

2 April 24

Halo

(Halogen)

$F > Cl > Br > I$

Alkanes

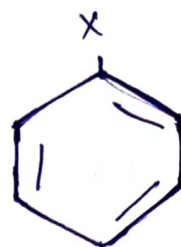
$R \rightarrow CH_3$ - Alkanes.

$CH_2 = CH$ - Alkenes

$CH \equiv C$ - Alkynes.

Arenes

Benzene.



* Classification of Haloalkanes & Halobenzenes :-

→ On the basis of no. of halogens.

(Haloalkanes)

① Monohaloalkanes.

(1 halogen R.)

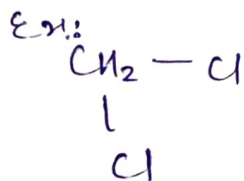
Ex: $CH_3 - Cl$.

$CH_3 - CH_2 - Cl$.

② Dihaloalkanes (2 halogen)

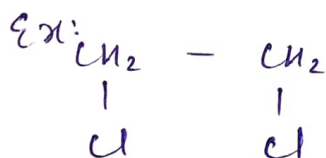
(a) Gem halide

C to 2 halo.



(b) Vicinal dihalide

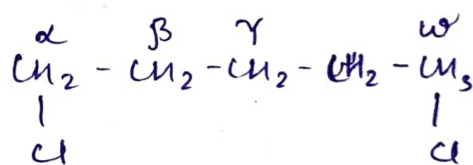
adjacent C to 2 halo.



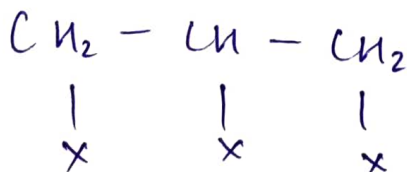
(c) α, ω dihalide.

α, ω to halo.

Ex:



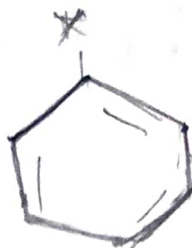
③ Tri haloalkane (3 halogen).



(Haloarenes)

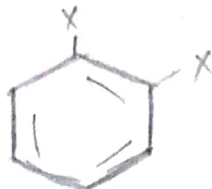
① Monohaloarenes.

Ex.:



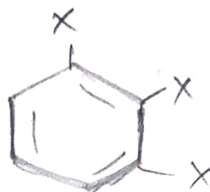
② Dihaloarenes.

Ex.:



③ Trihaloarenes.

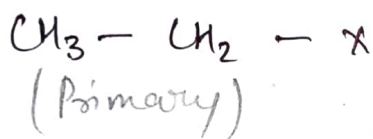
Ex.:



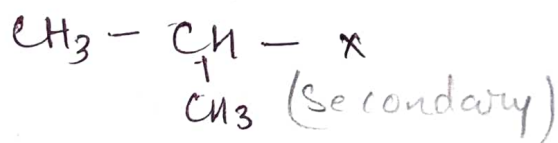
→ On the basis of sp^3 carbon :-

Alkyl

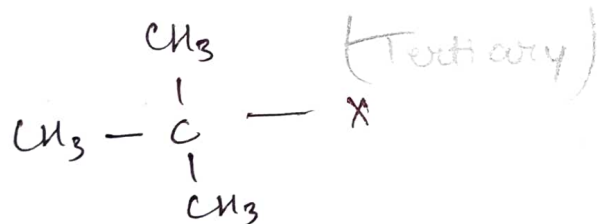
1° Haloalkane



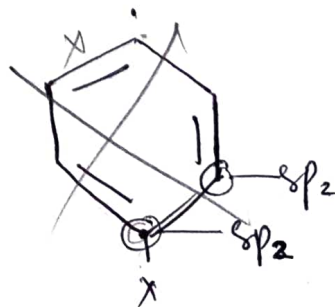
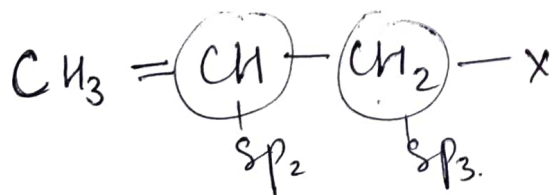
2° Haloalkane,



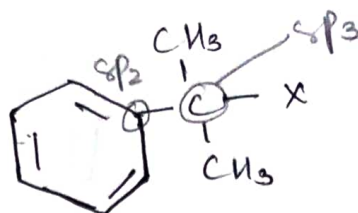
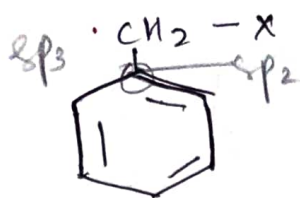
3° Haloalkane.



Allylic Halide.

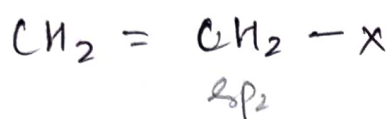


Benzylic

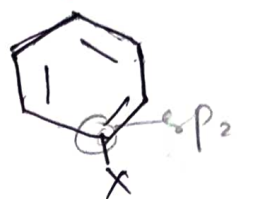


→ On the basis of sp^2 Carbon:-

Vinylic group



Aryl group.



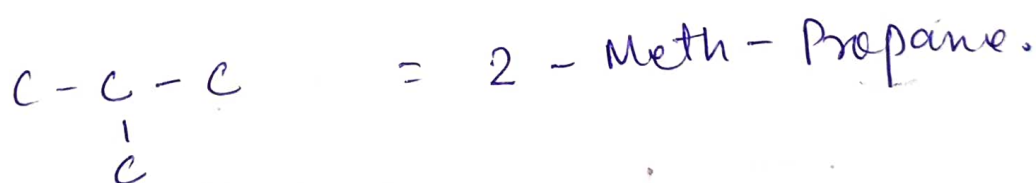
(Benzene).

ISOMERISM.

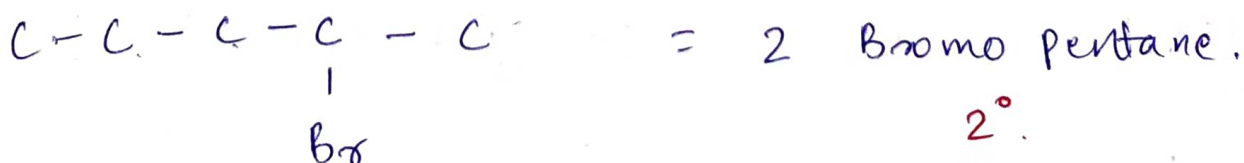
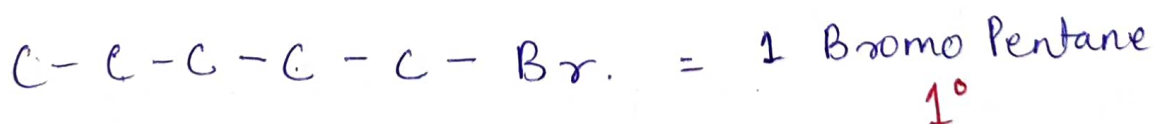
Chain

Position.

① Chain Isomer: C_4 .



② Position Isomer: $C_5 H_{11} Br$.

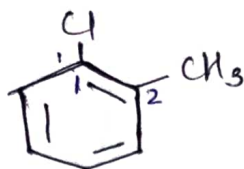


IUPAC

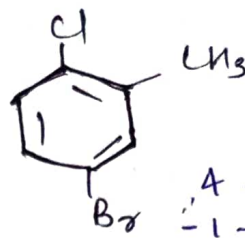
Name of cyclic / Aromatic.



Chloro Benzene

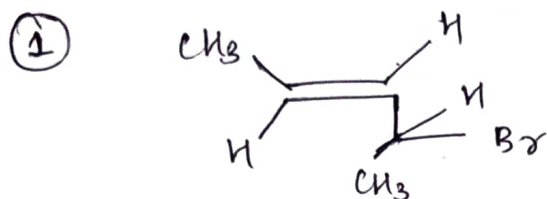


1-chloro-2-methyl Benzene.

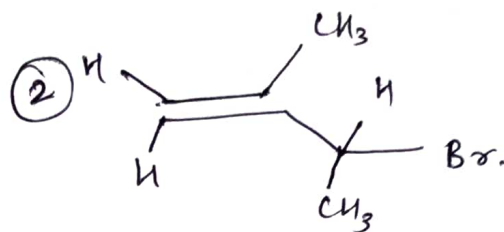


4-bromo-1-chloro-2-methyl Benzene.

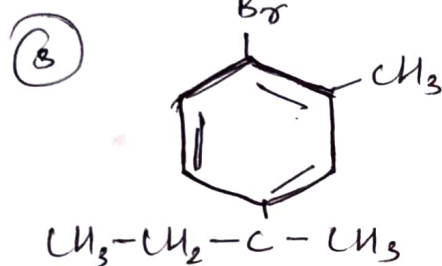
Example:



4-bromo-pent-2-ene

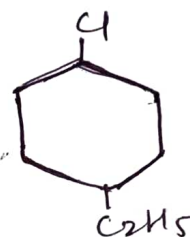


3-bromo-2-methyl but-1-ene.



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

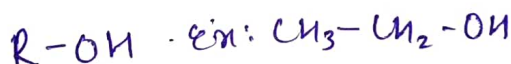
④



1-chloro-4-ethyl cyclohexane.

METHOD OF PREPARATION.

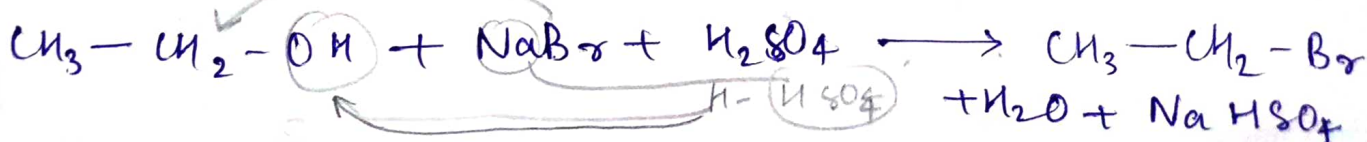
① From Alcohol.



(a) From Lucas Reagent

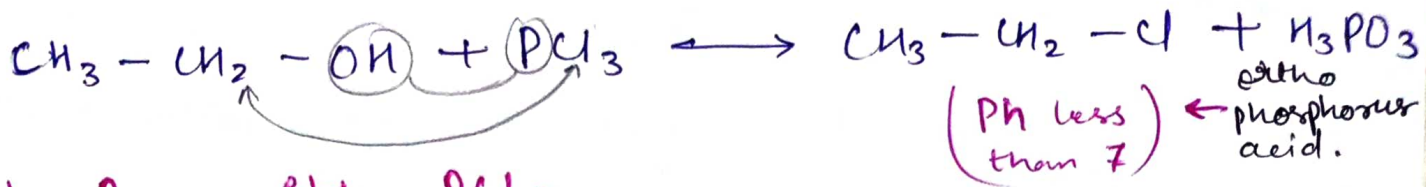


(b) From $\text{NaBr} + \text{H}_2\text{SO}_4$ (पानी निकालना)

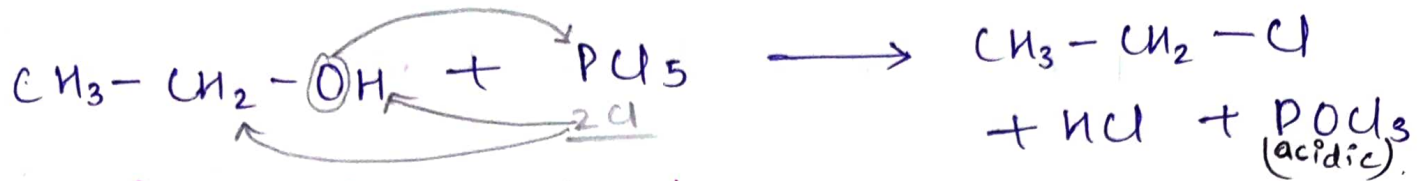


* Phosphorus (P) non metal oxide are acidic.

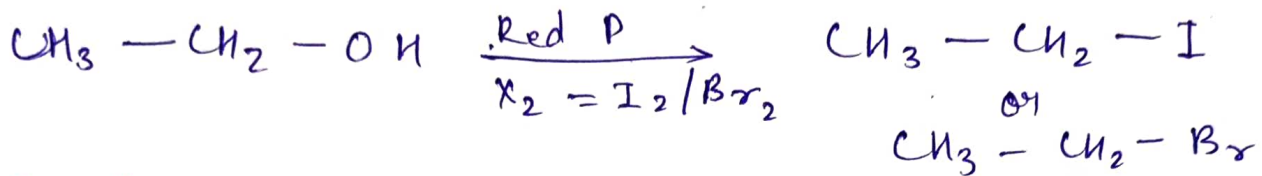
(c) From PCl_3



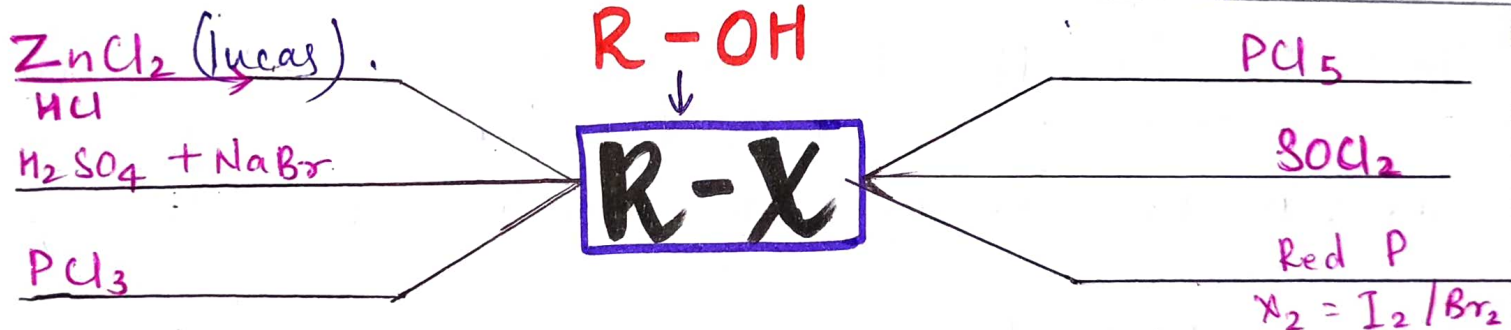
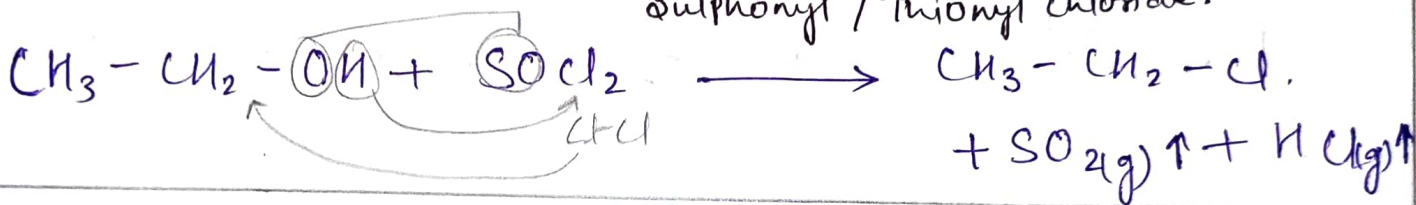
(d) Rxn with PCl₅



(e) Rxn with Red P / X_2 Br_2 or I_2 .

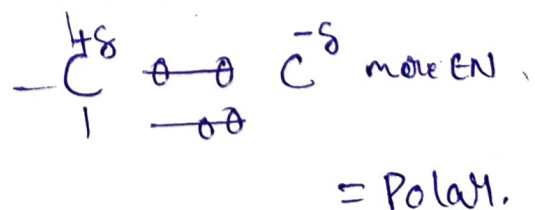


(f) Rxn with SOCl_2 . (Best Method)
Sulphonyl / Thionyl chloride.



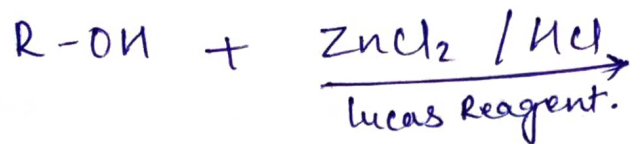
NATURE OF R-X BOND.

X = Halogen.



R-X bond are polar in nature because halogens are highly electro negative (EN).

Note :



★ Lucas Reagent shows the turbidity test of alcohol.



Reactivity order of Alcohol:



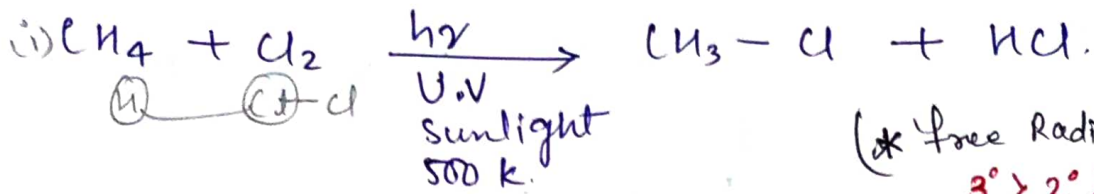
Note : The pH of system decreases when R-OH react with PCl_3 / PCl_5 / Red P.

Reason: Due to the formation of H_3PO_3 or H_3PO_4 .

