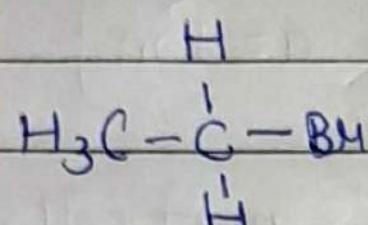


Haloalkanes And Haloalkenes

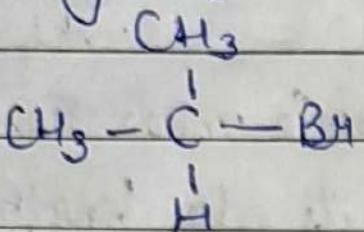
Perfect Date _____
Page _____

I.U.P.A.C.

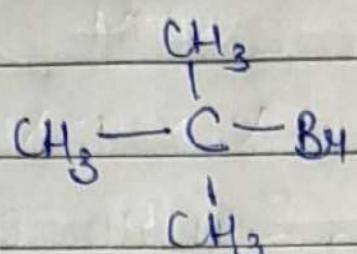
Nomenclature of Haloalkane —



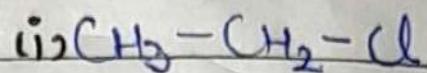
Primary ethyl bromide



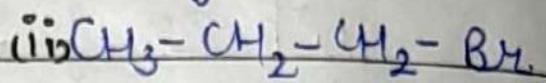
Secondary propyl bromide



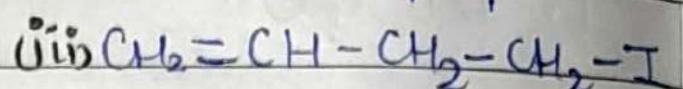
Tertiary butyl bromide



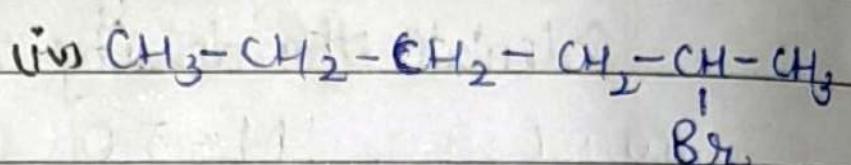
ethyl chloride



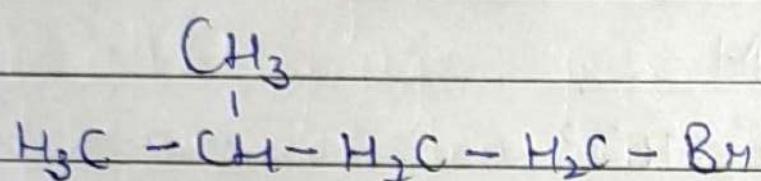
1-bromopropane



4-Iodo butene



2-bromohexane

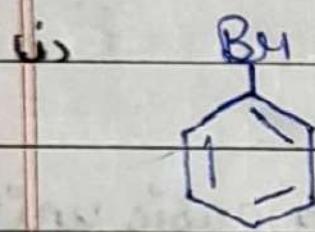


Iso pentyl bromide OR



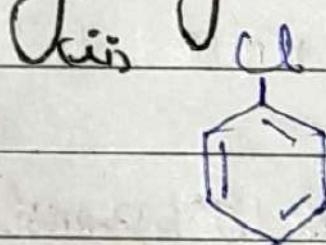
OR Neo hexyl bromide

I.U.P.A.C naming of Haloarenes —



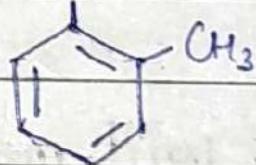
Bromo benzene

Or



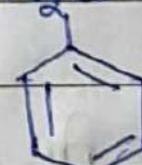
Chlorobenzene

viii, Cl



1-chloro-2-methyl benzene

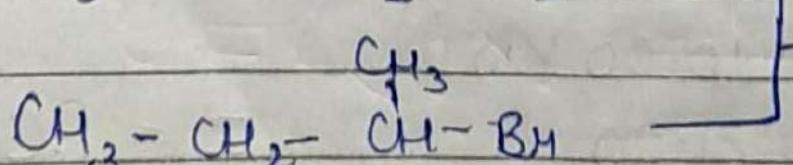
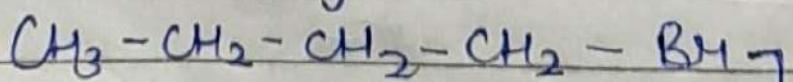
(ix), N_2Cl



Benzene diazonium chloride

Isomerism — the compounds having same molecular formula but different structures.

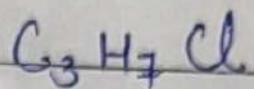
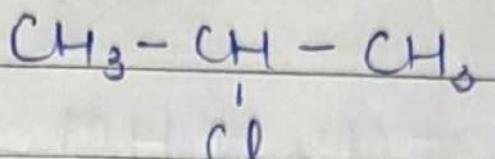
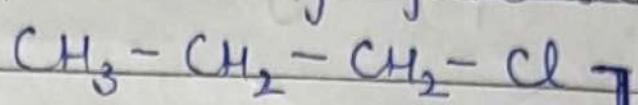
(i) Chain isomerism — the compounds having same molecular formula but different chain of carbon atom. for e.g. $\text{C}_4\text{H}_9\text{Br}$



$\text{C}_4\text{H}_9\text{Br}$

iii) Position isomerism: The compounds having same molecular formula but different positions of functional group.

for e.g. - C₃H₇Cl



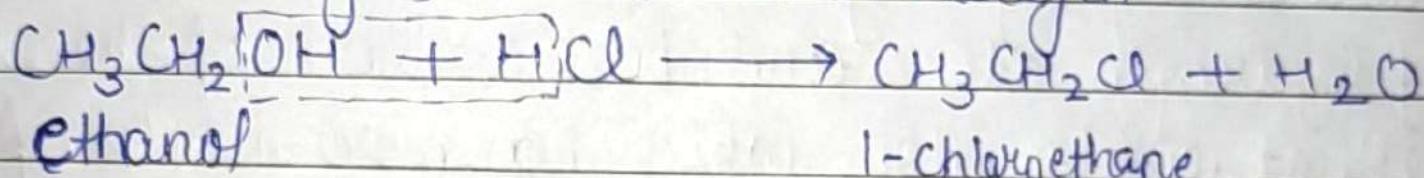
Methods of preparation of haloalkanes

1. From alcohol

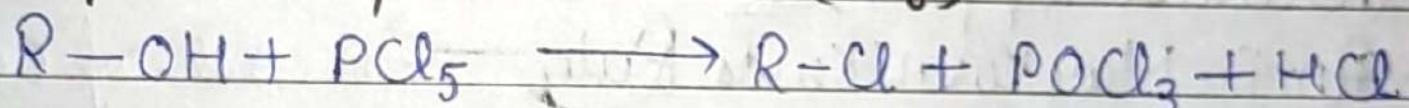
(a) with halogen acid -



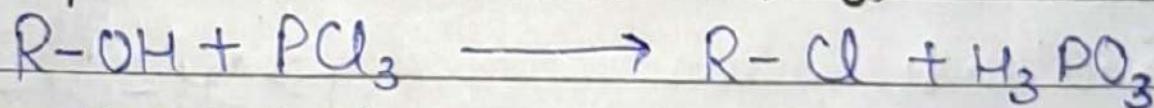
R — alkyl, X — halide or halogen



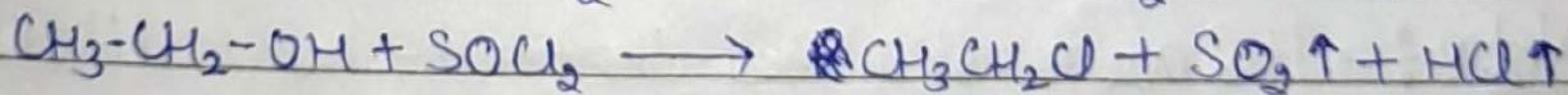
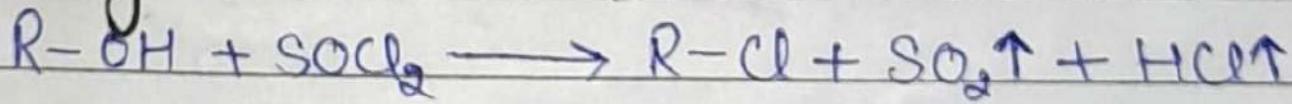
(b) with phosphorus pentachloride (PCl₅) —



(c) with phosphorous trichloride (PCl₃) —

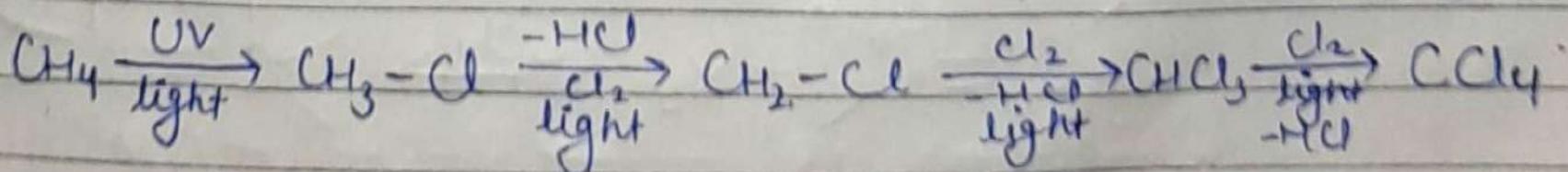
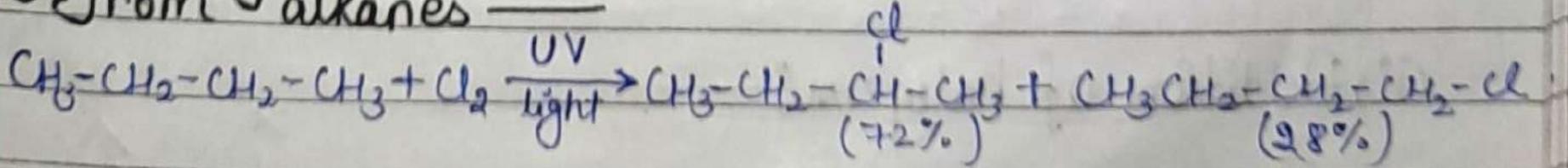


(d) with thionyl chloride (SOCl₂) —



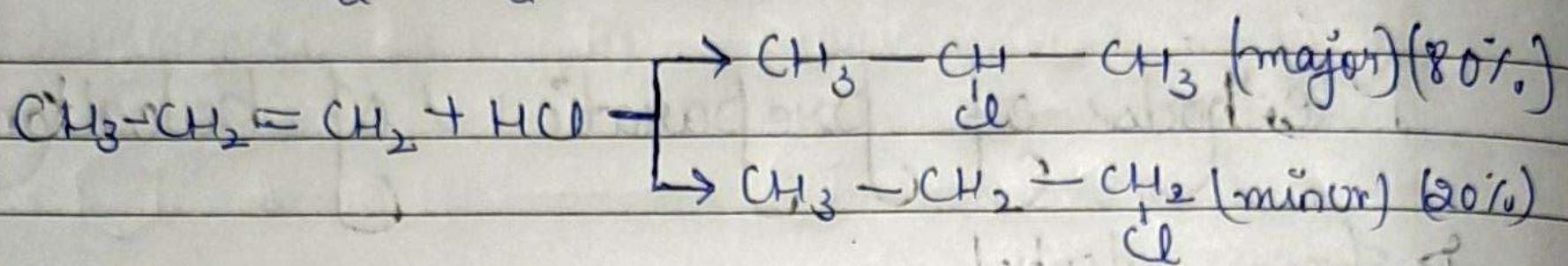
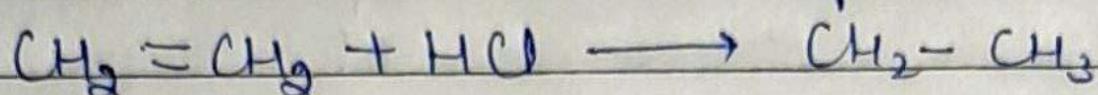
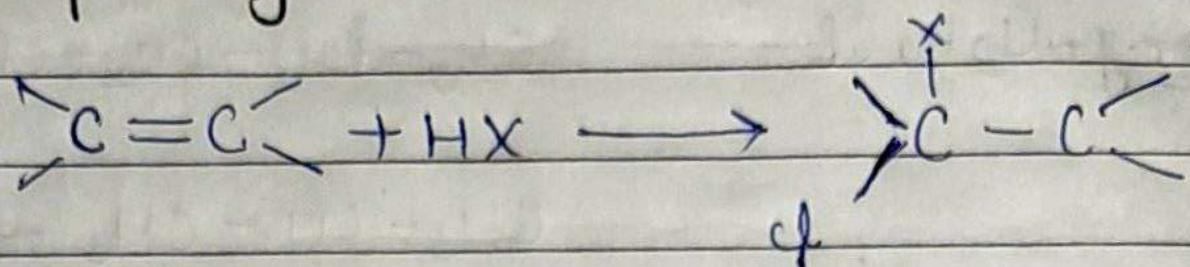
2. From hydrocarbon

(a) From alkanes —



(b) From alkenes —

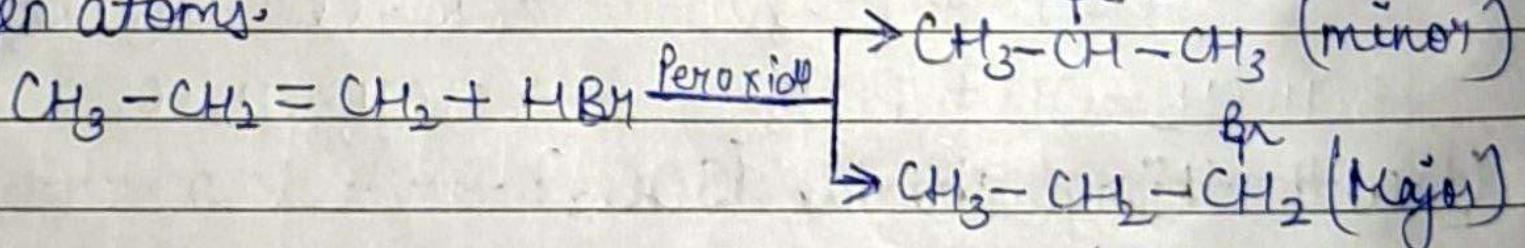
(i) Addition of halogen acid :-



Markovnikov's Rule — During the addition of halogen acid across unsymmetrical double bond, the negative part of the attacking agent goes to that carbon atom which has lesser no. of hydrogen atoms and positive part of the attacking agent goes to that carbon atom which has more number of hydrogen atoms.

