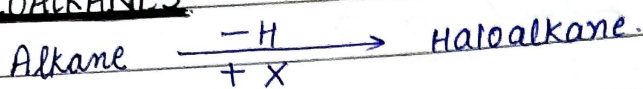


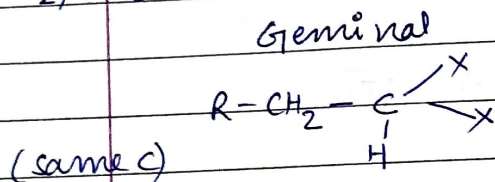
HALOALKANES AND HALOARENES

HALOALKANES

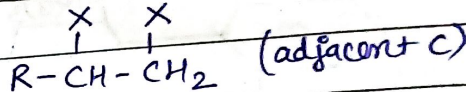


- 1) Monohaloalkane: Alkyl Halides $C_n H_{2n+1} X$
- | | | |
|----------------------------|---|--|
| $R-CH_2-X$
1° (Primary) | $\begin{matrix} R'' \\ \\ R-CH-X \\ \\ R' \end{matrix}$
2° (Secondary) | $\begin{matrix} R'' \\ \\ R-C-X \\ \\ R \end{matrix}$
3° (Tertiary) |
|----------------------------|---|--|

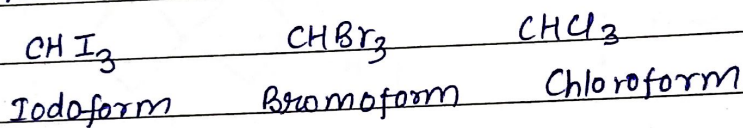
- 2) Di-haloalkane:



Vicinal

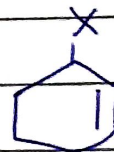
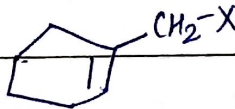
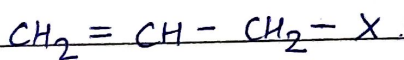


- 3) Tri-haloalkane: CHX_3 (Haloform)

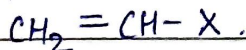


- 4) Tetrahaloalkane: $CX_4 \rightarrow CCl_4$ (Carbon Tetrachloride)

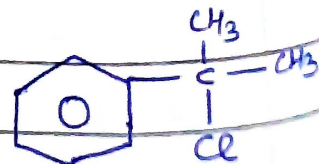
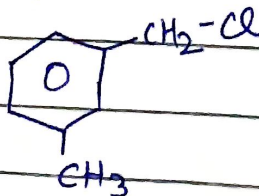
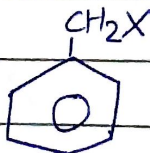
- 5) Allylic Halides \rightarrow Halogen attached to adjacent atom of double bond:



- 6) Vinylic Halides \rightarrow Halogen attached to double bonded carbon:



- 7) Benzylic Halides \rightarrow Halogen attached to carbon attached to Benzene ring:



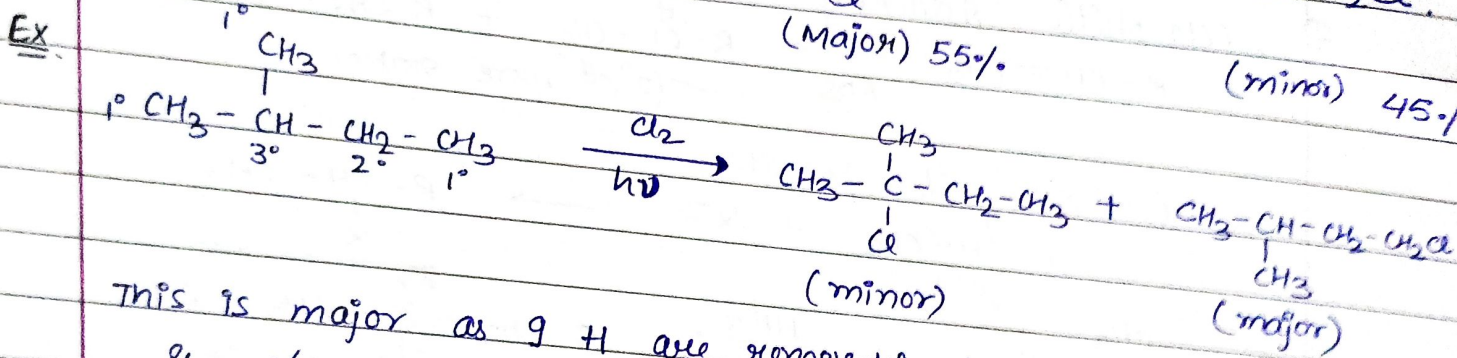
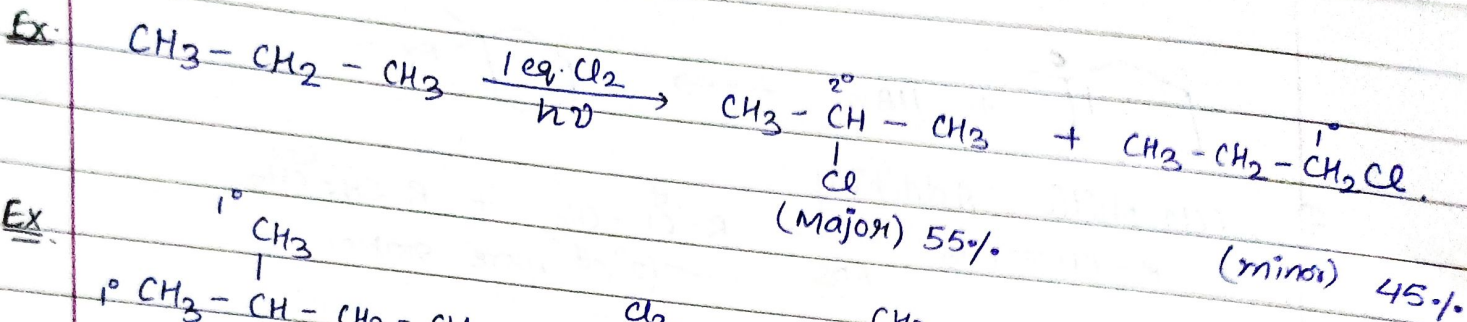
* PREPARATION OF ALKYL HALIDES (R-X)

1) From alkane. Direct Halogenation



But this isn't preferred in labs as mixed products are obtained. but preferred as industrial process.

Free Radical Mechanism



This is major as 9 H are removable from 1° C.

& $\%(\text{H}) = \frac{n_i r_i}{\sum n_i r_i} \times 100$

	3°	2°	1°
for Cl. Rate	5	3.0	1
for Br. Rate	1600	82	1

→ Bromination → proceeds in same way

→ Iodination: $\text{CH}_4 + \text{I}_2 \xrightarrow{h\nu} \text{CH}_3\text{-I} + \text{HI}$ → strong reducing agent.

for better yield of Alkyl Halide we use strong oxidising agent like HNO_3 or HIO_3 (conc)

$$\text{HIO}_3 + 5 \text{HI} \longrightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$$

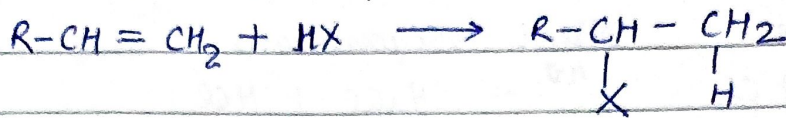
→ Fluorination: explosive and difficult to obtain

$$\text{CH}_3-\text{CH}_3 + 3\text{F}_2 \xrightarrow{h\nu} 2\text{C} + 6\text{HF}$$

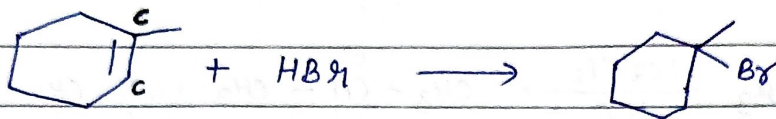
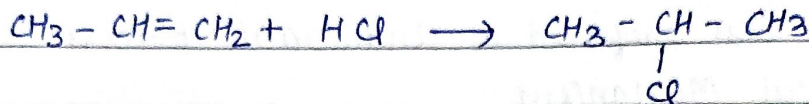
(carbon black)

$\Delta H < 0$ (highly exothermic)

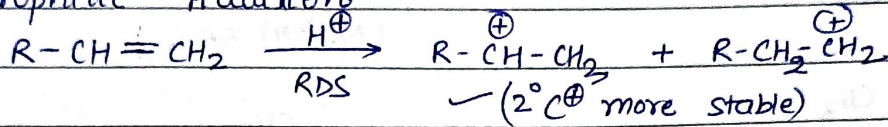
2) From Alkenes (Electrophilic Addition Rxⁿ).



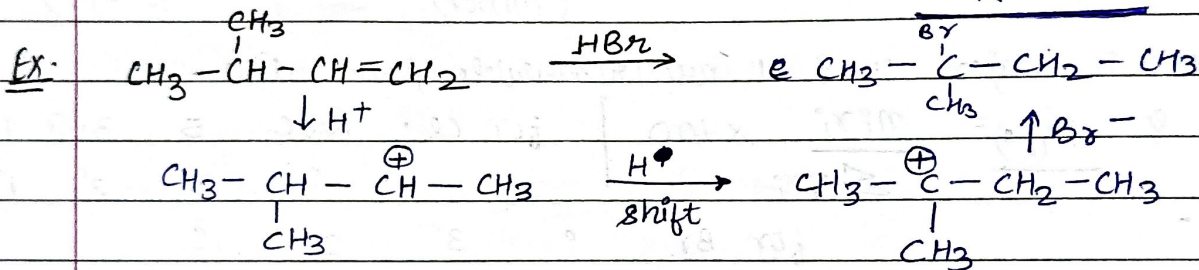
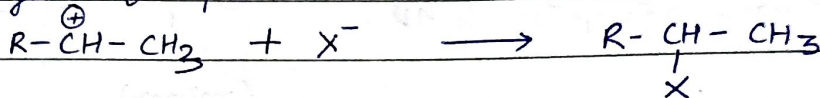
"MARKOVNIKOV'S RULE"



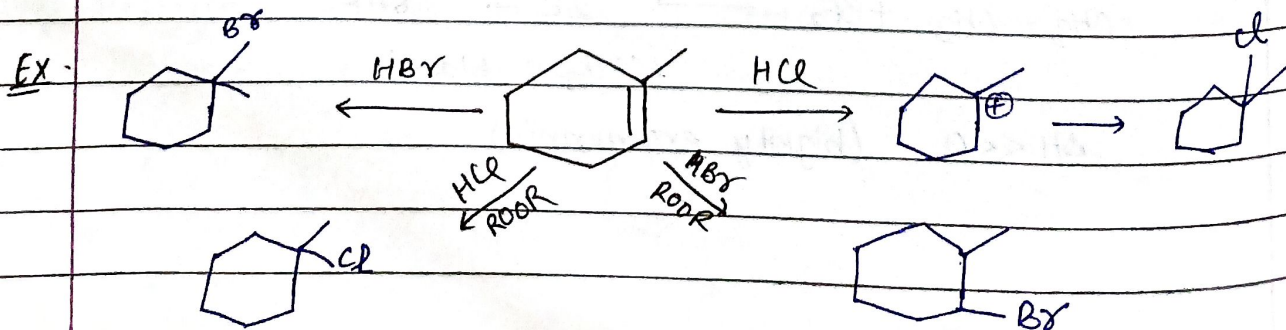
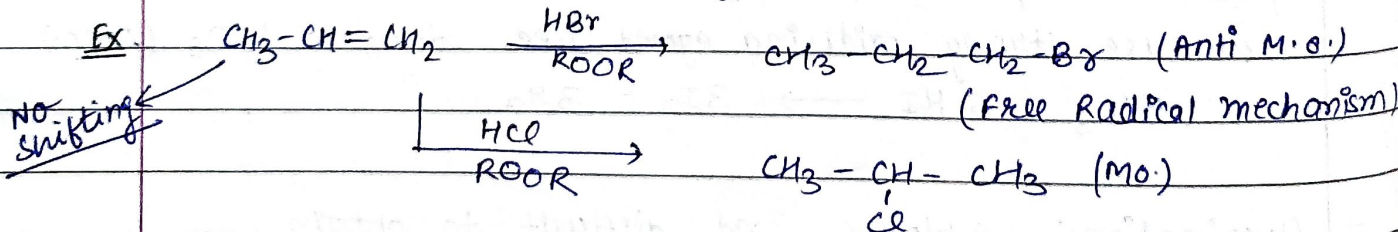
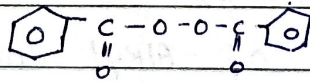
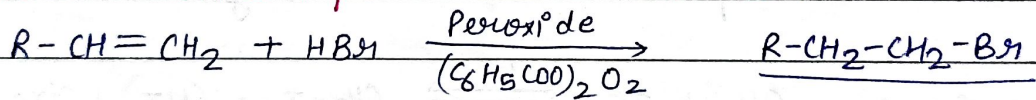
⊕ Electrophilic Addition



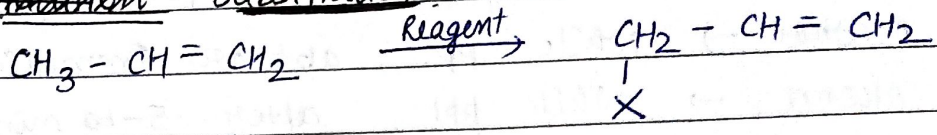
Rearrange if possible.



