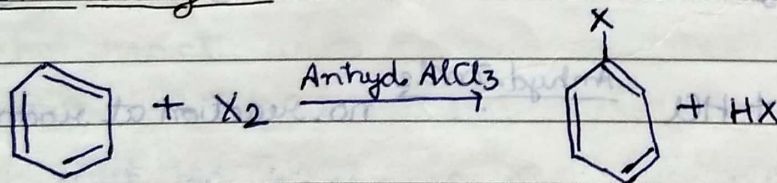


To overcome this difficulty a non-oxidising acid such as H_3PO_4 is used.



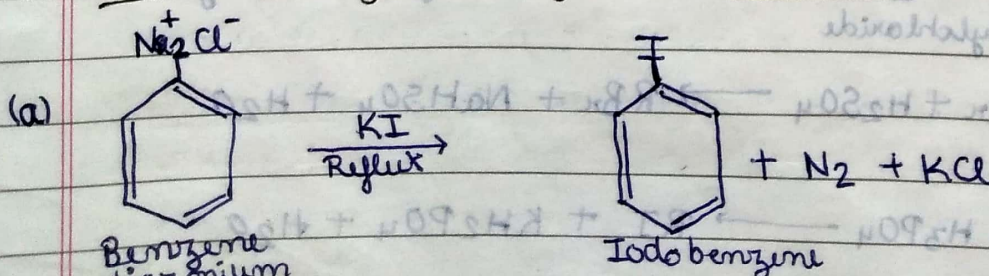
Preparation of Haloarenes

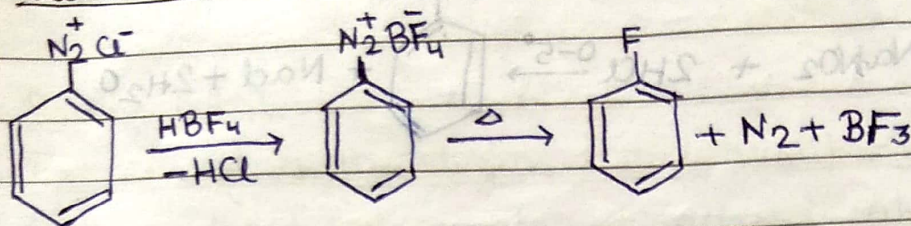
From Benzene



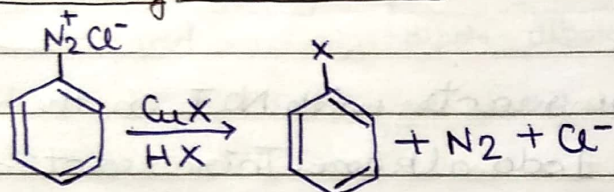
(where $\text{X}_2 = \text{Cl}_2, \text{Br}_2$)

From Benzene diazonium chloride



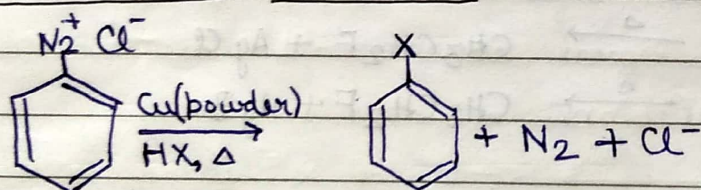
(b) Balz-Schiemann's reaction

Benzene diazonium chloride on heating with HBF_4 (Fluoroboric acid) to give fluoro benzene, this reaction is known as Balz-Schiemann's reaction.

(c) Sandmeyer reaction

where $\text{X} = \text{Cl}, \text{Br}, \text{CN}$

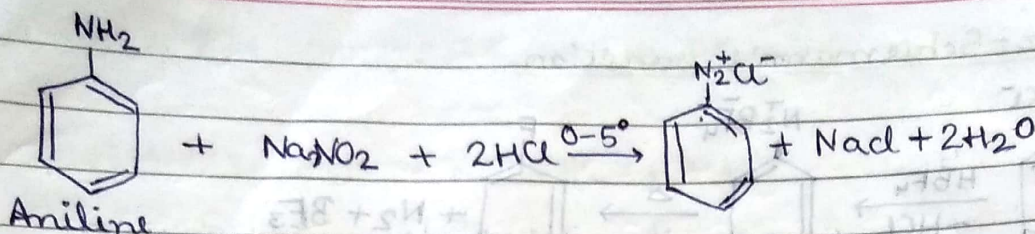
Benzene diazonium chloride reacts with Cu^+ halide in the presence of HX to give halobenzene, this reaction is known as Sandmeyer reaction.

(d) Gattermann reaction

Benzene diazonium chloride on heating with Copper powder in the presence of H-X to give halobenzene. This reaction is known as gattermann reaction.

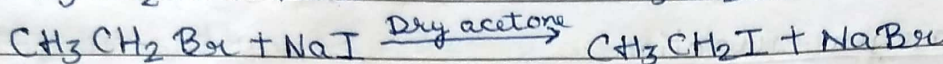
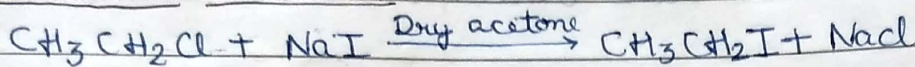
(e) Diazotization

Aniline reacts with NaNO_2 and HCl at 0 to 5°C to give benzene diazonium chloride. This reaction is called diazotization.



Halogen Exchange

1. Finkelstein reaction

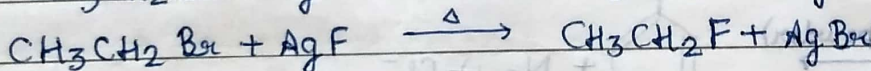
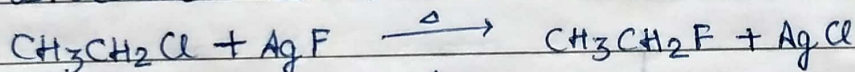


Chloro or Bromo alkane reacts with NaI in the presence of dry acetone to give Iodo alkane. This reaction is called finkelstein reaction.

2. Swarts reaction

Chloro or Bromo alkane on heating with metal fluoride such as AgF , COF_2 , Hg_2F_2 , SbF_3 , AsF_3 etc. to give fluoro alkane.

This reaction is called swarts reaction.



Physical Properties of Haloalkane and Haloarenes

Solubility

Compounds containing most electronegative element (F, O, N), are soluble in water because they form intermolecular hydrogen bond with water molecule. The solubility of compounds in water decrease with increase in size of alkyl group which is hydrophobic in nature.

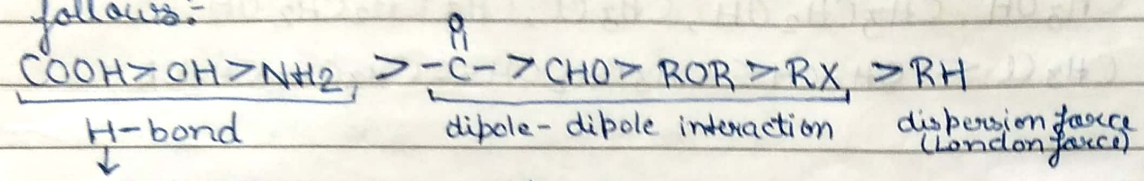
Haloalkanes ($\text{CH}_3\text{CH}_2\text{Cl}$, $\text{CH}_3\text{CH}_2\text{Br}$, $\text{CH}_3\text{CH}_2\text{I}$) are polar molecule but they are insoluble in water because they

don't form hydrogen bond with water molecules.

Boiling point

(a) In case of different functional group containing compound
Boiling point of compounds depends upon intermolecular force. With increase in magnitude of inter molecular force boiling point increases.

The decreasing order of boiling point of compound are as follows:-



Due to higher magnitude of hydrogen bond.

(b) In case of same functional group containing compound
Boiling point of compound increase with increase in molecular mass.

In case of isomer, straight chain isomer have higher boiling points than branch chained compounds. This is because straight chain compounds are large. As a result the magnitude of van der waal force are large.

Melting point

Similar to boiling point.

Exception

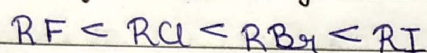
Exception in boiling melting point is due close packing in their crystal lattice.

* p-dichlorobenzene is a more symmetrical molecule therefore it closely packed in their crystal lattice and has highest melting point and less solubility than that of o-dichlorobenzene and m-dichlorobenzene.

* Lewis concept of Acids and Bases

An acid is defined as substance which is capable of accepting a pair of electrons and a base is defined as a substance which is capable of donating an unshared (lone) pair of electrons. In other words, an acid is an electron pair acceptor while a base is an electron pair donor.