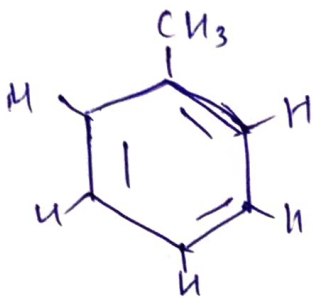
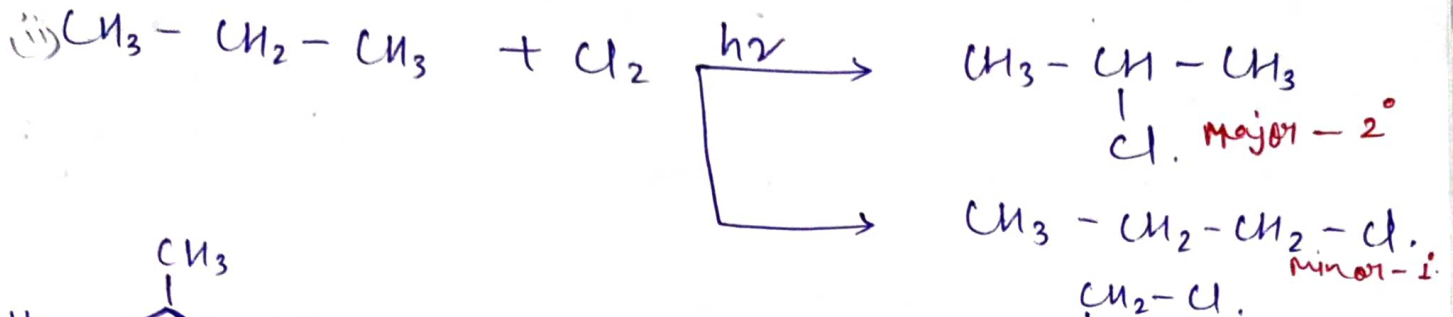
Note : Best method for making R-X from R-OH are $SOCl_2$ (sulbonyl chloride) Due to all the biproducts are in gaseous form (HCl, SO_2) which is eliminated.

Mono Chloro derivative
= 1 Cl product.

② From Alkanes:

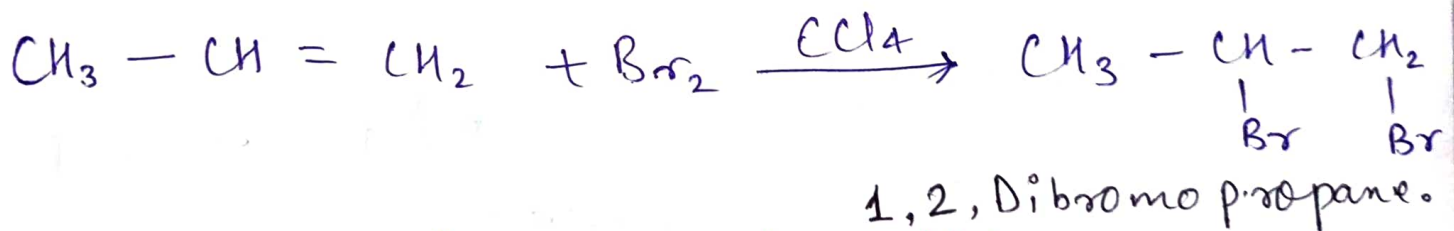
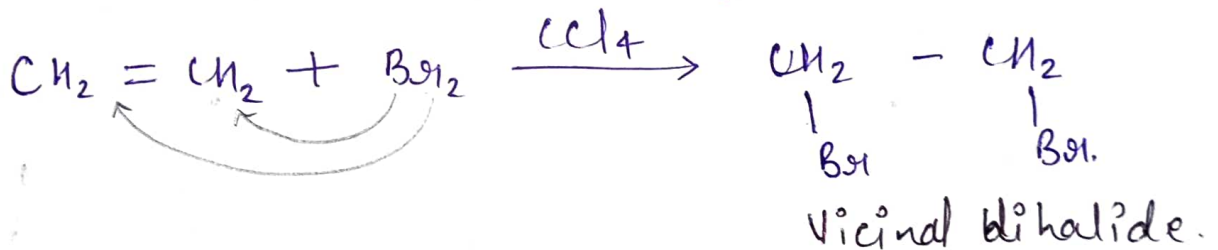


(* Free Radical mechanism)
 $3^\circ > 2^\circ > 1^\circ$

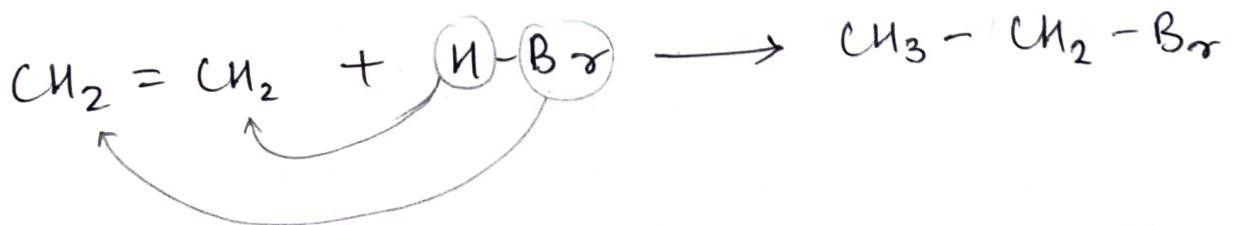


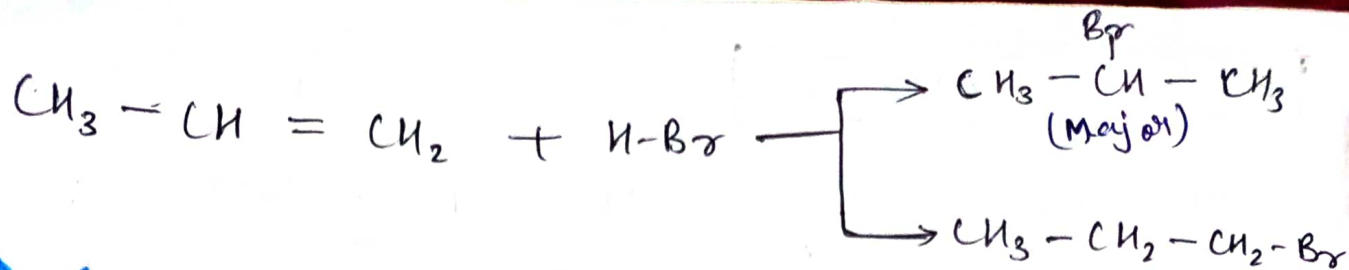
③ From Alkenes:

(a) Rxn. with Br_2 in the presence of CCl_4 .



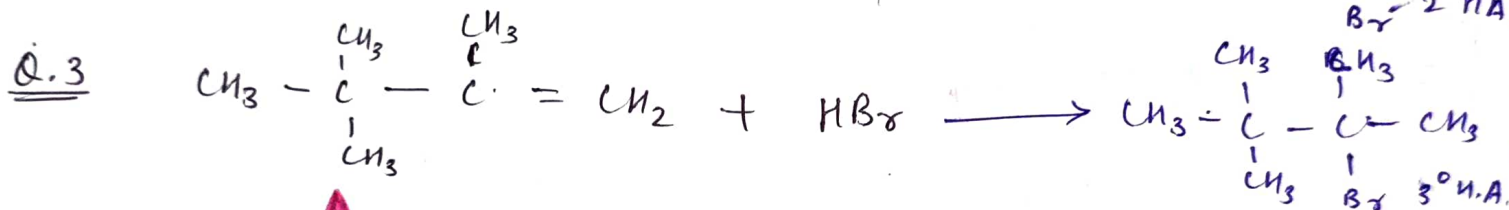
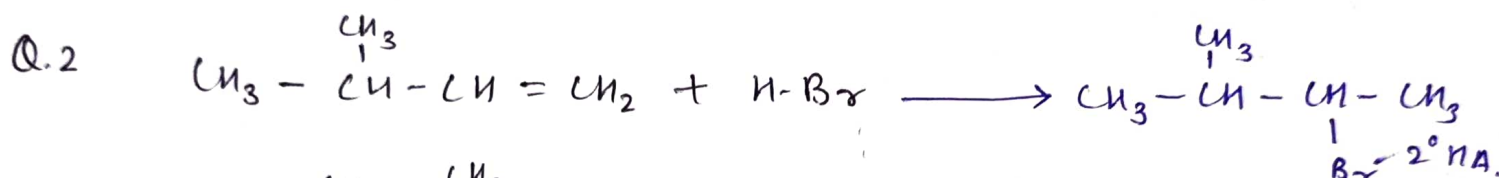
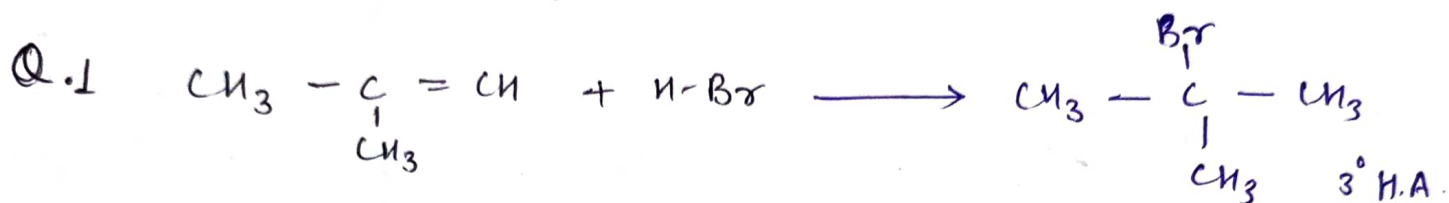
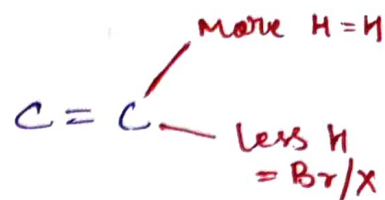
(b) Addition of Hydrohalogenation.
(H-X)





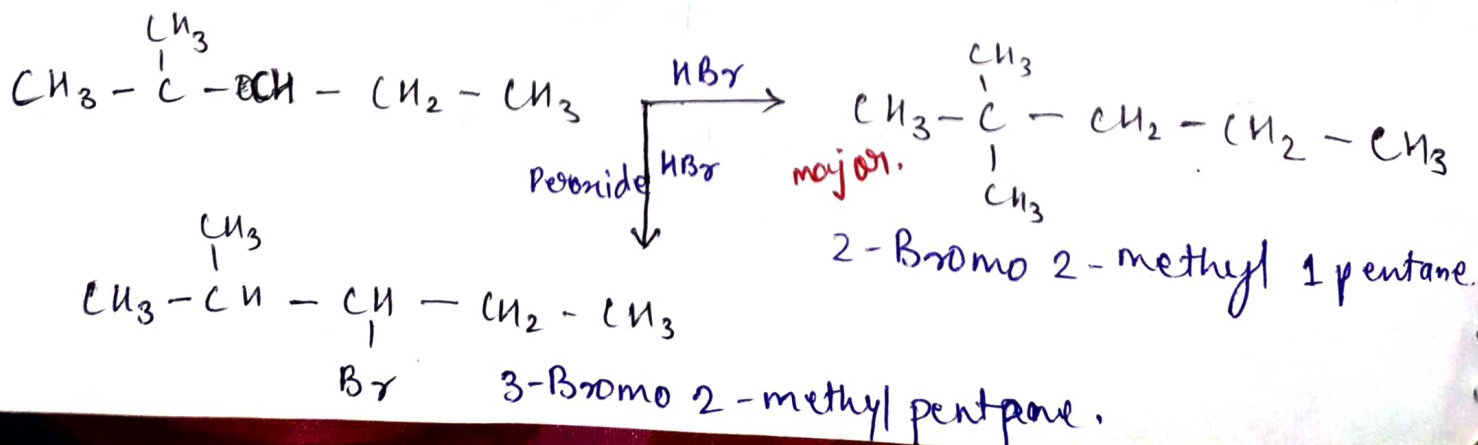
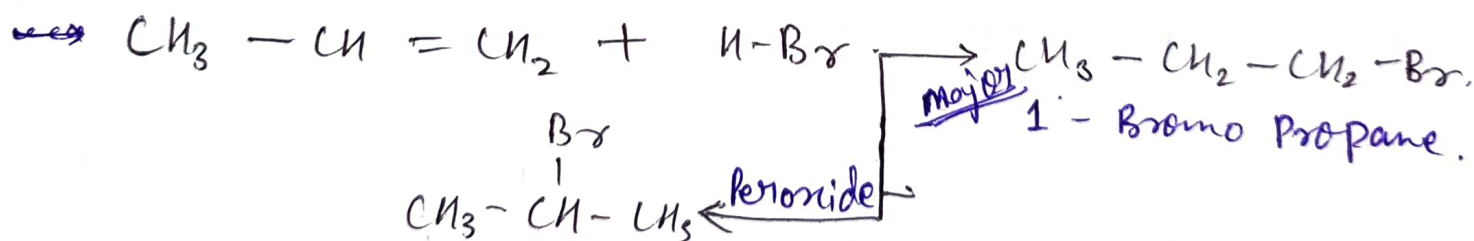
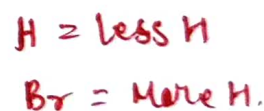
MARKONIKOV Rule:

- ~~H~~ not give mark addition
- Intermediate = Carbocation.

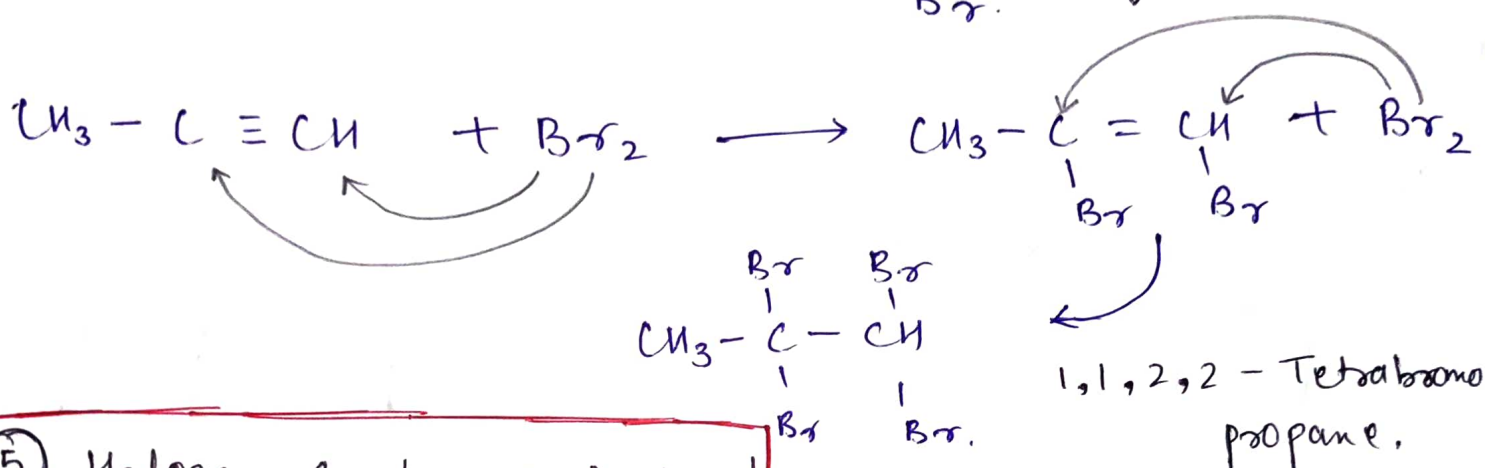
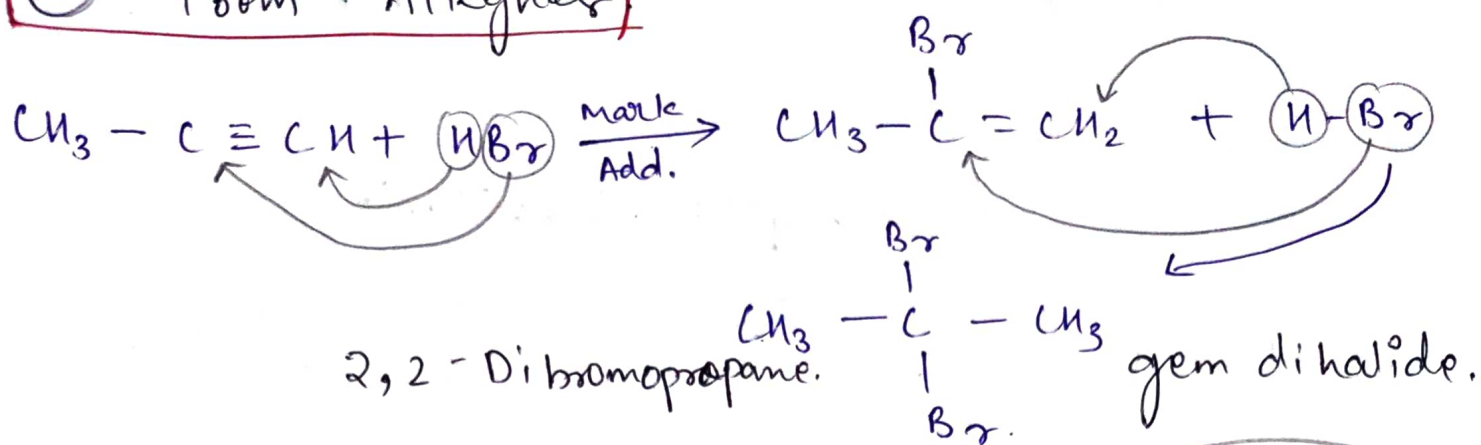


ANTIMARKONIKOV Rule :- (Kharasch Effect) (Peroxide effect)

- Intermediate = Carbon free Radical.



④ Form Alkynes

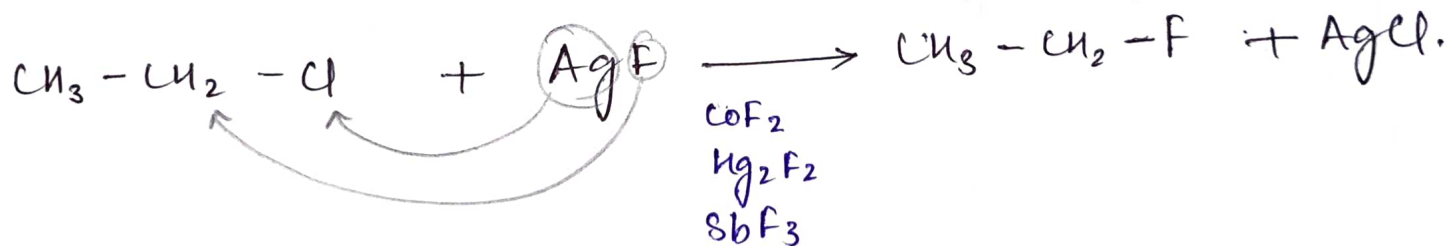


⑤ Halogen Exchange Method

(a) Finkelstein Rxn.