⊕ KHARASH EFFECT / ANTI MARKOVNIKOV RULE

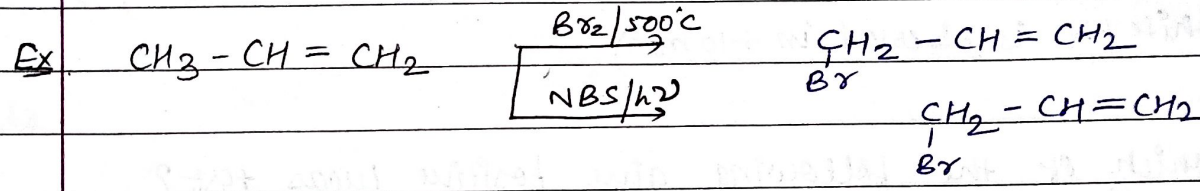
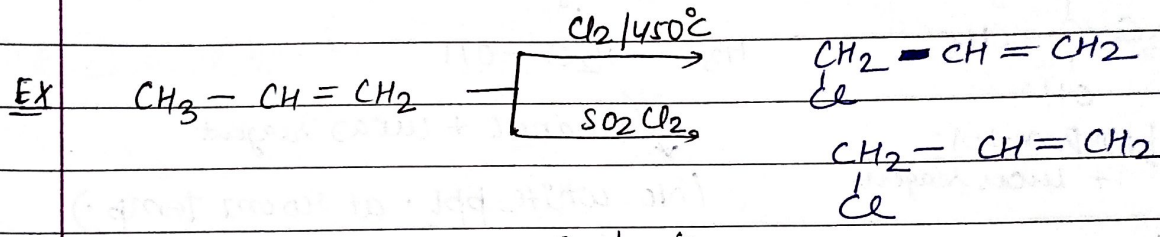


③ Allylic Substitution



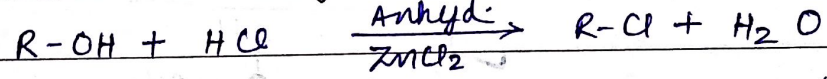
- Reagent: 1) Halogen at high temp (400-500°C)
 2) NBS → Allylic substitution of Br } room temp
 3) SO₂Cl₂ → Allylic substitution of Cl.

→ Proceeds with free radical mechanism.

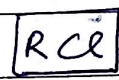
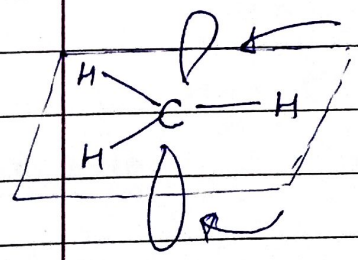
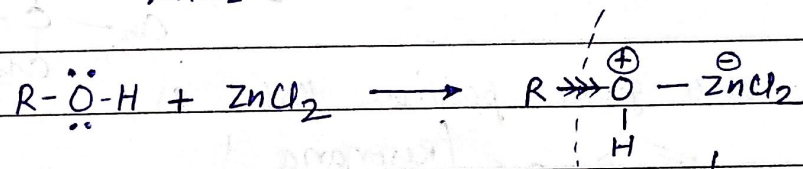


3) Preparation from Alcohols:

A) Conc. HCl + Anhyd. ZnCl₂ **LUCA'S REAGENT**

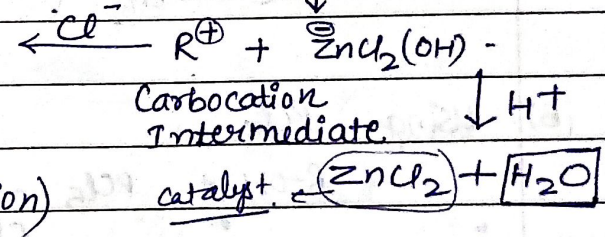


SN¹ Mechanism:

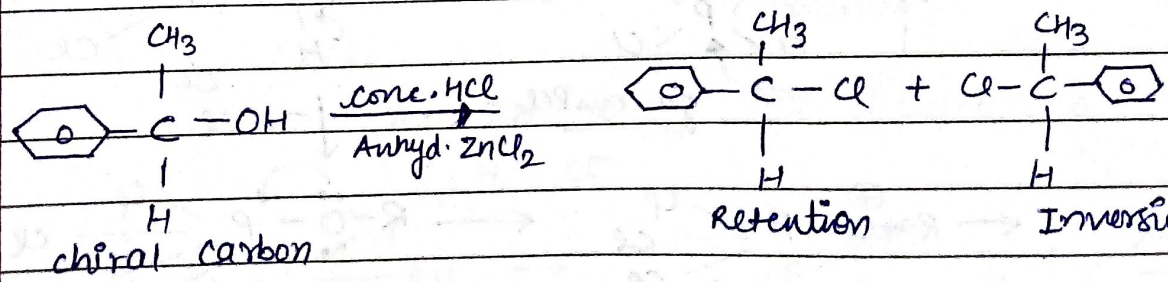


(Racemic mixture)

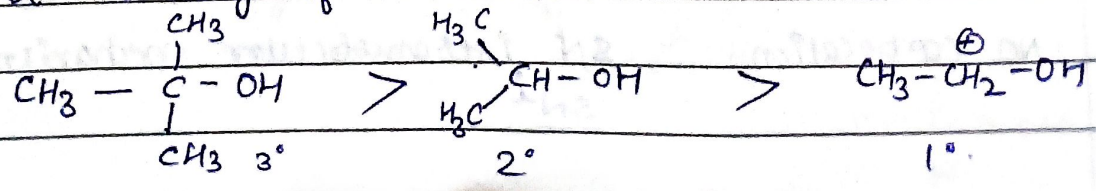
of Retention & Inversion)

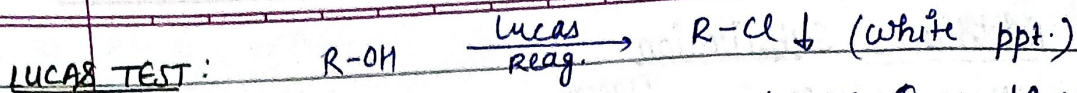


Ex



* Rate α stability of Carbocation.



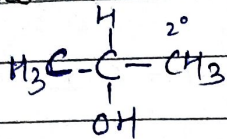


3° Alcohol \rightarrow white ppt. appears immediately

2° Alcohol \rightarrow white ppt. after 5-10 min.

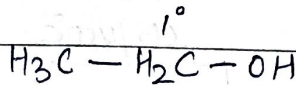
1° Alcohol \rightarrow No white ppt. at room temperature!
 \rightarrow Heat \checkmark

Ex Give chemical test to distinguish b/w propan-2-ol & ethanol:



\downarrow propan-2-ol + Lucas reagent

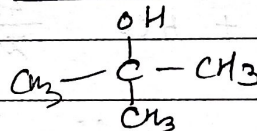
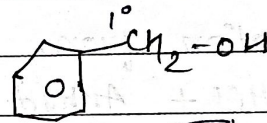
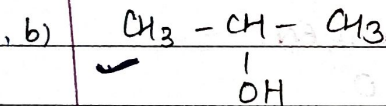
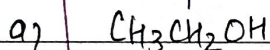
(white ppt is observed in 5-10 min)



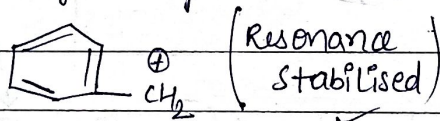
\downarrow ethanol + Lucas reagent

(No white ppt. at room temp.)

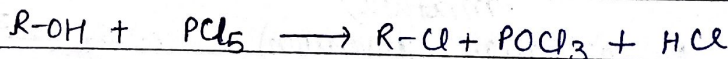
Ex Which of the following give positive Lucas test?



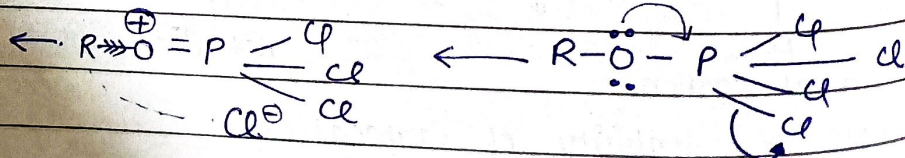
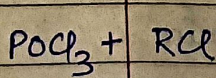
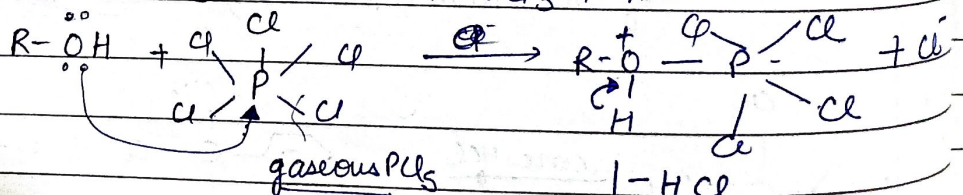
(c) also gives positive test as



(B) Using PCl_5



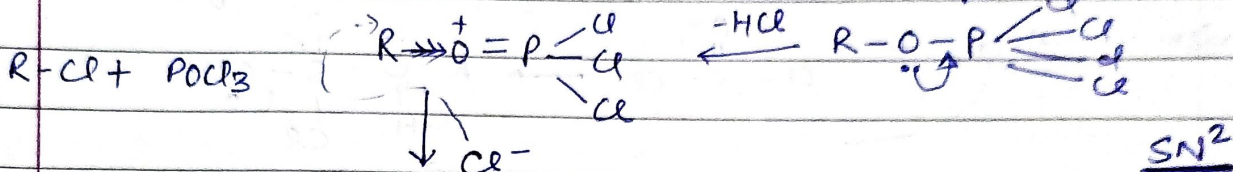
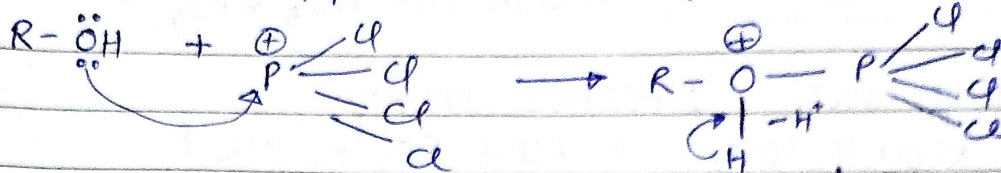
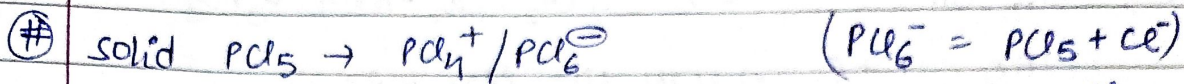
Mechanism:



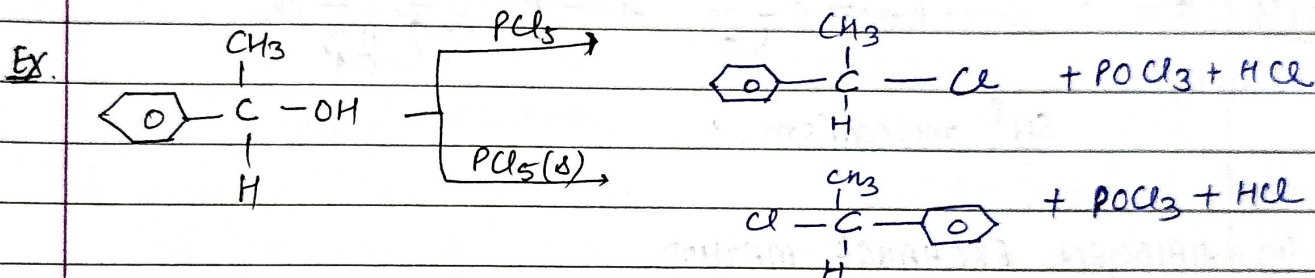
No carbocation.