Reactivity order of Haloalkane towards SN reaction



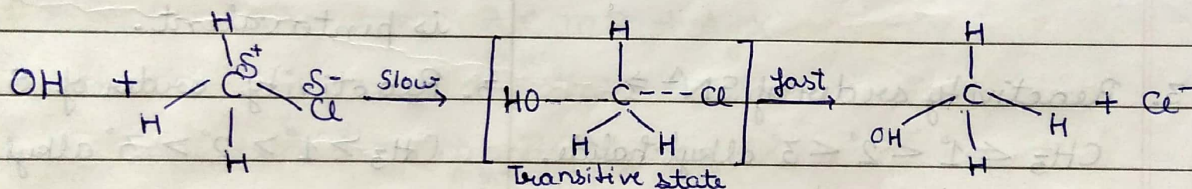
Because I^- is the best leaving group.

* Weak base behave as a best leaving group.

Mechanism of SN reaction

SN reaction takes place in the following two path:

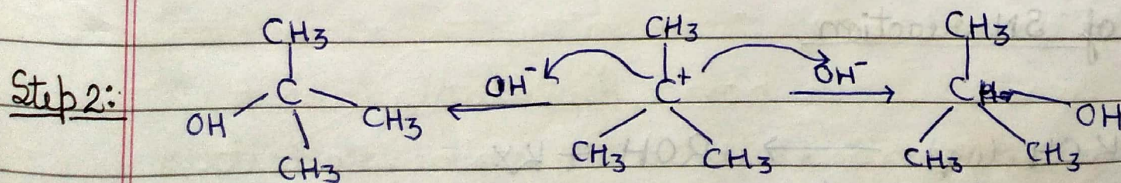
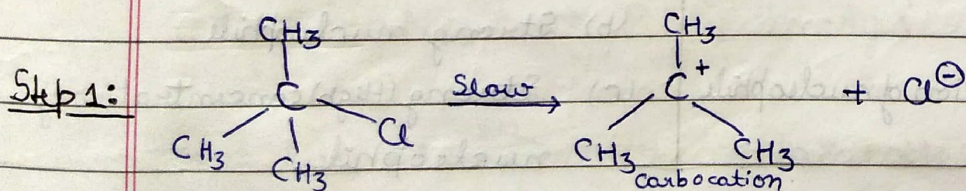
SN² (bi-molecular substitution nucleophilic reaction)



Reactivity order of SN² ⇒ CH₃X > 1° alkyl halide > 2° alkyl halide > 3° alkyl halide

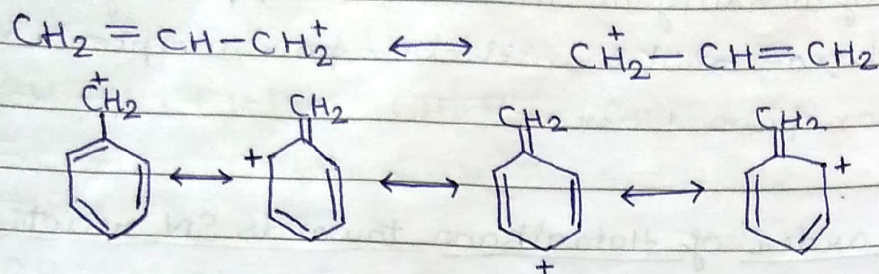
SN¹ (uni-molecular substitution nucleophilic reaction)

It takes place in 2 step:



Reactivity order of SN¹ ⇒ CH₃X < 1° alkyl halide < 2° alkyl halide < 3° alkyl halide.

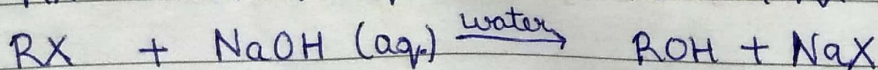
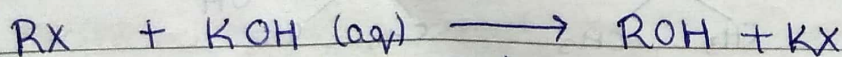
- * (a) Benzylic halide and Allylic halide follows S_N^1 path. This is because allylic and benzylic carbocation are stable due to resonance.

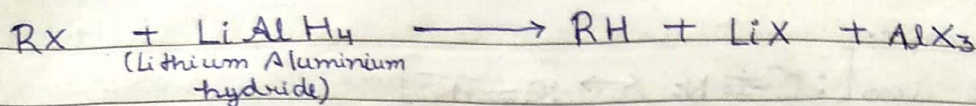


Difference between S_N^1 and S_N^2

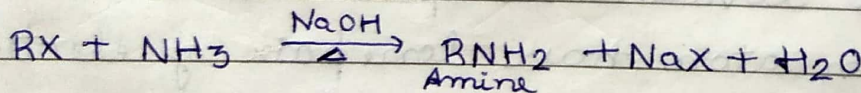
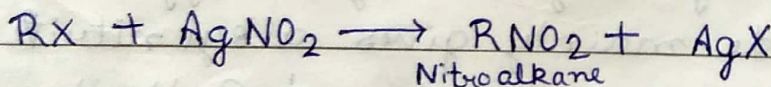
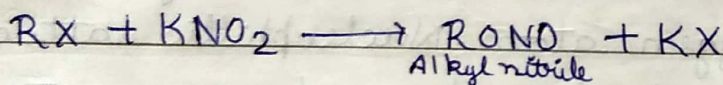
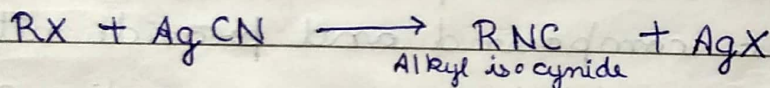
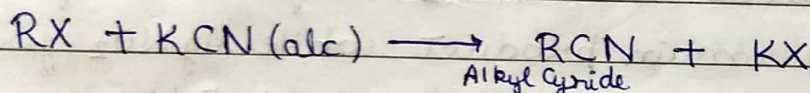
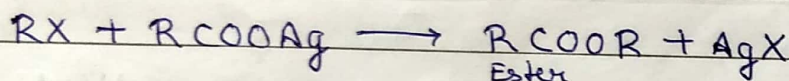
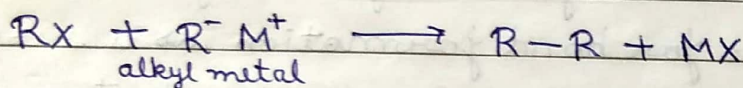
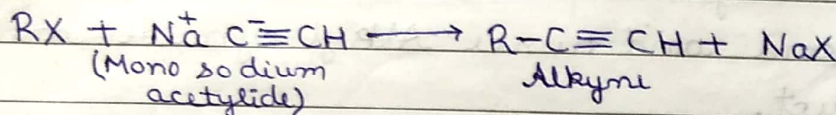
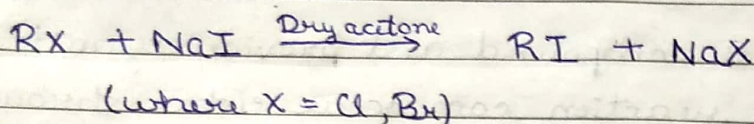
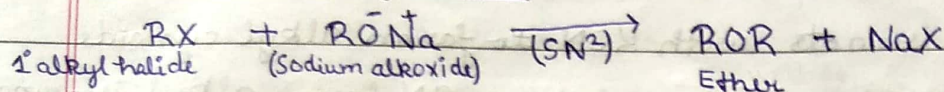
S_N^1	S_N^2
1. Its molecularity is 1	1. Its molecularity is 2
2. Its intermediate is carbocation.	2. Its intermediate is transition state in which carbon atom is pentavalent.
3. Reactivity order of $S_N^1 \Rightarrow$ $\text{CH}_3 < 1^\circ < 2^\circ < 3^\circ$ alkyl halide.	3. Reactivity order of $S_N^2 \Rightarrow$ $\text{CH}_3 > 1^\circ > 2^\circ > 3^\circ$ alkyl halide.
4. If a compound contain chiral carbon, racemic mixture is obtained during this reaction.	4. Inversion in configuration takes place in this reaction.
5. Favourable conditions for S_N^1	5. Favourable conditions for S_N^2
(a) Polar solvent	(a) Non-polar solvent
(b) Weak nucleophile	(b) Strong nucleophile
(c) Low concentration of nucleophile	(c) Strong (High) concentration of nucleophile.