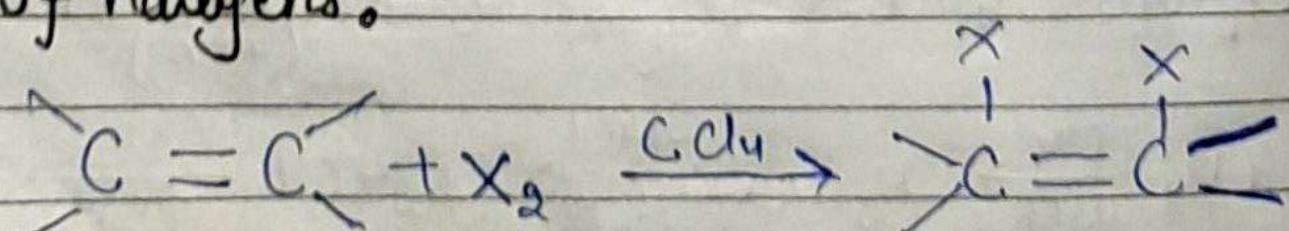
(Peroxide effect)

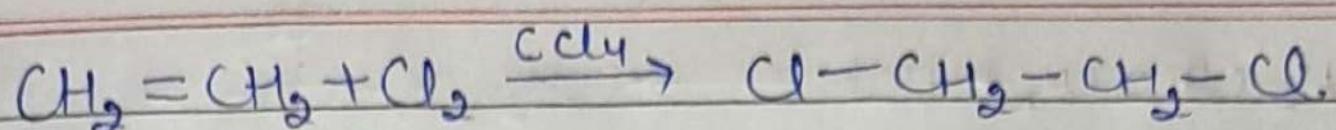
Anti-Markovnikov's Rule — In case of addition of HBr to unsymmetrical double bond, the negative part of the attacking agent goes to that carbon atom which is carrying more number of hydrogen atoms.



Note :- It may be noted that the anti-markovnikov's rule or peroxide effect applies to the addition of HBr only and not to the addition of HI or HCl.

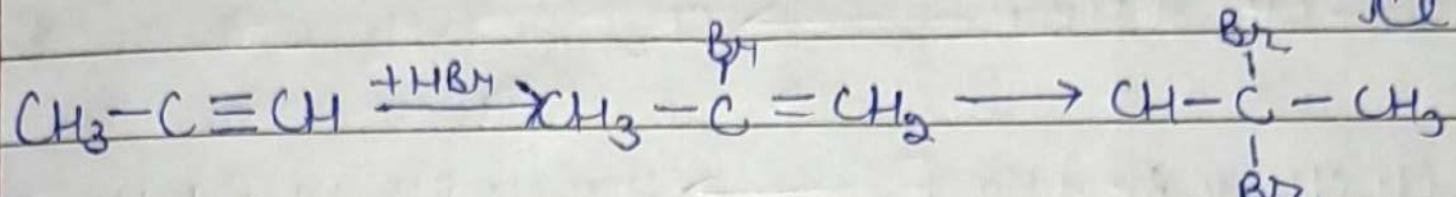
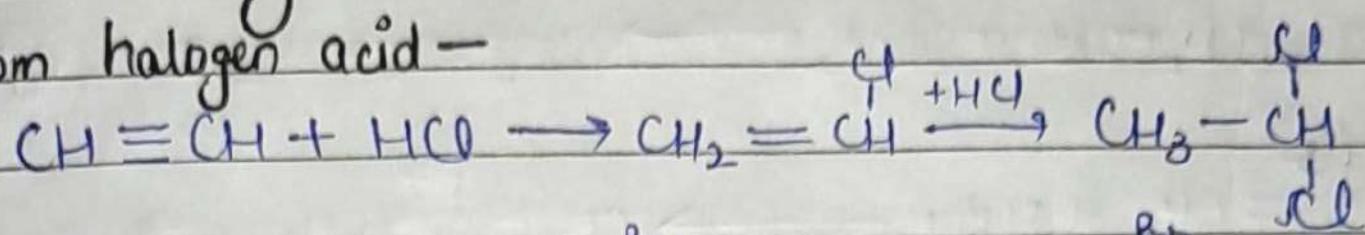
(ii) Addition of halogens :-



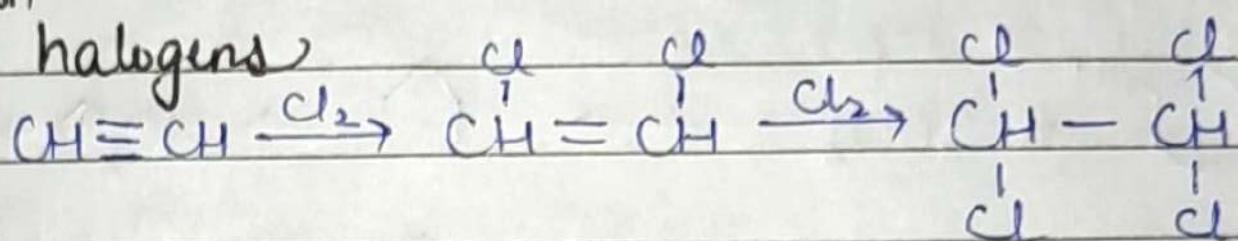


(c) From alkynes —

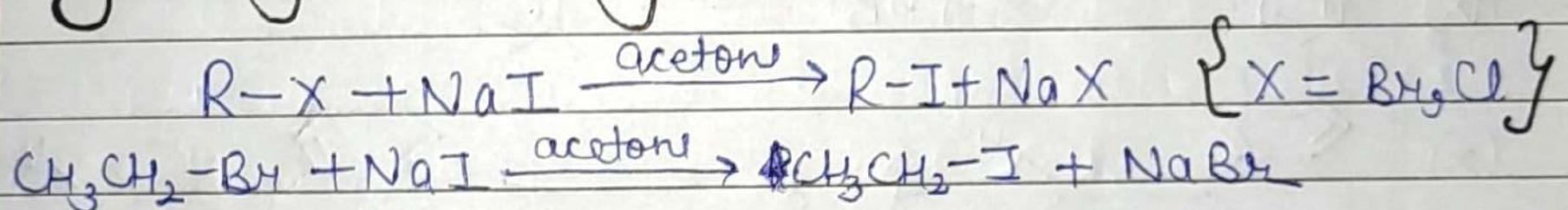
(i) from halogen acid —



(ii) from addition of halogens —

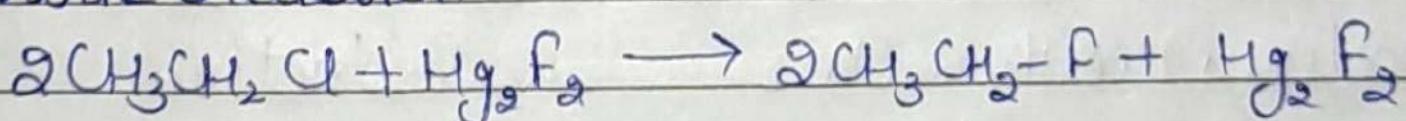


3. By halogen Exchange —

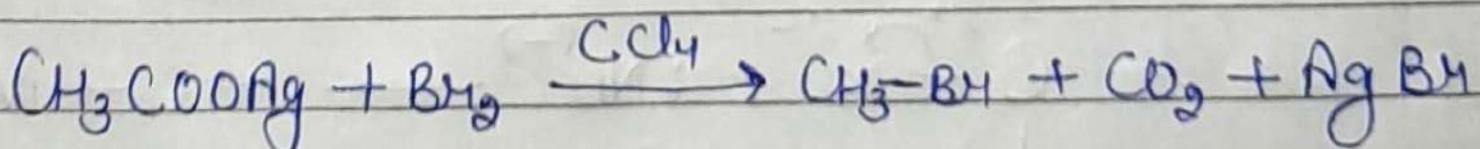


This Reaction is known as Finkelstein Reaction
for fluorine) Special rxn —

Swartz Meaction

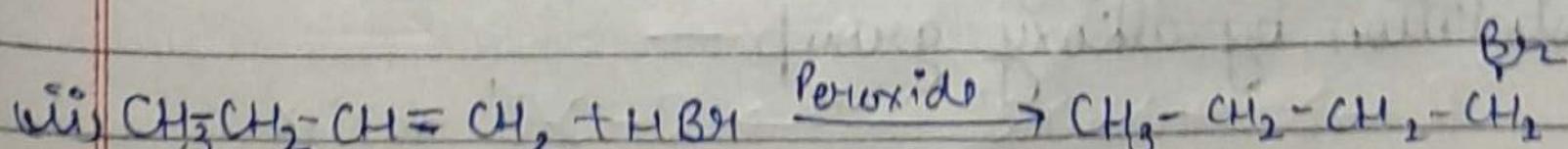
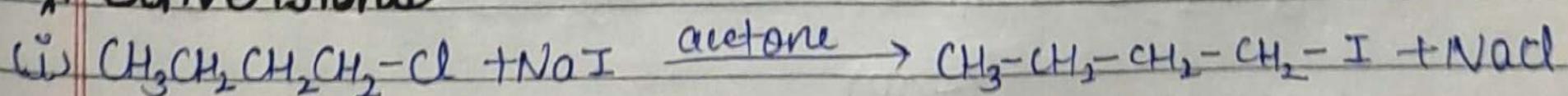


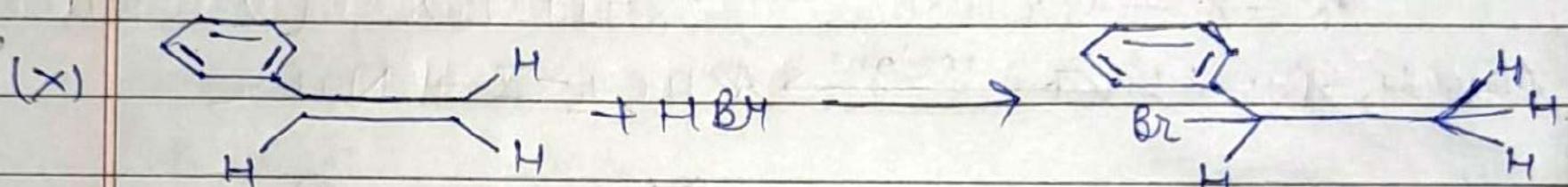
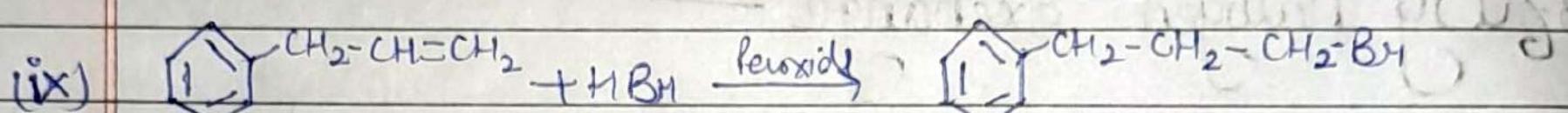
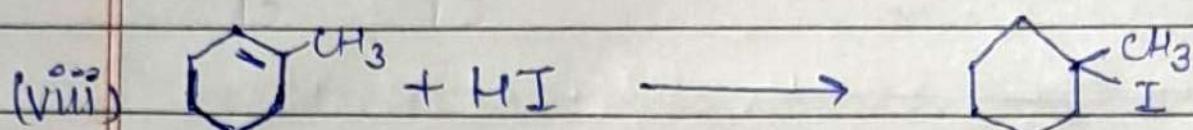
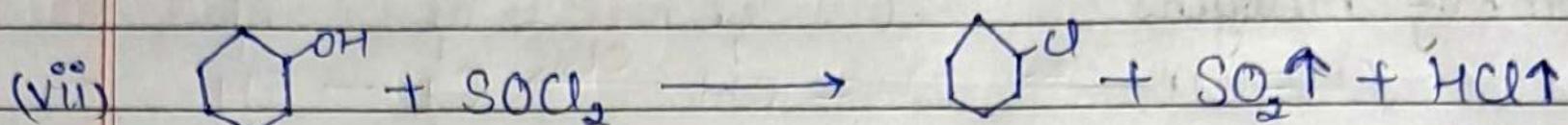
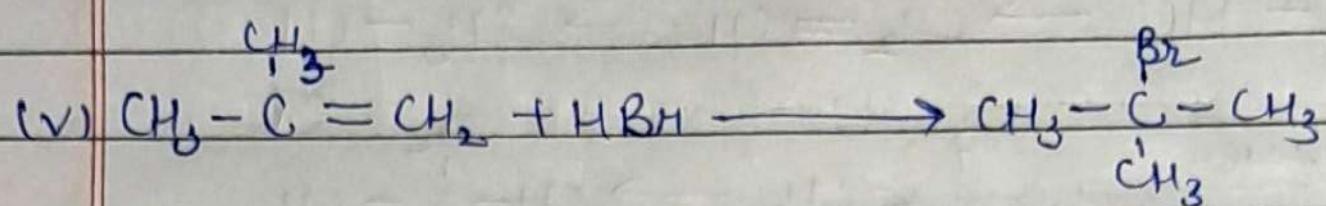
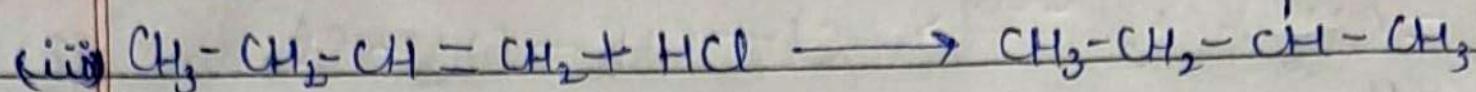
4. Preparation from Silver Salt of acid —