$\text{S}_\text{N}1$ intramolecular mechanism $\text{S}_\text{N}2$.

Product is "Retention Product"

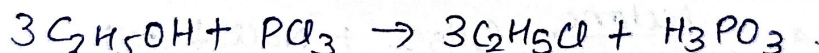


Product is "Inversion Product"

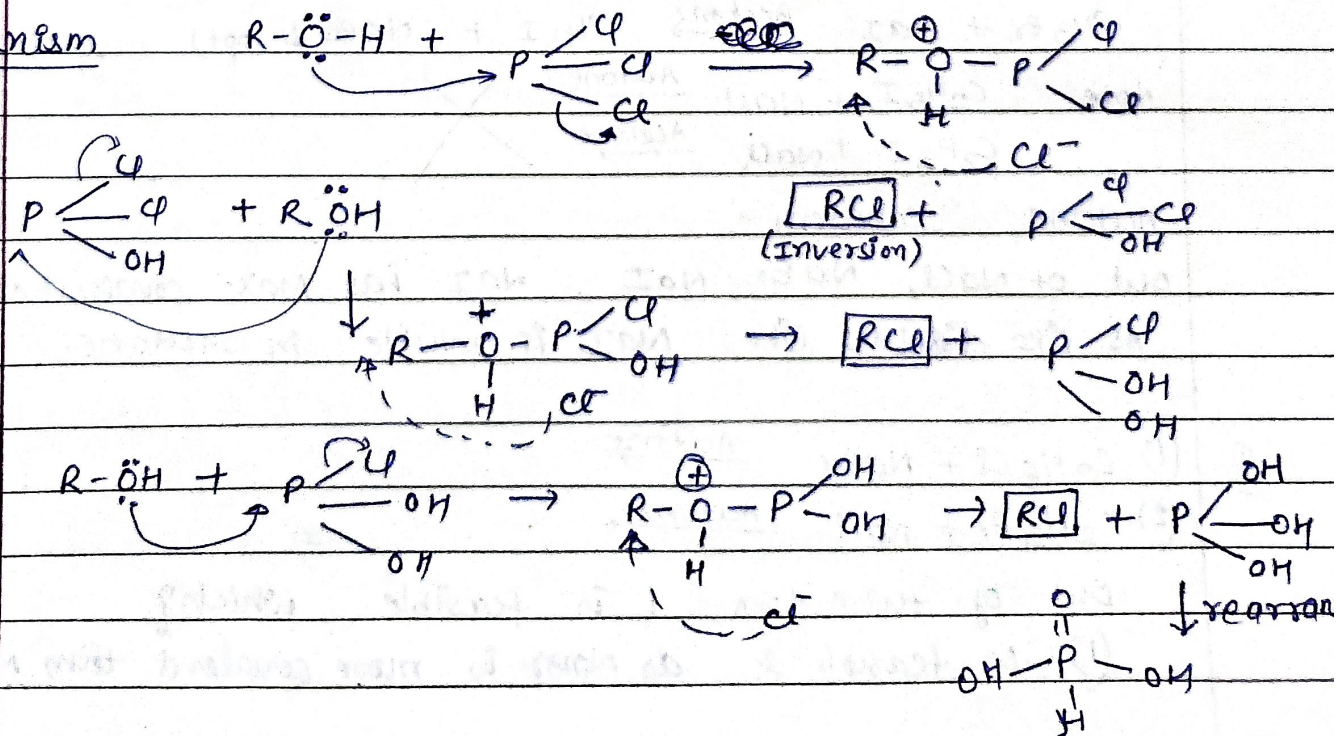


⊕ PBr_5 and PI_5 doesn't exist.

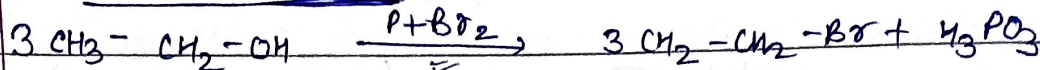
(c) using PCl_3 .



Mechanism

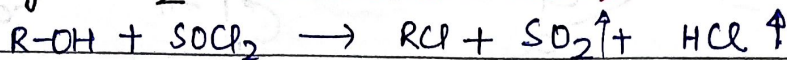


"Inversion product", S_N^2 mechanism.

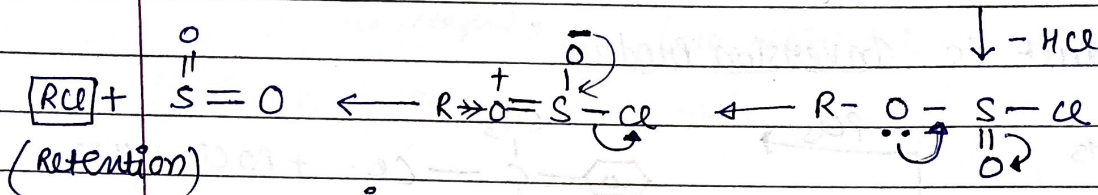
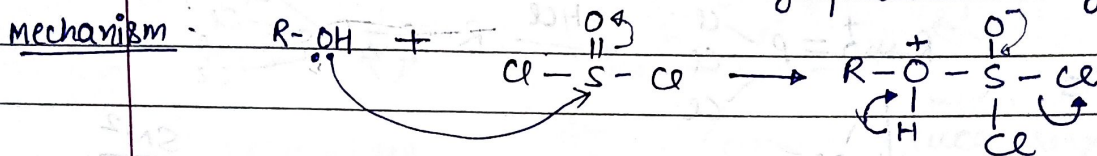


$\text{P+Br}_2, \text{P+I}_2 \rightarrow$ react like PBr_3 & PI_3 .

*** D) using SOCl_2 DARZEN'S METHOD



It is the best method as by products are gaseous.

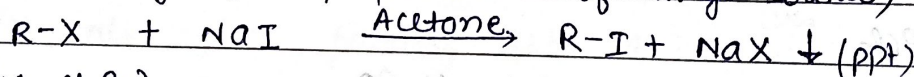


S_N^i mechanism.

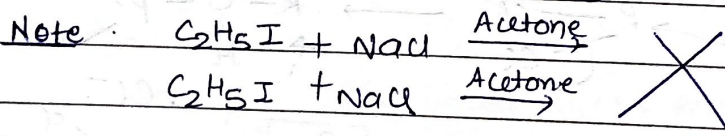
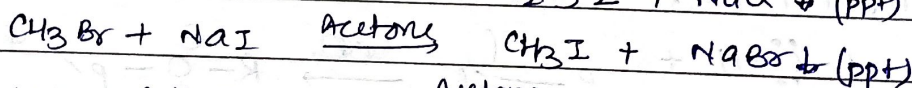
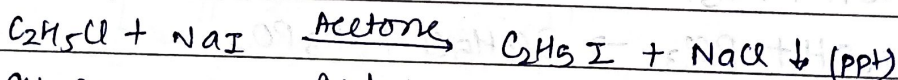
(4) HALOGEN EXCHANGE METHOD.

(A) FINKELSTEIN REACTION

(exclusively for preparation of Alkyl Iodide).

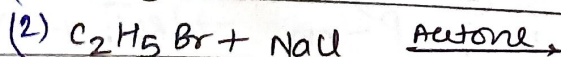
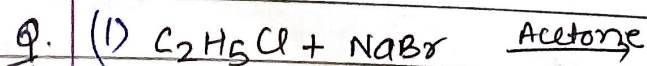


(X = Cl, Br)



Acetone = covalent.

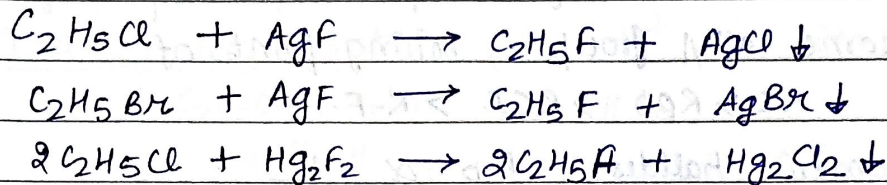
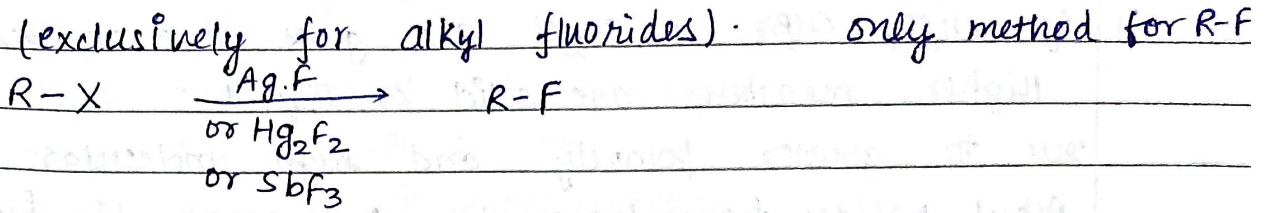
out of $\text{NaCl}, \text{NaBr}, \text{NaI}$, NaI has max. covalent character. As like dissolves like, NaI is soluble in Acetone.



Out of these two, 1 is feasible. which?

(1) is feasible & as NaBr is more covalent than NaCl .