Examples of S_N reaction





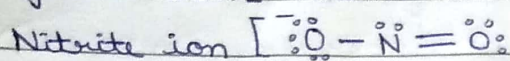
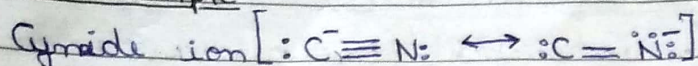
* Williamson Synthesis



Ambident Nucleophile

Nucleophile which can attack through two different sites are called ambident nucleophile.

For example



Haloalkane reacts with KCN to form alkyl cyanide as the major product while AgCN form alkyl iso-cyanide. Explain.

KCN is a ionic compound and provide cyanide ion in solution. The reaction can occur either through carbon or nitrogen. Since C-C bonds are stronger than C-N bond and hence Alkyl cyanide are the main product.

AgCN is covalent. Therefore only nitrogen electron pair is available for bond formation as a result Alkyl iso-cyanide are the main product.

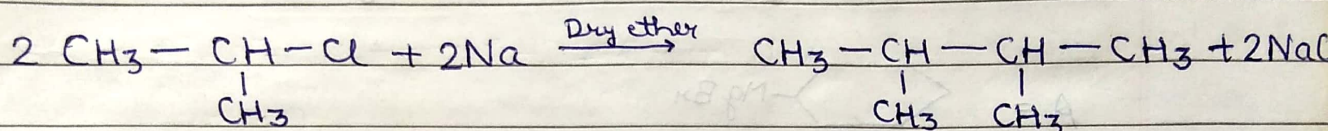
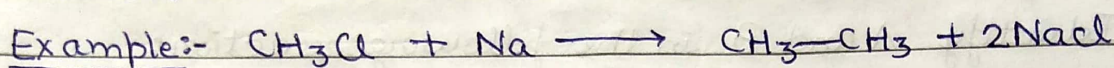
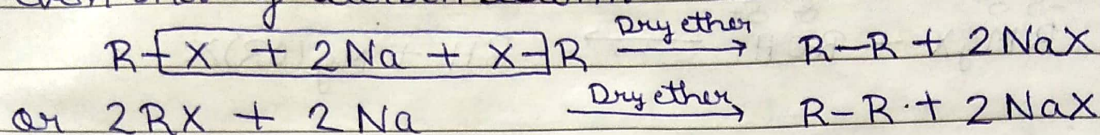
Haloalkane reacts with KNO_2 to form alkyl nitrite as the main product while AgNO_2 form nitro-alkane as the main product. Explain.

KNO_2 is a ionic compound and provide nitrite ion in the solution which have a negative charge on one of the oxygen atom. Nucleophilic attack through this negatively charged oxygen atom on alkyl halide mainly gives alkyl nitrite.

AgNO_2 is a covalent compound. Both the oxygen and nitrogen atom have lone pair of electrons. Since nitrogen is less electronegative than oxygen. Therefore lone pair of e^- on nitrogen atom is more easily available for bond formation and nitro compound formed as the main product.

Reaction with metal

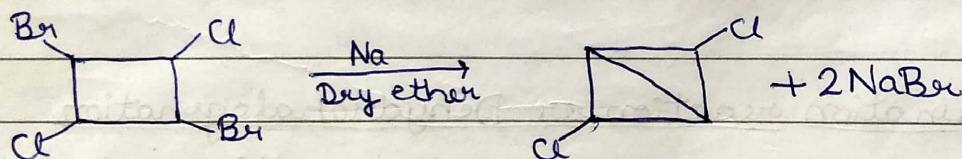
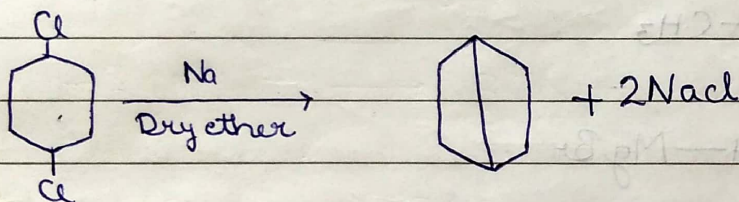
Reaction with sodium metal (Wurtz reaction) → Haloalkane reacts with sodium metal in the presence of dry ether to give symmetrical alkane which contain even no. of carbon atoms.



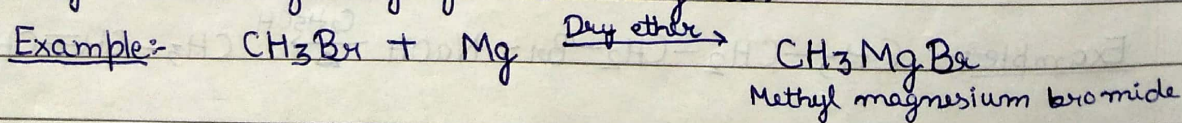
Wurtz reaction takes place by SN^2 path.

Intra molecular wurtz reaction

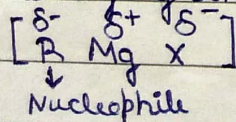
By cyclo compound form as a product.

1 Reaction with Mg metal

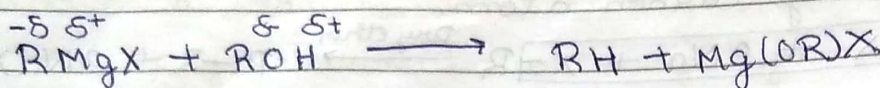
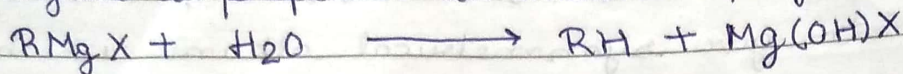
Haloalkane reacts with magnesium metal in the presence of dry ether to give grignard reagent.



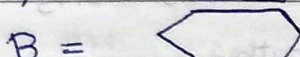
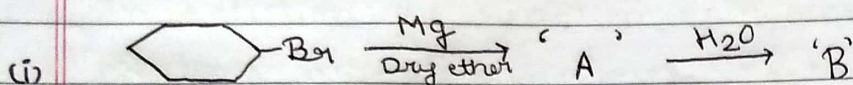
In case of grignard reagent, Always $R-\overset{\ominus}{C}-Mg^{\oplus}-X$ bond break.



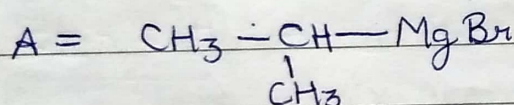
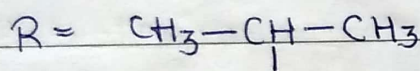
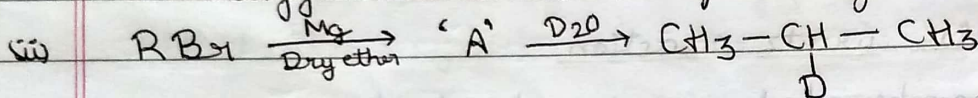
** Grignard reagent is a highly reactive reagent. It reacts with water to give alkane. Therefore Grignard reagent is prepared in moisture proof container.



Identify A and B in the following reaction:

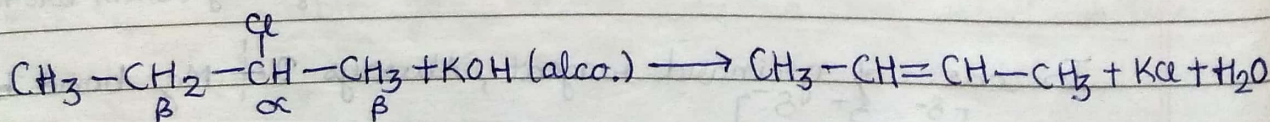
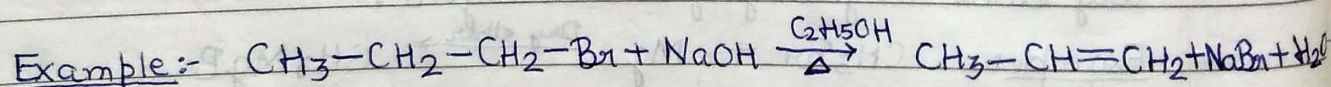
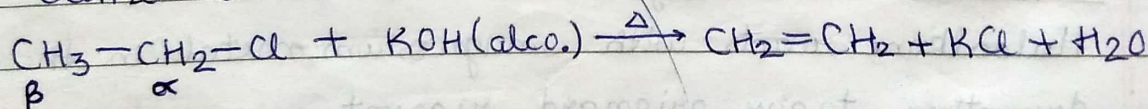


Identify R and A in the following reaction:



β -Elimination reaction or Dehydrohalogenation

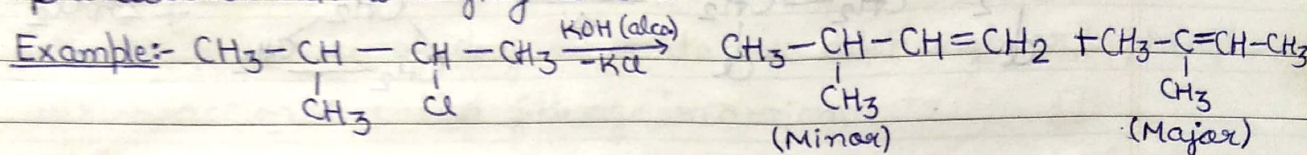
Haloalkane on heating with alcoholic KOH or alcoholic NaOH to give alkene. This reaction is known as β -elimination reaction.