This Reaction is known as Borodine-Hunsdieker rxn

* Conversions —





Chemical properties of Haloalkanes —

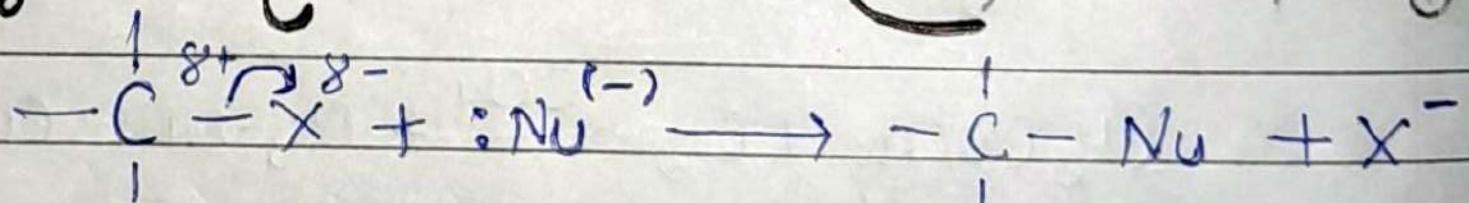
(i) Nucleophilic substitution

(ii) Elimination reaction

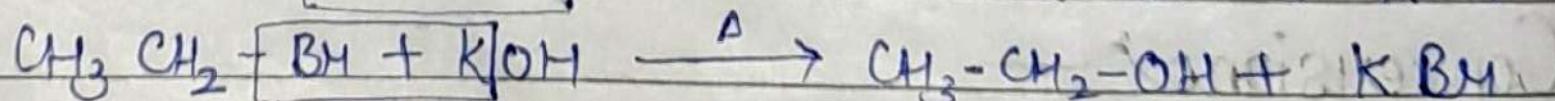
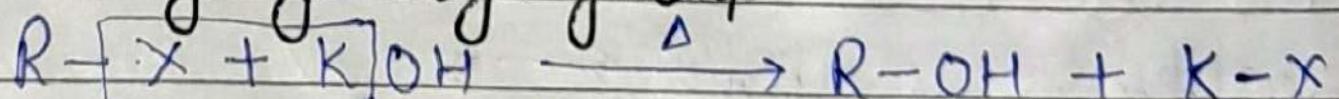
(iii) Reactions with metals

(iv) Reduction

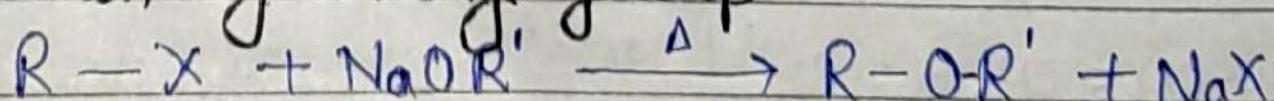
(i) Nucleophilic Substitution Reaction :-

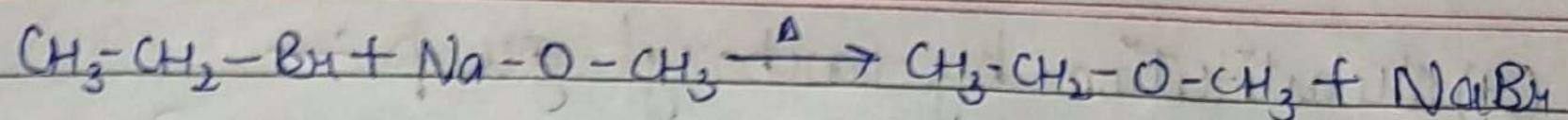


(a) Substitution by hydroxyl group —



(b) Substitution by alkoxy group —

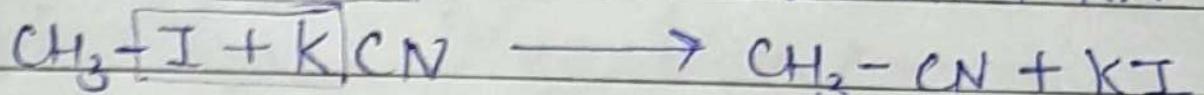
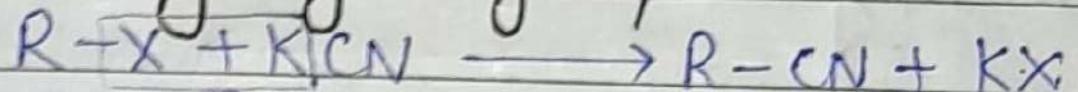




Methoxy ethane

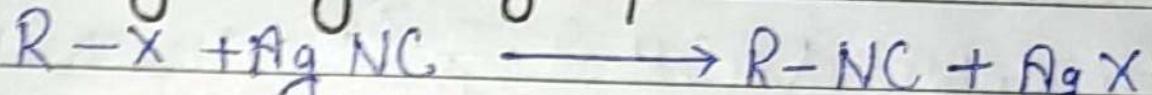
This reaction is known as **Williamson Synthesis**.

(c) Substitution by (-CN) group -



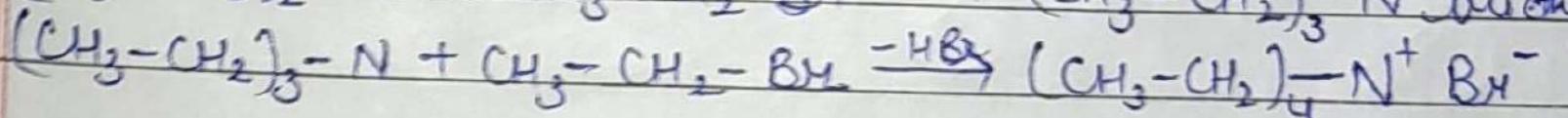
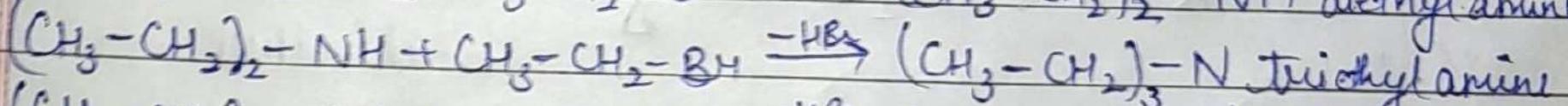
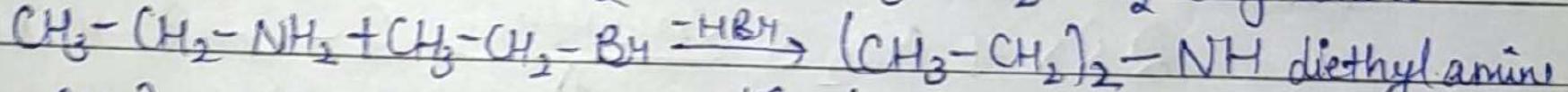
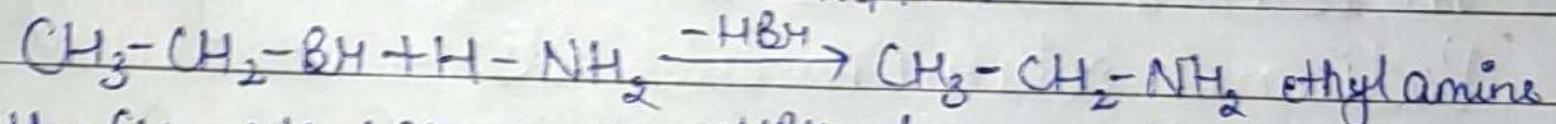
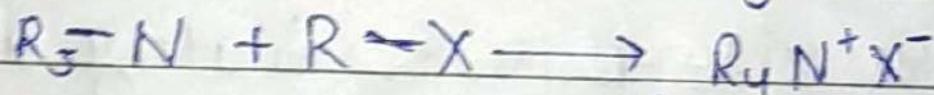
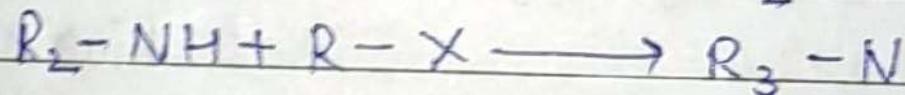
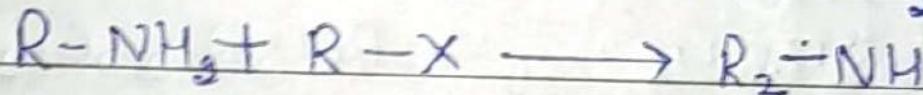
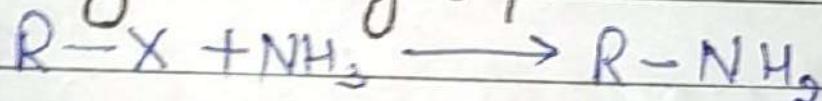
Ethanenitrile

(d) Substitution by (-NC) group -



ethyl isocyanide

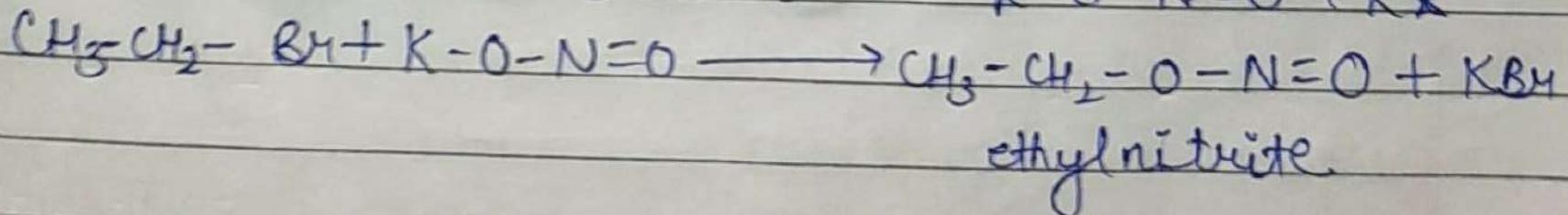
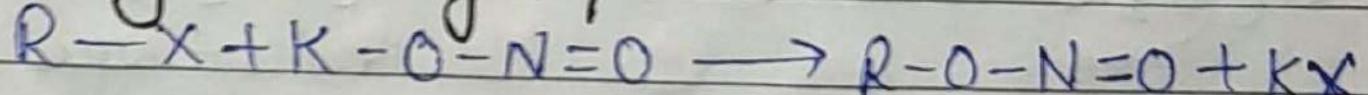
(e) Substitution by amino group -



Quaternary salt

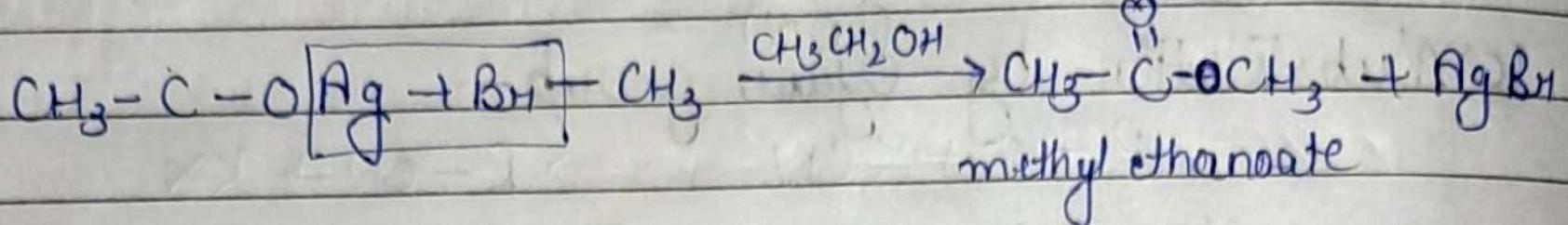
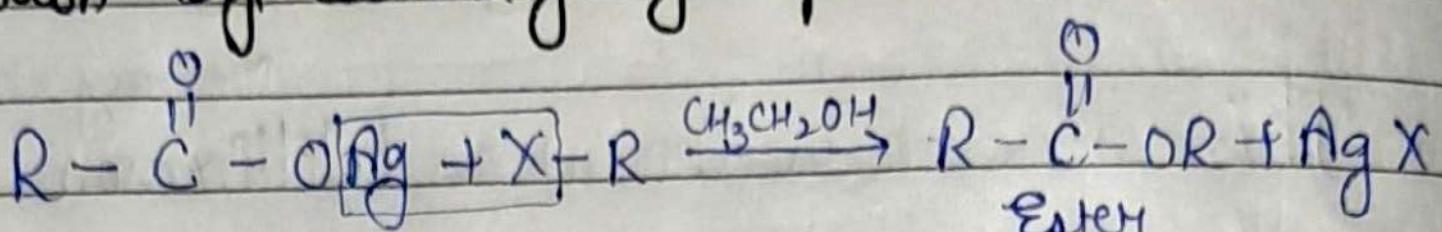
This reaction is known as **Hoffmann Ammonolysis Reaction**.