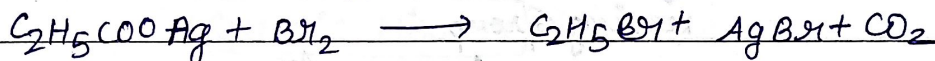
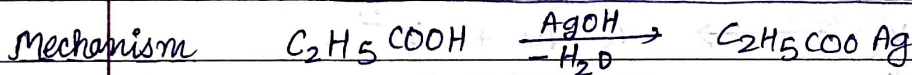
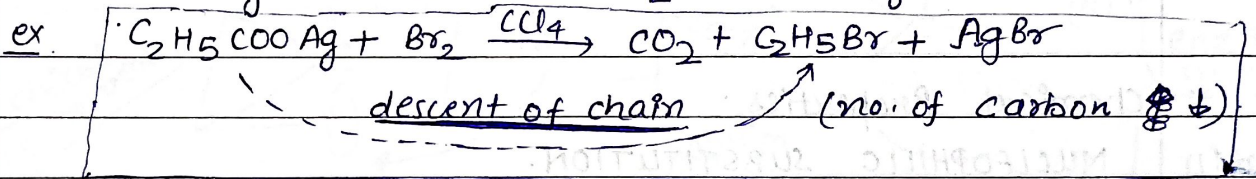
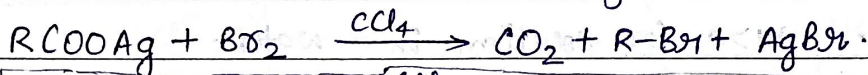
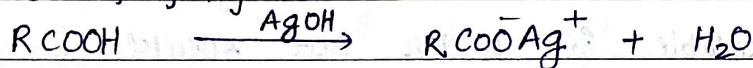
B) SWART'S REACTION



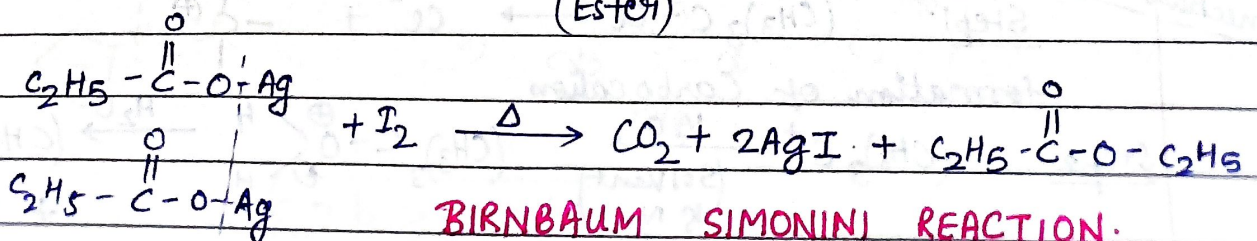
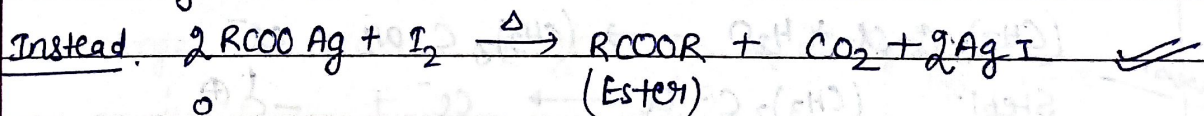
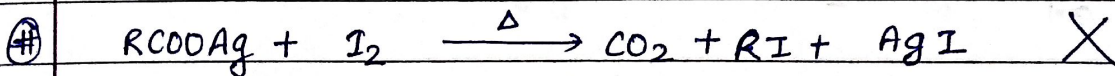
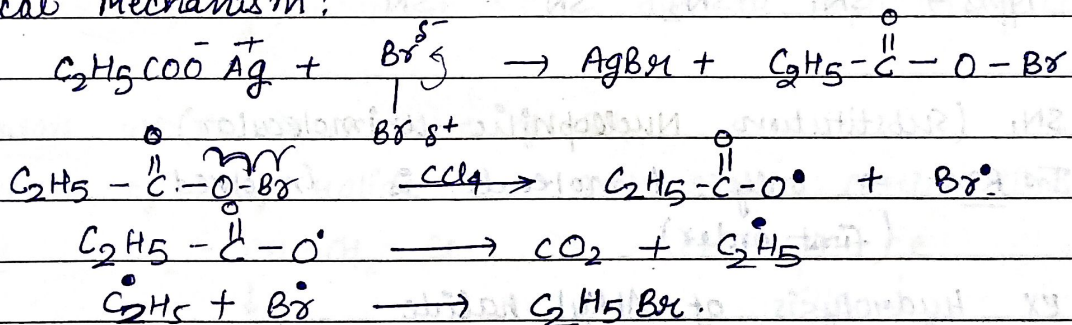
(5) BORODINE - HUNSDIECKER REACTION

(exclusively for preparation of Alkyl Bromide)

→ silver salt of fatty acid



free radical mechanism:



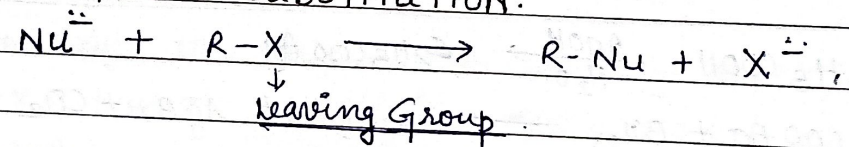
BIRNBAUM SIMONINI REACTION.

*** PHYSICAL PROPERTIES.**

- (1) CH_3Cl , CH_3Br , $\text{CH}_3\text{CH}_2\text{Cl}$ are gases at room temp. Higher members are solid or liquid. Due to greater polarity and high molecular mass, Alkyl halides have higher b.p than corresponding hydrocarbons.
- (2) For same alkyl group, boiling point of $\text{RI} > \text{RBr} > \text{RCl} > \text{R-F}$.
- (3) for isomeric halides, b.p \propto branching.
- (4) Bromo, iodo, polychloro derivatives have higher density than water. Density increases with no. of carbon atoms, Halogen atoms and atomic mass of halogen atom.
- (5) slightly soluble in water but soluble in other organic solvents. $\Delta H > 0$ for solution in water.

*** Chemical Properties.**

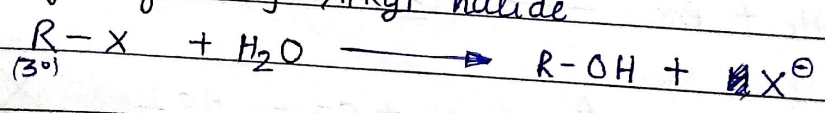
Property (1) **NUCLEOPHILIC SUBSTITUTION.**



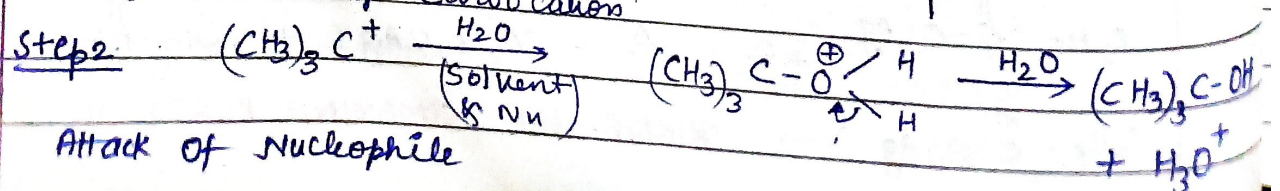
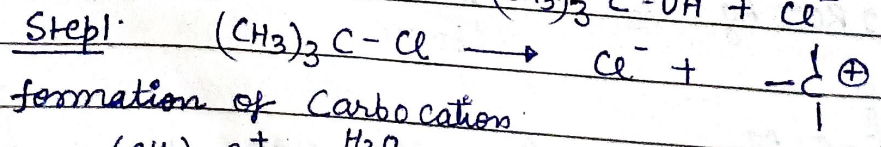
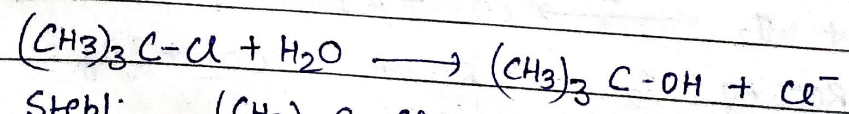
Types \rightarrow $\text{S}_{\text{N}}1$, $\text{S}_{\text{N}}2$, $\text{S}_{\text{N}}\text{i}$, $\text{S}_{\text{N}}\text{Ar}$

(#) $\text{S}_{\text{N}}1$ (Substitution Nucleophilic Unimolecular)
 In RDS \rightarrow only 1 molecule is involved (first order).

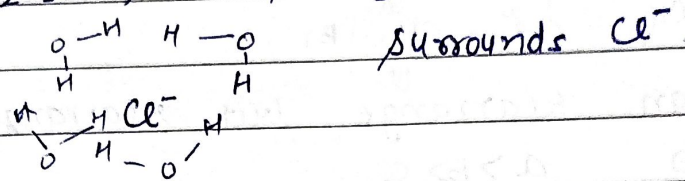
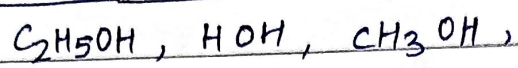
EX Hydrolysis of Alkyl halide



Mechanism

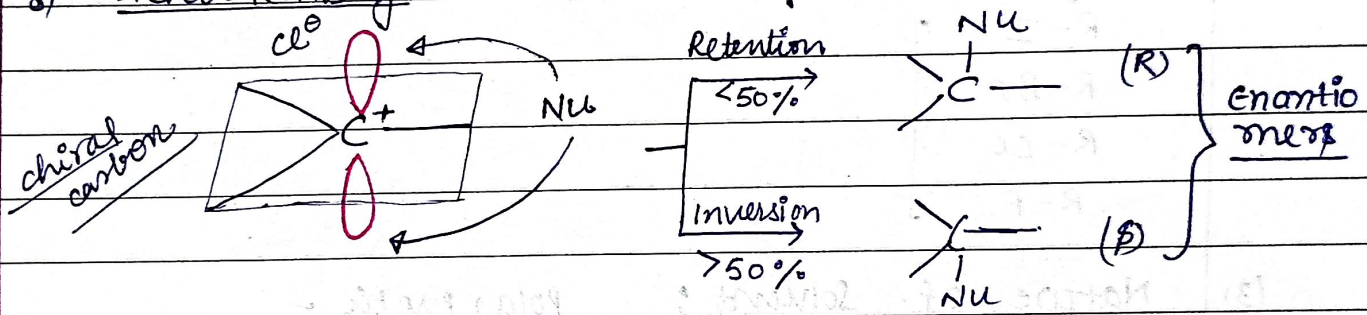


- 1) Rate \propto stability of carbocation
- 2) Rate $\propto [R-X]^1$
- 3) Rate = independent of [Nucleophile]
- 4) formation of C^\oplus is RDS
- 5) Rearrangement of C^\oplus takes place.
- 6) Polar protic solvent: have H^+ by dielectric property



7) Exothermic. $\Delta H < 0$ as more strong bond forms.
preferred at low temperature.

a) Stereochemistry: C^\oplus has sp^2 .

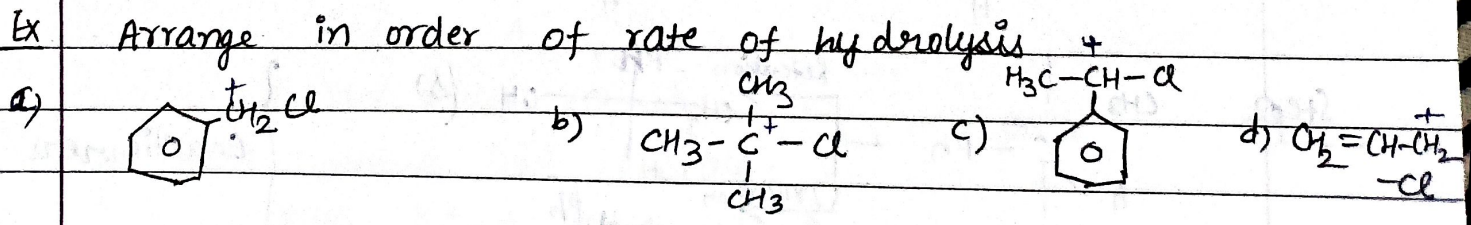
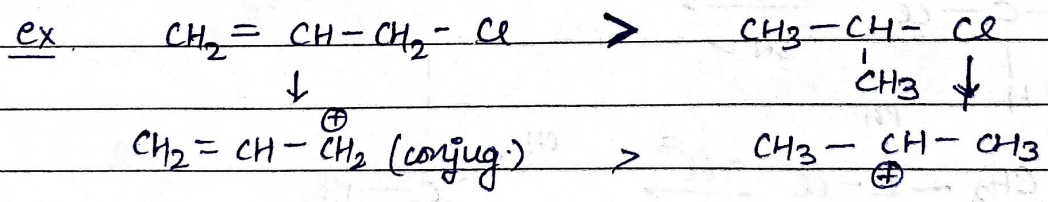


Racemic Mixture

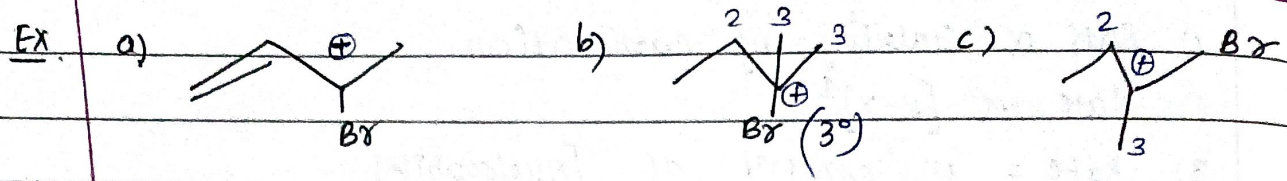
actually, Retention $< 50\%$ due to repulsion of Cl^- & Nu^- .