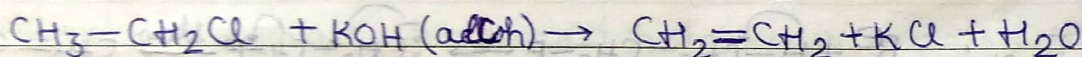
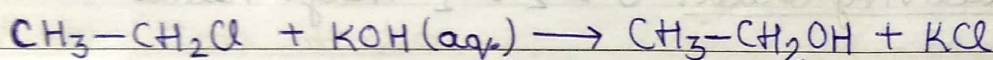
In dehydrohalogenation or β elimination reaction, remove X from α carbon and hydrogen from β carbon containing less no. of hydrogen atom.

* Saytzeff's rule

In dehydrohalogenation reaction that alkene is the major product which is highly substituted.



Q. Haloalkanes reacts with aqueous KOH to give alcohol but in the presence of alcoholic KOH, alkenes are the major product. Explain.



In aqueous solution, KOH is completely ionised to give OH^- ion which is a strong nucleophile and hence substitution reaction takes place on alkyl halide to form alcohol.

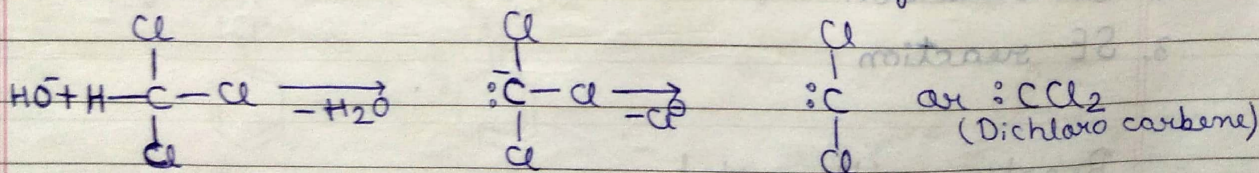
Alcoholic solution of KOH contain alkoxide ion (RO^-) which is a stronger base than OH^- ion and hence elimination reaction takes place to form alkene.

Types of Elimination reaction

There are three types of elimination reaction.

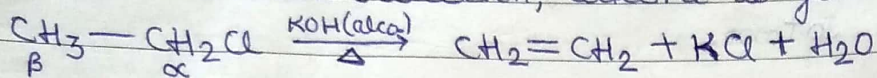
① α -Elimination or 1-1-elimination

In α -elimination reaction, carbene is formed.

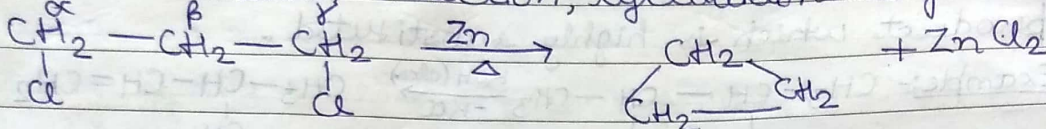
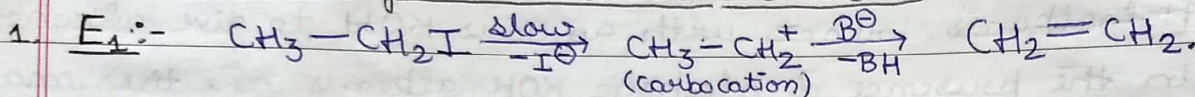


2. β -elimination or 1,2 elimination

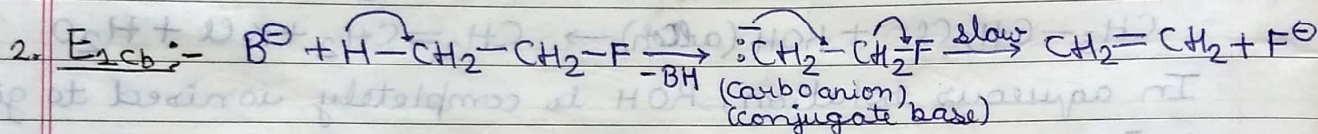
In β -elimination reaction, alkene is formed.

3. γ -elimination or 1,3 elimination

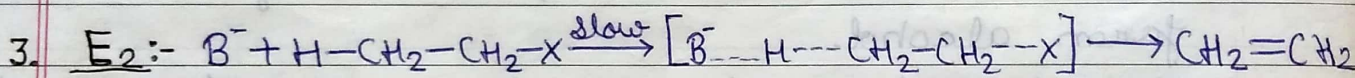
In γ -elimination reaction, cycloalkene is formed.

Mechanism of β -elimination reaction

Reactivity order:- $3^\circ > 2^\circ > 1^\circ$ Alkyl halide



Reactivity order:- $1^\circ > 2^\circ > 3^\circ$



Reactivity order:- $3^\circ > 2^\circ > 1^\circ$

↓
No. of β -Hydrogen

Chemical reactions of Haloarenes

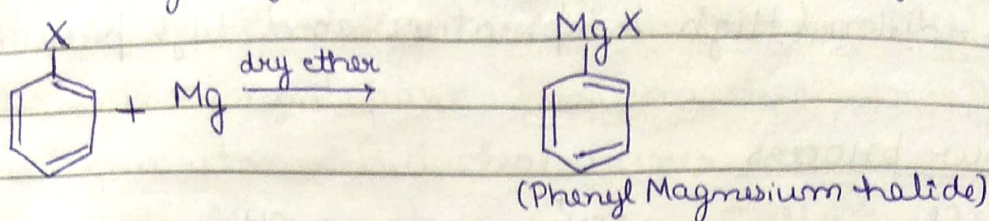
Haloarenes undergo the following reaction:-

1. Reaction with metal.
2. SN reaction
3. SE reaction

Reaction with metal(i) Reaction with Mg metal

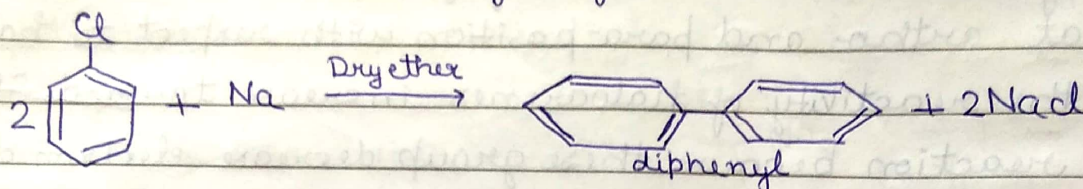
Haloarenes react with magnesium metal in the

presence of dry ether to give grignard reagent.



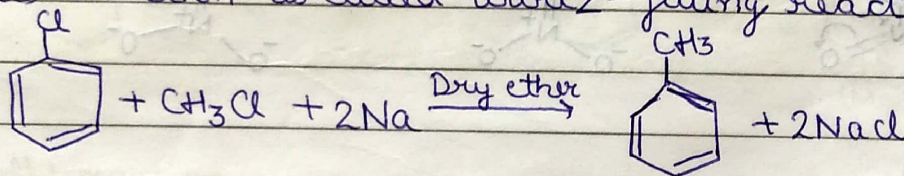
(ii) Reaction with Na metal

Fitting reaction:- Haloarenes reacts with sodium metal in the presence of dry ether to give diphenyl or biphenyl. This reaction is called fitting reaction.



Wurtz fitting reaction

A mixture of haloalkane and haloarenes reacts with sodium metal in the presence of dry ether to give alkyl benzene, this reaction is called wurtz-fitting reaction.

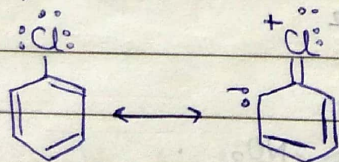


* Substitution nucleophilic reaction

Haloarenes do not undergo substitution nucleophilic reaction due to the following reasons:-

- (i) Repulsion between π -electrons of benzene ring and nucleophile.
- (ii) Partial double bond character of C-X bond due to resonance.