(f) Substitution by nitro group -

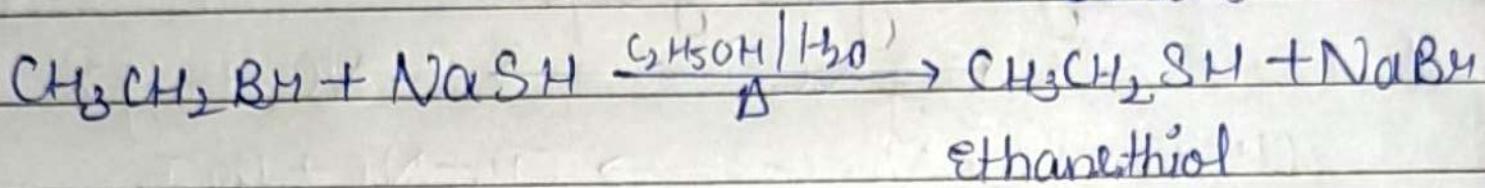
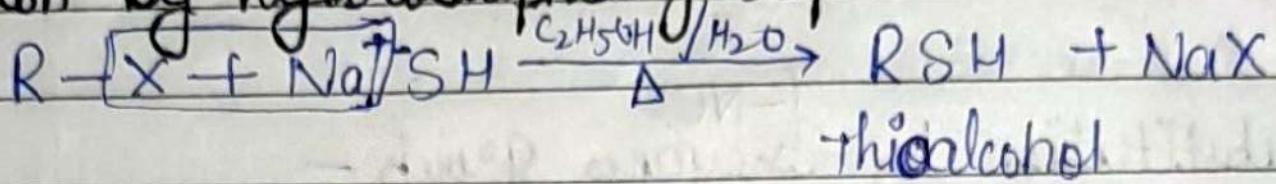


ethyl nitrate

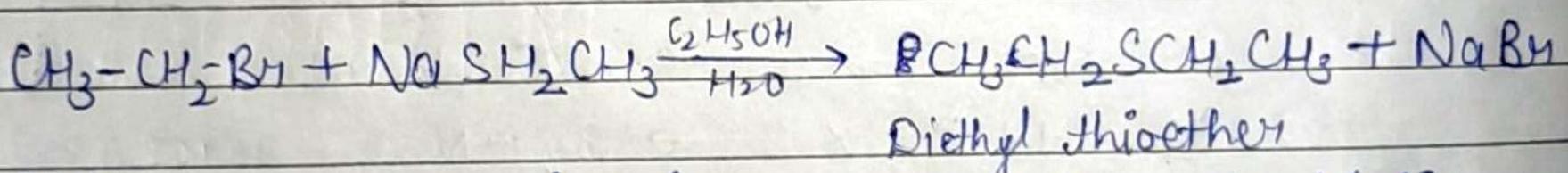
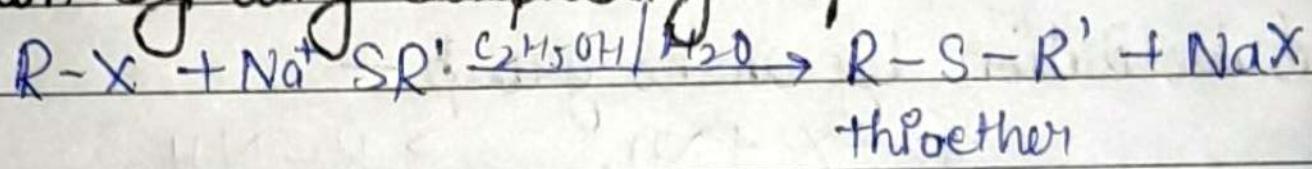
(g) Substitution by Carboxyl group :-



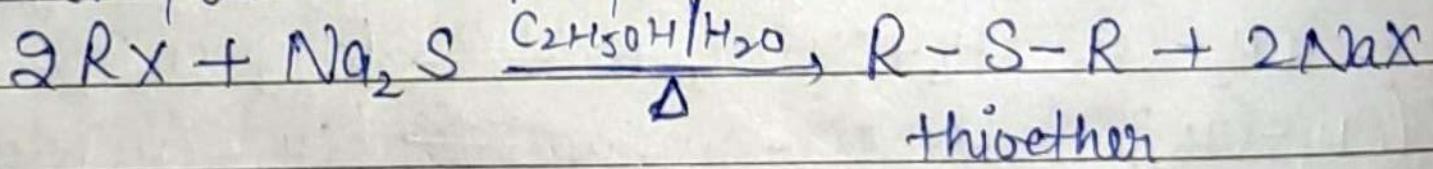
(h) Substitution by hydrosulphide group :-



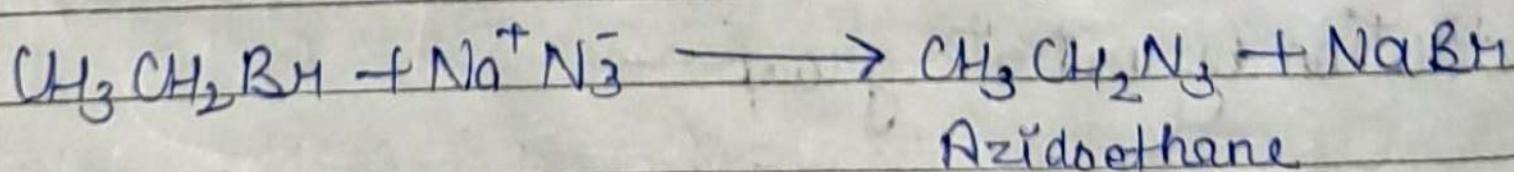
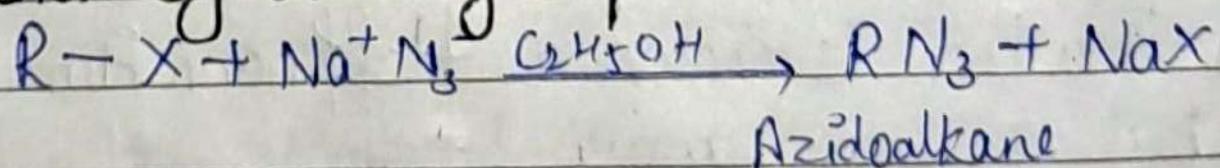
(i) Substitution by alkyl sulphide group :-



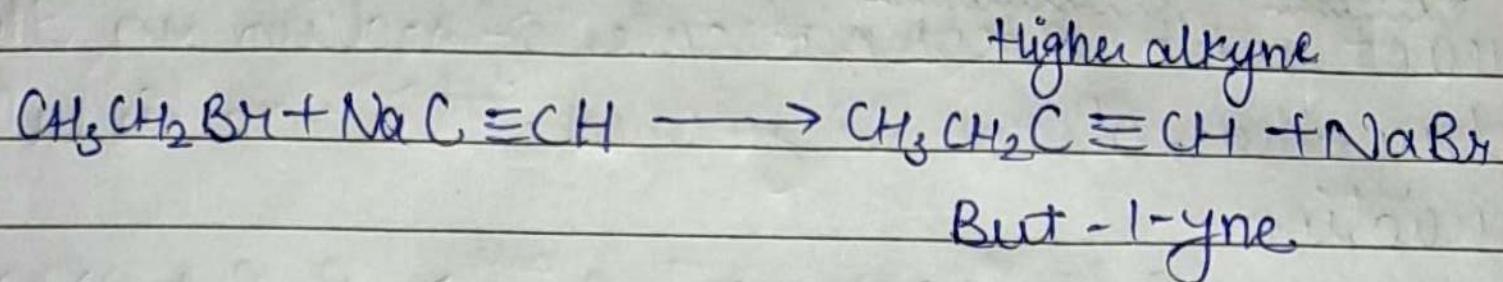
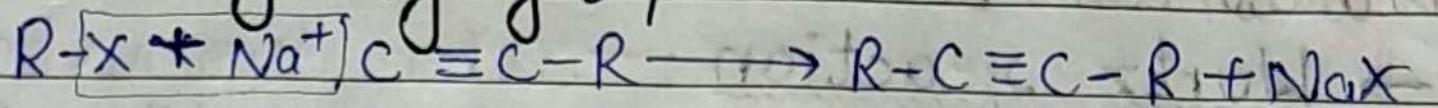
Thioethers are also formed by heating alkyl halide with Sodium or potassium sulphide.



(j) Substitution by azide group :-

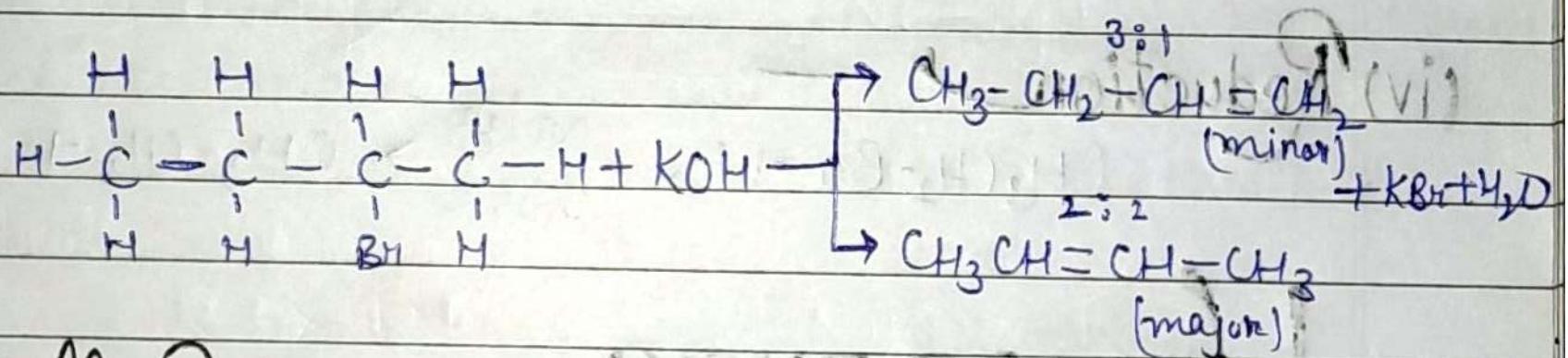
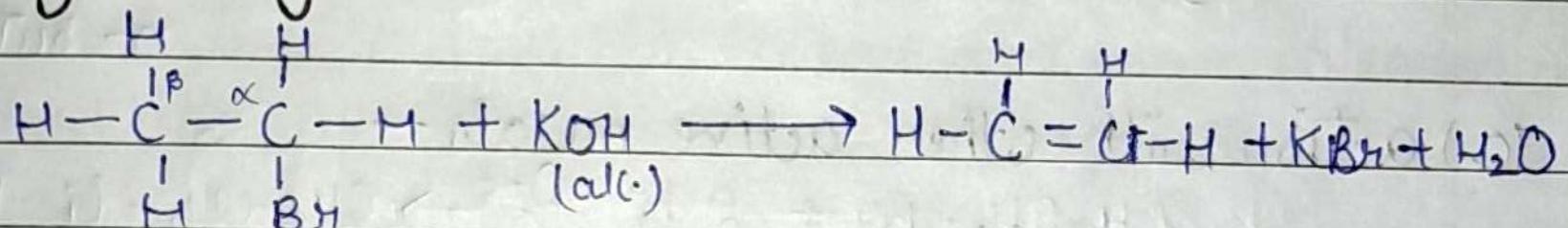


(k) Substitution by alkyl group —

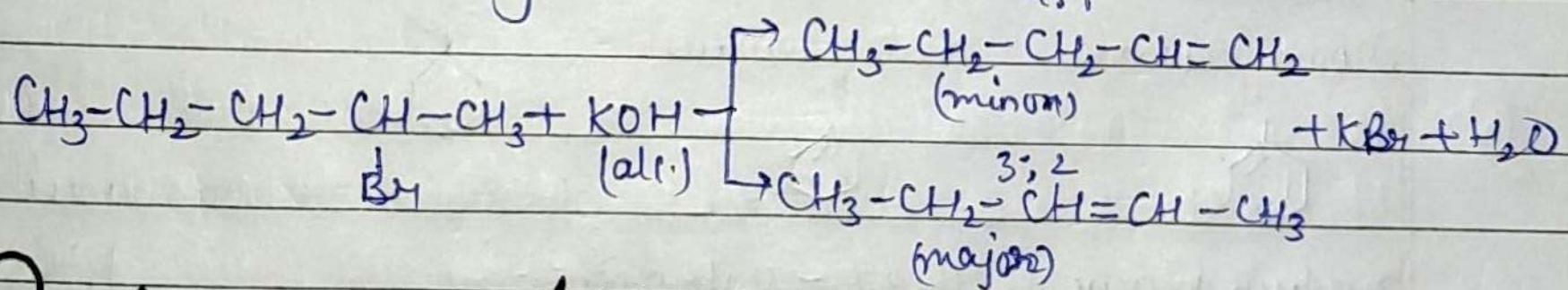


(ii) Elimination Reaction —

(a) Dehydrohalogenation —

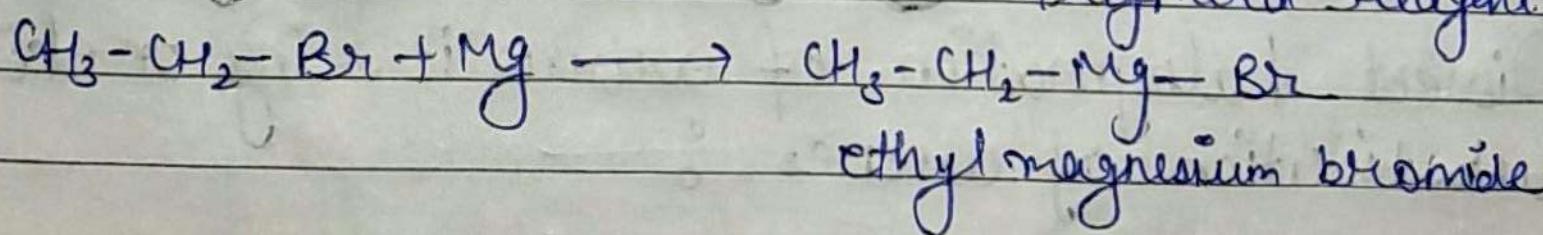
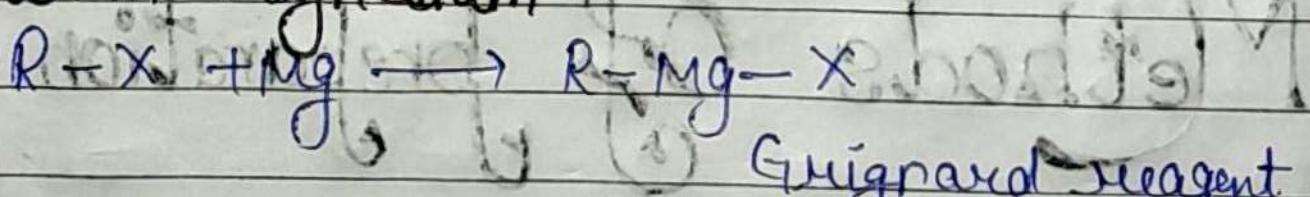


Polytzeff's Rule — In case of haloalkane can eliminate hydrogen halide in 2 different ways then, that alkane will be prefer in which carbon atom joined by the double bond are more alkylated.