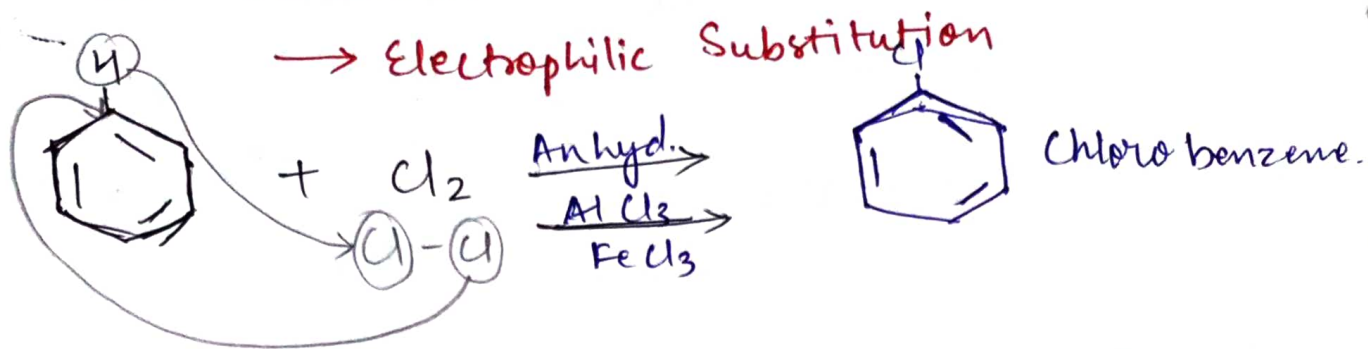


(b) Swarts Rxn. one & only method for making fluoroalkane.

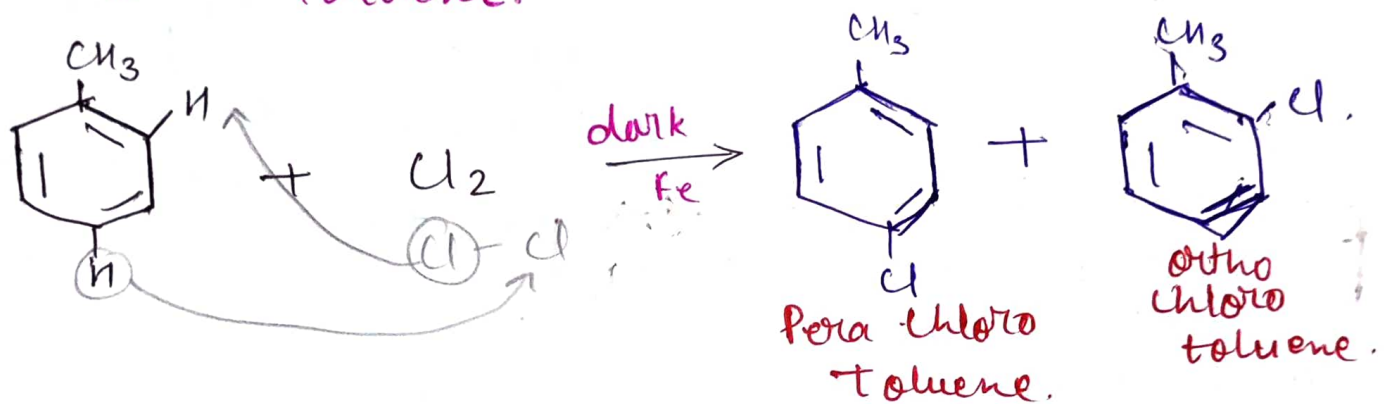


PREPARATION OF HALOARENES.

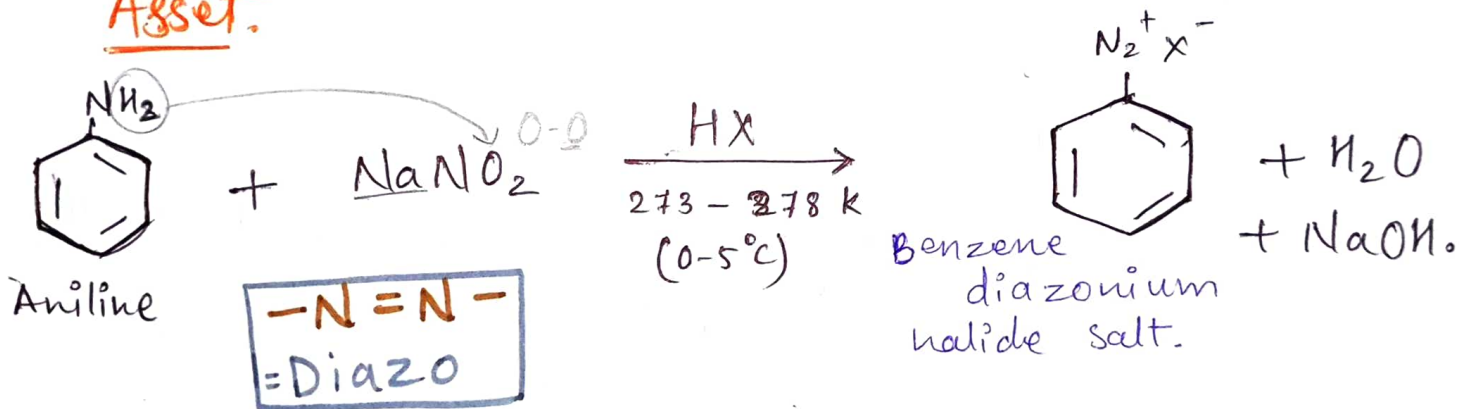
① From Benzene.



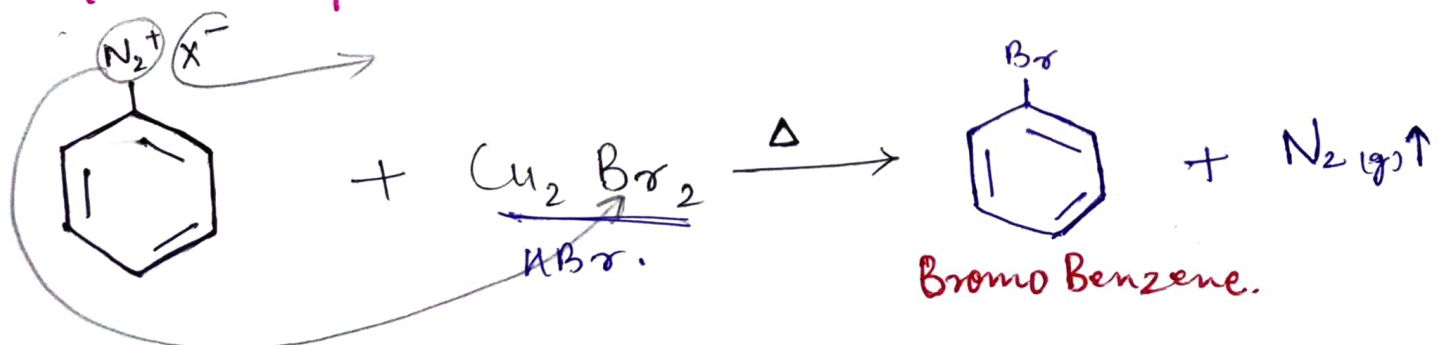
② From Toluene.

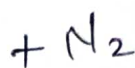
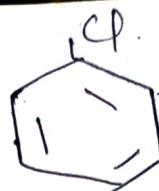
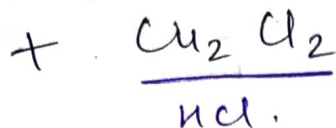
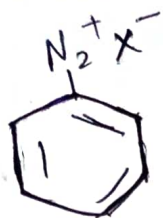


③ From Aniline Asset.

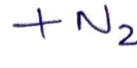
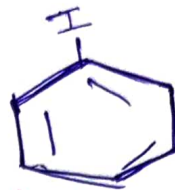
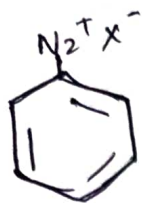


(a) Sand Meyer's Reaction



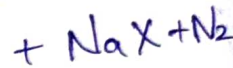
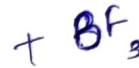
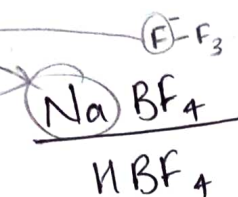


Chlorobenzene.



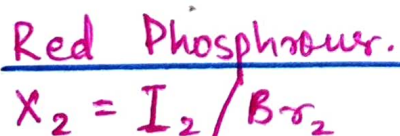
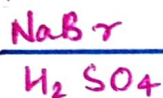
Iodobenzene.

(b) Balz Schizmann Rxn.



Fluorobenzene.

R-OH.



Alkanes.

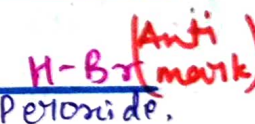


Alkene

Alkene



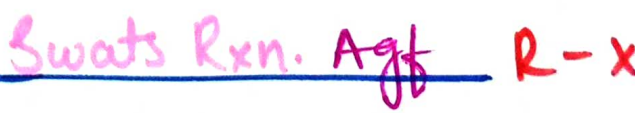
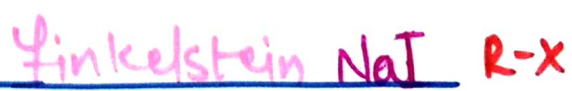
Alkene

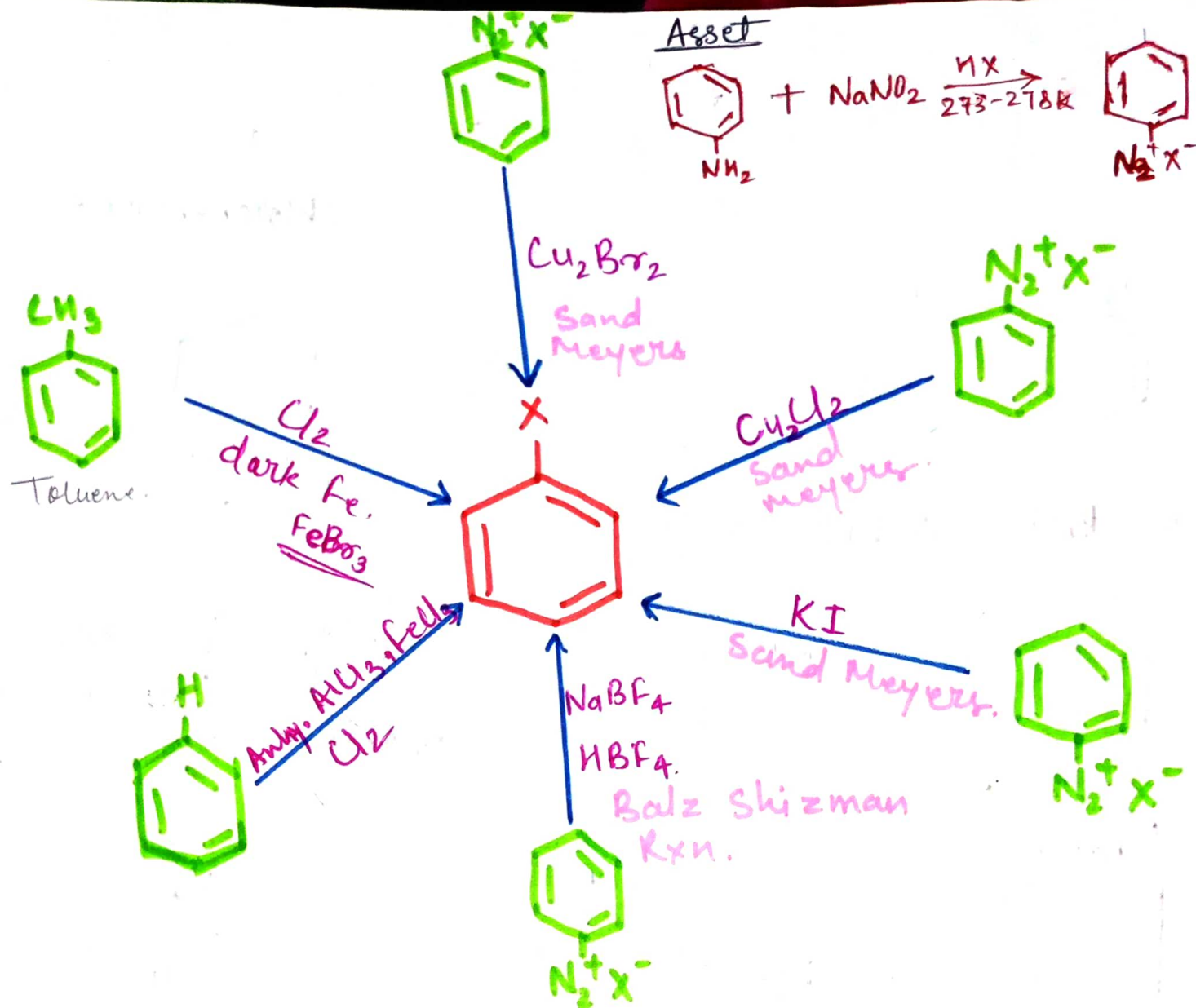


Alkyne



Alkyne





Q. Which of the following sequence of reactions is suitable to synthesise chlorobenzene?

(a) Phenol, NaNO_2 , HCl , CuCl .

(b) , HCl .

(c) , HCl , heating.

☒ (d) Benzene, Cl_2 , anhydrous FeCl_3 .

6, 2 $\rightarrow$ Ortho.

3, 5 $\rightarrow$ Meta

4 $\rightarrow$ Para.

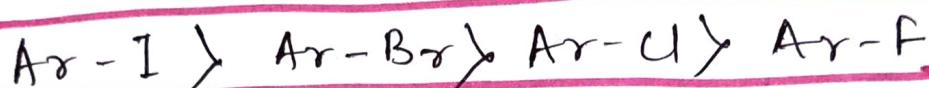
Physical Property

HALOALKANES

- ① State: $C_1 - C_3$: gas CF_3Cl , $CHCl_3$; CF_3Cl : gas.
 $C_3 < C_x$: liq + solid. $CH_3 - Br$ exception.
- ② Colour: Colourless but Bromo & Iodo derivatives
(only in the presence of sunlight) colourful.
- ③ Taste: Tasteless.
- ④ Odour: Lower $R-X$ have sweet smell & others are odourless.
- ⑤ Solubility: Polar Nature, No. of C $\uparrow$ = solubility $\downarrow$
 $\propto EN \propto \frac{1}{\text{group of R}}$ $\propto \frac{1}{R(C)}$
- ⑥ MP / BP : $MP / BP \propto MW$
 $R-I > R-Br > R-Cl > R-F$
 $M.P. / B.P. \propto \frac{1}{\text{Branching}}$
- ⑦ Density: Density $\propto MW$ lighter than water.
 $CH_3 \frac{F}{9} < CH_3 \frac{Cl}{35.5} < CH_3 \frac{Br}{80.5} < CH_3 \frac{I}{127}$

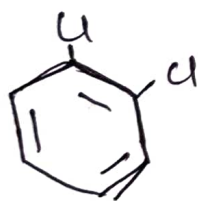
HALOARENES

- ① State : Liquid.
- ② Colour : Colourless.
- ③ Taste : Tasteless
- ④ Odour : odourless.
- ⑤ Solubility : slightly Soluble. $\frac{\text{Insoluble}}{\text{Due to Benzene Ring.}}$
- ⑥ Density : Density & Mw higher than water



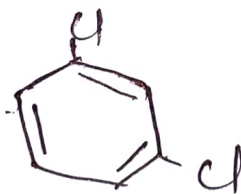
- ⑦ Melting Point / Boiling Point (Di halo derivative)
Approximately same (Boiling Point)
 $\text{R-I} \approx \text{R-Br} \approx \text{R-Cl} \approx \text{R-F}$

But in Melting Point.



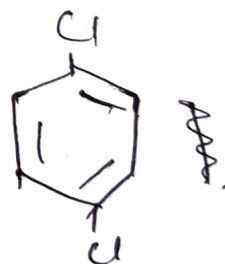
Ortho

<<



Meta

<<



Para.

→ Difference in MP in Para group is due to symmetry of para groups.

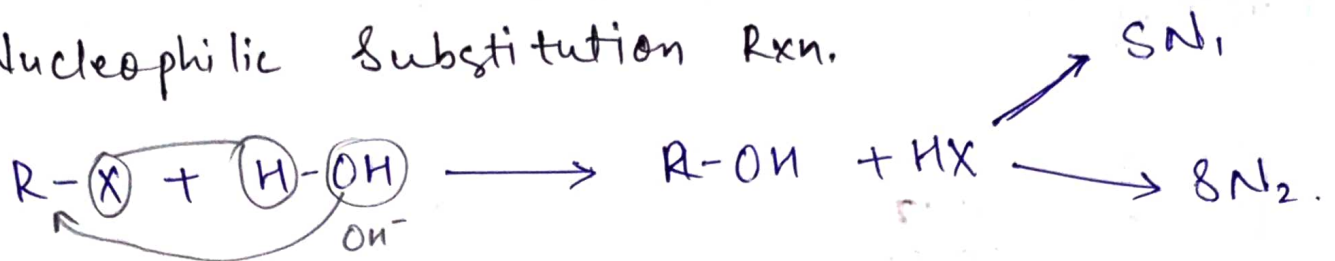
Para > ortho > Meta.

Chemical Property

HALOALKANES.

① Nucleophilic Substitution Rxn.