Factors which affect rate of SN_1

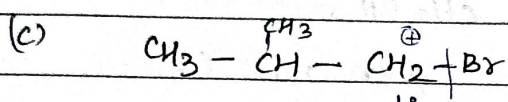
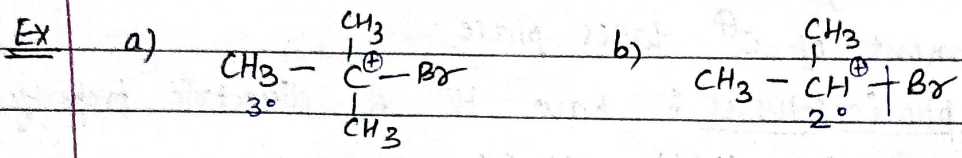
1) Nature of Alkyl Halide \rightarrow most stable carbocation.



$c > b > a > d$



~~a~~ $b > a > c$



(c) can rearrange but rearrangement isn't RDS.
 $\Rightarrow a > b > c$

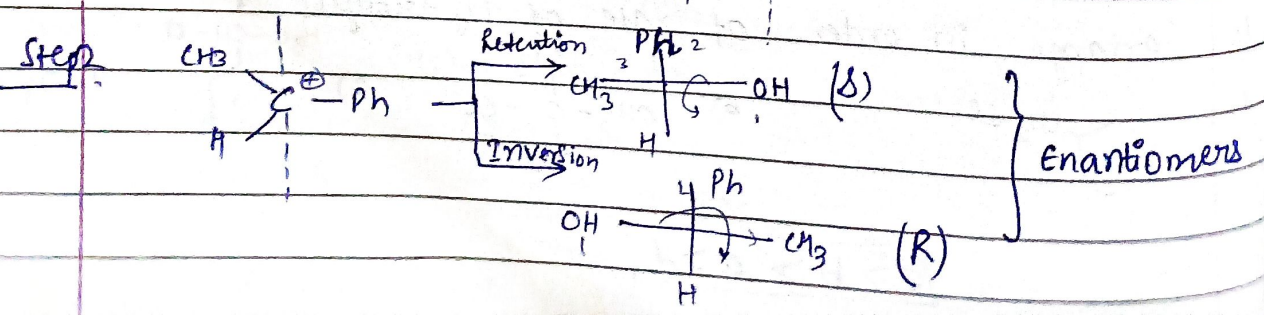
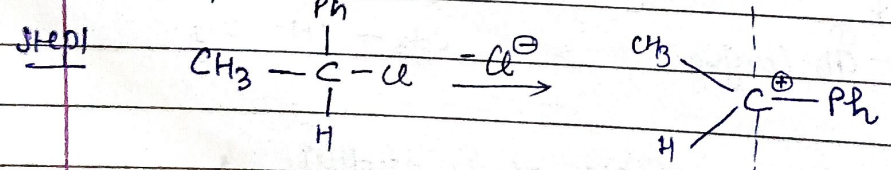
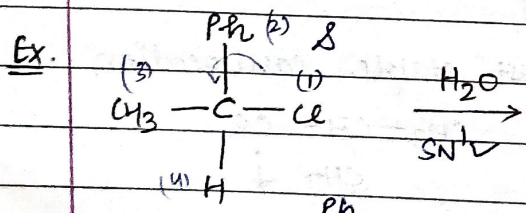
(2) Nature of Leaving Group

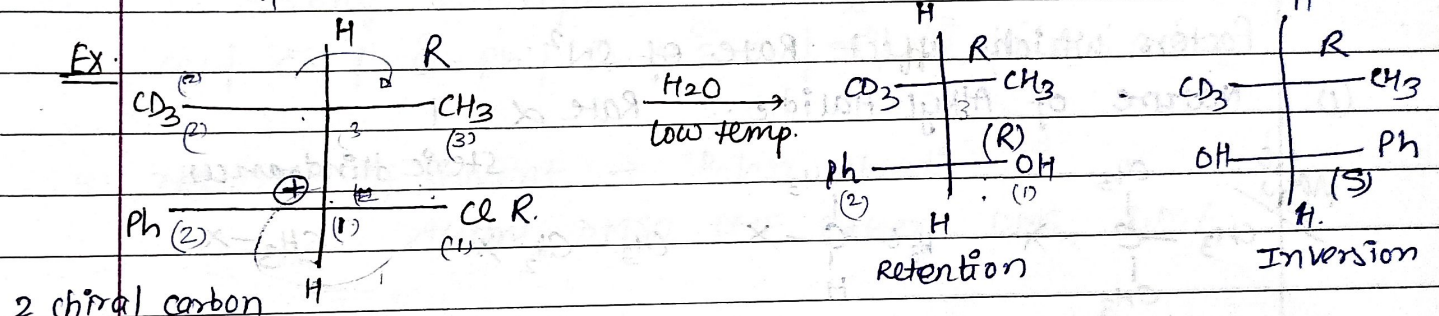
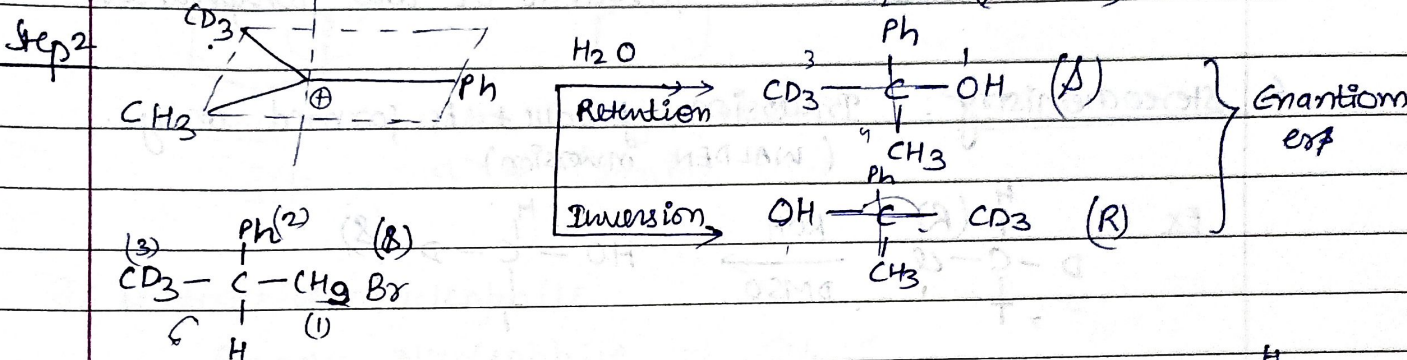
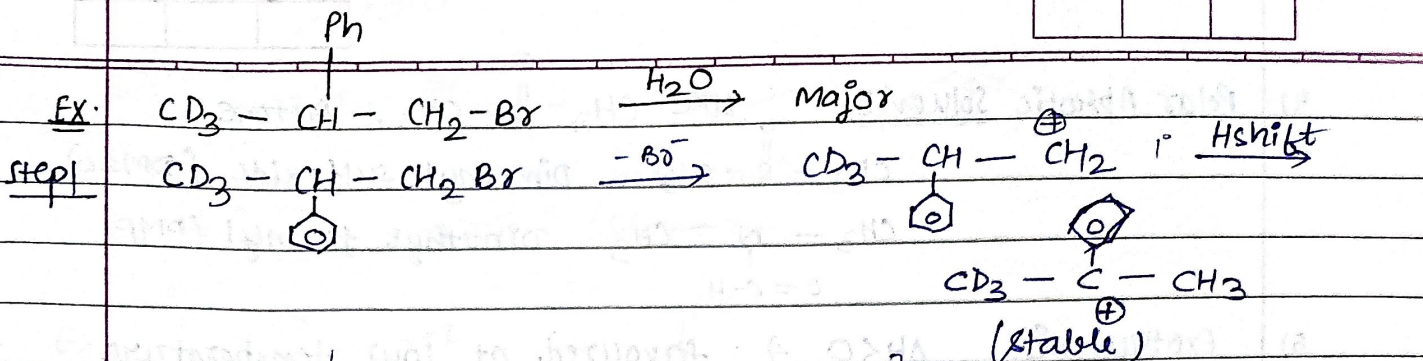
Easily leave \Rightarrow Rate \uparrow $I^- > Br^- > Cl^- > F^-$

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

(3) Nature of Solvent: Polar protic \checkmark

ex		Rate
H ₂ O	80	1.5 lakh x
C ₂ H ₅ OH	35	4x \Rightarrow H ₂ O > C ₂ H ₅ OH > CH ₃ COOH
CH ₃ COOH	5	x

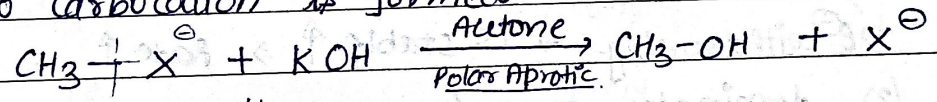




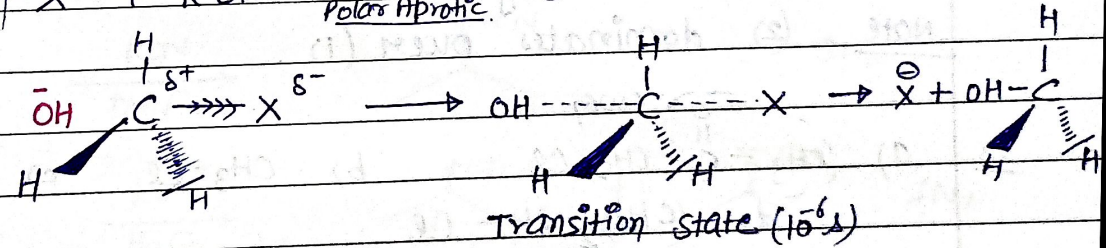
They aren't mirror images \Rightarrow Diastereomers

SN² (substitution Nucleophilic Bimolecular)

No Carbocation is formed.



mechanism



only Inversion product is formed.

1) Single step. RDS \Rightarrow Two molecules are involved.

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

2nd order reaction

2) Rearrangement isn't possible.

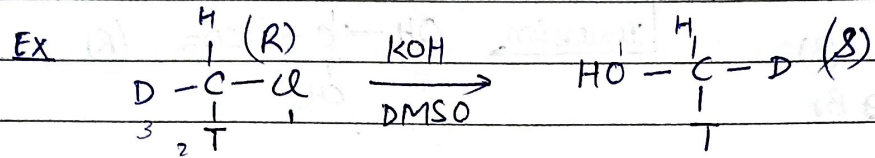
Stable T.S. \Rightarrow Rate SN² \uparrow

3) Nu⁻ donates its lone pair in antibonding orbitals of C.