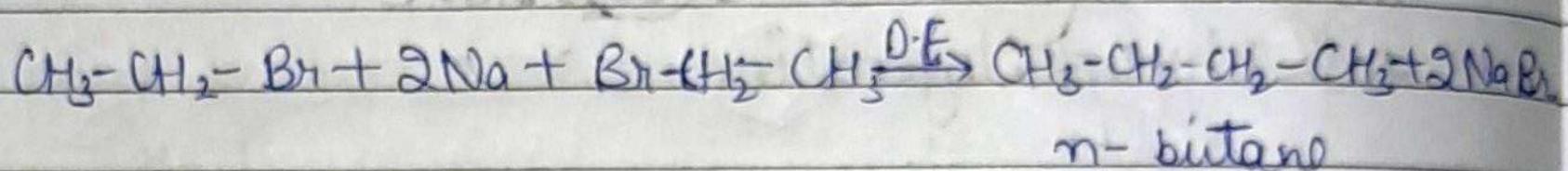
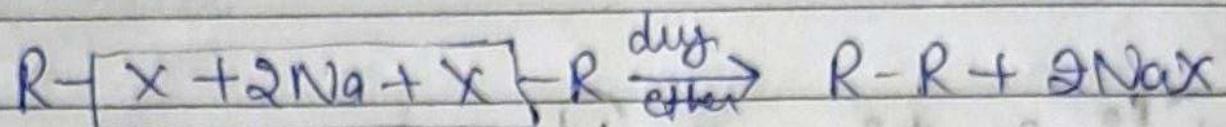
(iii) Reaction with Metals —

(a) Action with magnesium +

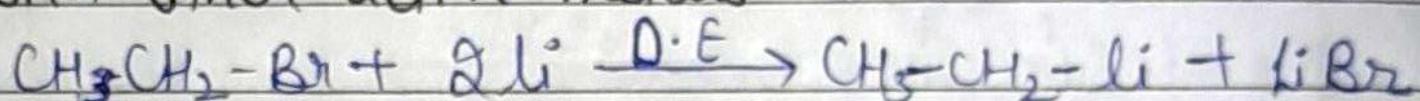


(b) action with sodium —

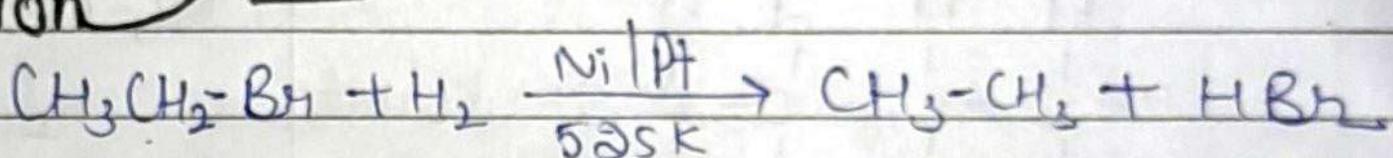
→ Wurtz reaction — when two molecules of alkyl halide react with two molecules of sodium in the presence of dry ether, alkane is formed. This reaction is called as Wurtz reaction.



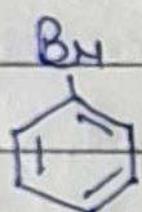
(c) action with other active metals —



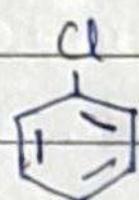
(iv) Reduction —



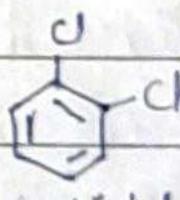
HALOARENES



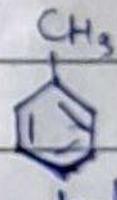
Bromo benzene



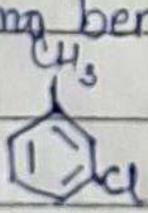
chlorobenzene



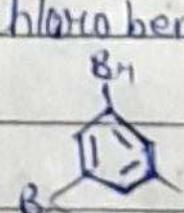
1, 2 - dichlorobenzene



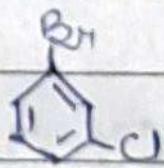
toluene



3-chloro toluene



1, 3, 5 - tribromobenzene



1 - bromo - 3 - chlorobenzene

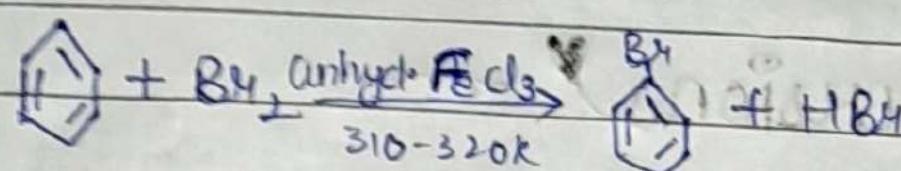
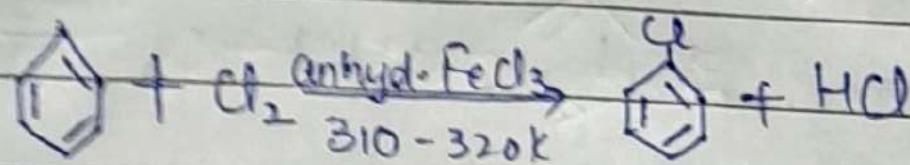
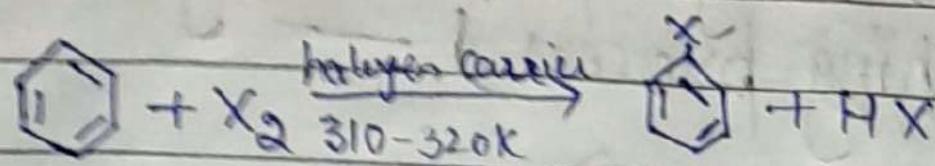


1, 4 - diiodobenzene

Methods Of Preparation of Haloarenes:-

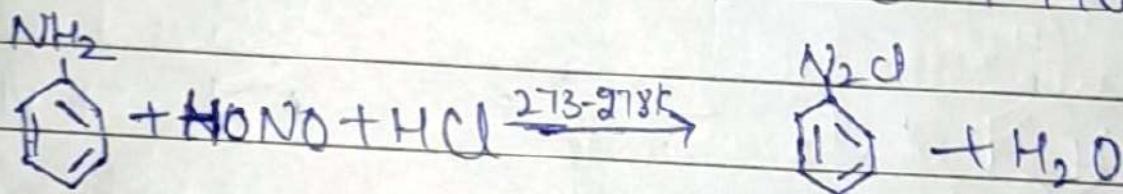
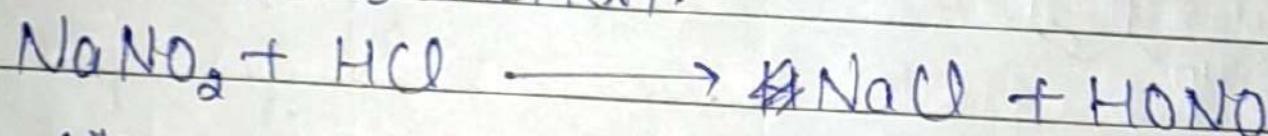
① Direct halogenation of aromatic ring or electrophilic substitution of arenes

(1) Nuclear halogenation :

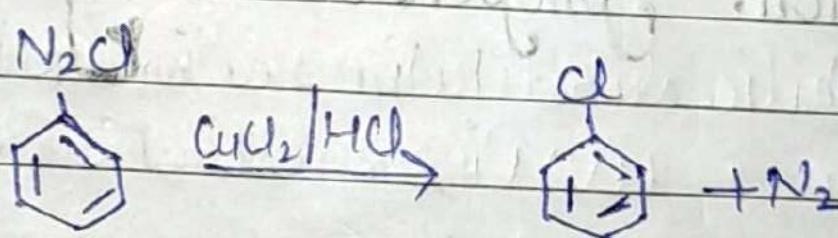


(2) From diazonium salt :

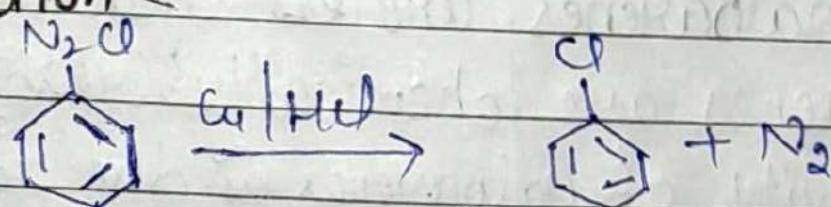
Diazotisation rxn — The benzene diazonium chloride is prepared by treating ice-cold solution of aniline in excess of dilute HCl with an aqueous solution of sodium nitrite at low temperature, 273–278 K. The reaction is known as diazotisation reaction.



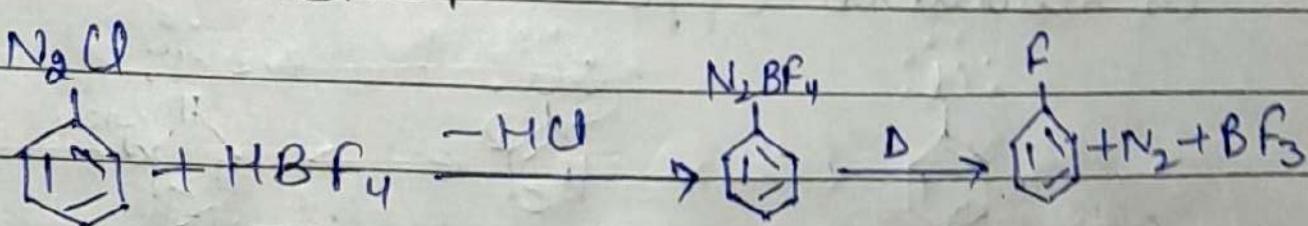
(Sandmeyer reaction)



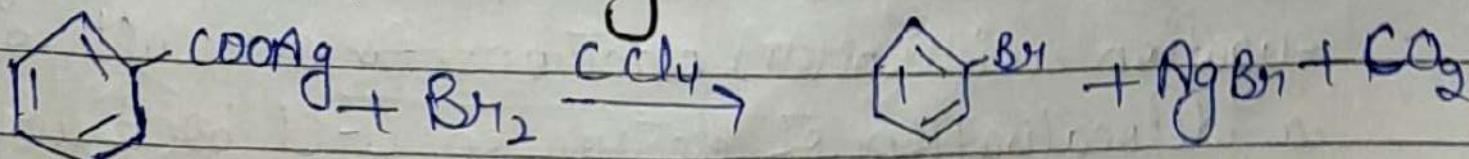
Gattermann reaction



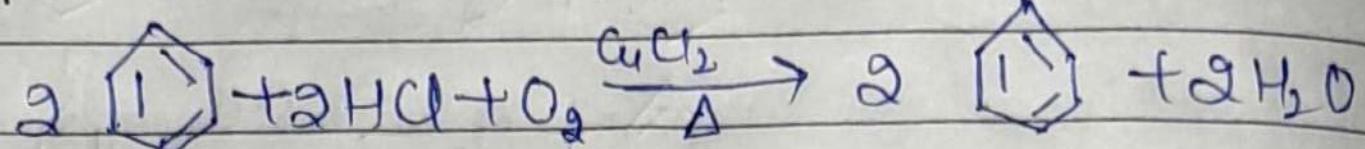
Balz Schiemann reaction



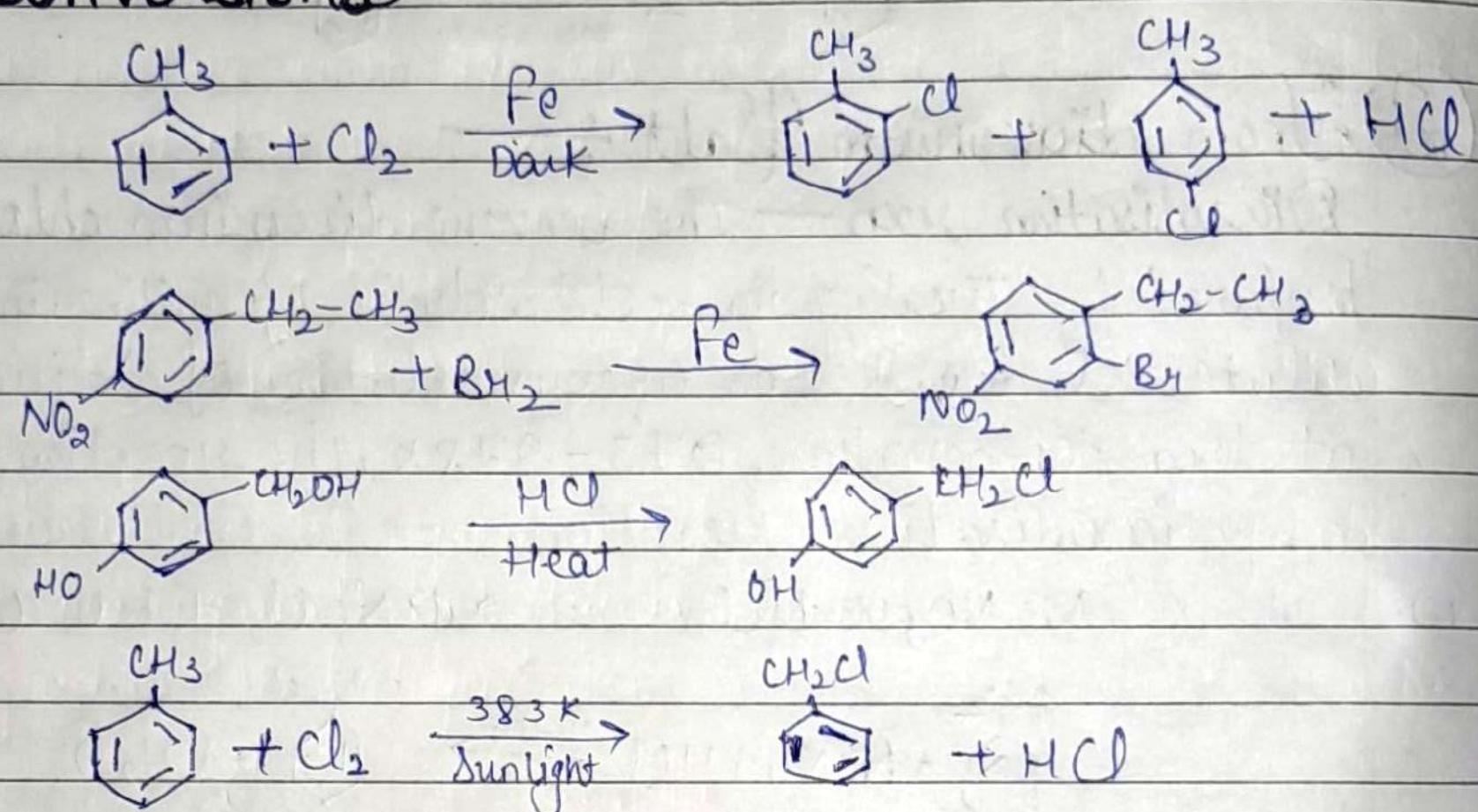
(3) From Willey Salt of aromatic acid :