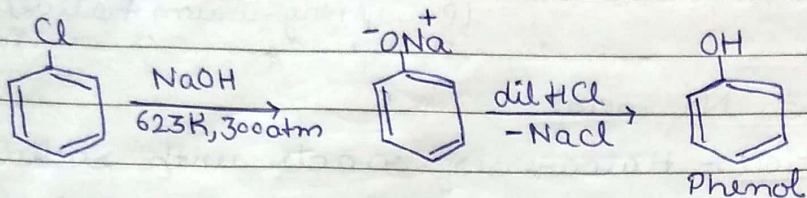
Therefore, C-X bond is not easily broken.



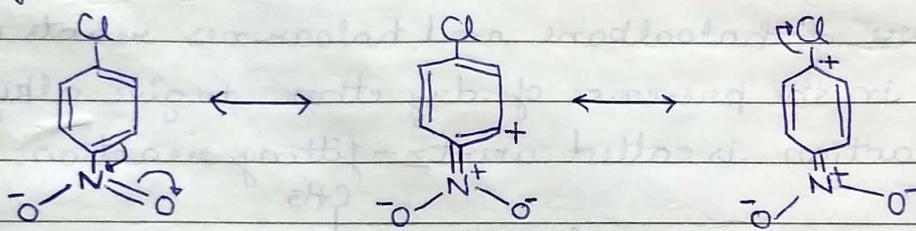
- (iii) Unstability of phenyl carbocation formed by $\text{S}_{\text{N}}^{\text{A}}$ path.

Haloarenes undergo S_N reaction under drastic condition (High temperature and high pressure).

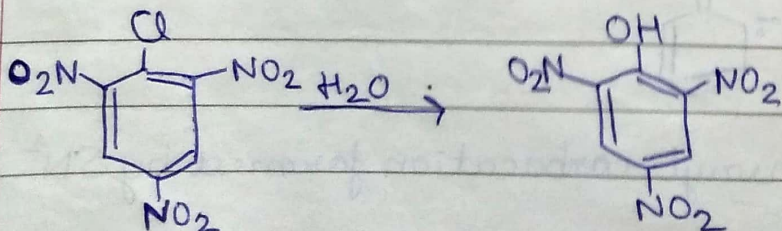
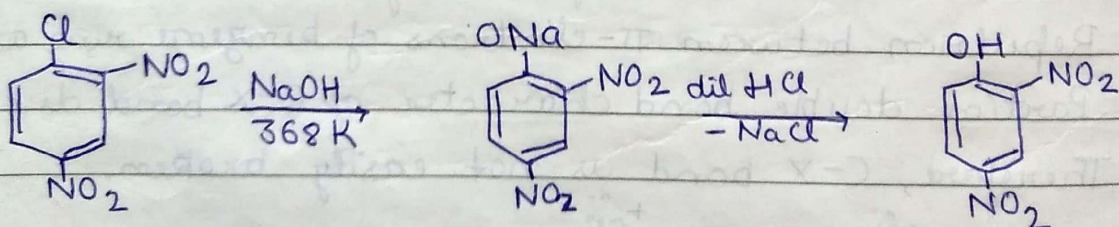
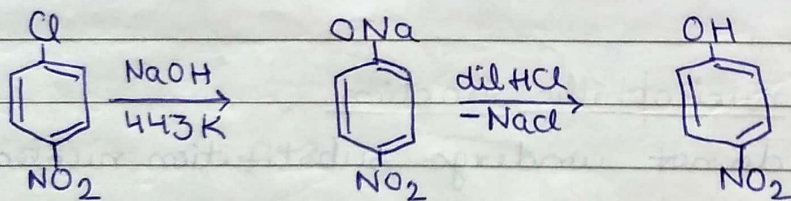
Dow process



If electron withdrawing group, NO_2 , CN are present at ortho and para-position with respect to halogen, the reactivity of haloarenes increase towards S_N reaction because these group decrease electron density on benzene ring and attack of nucleophile becomes fast.

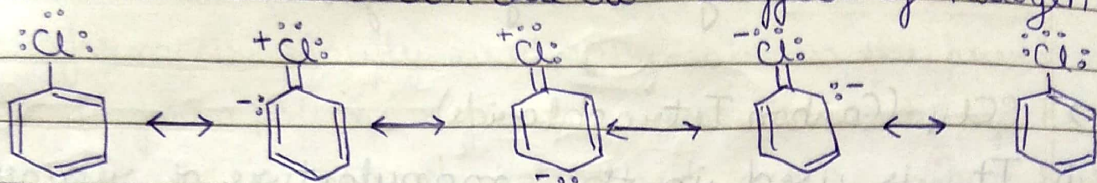


Examples

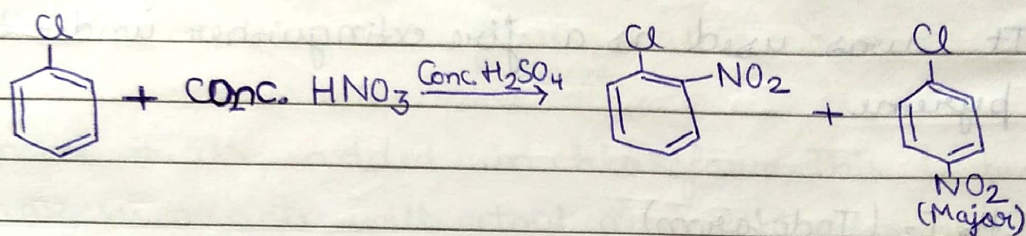


SE (Substitution electrophilic) reaction

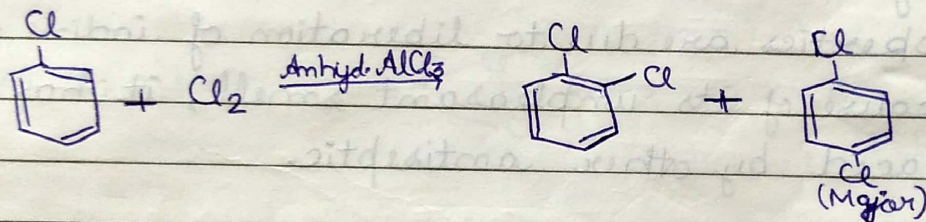
Haloarenes undergo substitution electrophilic reaction at ortho and para position due to +R effect of halogen atom. But haloarenes act as a deactivating towards SE reaction due to -I effect of halogen atom.



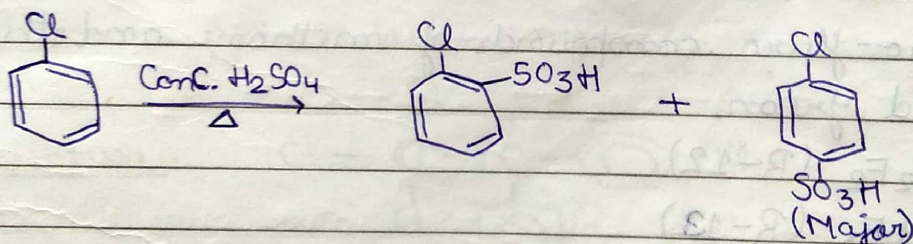
1. Nitration



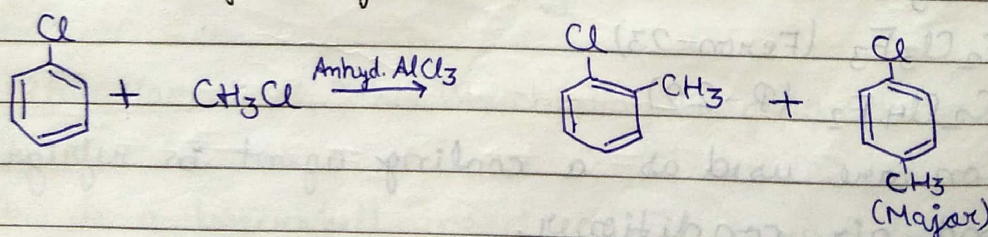
2. Halogenation



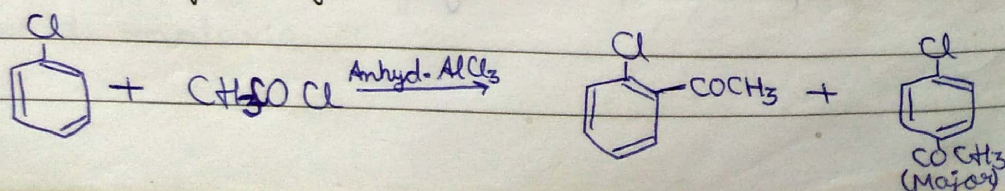
3. Sulphonation



4. Friedel Craft Alkylation



5. Friedel Craft Acylation



Polyhalogen Compounds

1. CH_2Cl_2 (Dichloro methane or Methylene dichloride)

It is used as a solvent for paint remover, as a propellant for aerosols and as a process solvent in the manufacture of drugs.