2.5★

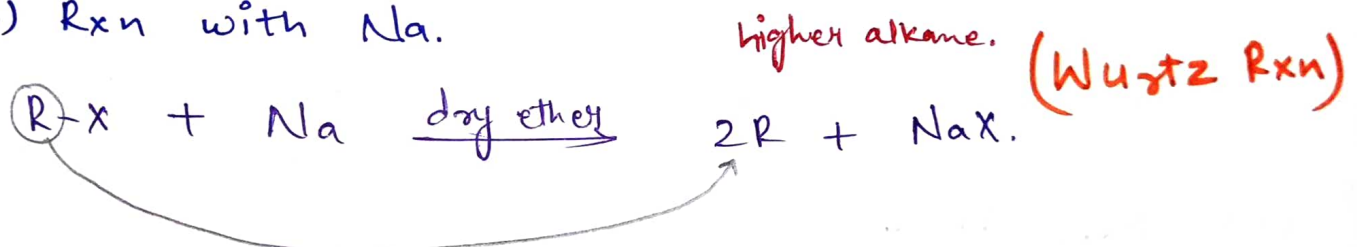


② Elimination Rxn (α, β) (Saytzev Rule)

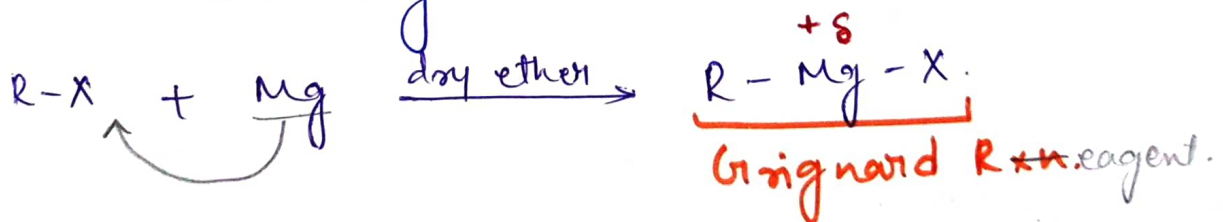


③ Rxn with Metal.

(a) Rxn with Na.



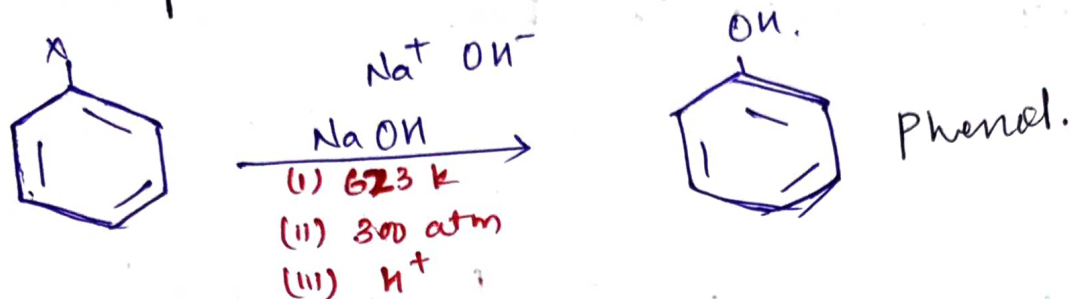
(b) Rxn with Mg.



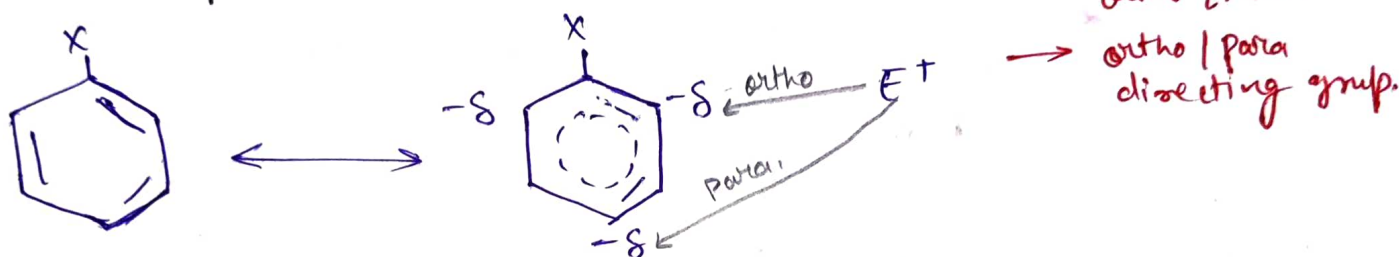
HALOARENES.

Attacking agent is always electrophilic when it reacts on benzene.

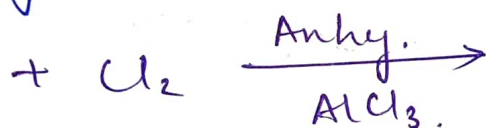
① Nucleophilic Substitution Rxn.



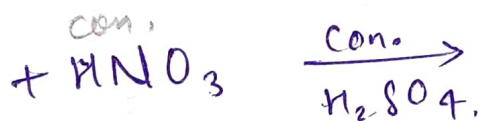
② Electrophilic Substitution Rxn.



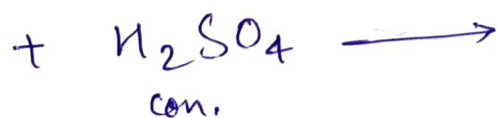
(a) Halogenation. / Chlorination.



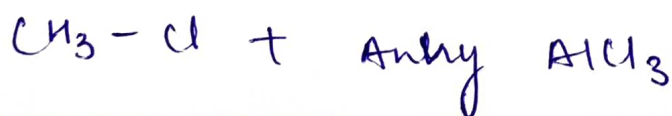
(b) Nitration.



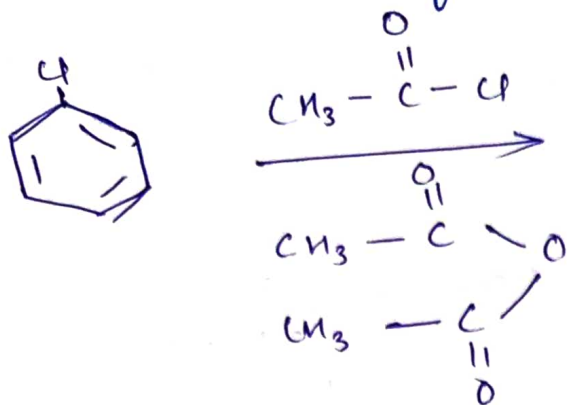
(c) Sulphonation.



(d) Friedel Craft Alkylation Rxn.

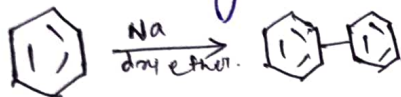


(e) Friedel craft Acylation Rxn.

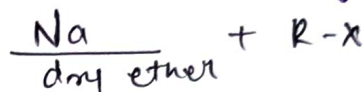


③ Rxn with Metal.

(a) Fittig Rxn



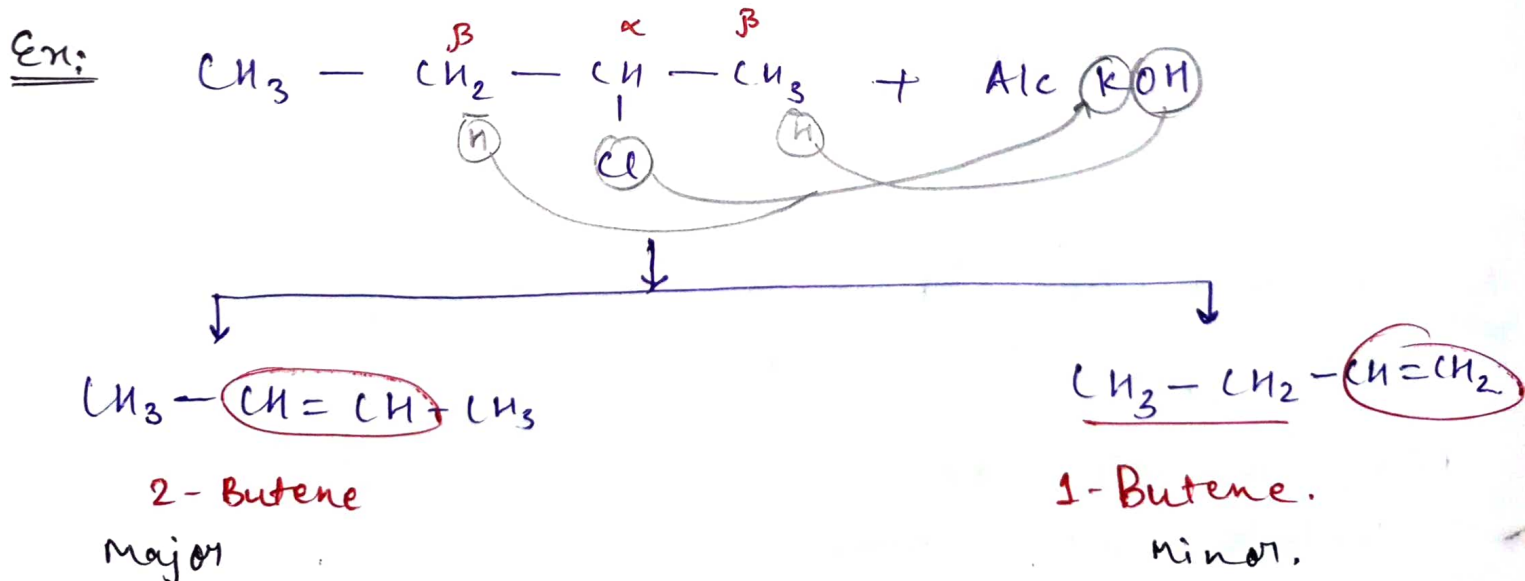
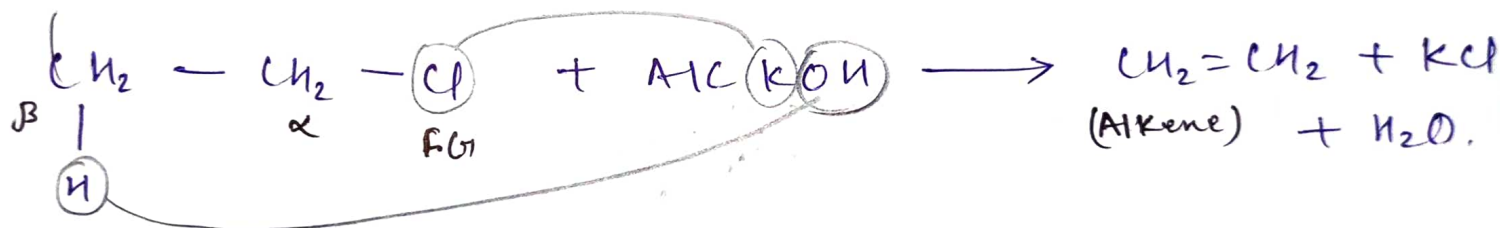
(b) Wurtz Fittig Rxn.



EXPLANATIONS:

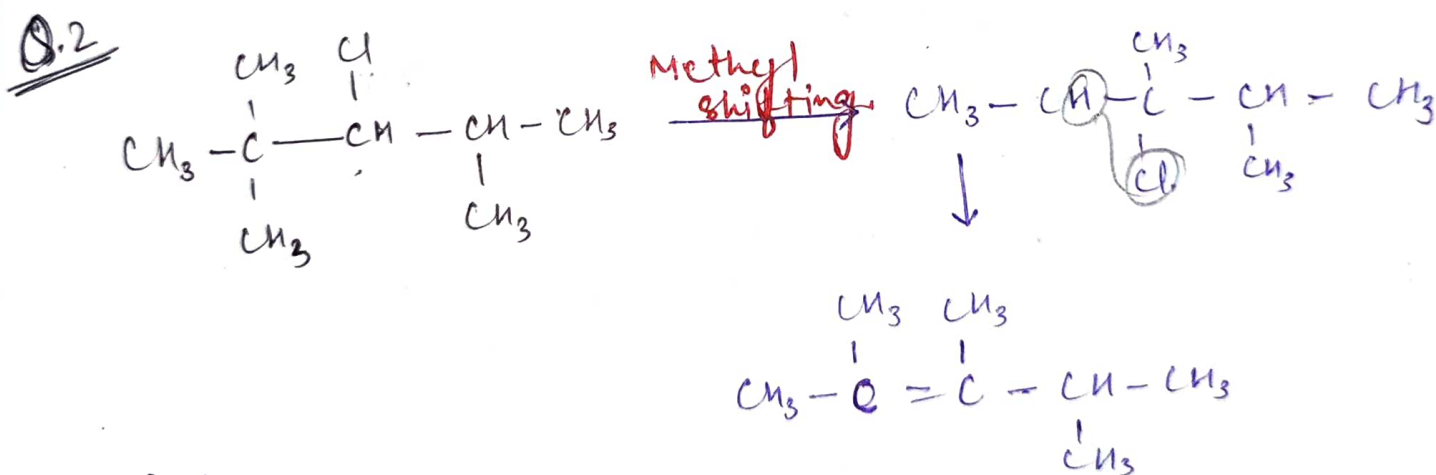
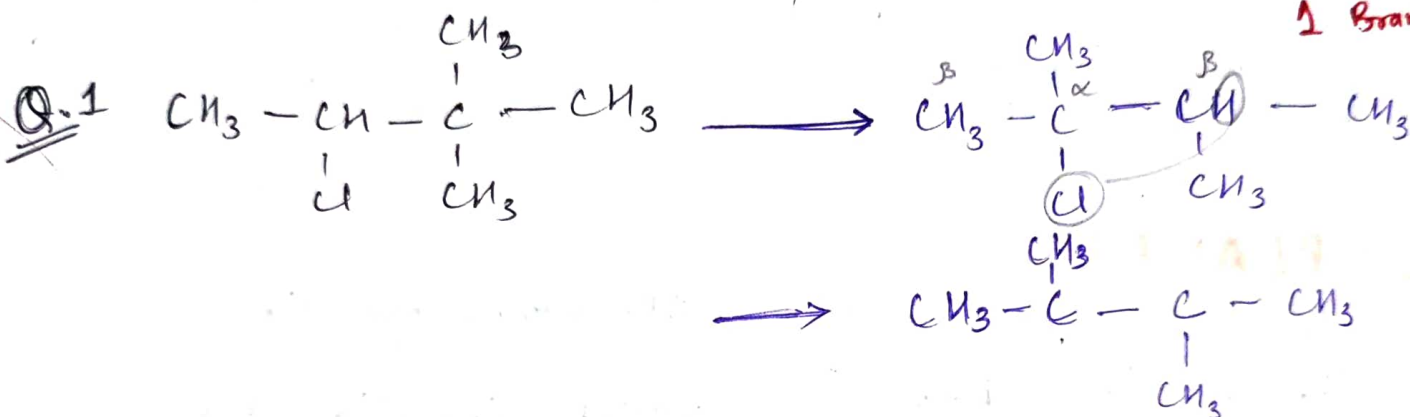
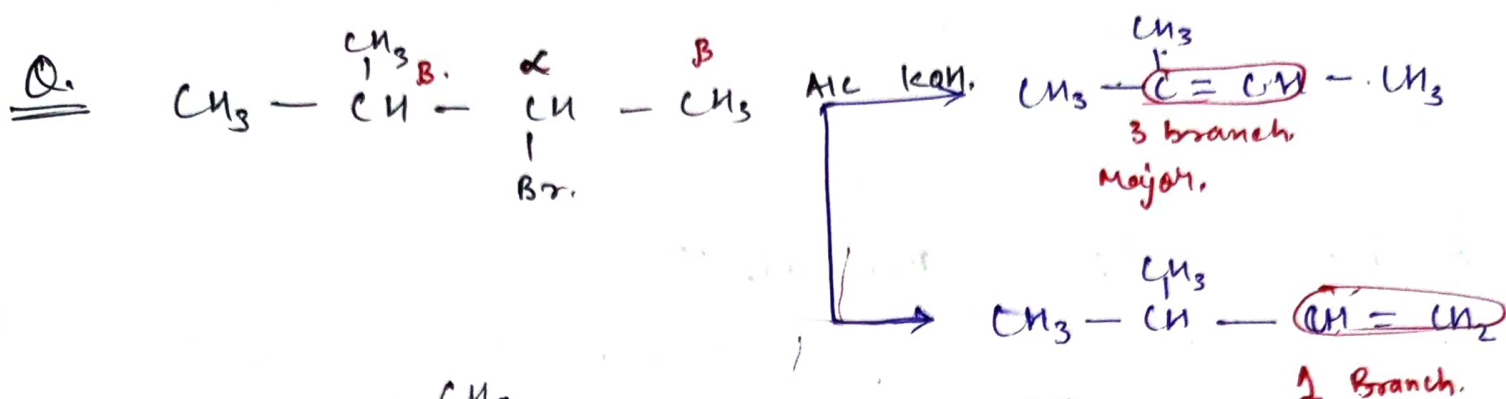
Haloalkanes.

② Elimination Rxn.
 ① Dehydro halogenation.
 ② α, β elimination Rxn.



↑ **Saitzev (Saytzeff) Product.**

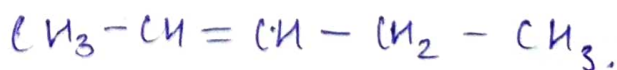
- More branch of $-\overset{|}{C}=\overset{|}{C}-$
C have more stability.



Q. Elimination rxn of 2-bromo-pentane to form pent-2-ene is:

$$\begin{array}{c}
 \text{CH}_3 \\
 | \\
 \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \\
 | \\
 \text{Br}
 \end{array}$$

1. β -elimination rxn.
2. Follows Zaitsev rxn.
3. Dehydrohalogenation rxn.
4. Dehydration rxn.



(a) 1, 3, 4 (c) 1, 2, 4

(b) 2, 3, 4 (d) 1, 2, 3

Q. For the following reactions. (NEET 2016).

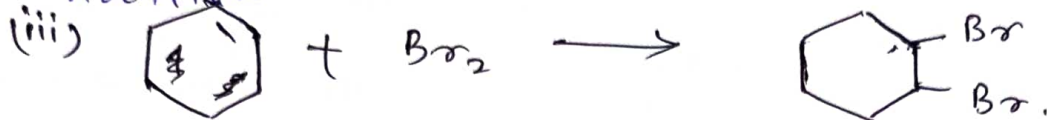
elimination.



substitution.



Addition.