(4) Commercial preparation of Chloro Benzene (Rasching process) —



* Conversions —



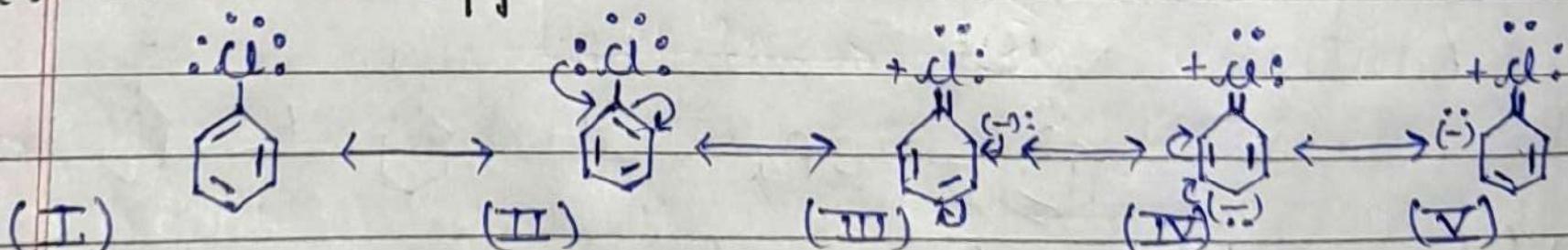
Chemical properties of haloarenes —

- (i) Nucleophilic substitution reaction
- (ii) Reaction with metals.
- (iii) Reduction.
- (iv) Ring substitution or electrophilic substitution.

Q:- Why haloarenes are less reactive than haloalkanes?

Haloarenes are chemically less reactive than haloalkanes. The low reactivity of haloarenes is due to the following reasons —

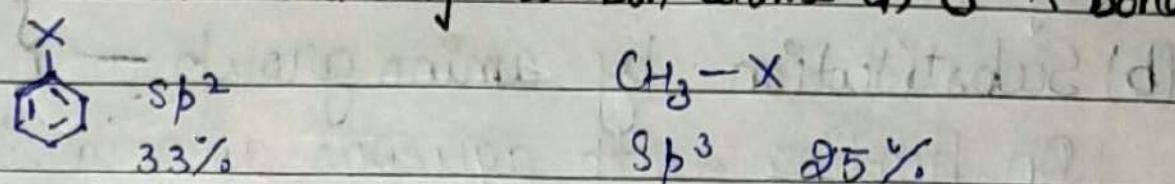
(i) Resonance effect —



In haloarenes the electron pairs on the halogen atom are in conjugation with pi (π) electrons. As a result of resonance, there is a delocalisation of electron on C-Cl bond which acquire a partially

double bond character. This is also evident from the contribution of structures II, IV & V. As a result, the bond cleavage in halo-arene is difficult than haloalkanes, therefore, haloarenes are less reactive towards nucleophilic substitution reaction.

(ii) Difference in hybridisation states of carbon atoms in C-X bond —



In haloalkanes the carbon atom of the C-X bond is sp^3 hybridised whereas, in haloarenes the carbon atom is attached to halogen is sp^2 hybridised. The sp^2 hybridised carbon atom with a greater S character is more electronegative. It can hold the electron pair of the bond more tightly than the sp^3 hybridised carbon atom in alkyl halide with less S character.

(iii) Polarity of carbon halogen bond —

The sp^2 hybridised carbon atom involved in C-X bond in haloarene is more electronegative than the sp^3 hybrid carbon atom in alkyl halide; therefore, this sp^2 hybridised carbon has less tendency to release electrons of the chlorine atom and C-Cl bond in ~~is~~ aryl halide is less polar than in alkyl halide. Thus, lesser is the polarity of C-Cl bond lesser is the reactivity.

(iv) Repulsion between the electron rich attacking nucleophile & electrode rich arenes —

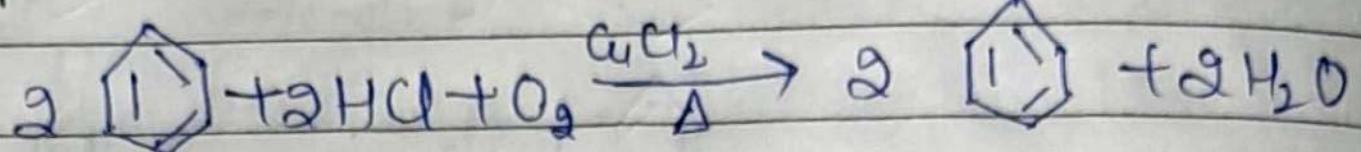
Because of electron rich arenes electron rich nucleophile will not approach for the attack because of the repulsion.

① Nucleophilic Substitution Reaction —

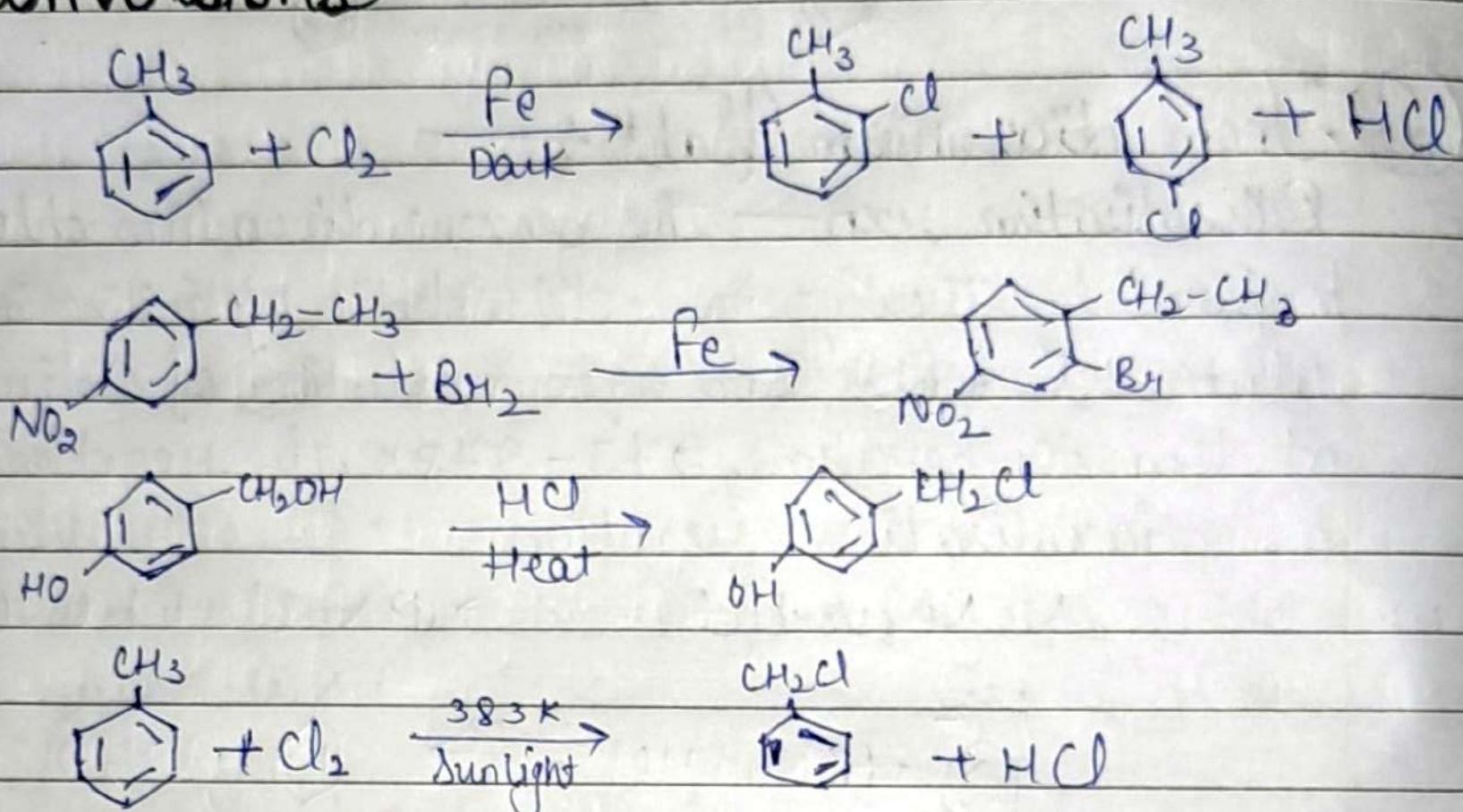
(a) Replacement of hydroxy group — {Formation of phenol}

On heating aryl halide with aqueous solution of sodium hydroxide at 623K and under pressure (300 atm.) the halogen atom is replaced by hydroxyl group forming phenol.

Q. Commercial preparation of Chloro Benzene (Rasching process) —



* Conversions —



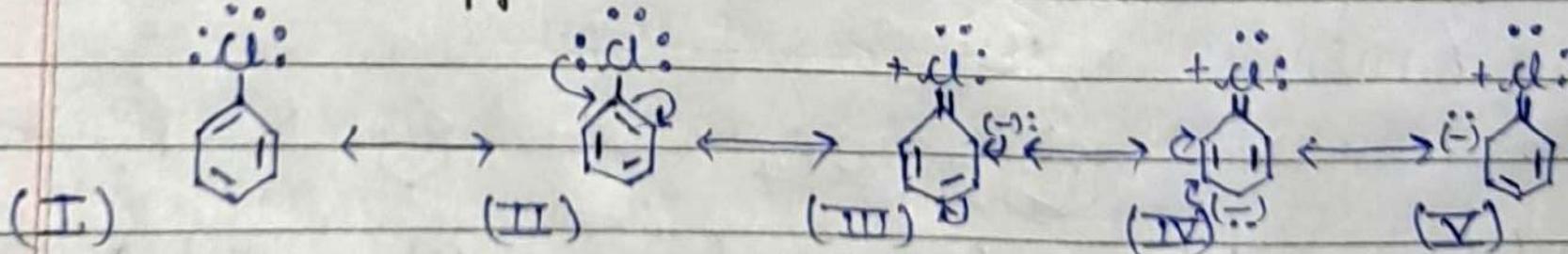
Chemical properties of haloarenes —

(i) Nucleophilic substitution reaction, (ii) Reaction with metals,
 (iii) Reduction, (iv) Ring substitution or electrophilic substitution.

Q:- Why haloarenes are less reactive than haloalkanes?

Haloarenes are chemically less reactive than haloalkanes. The low reactivity of haloarenes is due to the following reasons —

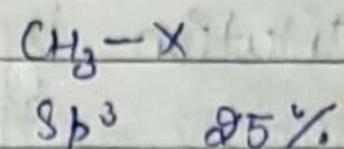
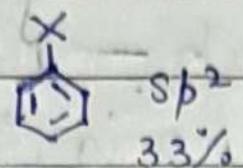
(i) Resonance effect —



In haloarenes the electron pairs on the halogen atom are in conjugation with pi (π) electrons. As a result of resonance, there is a delocalisation of electron on C-Cl bond which acquire a partially

double bond character. This is also evident from the contribution of structures III, IV & V. As a result, the bond cleavage in halo-arene is difficult than haloalkanes; therefore, haloarenes are less reactive towards nucleophilic substitution reaction.

(ii) Difference in hybridisation states of carbon atoms in C-X bond —



In haloalkanes the carbon atom of the C-X bond is sp^3 hybridised whereas, in haloarenes the carbon atom is attached to halogen in sp^2 hybridised. The sp^2 hybridised carbon atom with a greater S character is more electronegative. It can hold the electron pair of the bond more tightly than the sp^3 hybridised carbon atom in alkyl halide with less S character.

(iii) Polarity of carbon halogen bond —

The sp^2 hybridised carbon atom involved in C-X bond in haloarene is more electronegative than the sp^3 hybrid carbon atom in alkyl halide. Therefore, this sp^2 hybridised carbon has less tendency to release electrons of the chlorine atom and C-Cl bond in ~~aromatic~~ halide is less polar than in alkyl halide. Thus, lesser is the polarity of C-Cl bond lesser is the reactivity.