2. CCl_4 (Carbon Tetrachloride)

(i) It is used in the manufacture of refrigerants and propellant for aerosol.

(ii) It is used as a solvent in the manufacture of drugs.

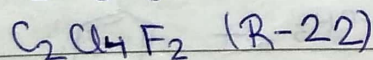
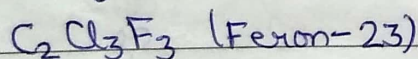
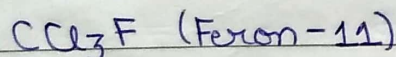
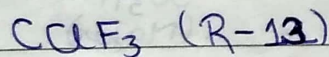
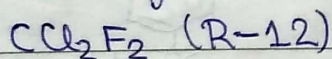
(iii) It was used as a fire extinguisher under the name pyrene.

3. CH_3I_3 (Iodoform)

Iodoform was used as an antiseptic. Its antiseptic properties are due to liberation of iodine atom. Because of its unpleasant smell, it has been replaced by other antiseptic.

4. Freons

Chloro-fluoro compounds of methane and ethane are called freon.



Freon are used as a cooling agent in refrigerator and air conditioner.

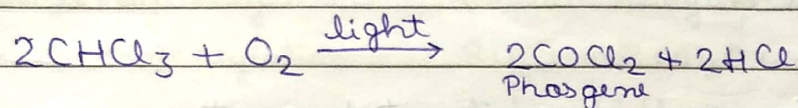
Freon depletes ozone layer.

5. CHCl_3 (Chloroform)

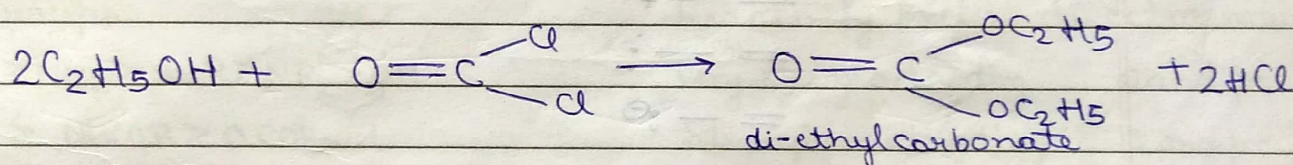
It is used as a solvent for rubber, oil, fats and iodine and other substances.

It is also used in the production of freon (R-22)

- * Chloroform is slowly oxidised by air in the presence of light to form poisonous gas phosgene or carbonyl chloride. Therefore it is stored in closed dark colour bottle to completely filled.

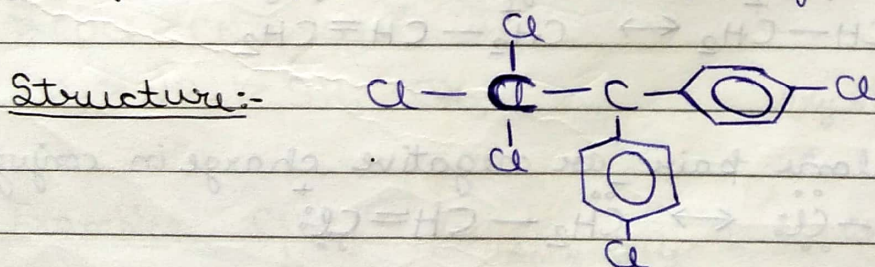


- * Alcohol is also added in chloroform. This is because phosgene reacts with ethyl alcohol to form a non-toxic diethyl carbonate.



6. DDT

Full form:- p,p'-Dichloro Diphenyl trichloro ethane



IUPAC Name:- 2,2 bis (4-chloro phenyl)-1,1,1 tri chloro ethane

Uses

It is a powerful insecticide. It is used for sugarcane. It is very effective against Anopheles mosquito which spread malaria.

Substitution Electrophilic (SE) reaction

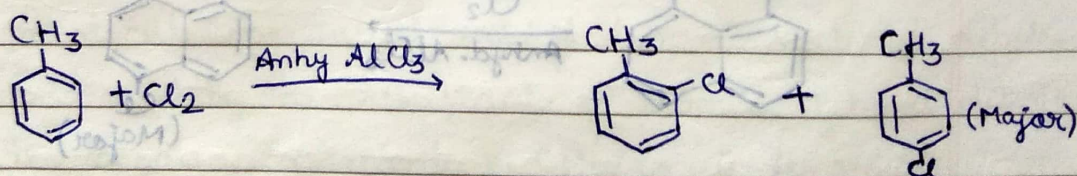
A reaction in which a strong electrophile displaces a weak electrophile from benzene ring is called SE reaction.

Examples of SE reaction	Reagents	Electrophile	Adding group
1 Nitration	$\text{HNO}_3(\text{conc.}) + \text{H}_2\text{SO}_4(\text{conc.})$	NO_2^+	NO_2
2 Halogenation	$\text{X}_2 (\text{Cl}_2 \text{ or } \text{Br}_2)$ with Anhyd. $\text{AlCl}_3 \text{ or } \text{BCl}_3 \text{ or } \text{FeBr}_3$	X^+	X
3 Sulphonation	Conc. H_2SO_4 or $\text{H}_2\text{S}_2\text{O}_7$	SO_3	SO_3H
4 Friedel craft alkylation	RX with anhyd. AlCl_3	R^+	$\text{R} (\text{CH}_3, \text{C}_2\text{H}_5)$ etc.
5 Friedel craft acylation	RCOCl or $(\text{RCO})_2\text{O}$ with Anhyd. AlCl_3	COR^+	COR

Reactivity order of different groups towards SE reaction

Groups	Reactivity order	directing nature
1. $\text{O}^- > \text{NH}_2 > \text{NHR} > \text{NR}_2 > \text{OH}$	very strong activating	o and p-
2. $\text{OR} > \text{NHCOR} > \text{OCOR}$	Strongly activating	o and p-
3. $\text{R} > \text{Ar} > \text{CH}_2=\text{CH}_2$	Activating	o and p-
4. $\text{X} (\text{F} > \text{Cl} > \text{Br} > \text{I}) > \text{NO} > \text{CH}_2\text{X} > \text{CHX}_2$	Deactivating	o and p-
5. $\text{CHO} > \text{COR} > \text{COOH} > \text{COOR} > \text{CONH}_2$ $> \text{COCl} > \text{CN} > \text{SO}_3\text{H}$	Strongly deactivating	m-
6. $\text{NO}_2 > \text{NR}_3^+ > \text{SR}_2^+ > \text{CX}_3$	very strongly deactivating	m-

Example \Rightarrow



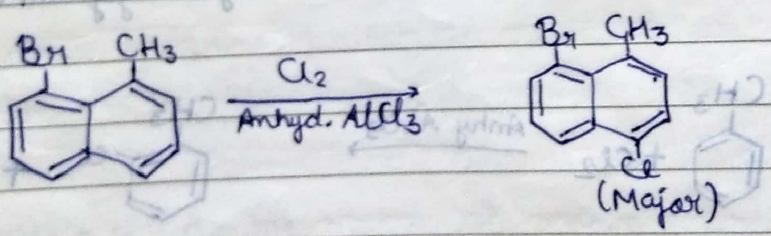
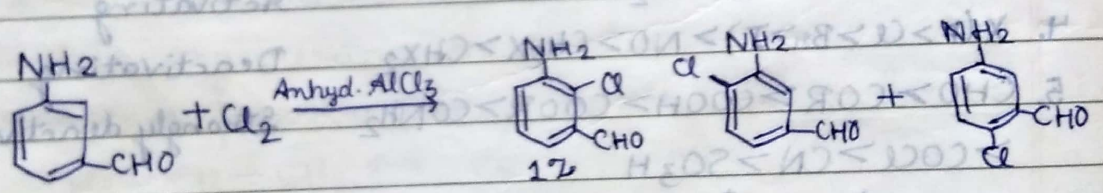
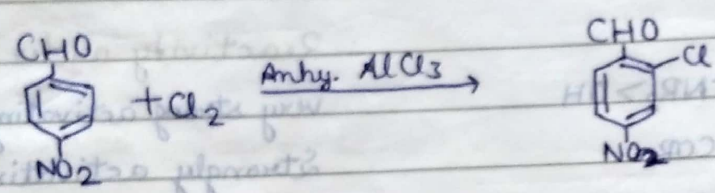
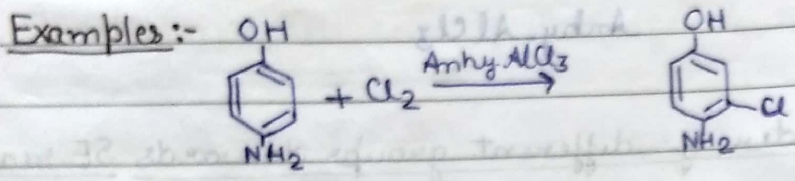
In case of disubstituted benzene

- (i) If activating and deactivating both group are present in a system then position of electrophile will be decided by activating group.