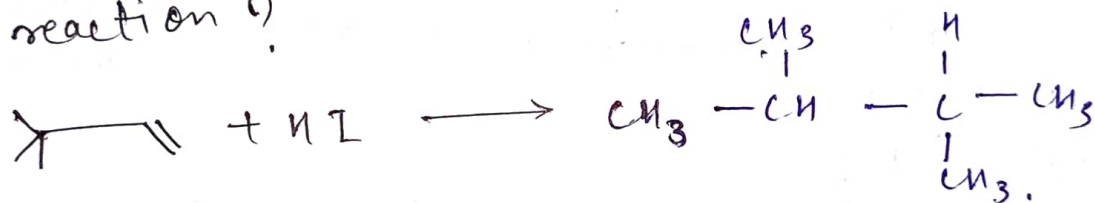
~~(a)~~ (i) is elimination rxn (ii) is substitution (iii) Addition rxn.

(b) (i) elimination rxn (ii) and (iii) are substitution.

(c) (i) substitution, (ii) and (iii) are addition rxn.

(d) (i) and (ii) are elimination rxn. and (iii) is addition rxn.

Q. What is the major product of following reaction?



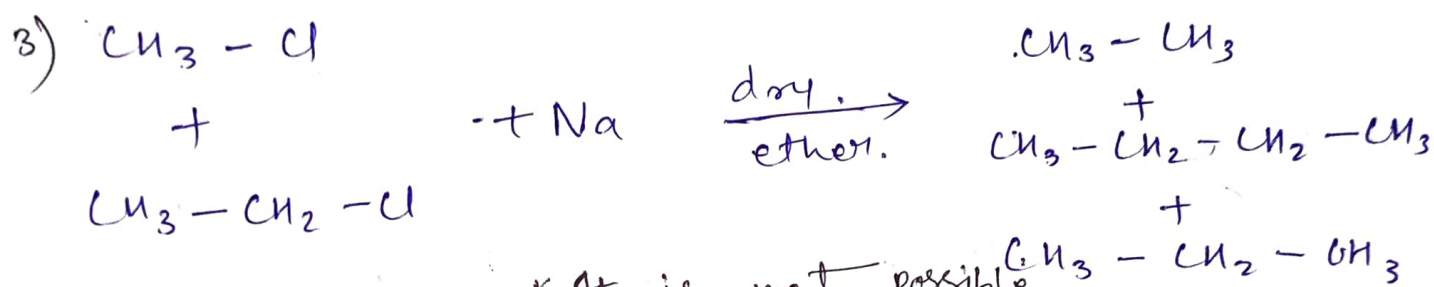
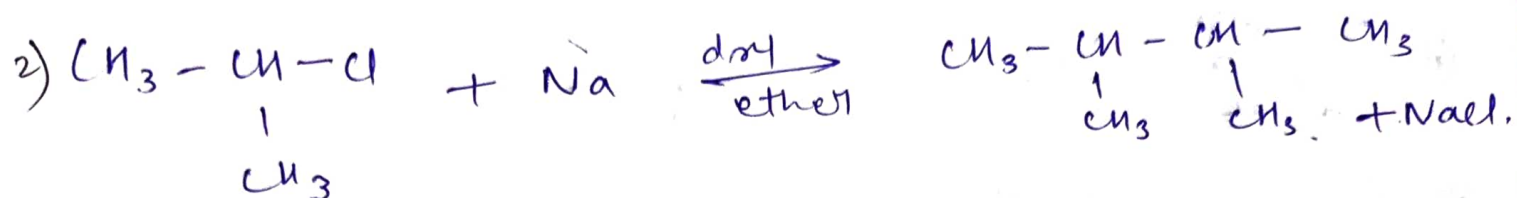
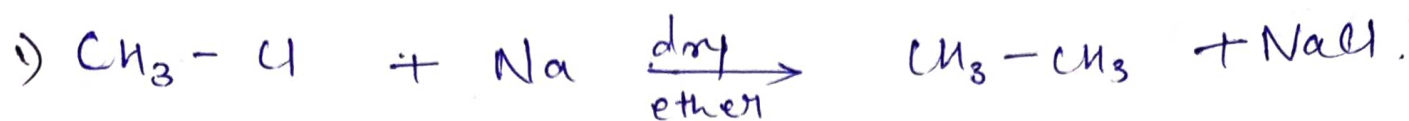
What is proton / Me^- shifting.

$\longrightarrow$ Saytzev Rule $\longrightarrow$ More branch.

$\longrightarrow$ Markov addition $\longrightarrow$

③ Rxn with metal.

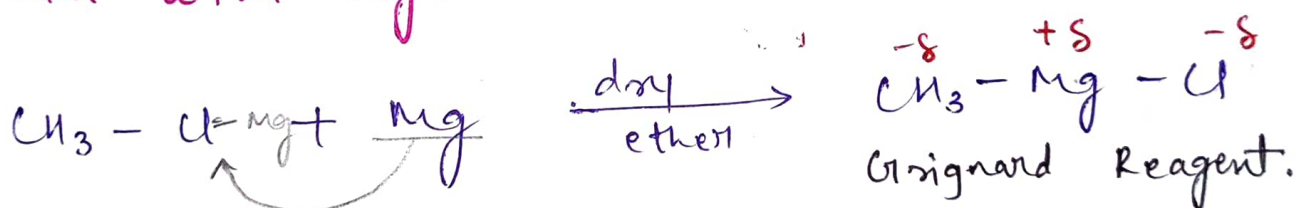
(a) Wurtz Rxn. $2C \rightarrow 4C, 3C \rightarrow 6C$] Even Carbon.



* Bcz they all have same B.P.
C₁ - C₅ = gas.

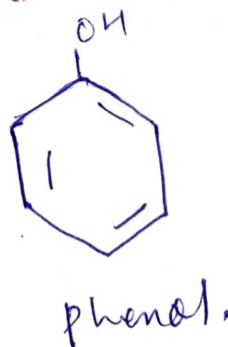
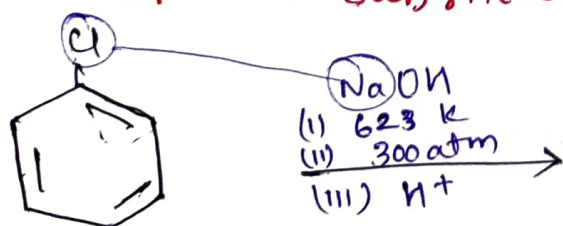
It is not possible to differ that hydrocarbon by simple distillation method.

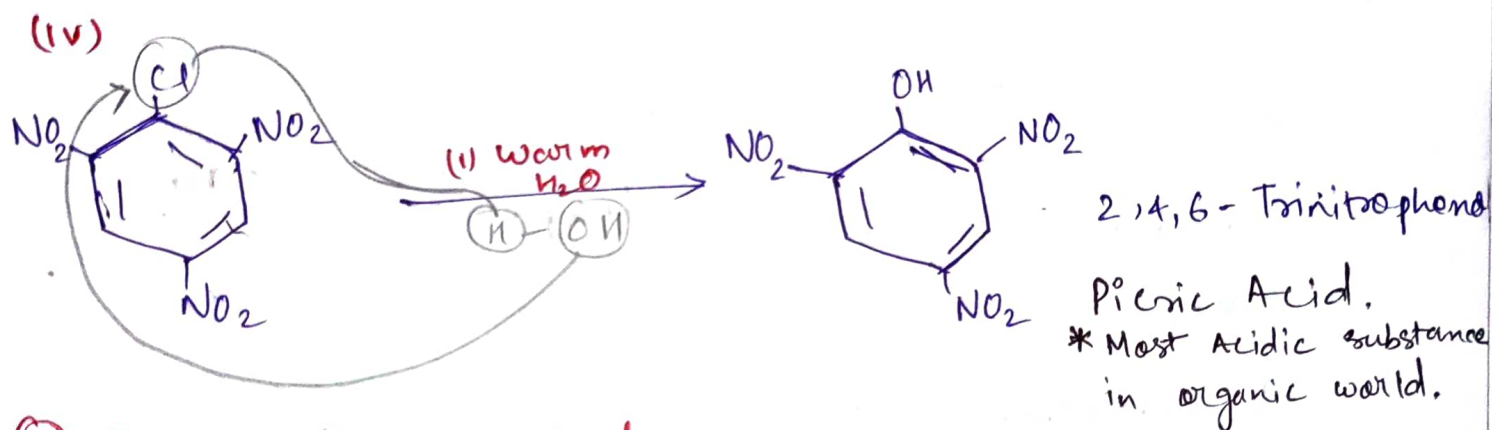
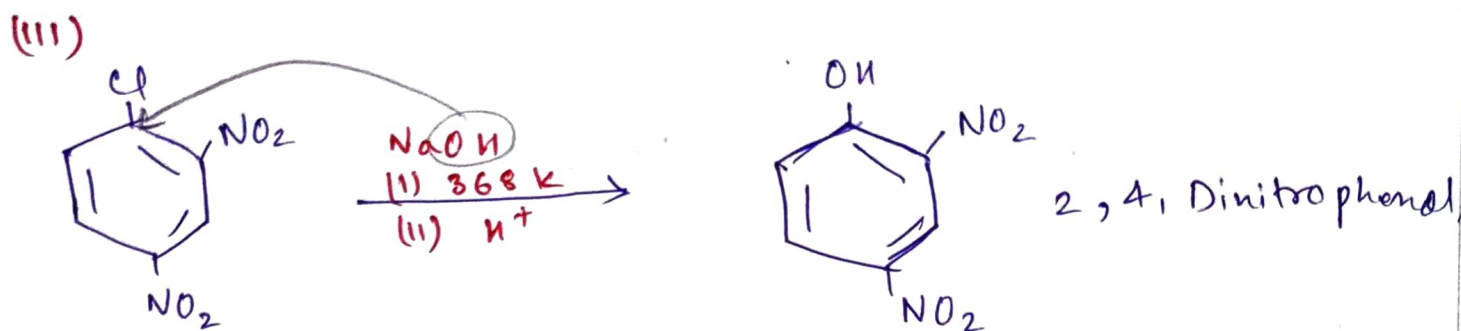
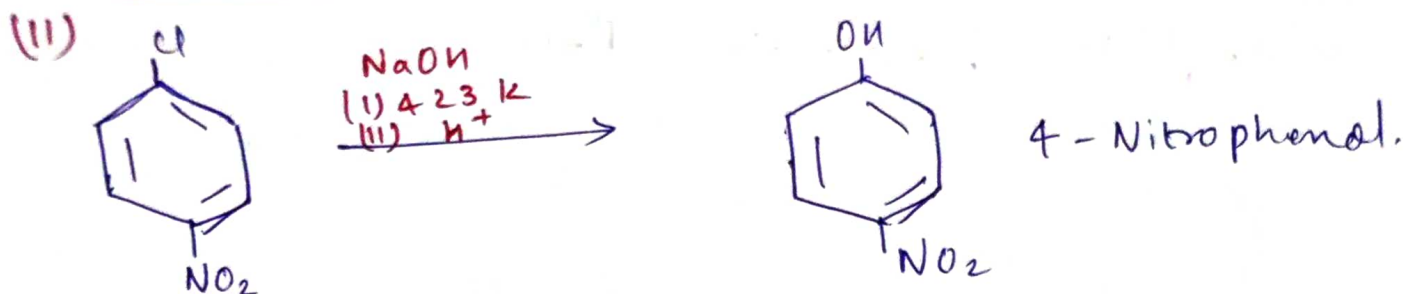
(b) Rxn with Mg.



Haloarenes.

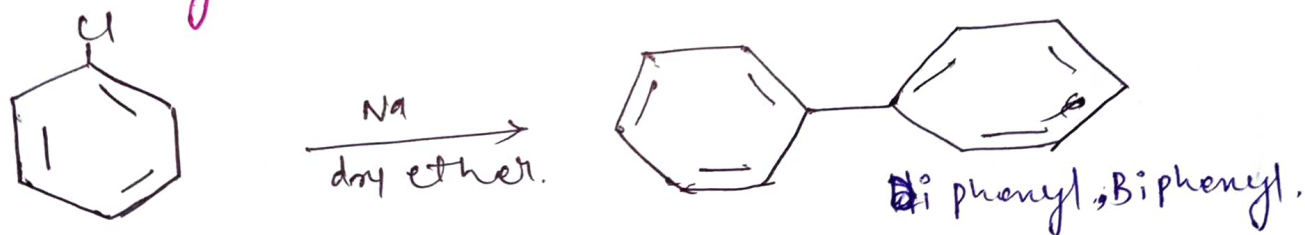
① Nucleophilic Substitution Rxn.



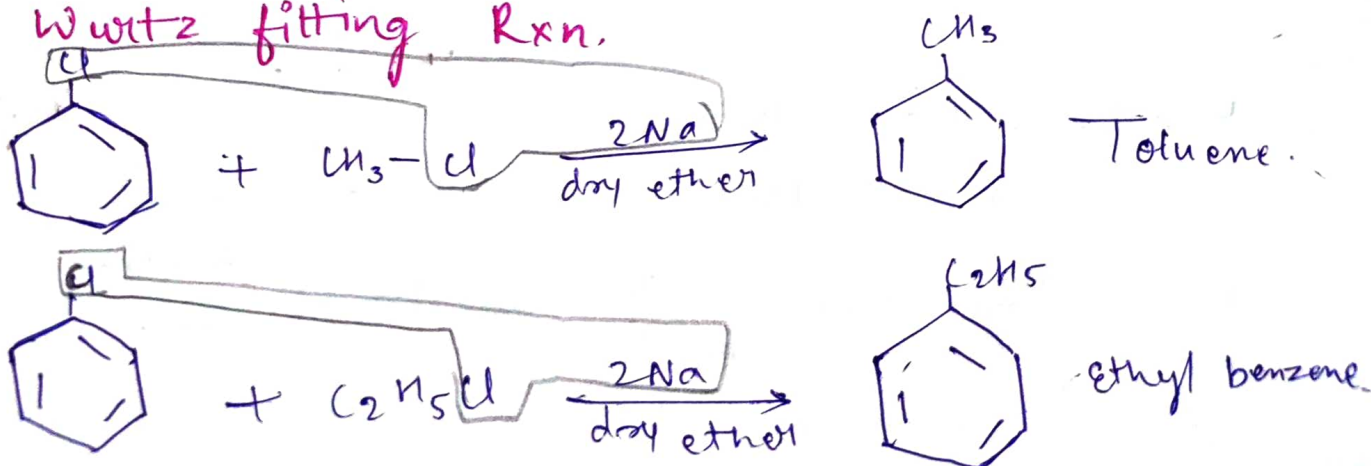


(2) Rxn with Metal.

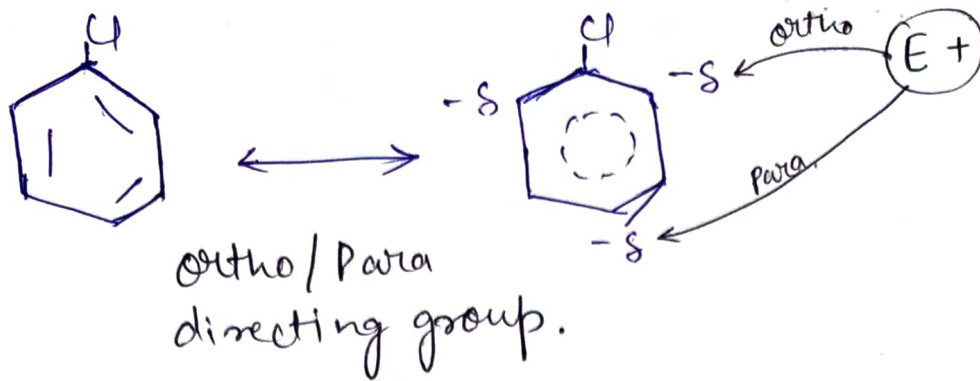
(a) Fitting Reaction.



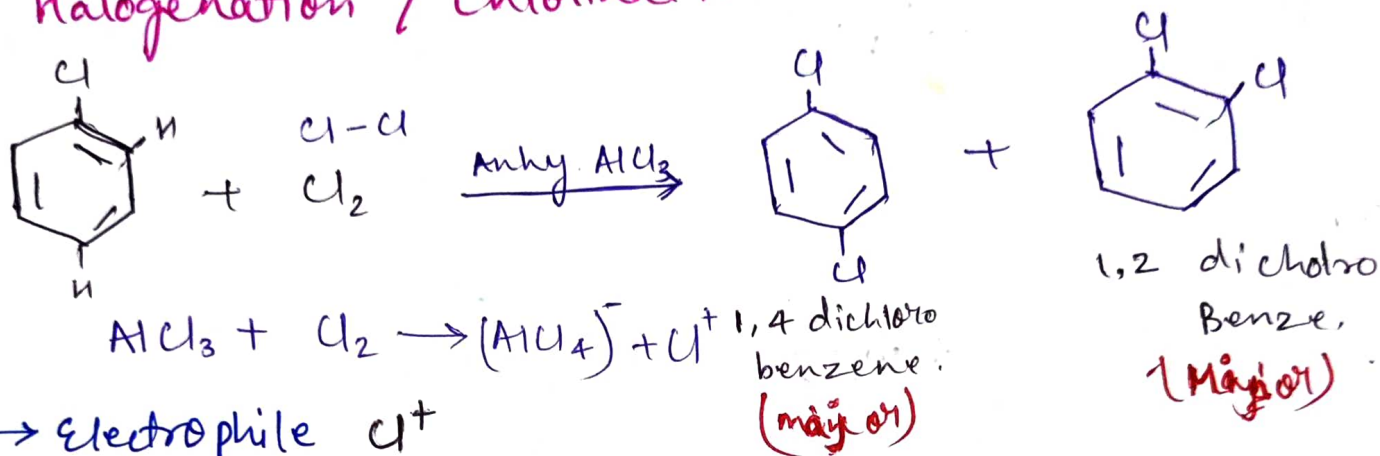
(b) Wurtz fitting Rxn.



③ Electrophilic Substitution Rxn.



(a) Halogenation / Chlorination.