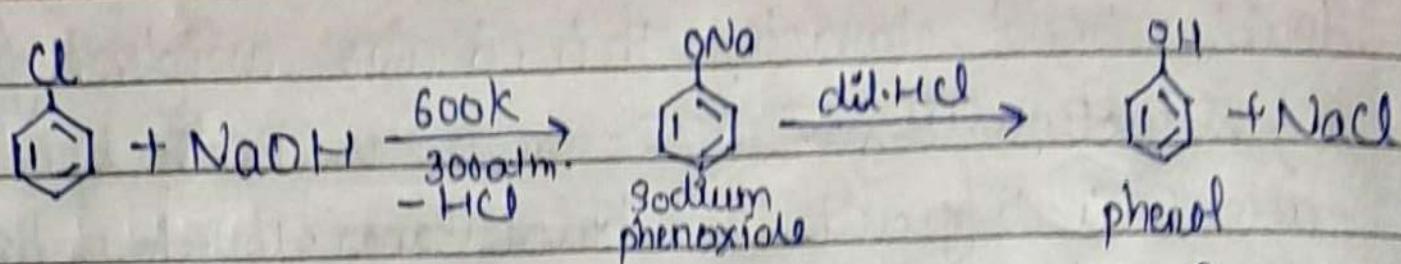
(iv) Repulsion between the electron rich attacking nucleophile & electron rich arenes —

Because of electron rich arenes electron rich nucleophile will not approach for the attack because of the repulsion.

① Nucleophilic Substitution Reaction —

(a) Replacement of hydroxy group — {Formation of phenol}

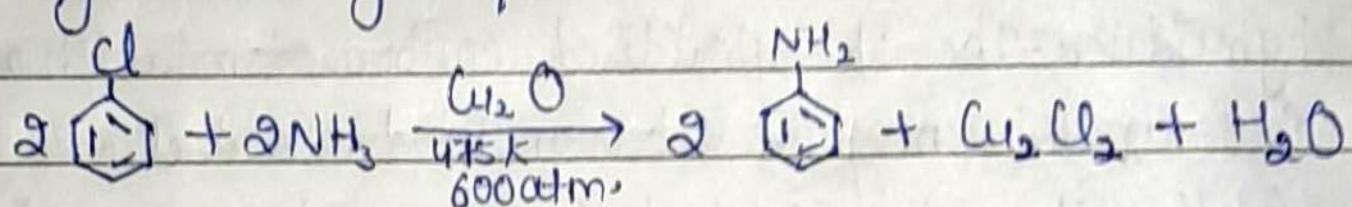
On heating aryl halide with aqueous solution of sodium hydroxide at 623K and under pressure (300 atm.) the halogen atom is replaced by hydroxyl group forming phenol.



This reaction forms the basis of down process for the manufacture of phenol.

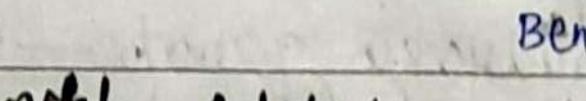
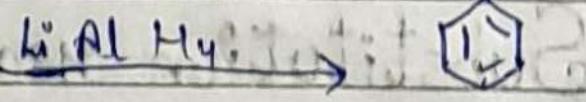
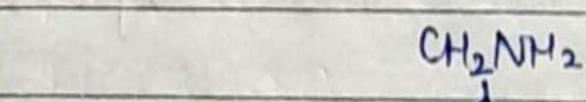
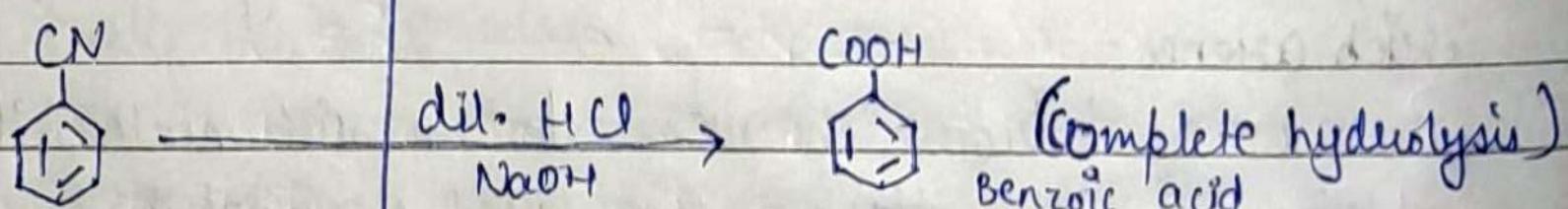
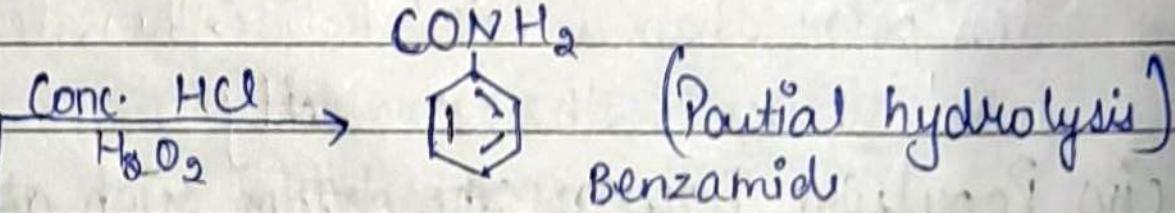
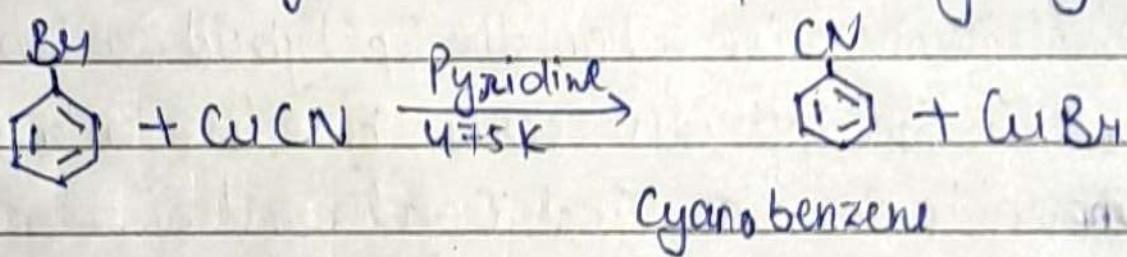
(b) Substitution by amino group — {Formation of aniline}

On heating with aqueous ammonia in the presence of cuprous oxide at 475 K under a pressure of 60 atm , the halogen atom is replaced by amino group.



(C) Substitution by cyano group — {Formation of cyanobenzene}

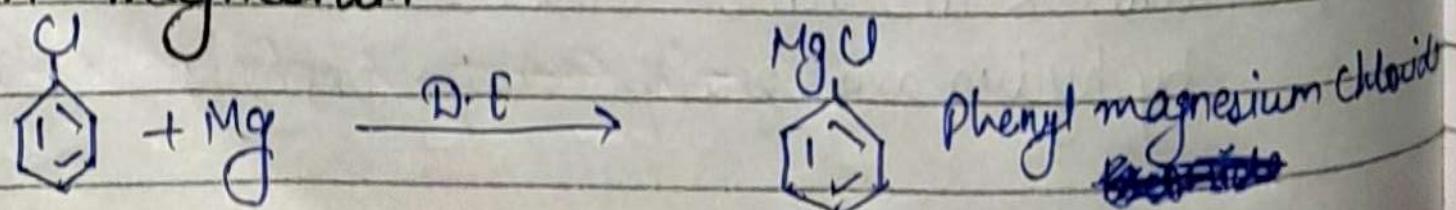
On heating with anhydrous cuprous cyanide in the presence of pyridine the halogen atom is replaced by cyano group.



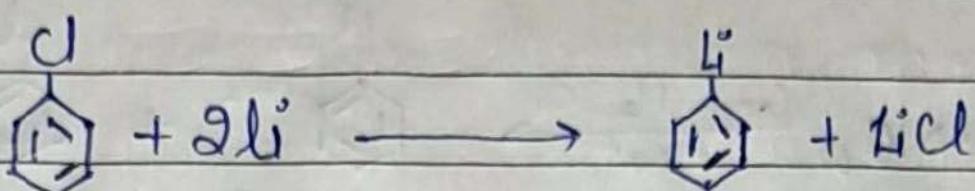
Benzylamin

(2) Reactions with Metals

(a) Reaction with magnesium -

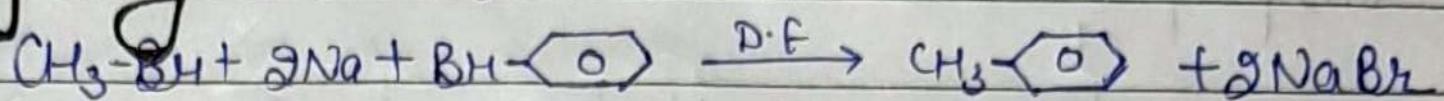


(b) Reaction with Lithium -

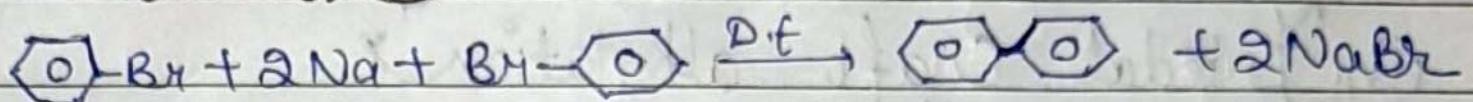


(c) Reaction with Sodium -

Wurtz Fittig reaction

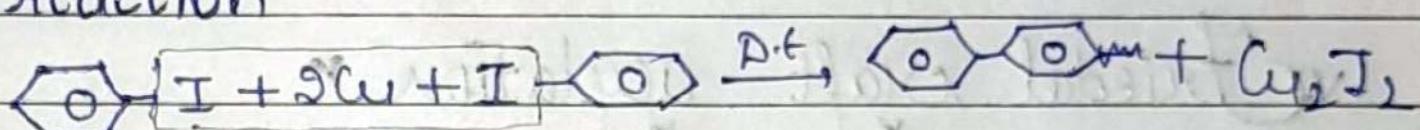


Fittig reaction

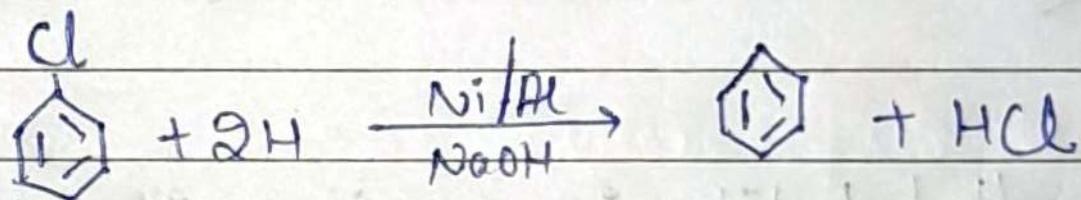


(d) Reaction with copper powder -

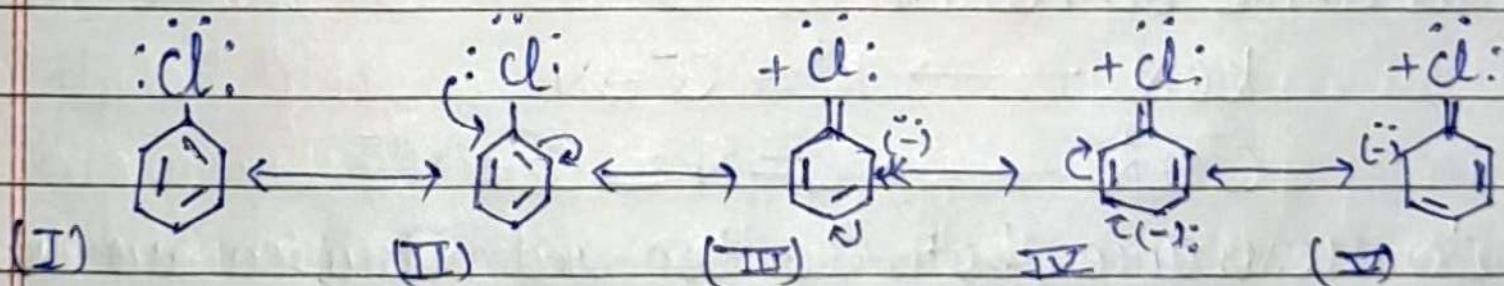
Ullmann reaction



③ Reduction -

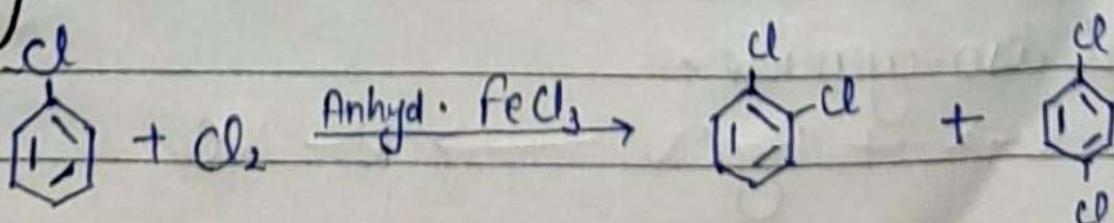


④ Ring Substitution OR

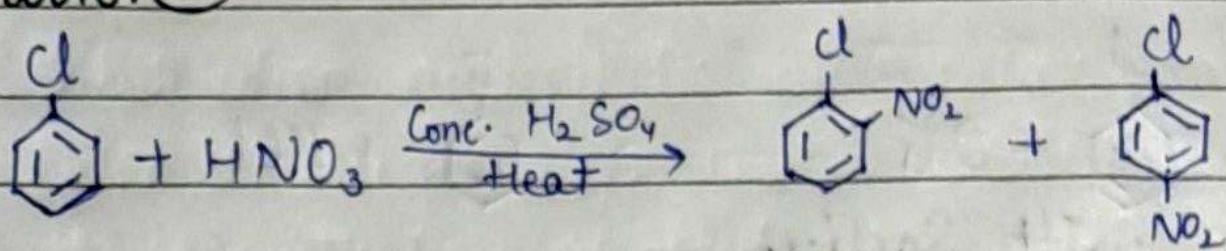


It has been seen in structure III, IV & V that the ortho & para position get negatively charged. In other words the electron density is relatively more at ortho & para positions and consequently the incoming electrophile is more likely to attack on these positions.