(ii) If both groups present in a system are activating then the position of electrophile will be decided by strongly activating group.

(iii) If both group present in a system are deactivating then position of electrophile will be decided by stronger deactivating group.

(iv) There is a little substitution between two groups that are meta to each other.



Dipole moment

$$\mu = q \times d \quad (\text{unit of } \mu = \text{Debye (D)})$$

(charge) (bond length)

Dipole moment depends on charge.

In case of diatomic molecule, dipole moment depends upon charge present on an atom. The magnitude of charge increase with increase in electronegativity.



In case of polyatomic molecule, the dipole moment of molecule depends upon resultant of bond dipole.

Bond dipole represent as follows:-

Less electronegative \rightarrow More electronegative

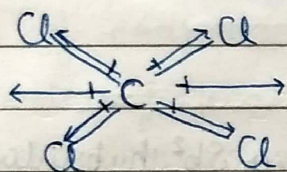
The resultant dipole moment calculated as follows:-

$$\mu_R = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$$

With increase in θ , the resultant of dipole moment decreases.

The magnitude of dipole moment of the following molecules:-

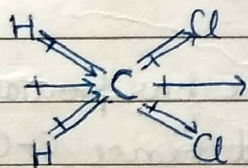
(i) CCl_4



$$\mu = 0$$

CCl_4 is a symmetrical molecule therefore dipole moment is 0.

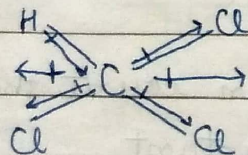
(ii) CH_2Cl_2



$$\mu = 1.62D$$

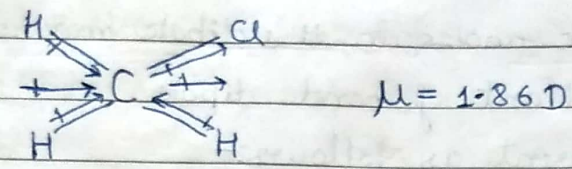
In CH_2Cl_2 molecule, the resultant of two C-Cl bond dipoles is reinforce (increase) by the resultant of two C-H bond dipole, therefore the dipole moment of CH_2Cl_2 is $\mu = 1.62D$.

(iii) $CHCl_3$



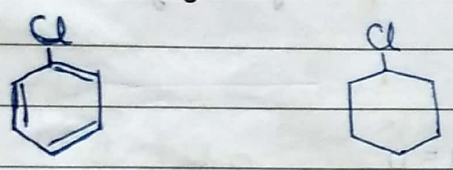
In CHCl_3 molecule, the resultant of two is oppose by the resultant of C-H and C-Cl bond dipole. Therefore the dipole moment of CHCl_3 is $\mu = 1.03 \text{ D}$.

(ii) CH_3Cl



In CH_3Cl , the resultant of two CH bond dipole is reinforce by the resultant of CH and CCl bond dipole. Therefore CH_3Cl has a dipole moment 1.86 D .

* Which of the following molecule has high dipole moment chlorobenzene or Cyclohexene chloride.



In chlorobenzene, carbon atom is Sp^2 hybridised and in cyclo-chloride hexile, carbon atom is Sp^3 hybridised. Sp^2 hybrid carbon atom has greater electronegativity than that of Sp^3 hybrid carbon atom therefore C-Cl bond in chlorobenzene is less polar.

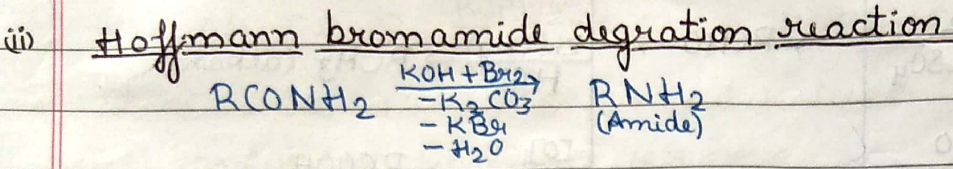
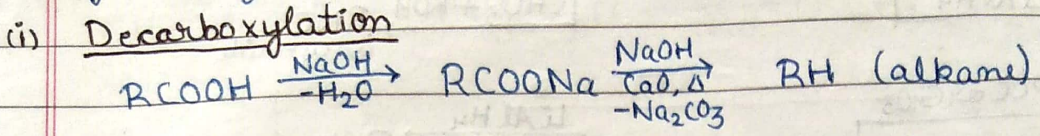
Further, C-Cl bond in chlorobenzene has partial double bond character due to resonance and hence C-Cl bond length is less in chlorobenzene.

As a result the dipole moment of cyclo hexile chloride is higher than that of chlorobenzene.

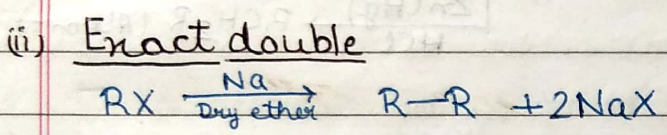
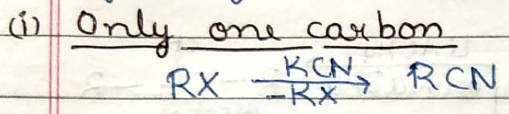
Rules for Conversion:-

1. Apply name reaction.
2. If name reaction is not apply, then count the no. of carbon atoms in product and reactant.

Three condition arise:- If no. of carbon atom decrease, apply following reaction:-

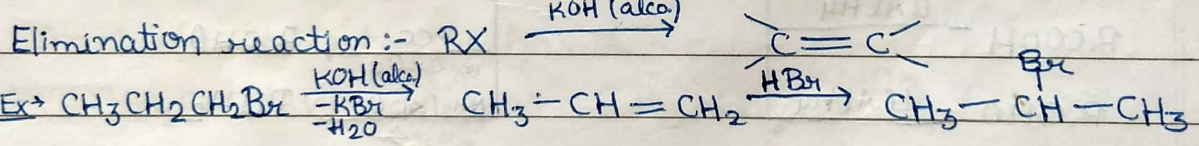
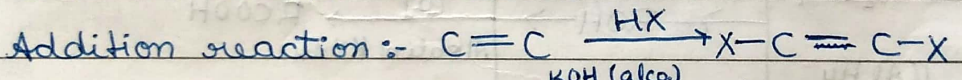