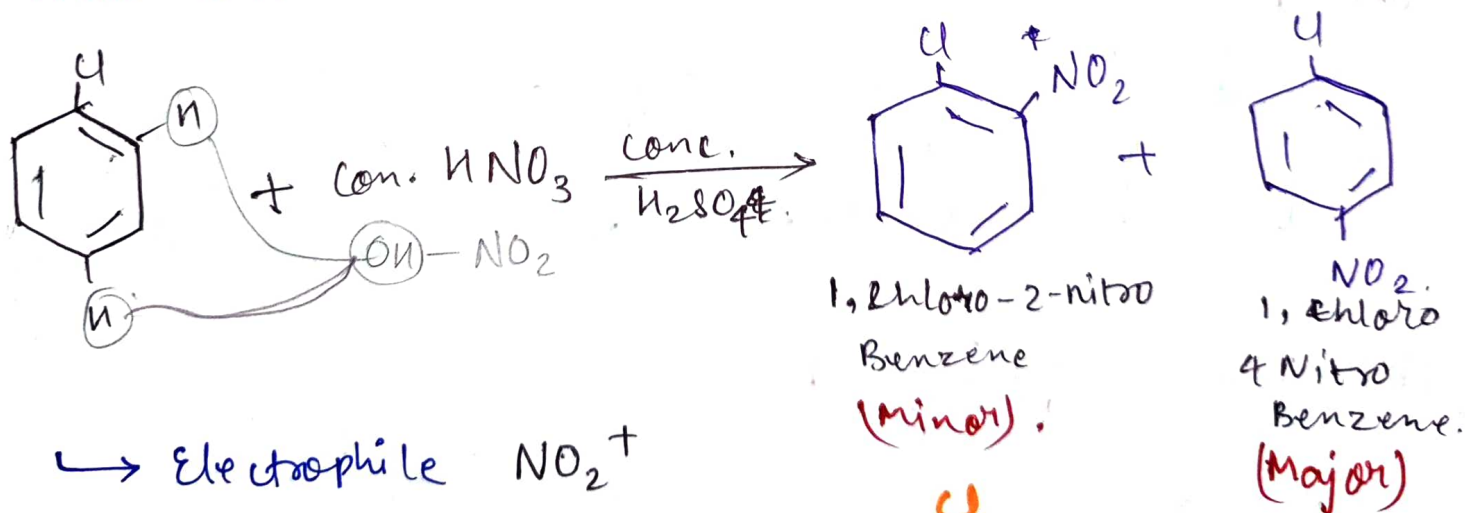


→ Electrophile Cl^+

→ Major. Para

→ Intermediate chlorarenium Ion.

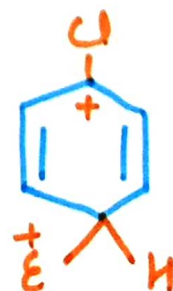
(b) Nitration.



→ Electrophile NO_2^+

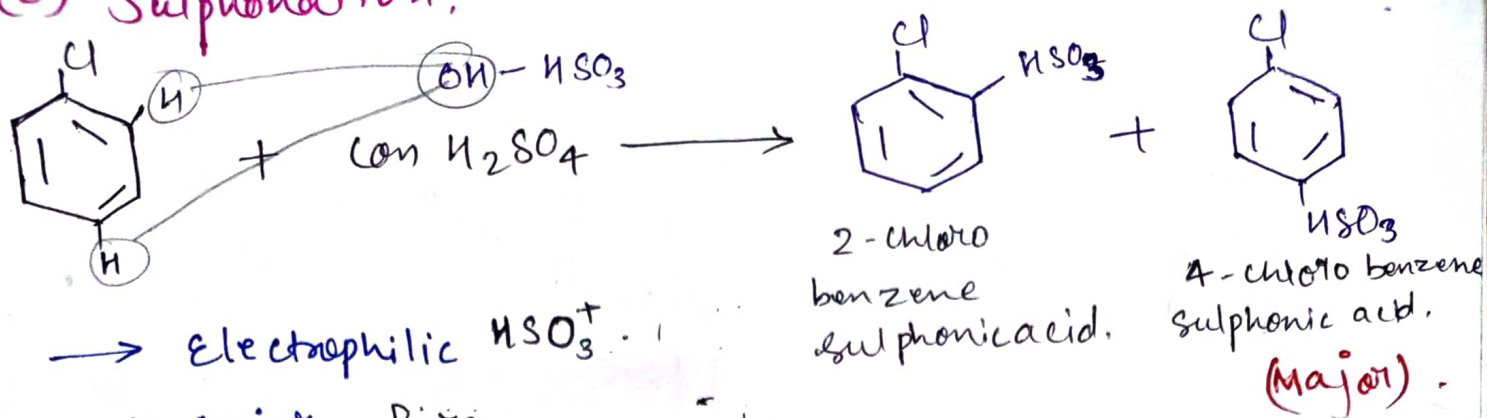
→ Major Para

→ Intermediate chloro Arenium Ion.



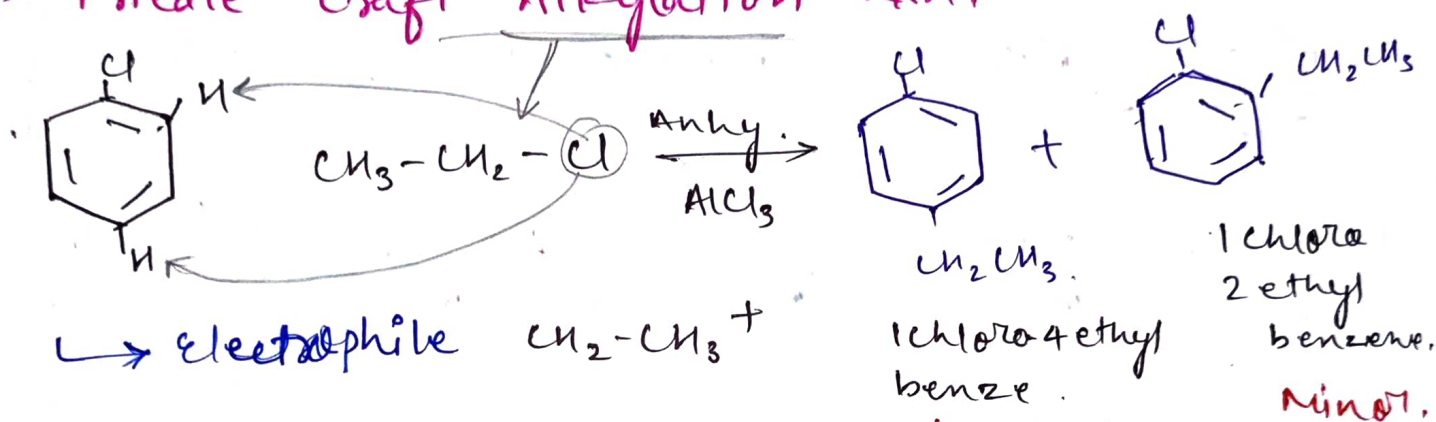
Chloro Arenium Ion.

(c) Sulphonation.



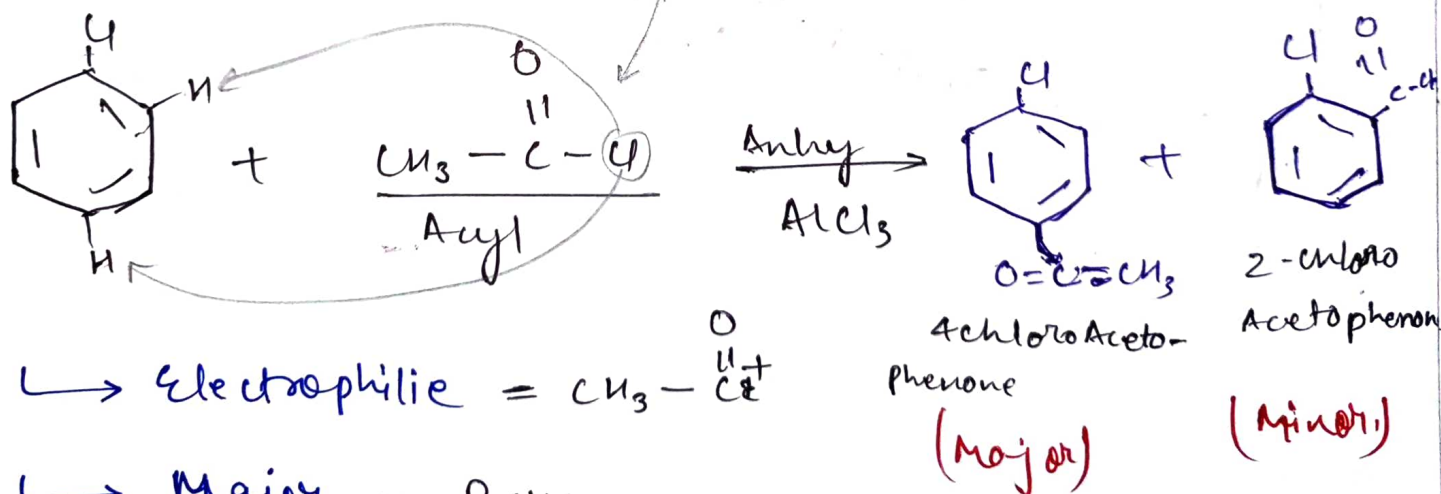
- Electrophilic HSO_3^+
- Major Para.
- Intermediate: Halo Arenium Ion.

(d) Friedle Craft Alkylation Rxn.

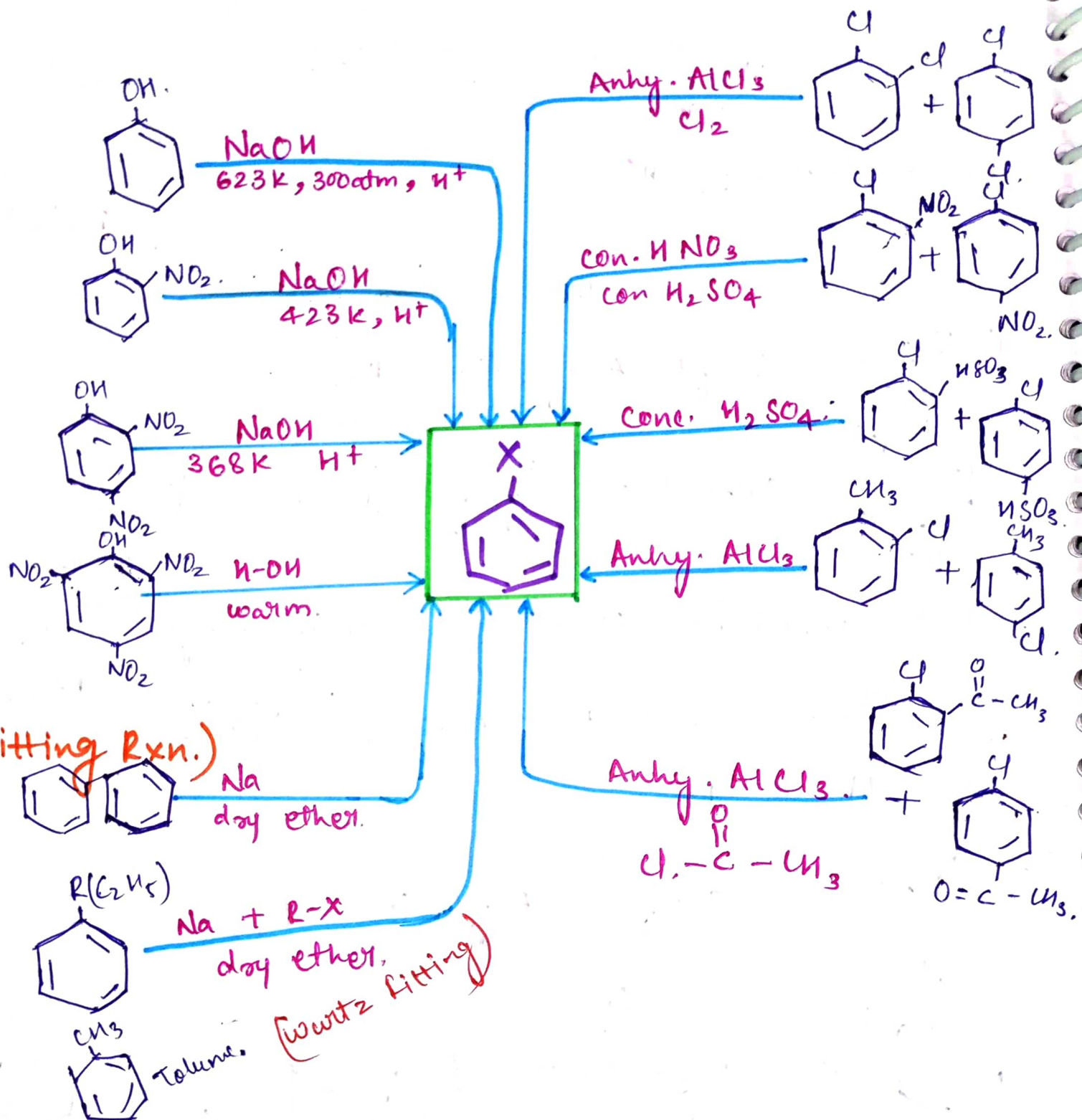


- Electrophile $\text{CH}_2 - \text{CH}_3^+$
- Intermediate chloro Arenium Ion.
- Major Para.

(e) Friedel Craft Acylation Rxn.



- Electrophile = $\text{CH}_3 - \text{C}(=\text{O})^+$
- Major = Para
- Intermediate = chloro Arenium Ion.



* Chemical Properties

Rxn with Na, dry ether
(Mustz Rxn)
Rxn with Mg, dry ether
(Grignard Reagent)



Nucleophilic Sub. Rxn.
Alc. KOH Elimination Rxn
(Saytzeff Rule)



Q. Physical properties in I.C order of boiling point.

1] Bromomethane, Bromoform, Chloromethane, Dibromomethane.
 $\text{CH}_3\text{-Br}$ CHBr_3 CH_3Cl CH_2Br_2 .

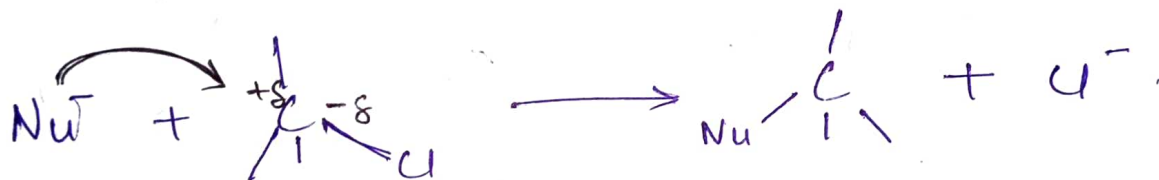
Ans. $\text{CH}_3\text{Cl} < \text{CH}_3\text{Br} < \text{CH}_2\text{Br}_2 < \text{CHBr}_3$.

2] 1-chloropropane, Isopropyl chloride, 1-chlorobutane.
 $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Cl}$, $\text{CH}_3\text{-CH(CH}_3\text{)-Cl}$ $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Cl}$.

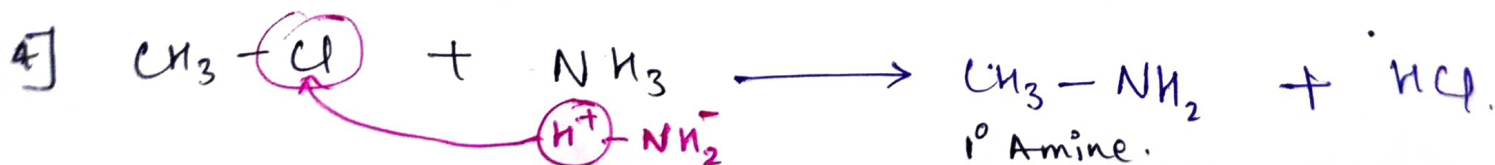
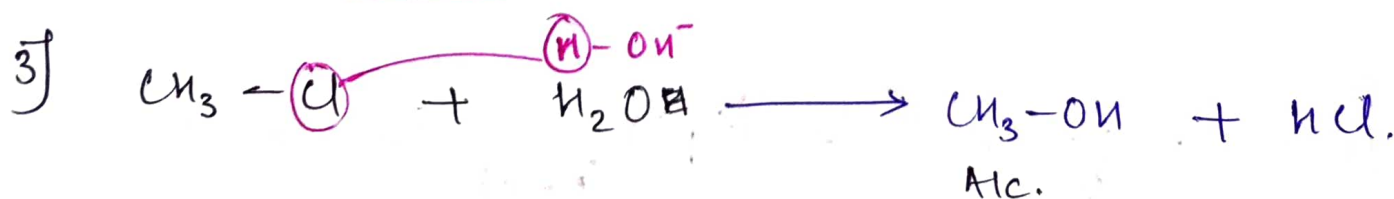
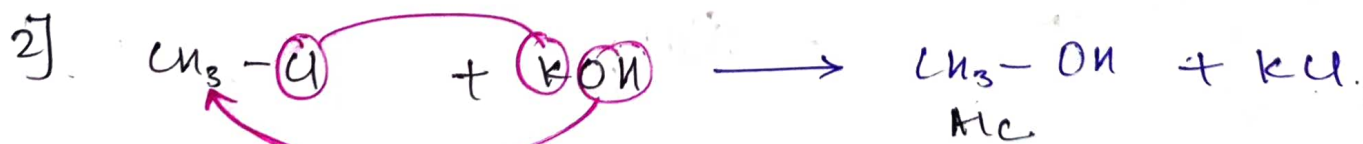
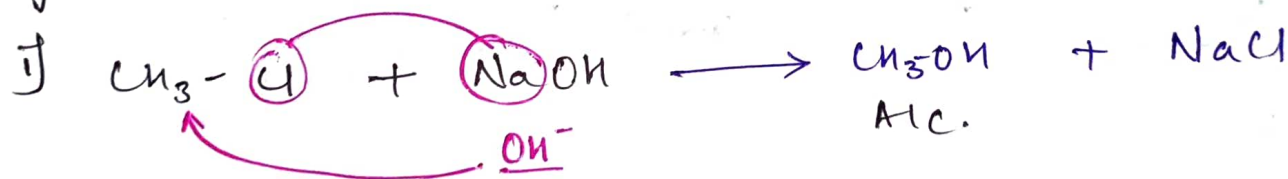
Ans. $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Cl} > \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Cl} > \text{CH}_3\text{-CH(CH}_3\text{)-Cl}$.