4) Polar Aprotic Solvent: Like $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$, Acetone
 $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{S}}-\text{CH}_3$ Dimethyl sulfoxide (DMSO)
 $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{N}}-\text{CH}_3$ Dimethyl formyl (DMF)
 $\text{O}=\text{C}-\text{H}$

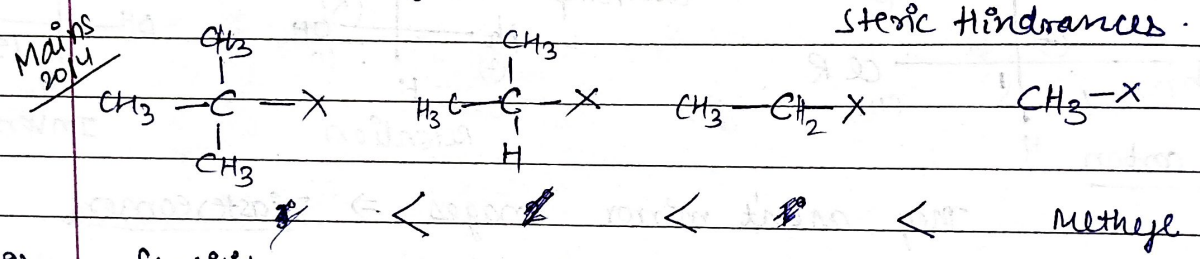
5) Exothermic. $\Delta H < 0 \Rightarrow$ favoured at low temperature

6) Stereochemistry: Inversion product is formed only.
 (WALDEN inversion)

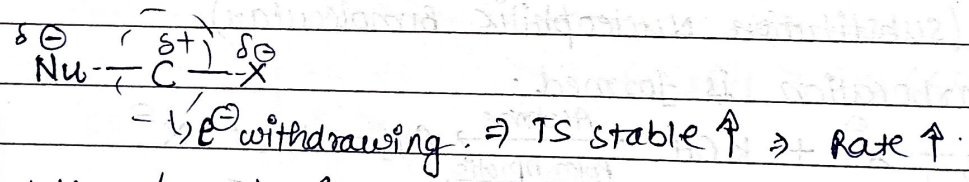


Factors which affect Rate of $\text{S}_\text{N}2$.

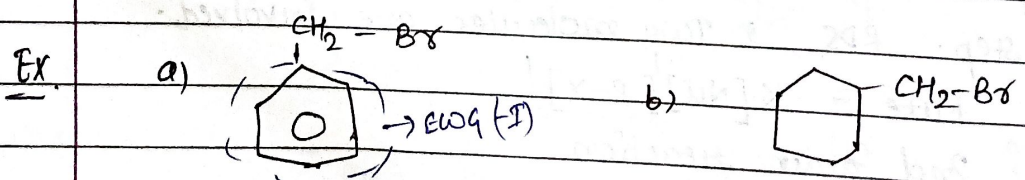
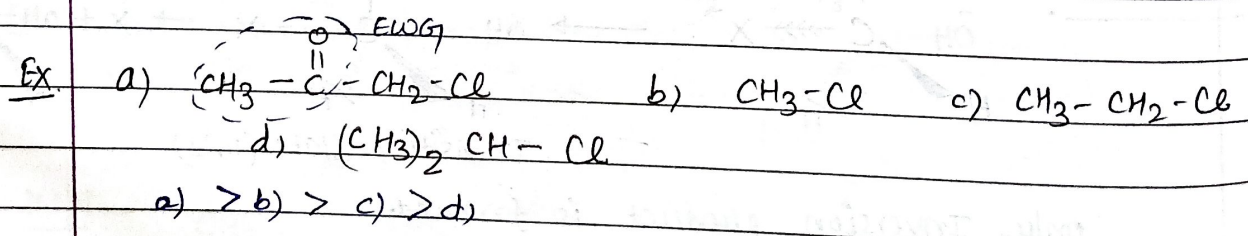
(1) Nature of Alkyl Halide: Rate \propto 1



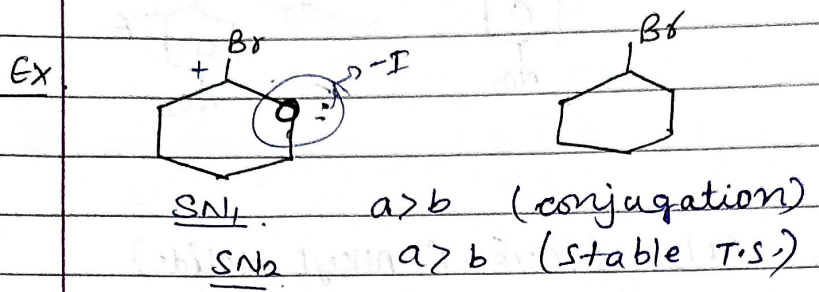
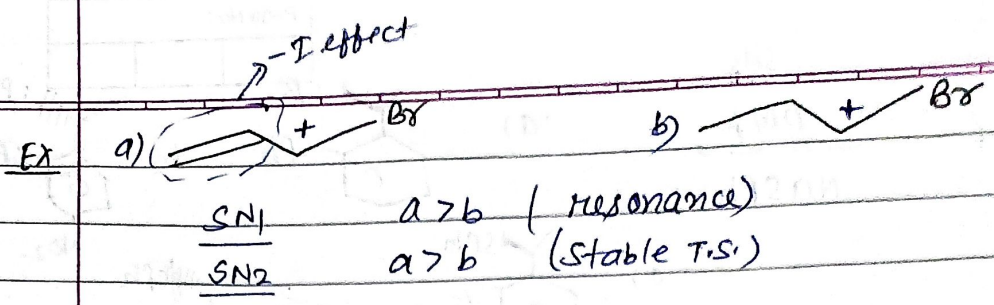
(2) Stability of Transition State.



NOTE (2) dominates over (1).



$\text{S}_\text{N}1$ $a > b$ (resonance)
 $\text{S}_\text{N}2$ $a > b$ (stable T.S.)

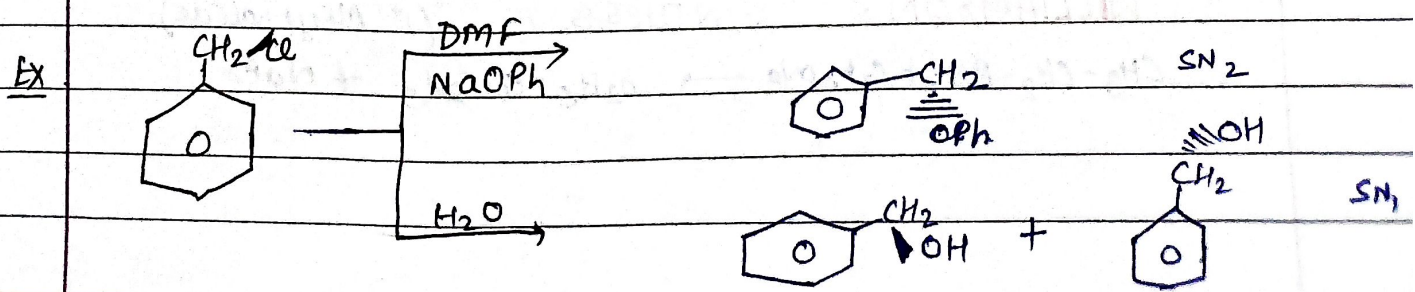
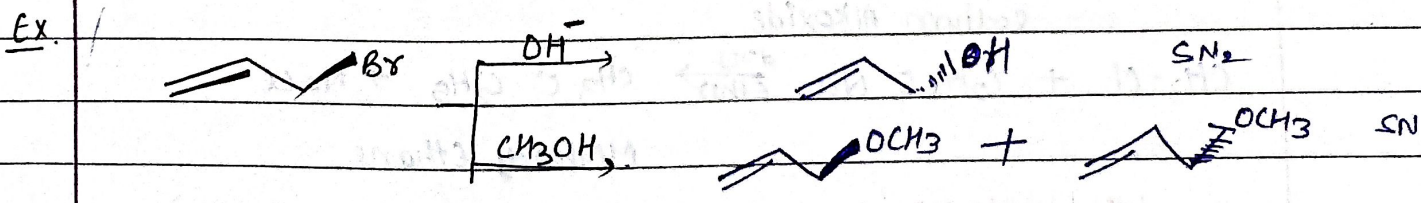
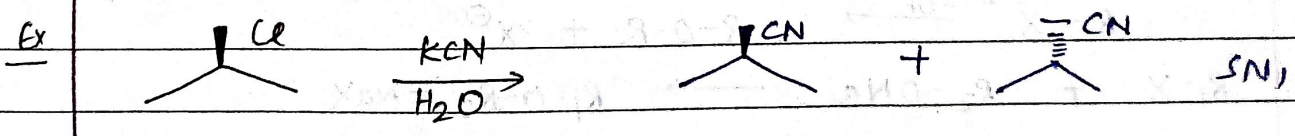
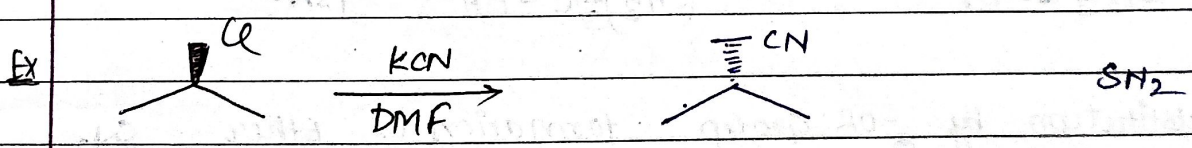
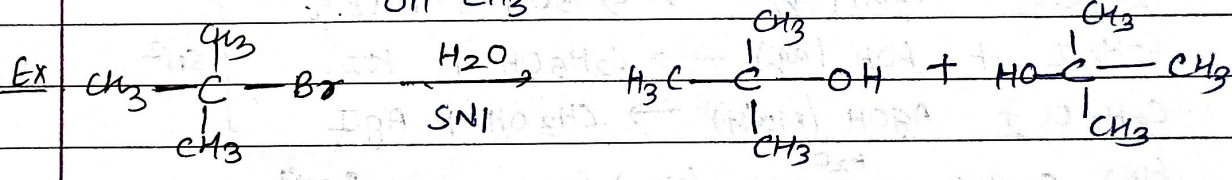
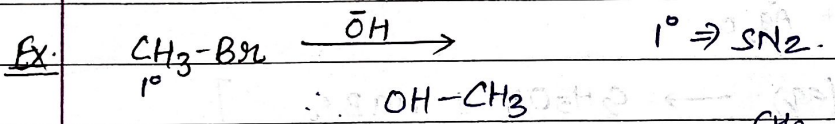


3) Nature of nucleophile.