If no. of carbon atom increase:-

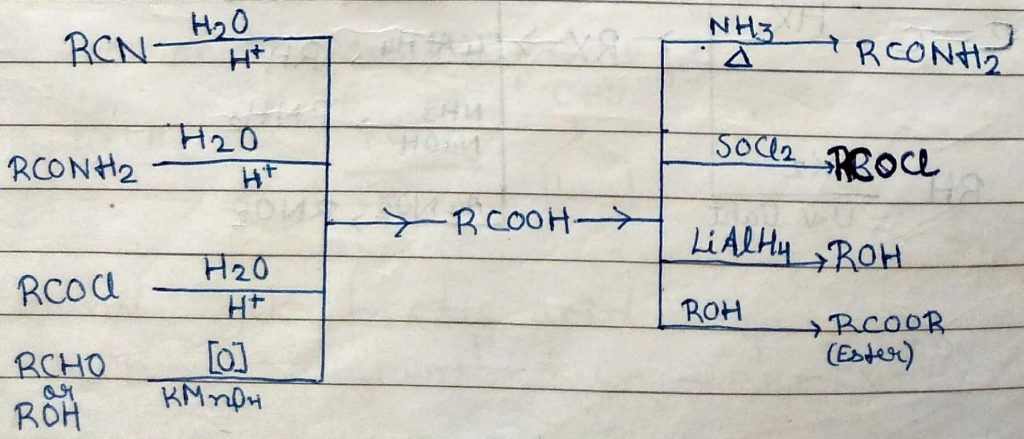


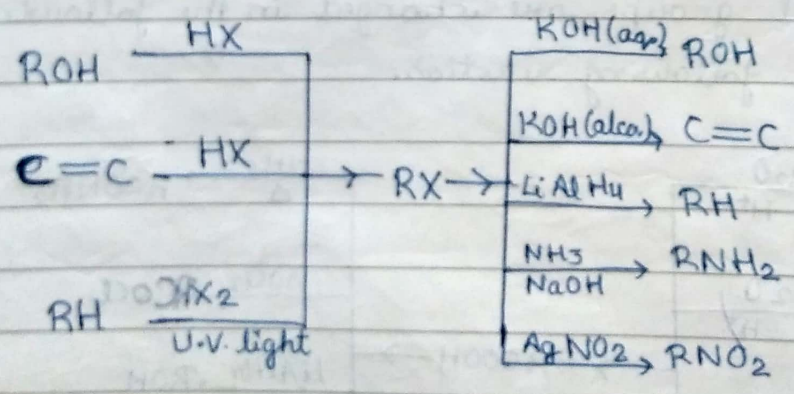
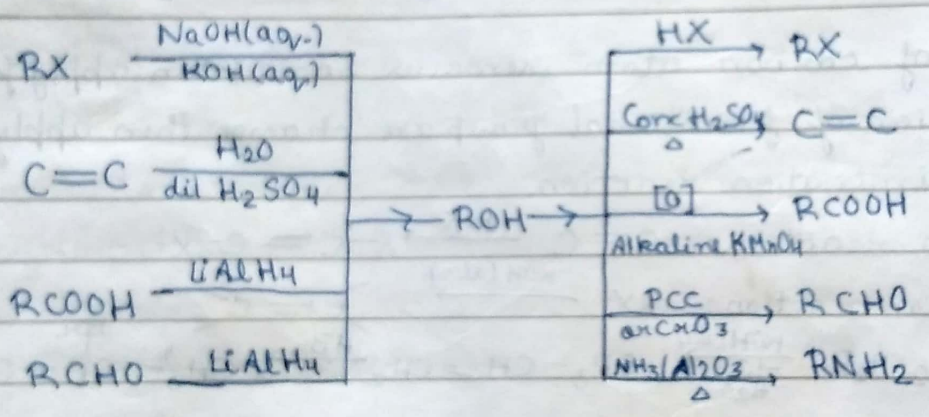
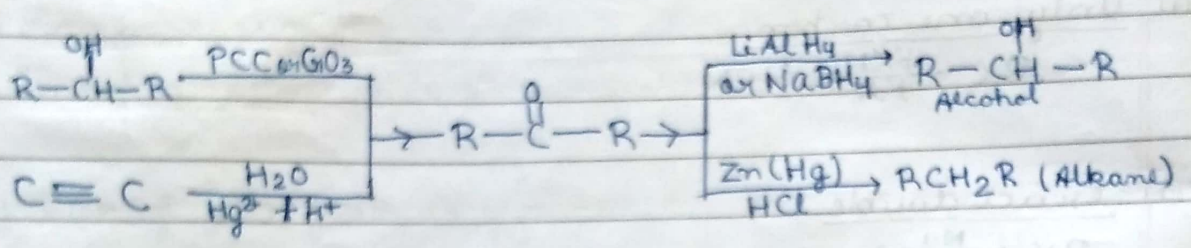
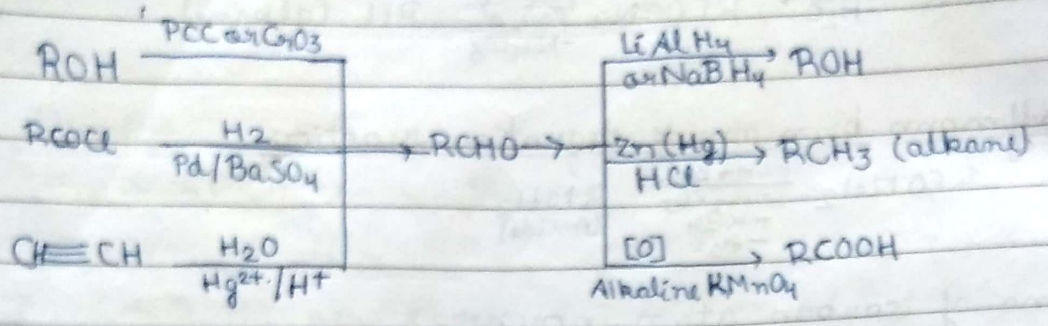
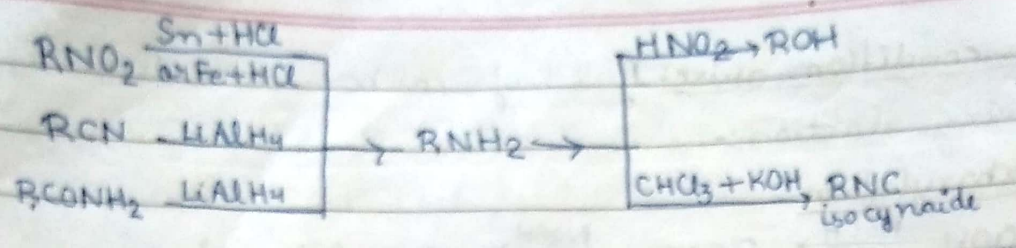
If no. of carbon atom remains same; then apply following react

(i) If position of functional group are change then apply addition and elimination reaction.



If functional groups are changed in the following conversion then apply following reaction.

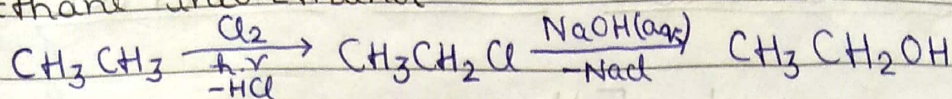




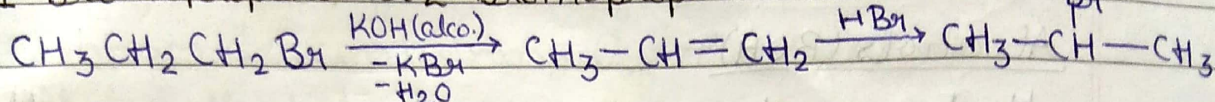
SBG STUDY

Conversion

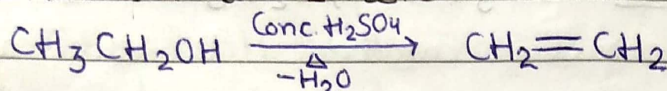
Ethane into Ethanol



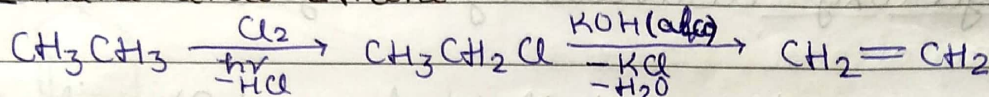
1-Bromopropane or 2-Bromopropane



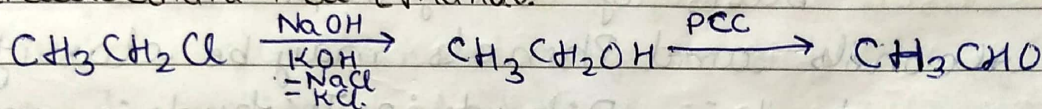
Ethanol into Ethene



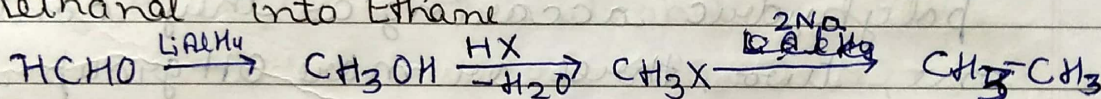
Ethane into Ethene



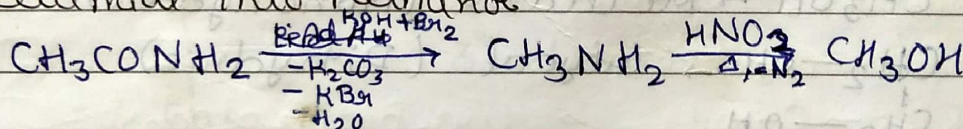
Chloroethane into Ethanal



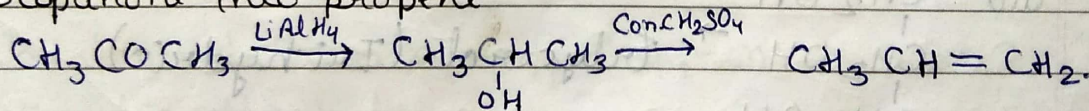
Methanal into Ethane



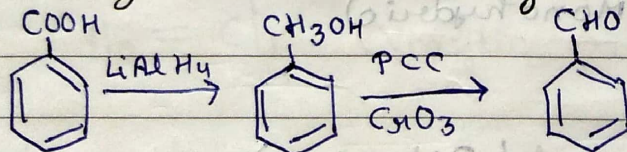
Acetamide into Methanol



Propanone into propene



Benzoic acid into Benzaldehyde



Ethanol into Lactic acid.