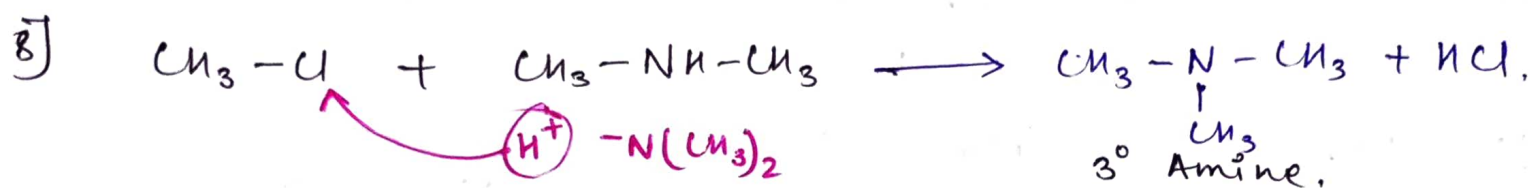
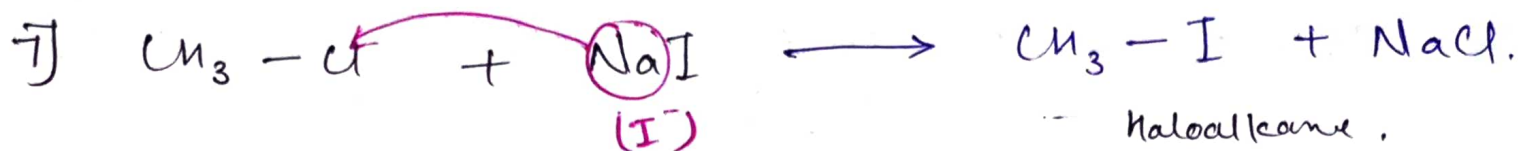
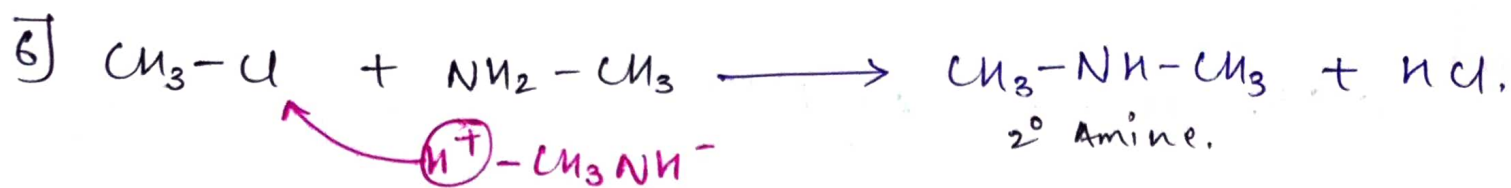
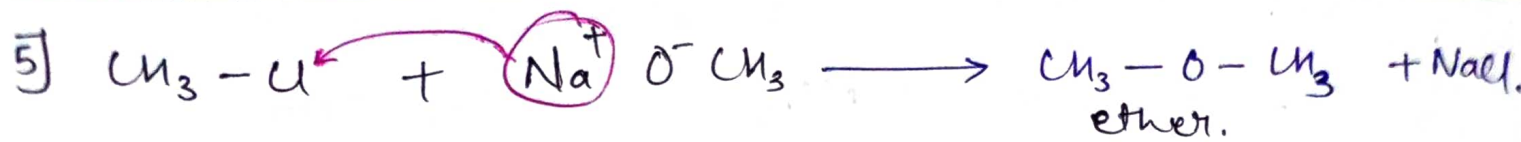
Halalkanes.

① Nucleophilic Substitution Rxn.



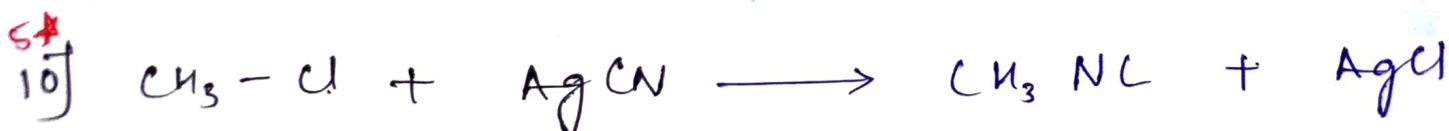
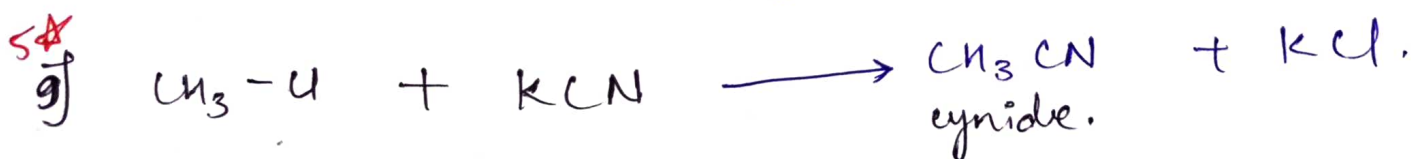
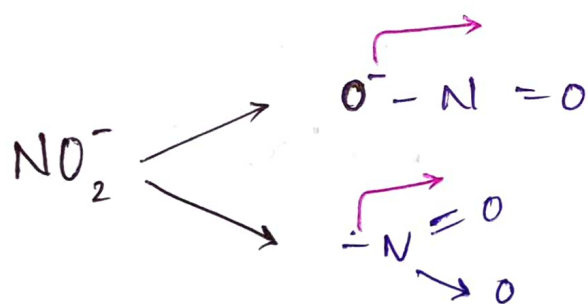
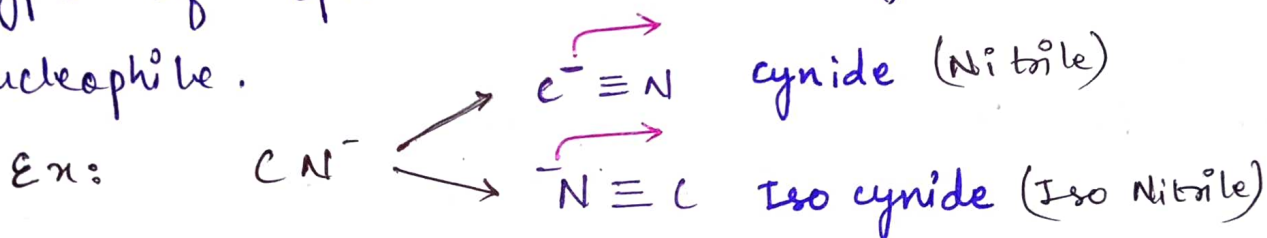
Eg:

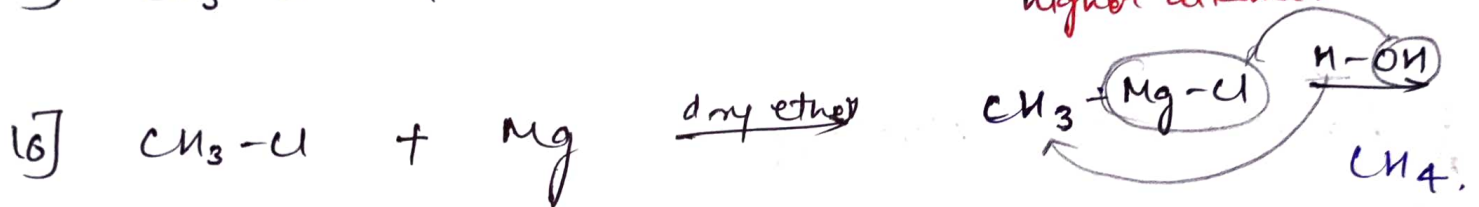
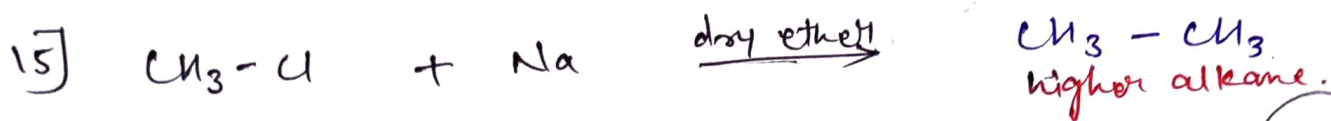
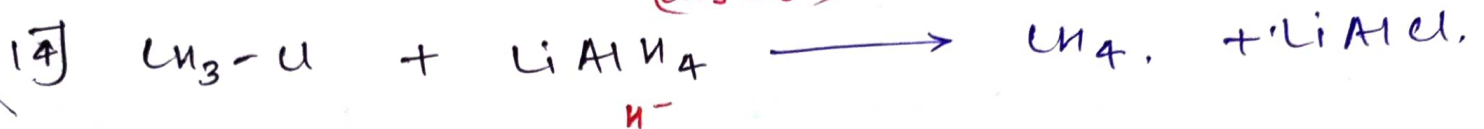
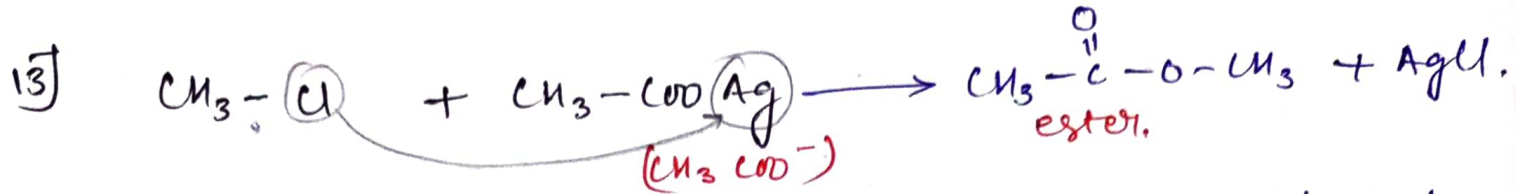
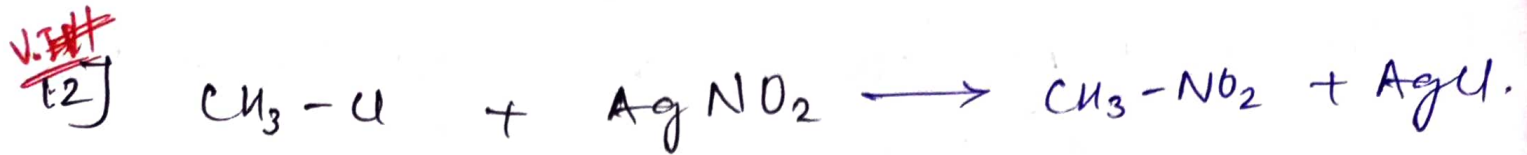
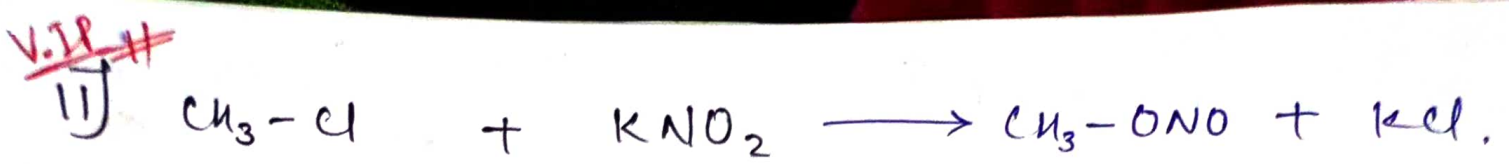




* Ambidentate Nucleophiles.

→ A Nucleophile which contain more than two types of species which can give or attack as nucleophile.





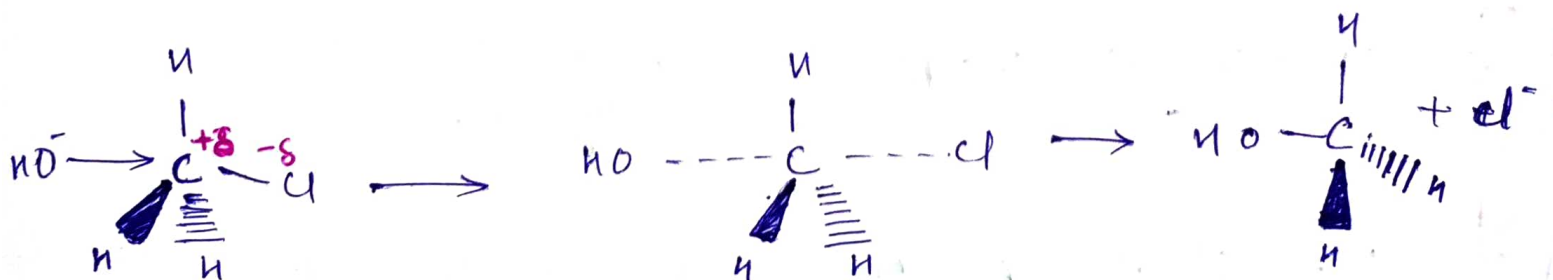
Mechanism of Nucleophilic Sub. Rxn.

1. S.N.2 Reaction $\longrightarrow$ When Non-polar solvent are present : ex CS_2 ; Benzene.



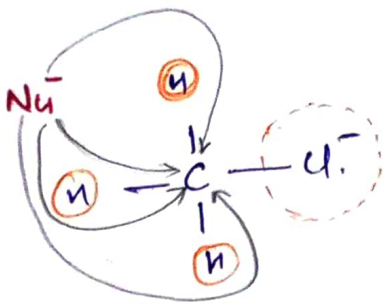
Rate of rxn = $r = k [\text{R-X}]^1 [\text{Nu}]^1$

Order = 2

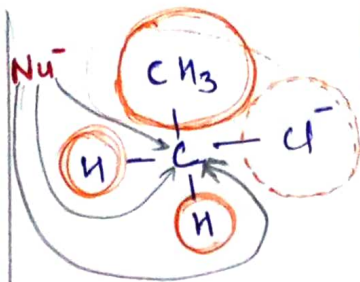


Transition State.

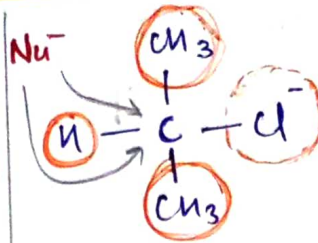
Reactivity Order.



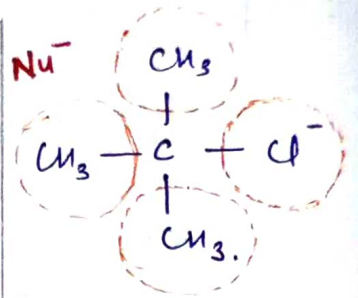
Rate - 10^{40}
 CH_3-Cl .
 methyl chloride.



Rate - 10^{30}
 $\text{CH}_3-\text{CH}_2-\text{Cl}$
 1° Haloalkane.
 Alkyl halide.



Rate - 10^{20}
 $\text{CH}_3-\text{CH}(\text{Cl})-\text{CH}_3$
 2° Haloalkane.
 Alkyl halide



Rate - 10^{10}
 $\text{CH}_3-\text{C}(\text{Cl})(\text{CH}_3)_2$
 3° Haloalkanes.
 Alkyl halide.

Reactivity Order:

Methyl halide $> 1^\circ > 2^\circ > 3^\circ$

Reactivity order is

defined by **Steric Effect**

↓
 Bade group ke karan
 attack na karne ki
 स्थिति.

SN-2

① Rate $r = k [\text{R-X}] [\text{Nu}^-]$.

② Reactivity order.

Methyl H.A $> 1^\circ > 2^\circ > 3^\circ$.

③ Steps - Single steps.

④ Inversion of configuration.

⑤ Intermediate - No.
 (Transition state)

⑥ Reactivity order defined by:
 Steric effects.

⑦ Order - 2.

⑧ Non polar solvent, CS_2 , 100% Benzene } SN_2

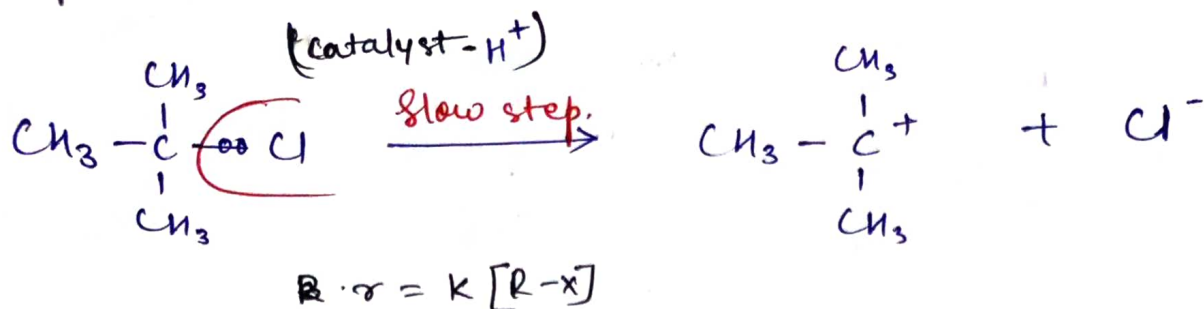
2. $\text{S}_\text{N}-1$ Reaction.

→ Protic / Polar Solvent (H^+)
 H_2O , R-OH , Acid etc.

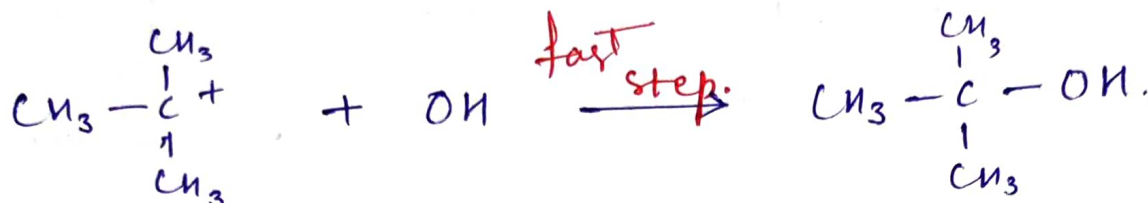
→ Steps - two.

→ Order - 1

Step. I.



Step. II



→ Intermediate - carbocation.