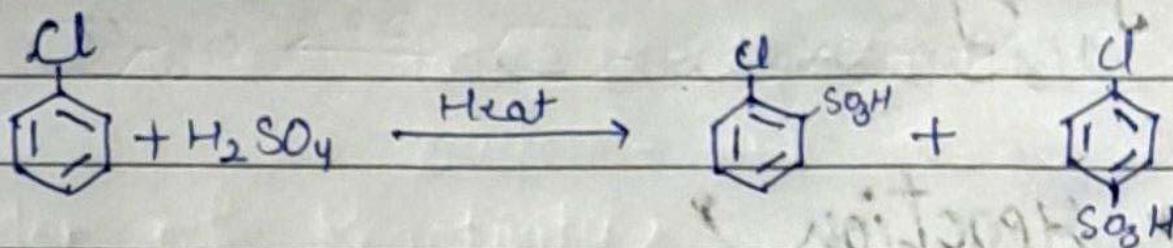
(i) Halogenation



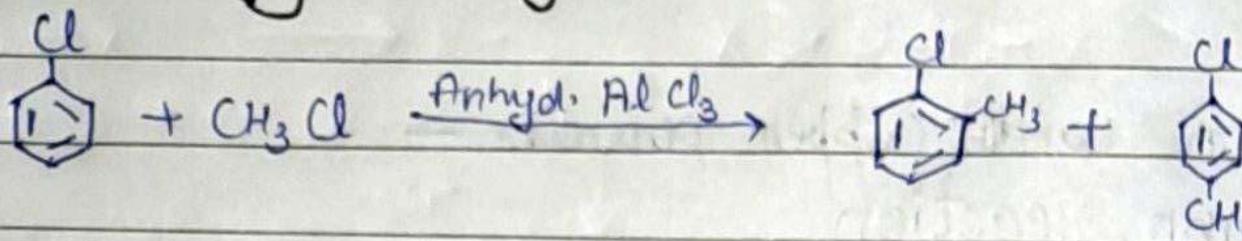
(iii) Nitration ↗



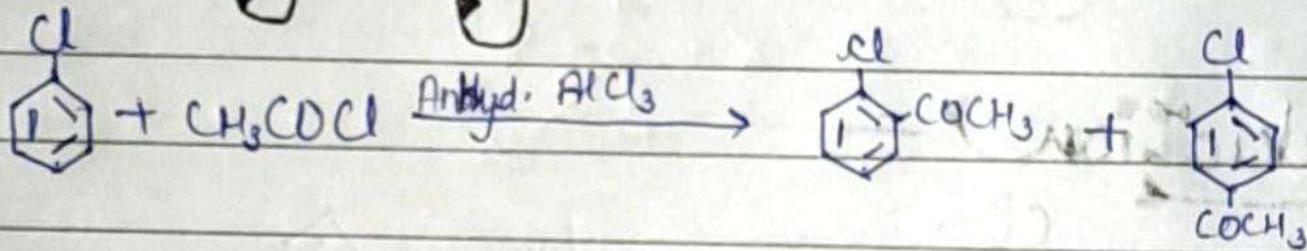
(iv) Sulphonation ↗



(v) Friedel-Crafts alkylation ↗

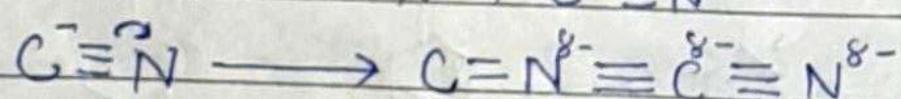
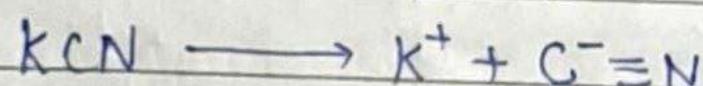


(vi) Friedel-Crafts acylation ↗



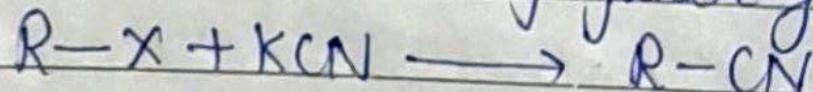
Q: Why alkyl halide give cyanide with KCN but iso-cyanide with AgCN ?

→ KCN is ionic in nature —

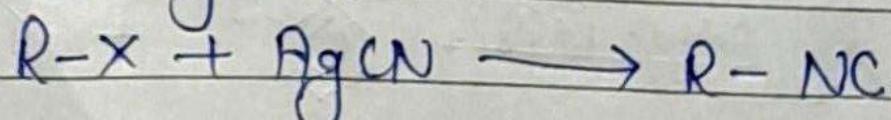


Due to resonance, both carbon and nitrogen are available to donate its electron pair but C-C bond are stronger than C-N bond.

To attack occurs on carbon of cyanide group to form alkyl cyanide



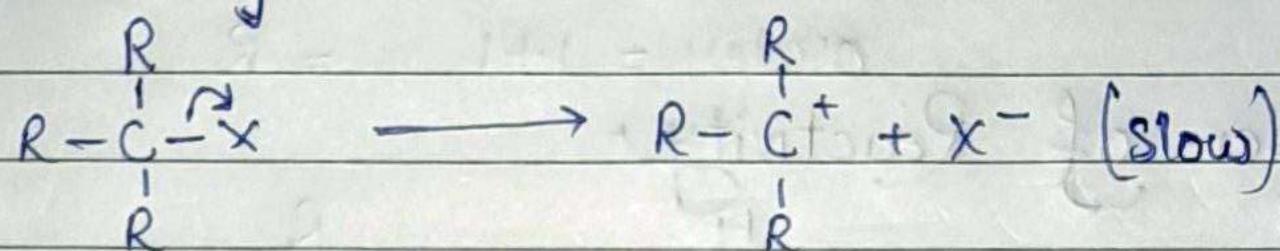
AgCN is covalent in nature only nitrogen is available to donate its electron pair so attack occurs on nitrogen of C-N group to form alkyl iso-cyanide.



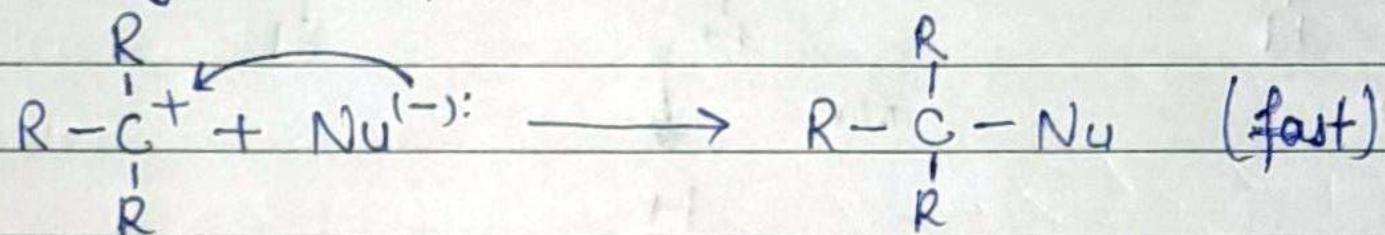
Q:- Give the mechanism of S_N^1 reaction.

S_N^1 (Substitution nucleophilic unimolecular reaction) are those which takes place in two steps and the rate of reaction depends upon only on the concentration of the alkyl halide and independent on concentration of nucleophile.

Step-I:- formation of carbocation (C^+)



Step-II:- Attack of nucleophile

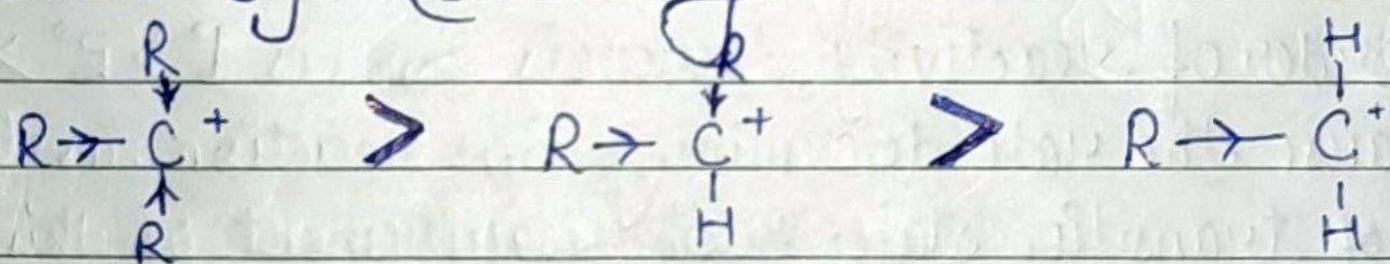


$$\text{Rate} = k [R_3C-X]$$

Order - 1

[Slowest step is the]
[rate determining step]

Order of Reactivity



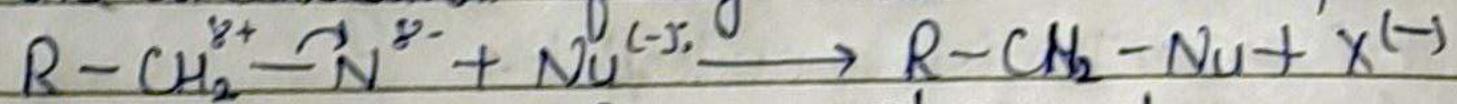
The order of reactivity is explained on the basis of inductive effect.

Due to $+I$ effect, R group is electron releasing group. It releases its electrons towards positively charged carbon atom, and the positive charge on the carbon decreases and stability increases.

Now, more the number of group of alkyl group more is the inductive effect and more the stability of carbocation. thus the order of reactivity of alkyl halide towards S_N^1 reaction is —

$$3^\circ > R^\circ > 1^\circ$$

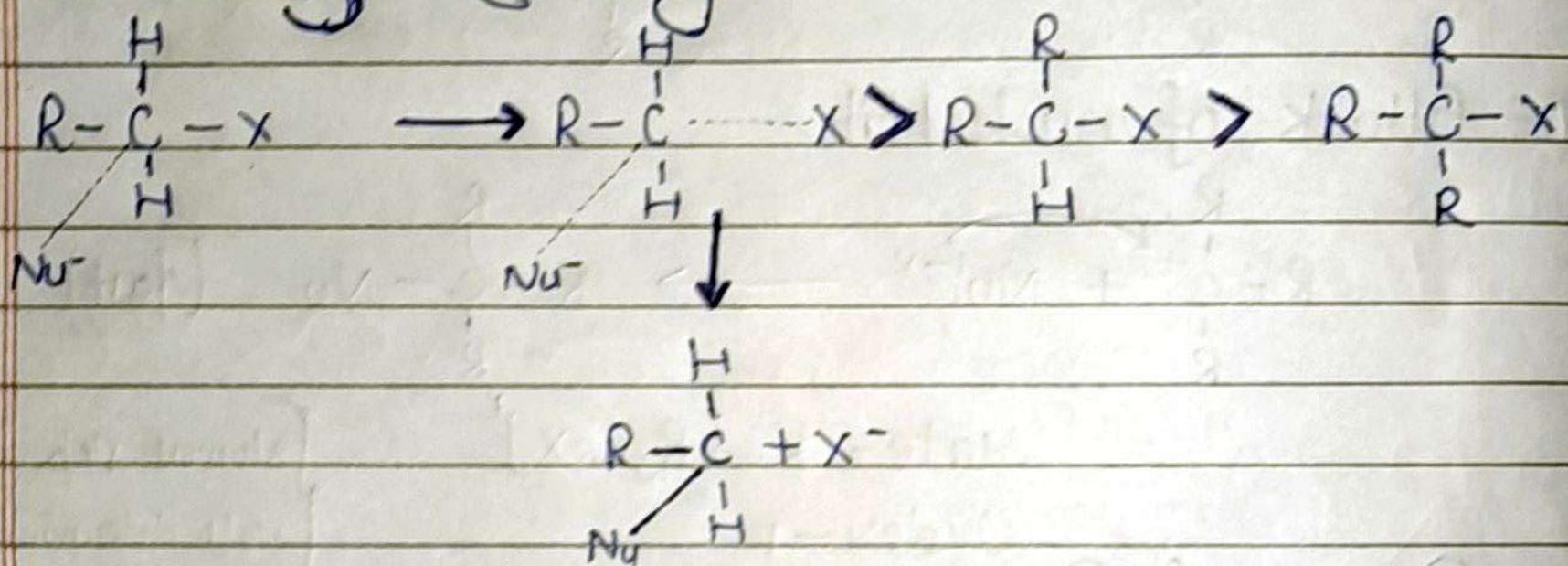
$S_{N}2$ (Substitution nucleophilic bimolecular reaction) are those which takes place in single step and the rate of reaction depends upon the concentration of alkyl halide and nucleophile.



$$\text{Rate} = [R-\overset{H}{\underset{H}{C}}-\overset{x}{|}] [Nu^-]$$

$$\text{order} = 1+1 = 2$$

Order of Reactivity



The order of reactivity towards $S_{N}2$ is $1^\circ > 2^\circ > 3^\circ$. This is because the rate determining $S_{N}2$ reactions involve the formation of transition state. Basic requirement of this is back side attack of nucleophile on carbon atom carrying halogen. This type of attack is easy in case of primary alkyl halide because in tertiary & secondary alkyl halide carbon atom attack to halogen further like to three alkyl groups & two alkyl groups which causes steric hindrance to attack of nucleophile.