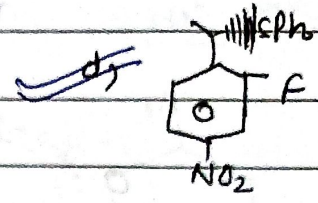
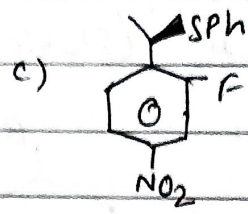
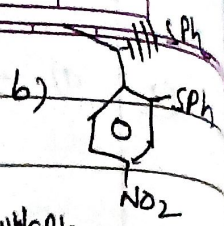
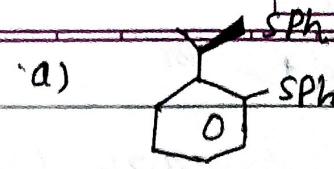
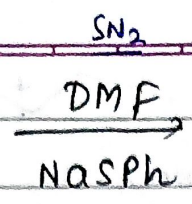
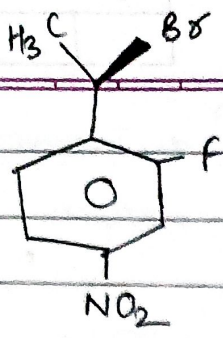
Strong Nucleophile → SN2 ✓
 OH^- | CN^- | O^- -Ph | SH^- | S^- -Ph | I^- | CH_2^- | NH_3 | RNH_2

4) Nature of solvent → Polar Aprotic

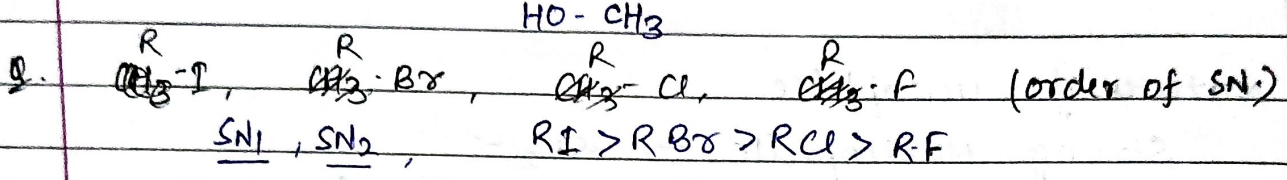
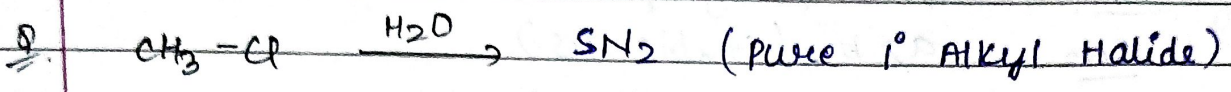
Aceton, DMSO, DMF, Ether, DMS, DMA



11/2/2008

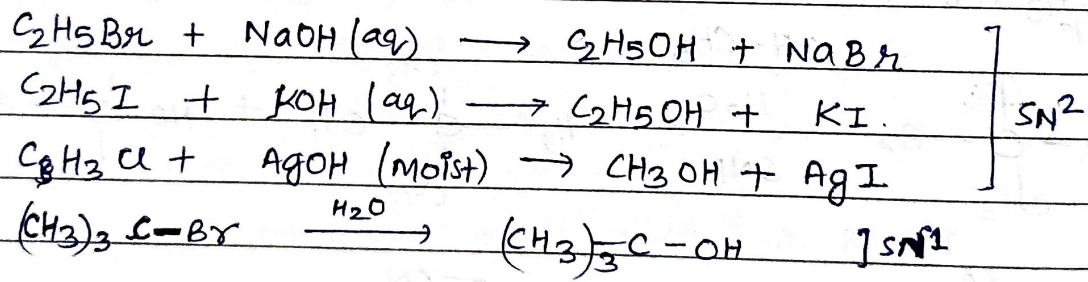
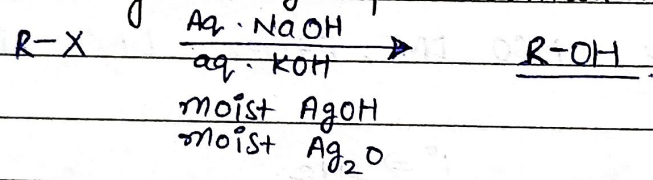


F doesn't leave
as Aryl halide doesn't
show SN.

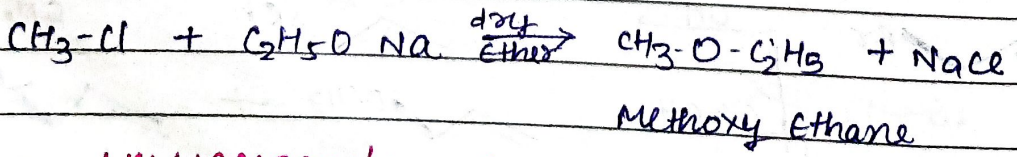
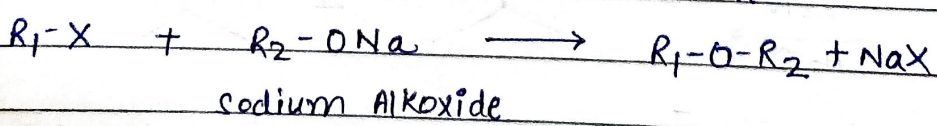
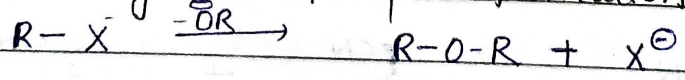


Nucleophilic Substitution Rxns. of Alkyl Halides

A) Substitution by -OH group: Formation of Alcohol

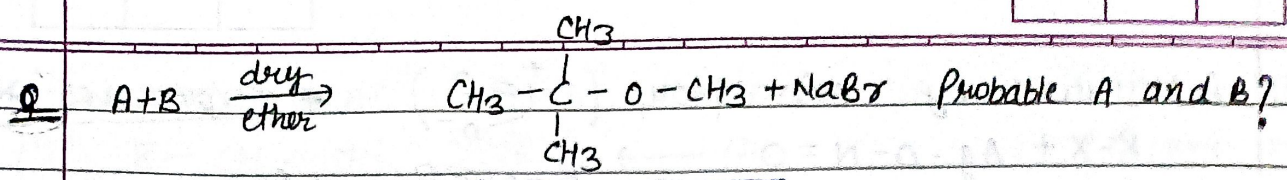


B) Substitution by -OR group: formation of Ether SN_2



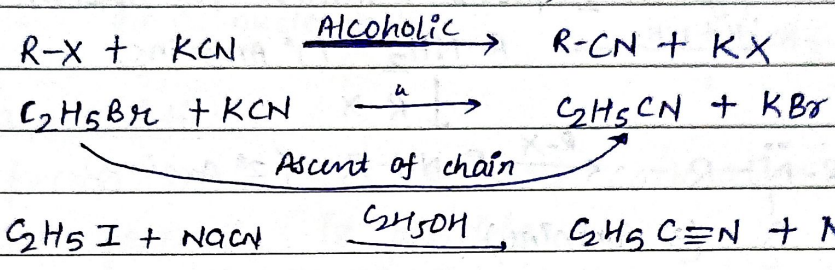
WILLIAMSON'S SYNTHESIS (1° Alkyl halide)



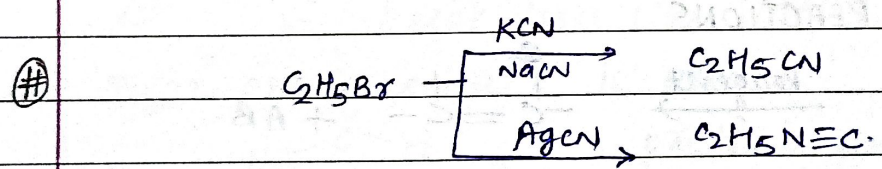
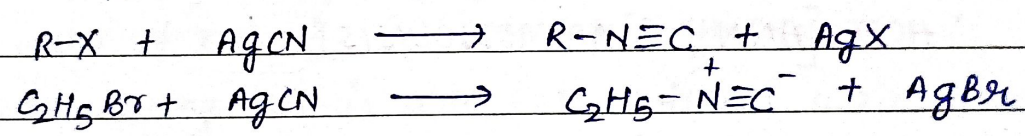


A = alkyl halide = $\text{CH}_3 - \text{Br}$ (1°)
 B = $(\text{CH}_3)_3 \text{C} - \text{ONa}$

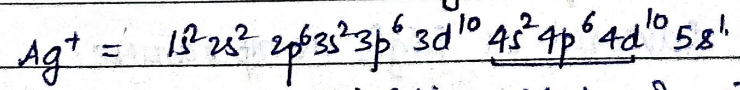
C) Substitution by $^- \text{CN}$ group: formation of Alkyl Cyanide $\text{S}_\text{N}2$
 $\text{R-X} \xrightarrow{\text{CN}^-} \text{R-CN}$
 (Alkane Nitrile)



D) Substitution by $^- \text{NC}$ group: formation of Alkyl Isoyanide $\text{S}_\text{N}2$
 $\text{R-X} \xrightarrow{^- \text{N}\equiv\text{C}^+} \text{R}-\overset{+}{\text{N}}\equiv\text{C}^-$

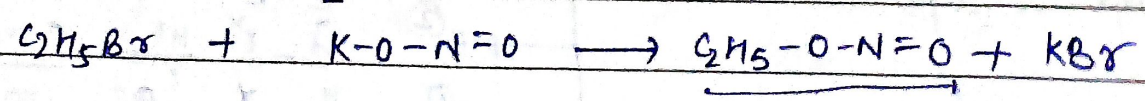
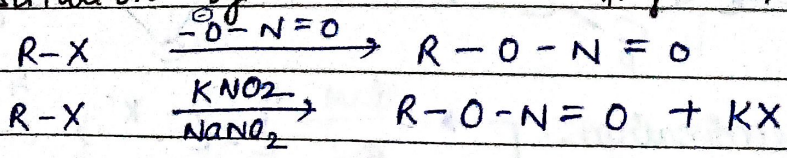


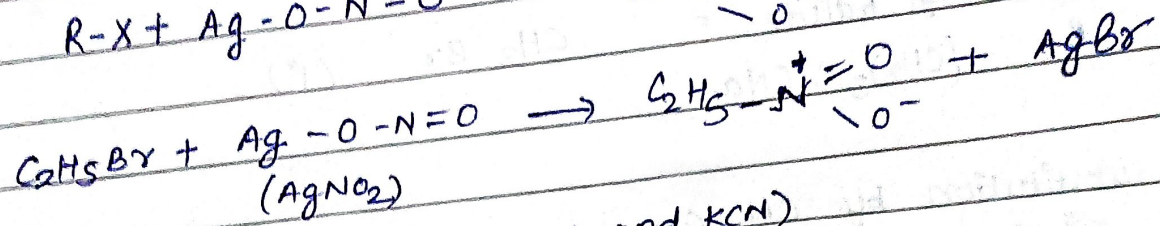
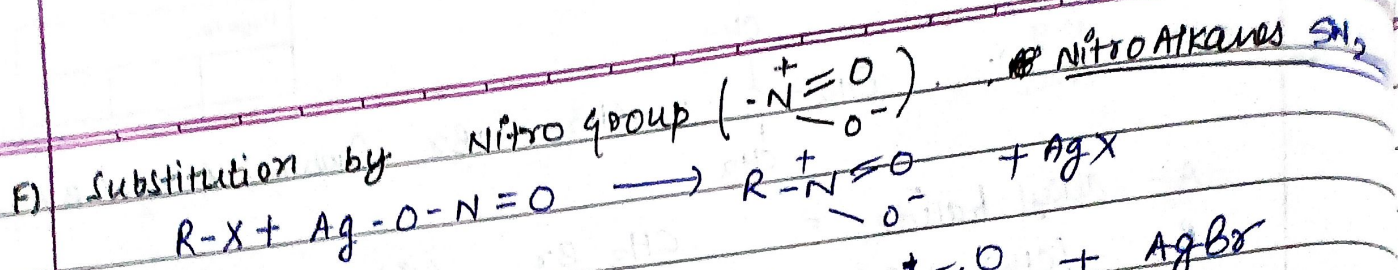
KCN bond is ionic \rightarrow Attack occurs from C side of CN group
 $\text{AgCN} \rightarrow$ Very covalent (Ag^+ = pseudo inert gas configuration)
 $\text{Ag}-\text{C}\equiv\text{N}$: Attack occurs from N of cyanide
 \hookrightarrow not break easily.