→ Reactivity Order - $3^\circ > 2^\circ > 1^\circ > \text{Methyl H.A.}$

→ ~~Order~~ - 1. Due to stability of Carbocation.

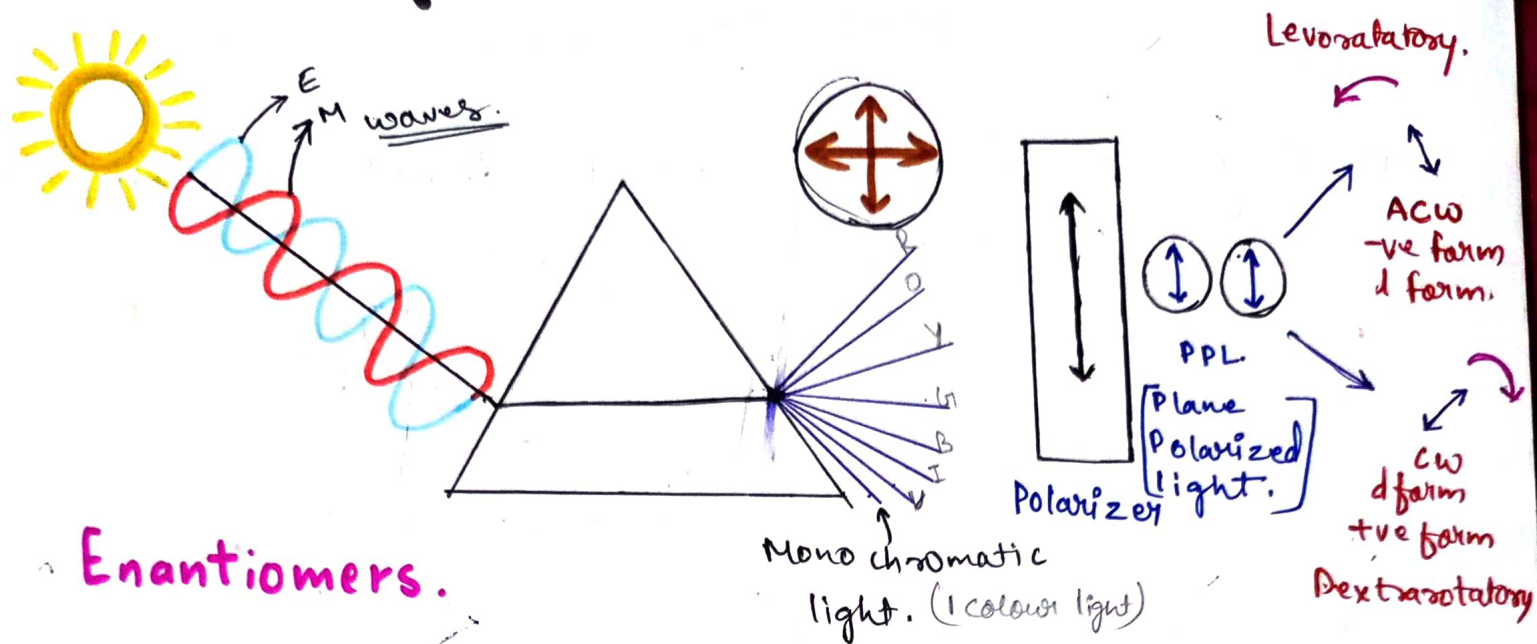
SN-2

SN-1

- Non polar / Non protic
- rate $x = k [R-x] [Nu^-]$
- step = one.
- Order = 2
- Intermediate - Transition state.
- Reactivity order.
 $\text{Methyl H.A} > 1^\circ > 2^\circ > 3^\circ$
- Due to steric effect.
- Inversion of configuration.
(Product)

- Protic / Polar (H^+ , OH^-)
- rate $= x k [R-x]$
- step = two.
- Order = 1.
- Intermediate - Carbo Cation.
- Reactivity order.
 $3^\circ > 2^\circ > 1^\circ > \text{Methyl H.A.}$
- stability of Carbo Cation.
- Optical Isomer.
- Product = Racemic Mixture

Optical Isomers.



Enantiomers.

Enantiomers: A compound which can rotate PPL in C.W or A.C.W directions that is called enantiomers. and the compounds are called optically active.

Levorotatory: -ve form / d form.

→ which can rotate light in A.C.W direction.

Dextrorotatory: +ve form / d form.

→ which can rotate light in C.W direction.

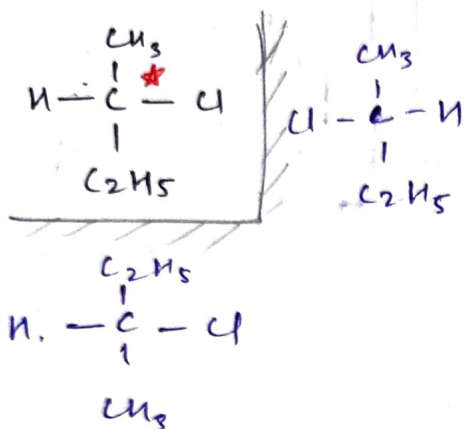
Racemic Mixture: 50% C.W / 50% A.C.W rotate.

that is called racemic mixture and the process are called racemisation

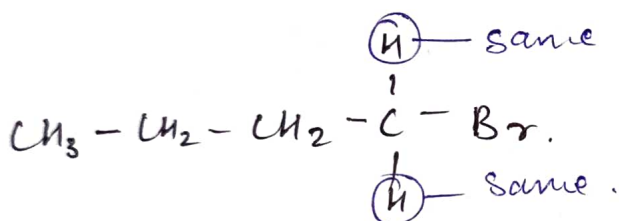
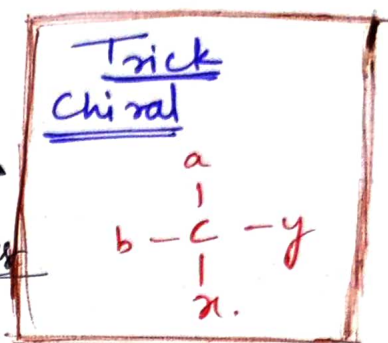
* Rotation are zero still optically active.

Meso Compounds: A compound which is optically inactive.

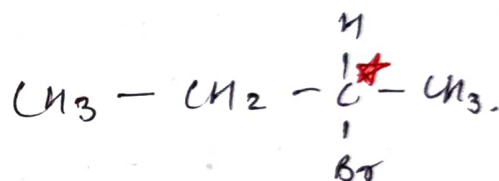
Chirality: A compound which does not superimpose on its mirror image.



It's a Condition

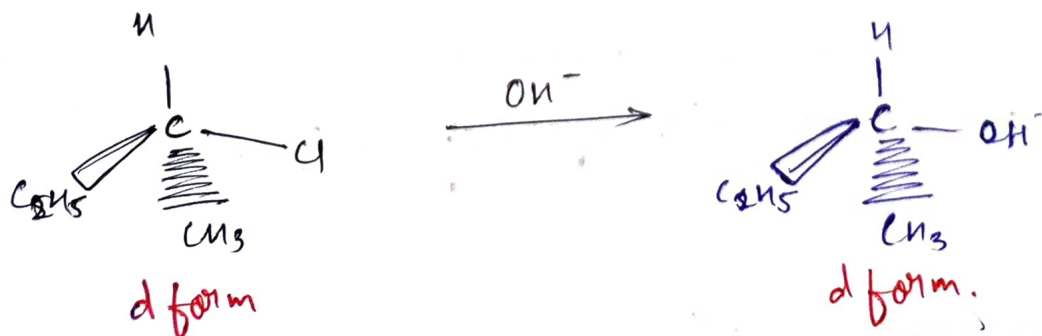


Non-chiral.

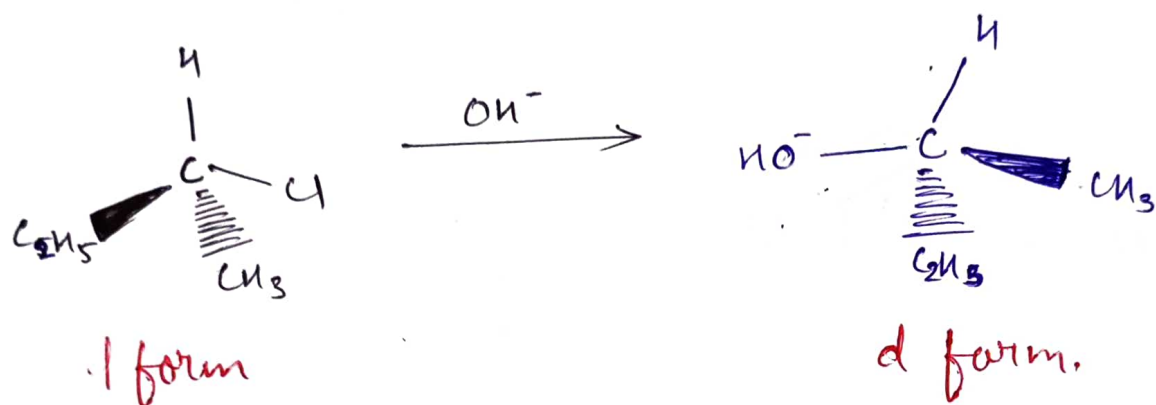


Chiral.

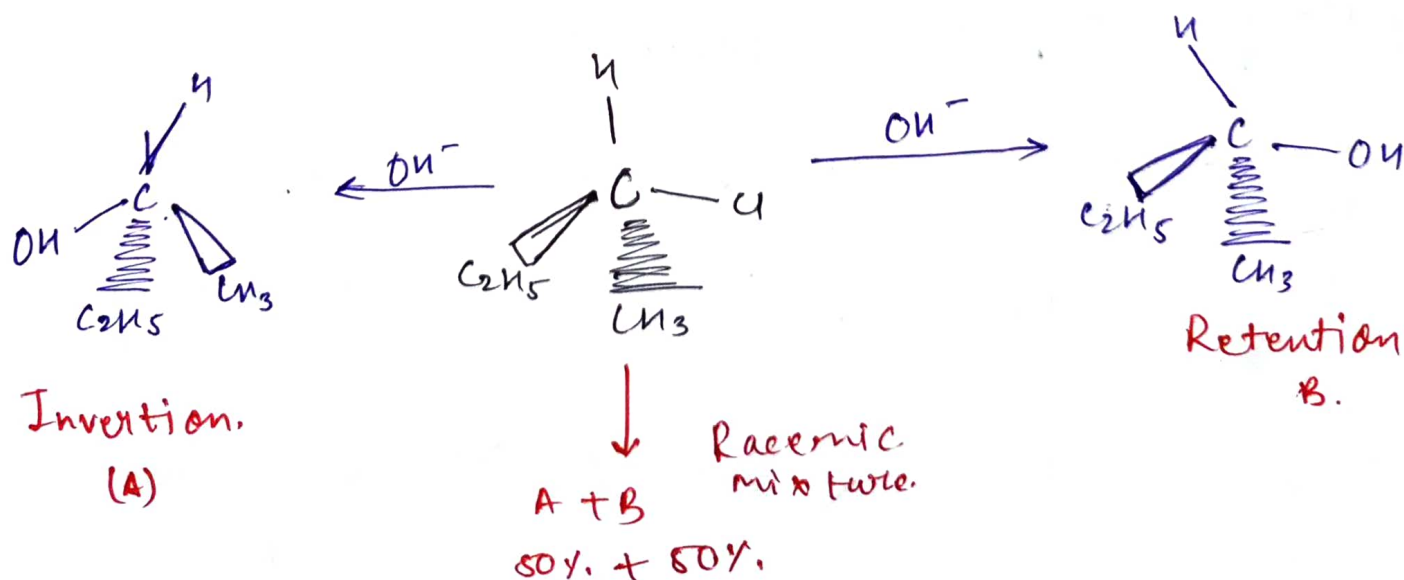
Retention: When configuration are completely same and only position of ~~electro~~ nucleophile are change that is called Retention (there is no change in configuration)



2. Inversion: When configuration are completely change from its initial and the place of nucleophile are completely different from its original place, that is called Inversion. In that case if initially the compound are in d-form it is converted into the l-form.

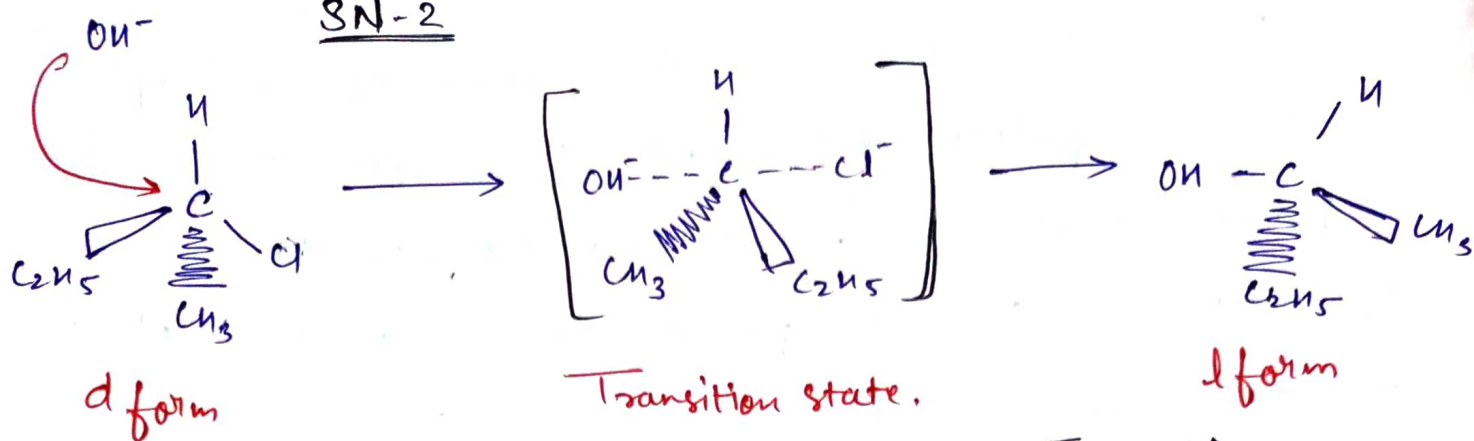


3. Racemic Mix: When the configuration are 50% retention and 50% Inversion that condition are called Racemic mixture. and the process are called Racemisation.



Let us Talk About S_N-2 & S_N-1 .

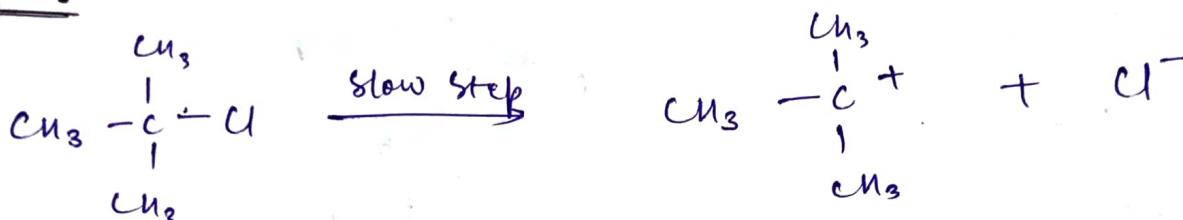
S_N-2



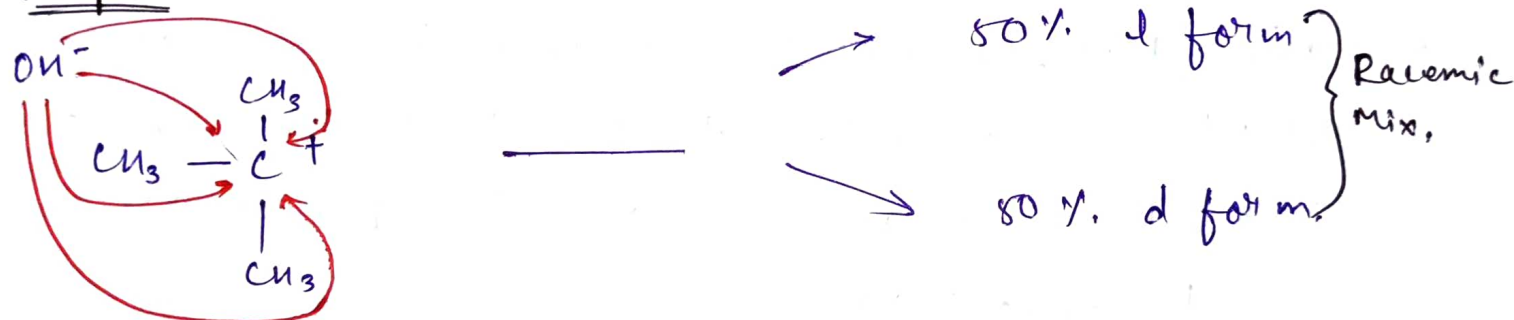
Inversion.

S_N-1

Step-1



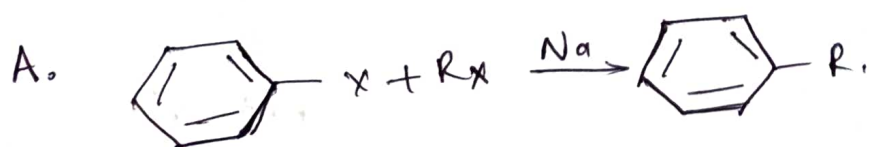
Step-2



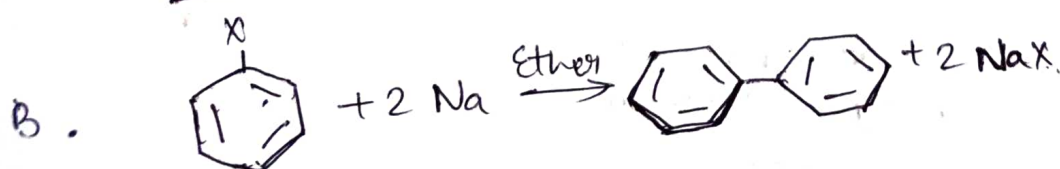
Poly Halogen Compounds.

NCERT.

Q.44. Match the reaction given in column I with the name.



1. Fitting Reaction.



2. Wurtz-Fittig Reaction.