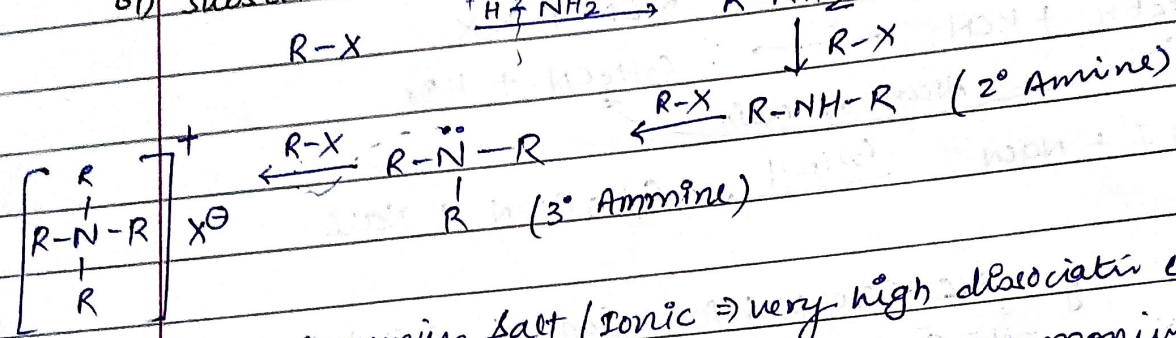
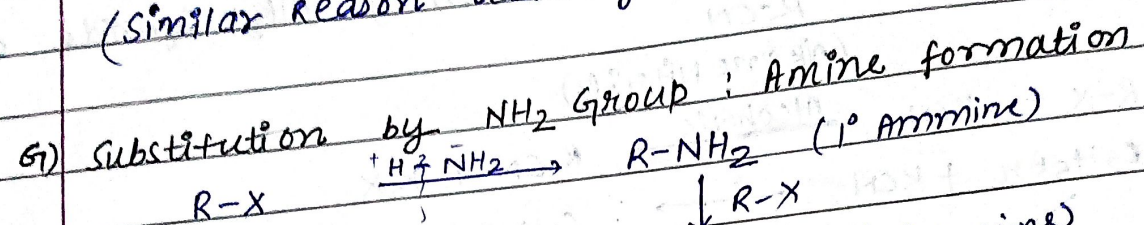
d has weak shielding effect $\rightarrow e^-$ attracted strongly to nucleus

E) Substitution by $^- \text{O}-\text{N}=\text{O}$: Alkyl Nitrite $\text{S}_\text{N}2$





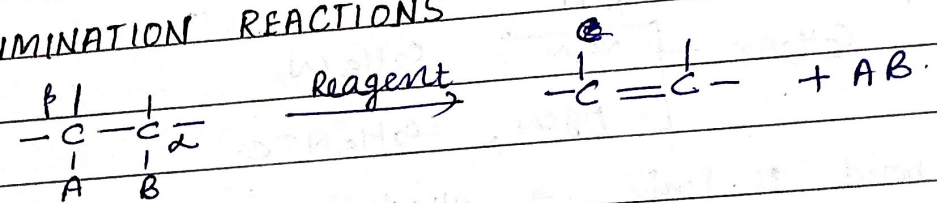
(Similar reaction like AgCN and KCN)



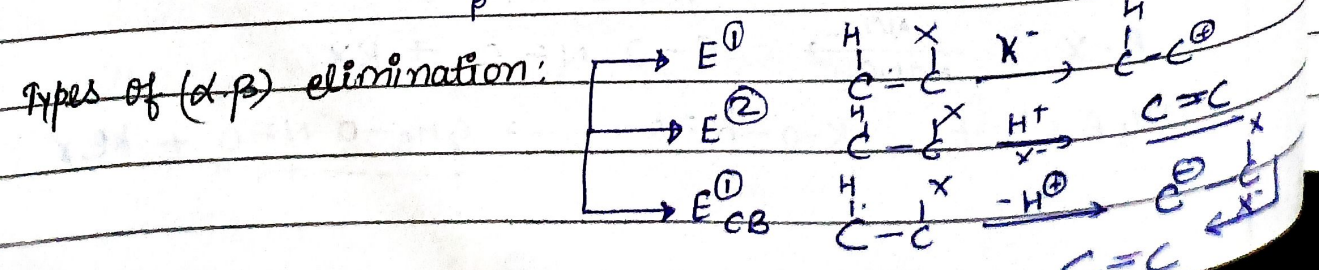
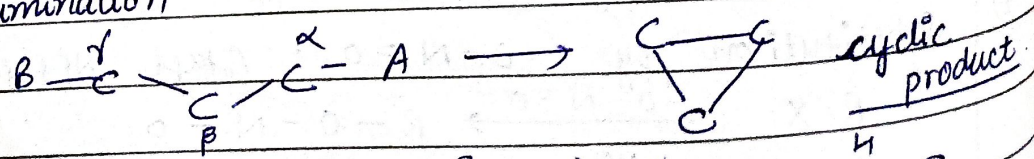
quaternary Ammonium salt (Ionic \Rightarrow very high dissociation constant)
 ex: $[C_2H_5]_4N^+ Cl^-$ Tetraethyl Ammonium chloride

HOFFMANN AMMONOLYSIS

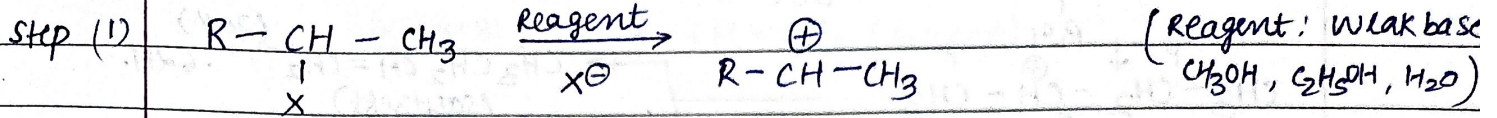
Property (2): ELIMINATION REACTIONS



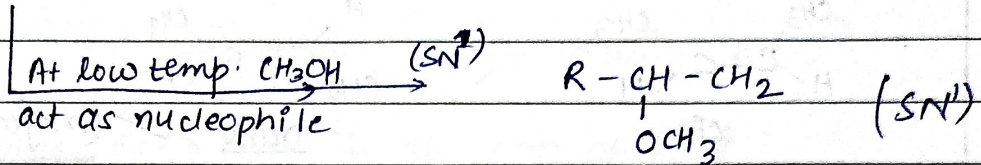
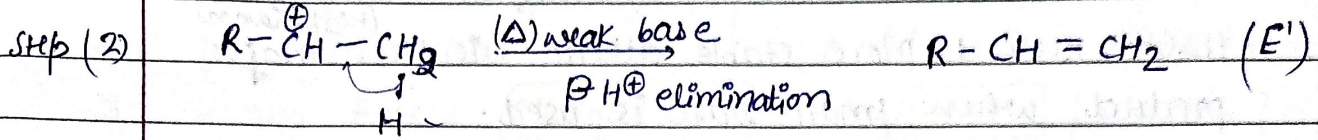
- 1) Smaller atoms/groups are eliminated.
- 2) Unsaturated compound is formed.
- 3) 2σ break $\rightarrow 1\sigma + 1\pi$ form.
 $\Rightarrow \Delta H > 0$ favoured at high temperature.
- 4) α - β elimination \rightarrow adjacent C show elimination.
 α - γ elimination \rightarrow



UNIMOLECULAR ELIMINATION (E¹) REACTION.



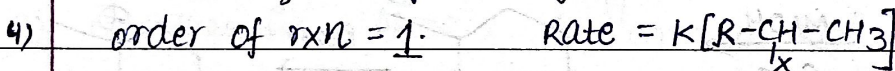
RDS (C[⊕] formation ⇒ Rearrange)



Characteristics

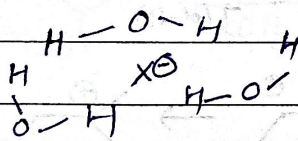
- 1) C[⊕] formation is RDS. ⇒ stable carbocation ⇒ more E¹
- 2) Rearrangement is possible.
- 3) carbocation $\begin{cases} \xrightarrow{\text{NU}^-} \text{S}_{\text{N}}^1 \text{ (exothermic, Temp } < 20^\circ) \\ \xrightarrow{\text{base}} \text{E}^1 \text{ (Endothermic, Temp } > 50^\circ). \end{cases}$

S_N¹ & E¹ goes together.



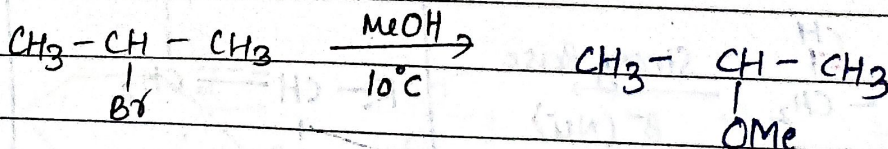
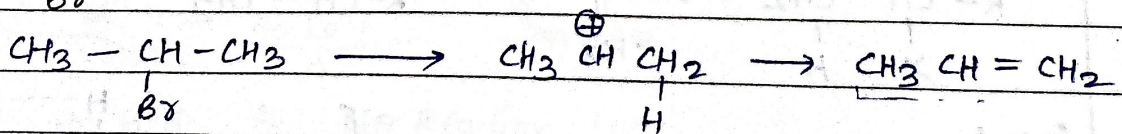
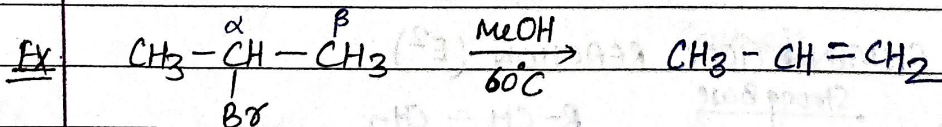
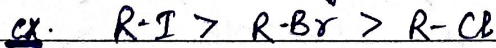
5) If strong base is used, it will not wait for removal of X[⊖]. So, weak base like (MeOH, EtOH, H₂O) is used.

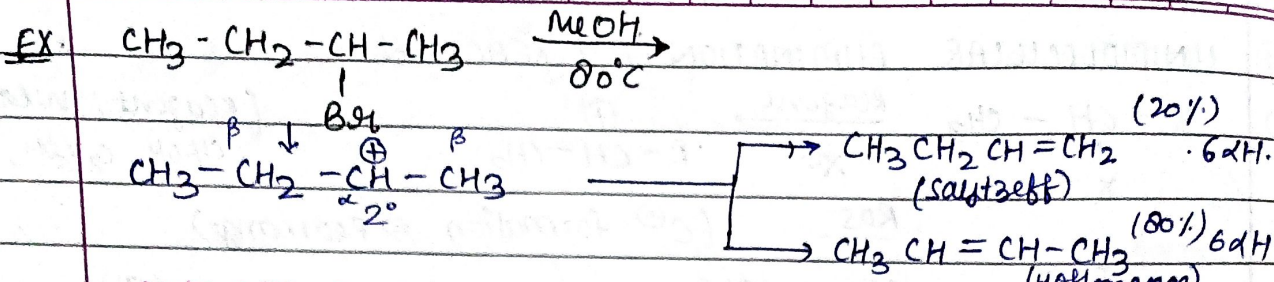
6) Polar protic solvent is used.



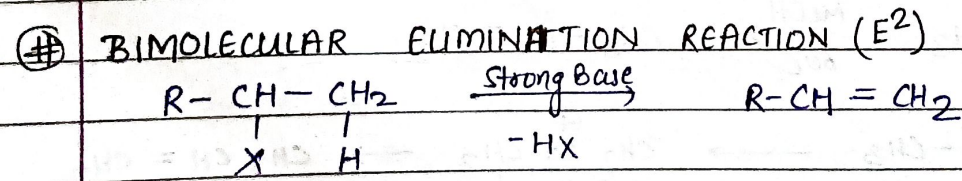
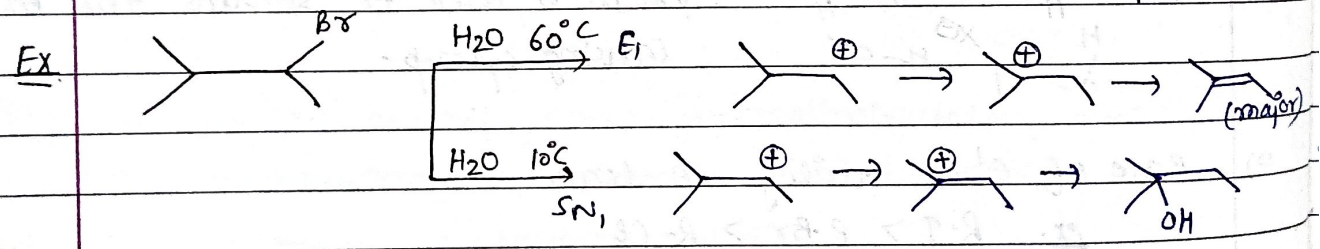
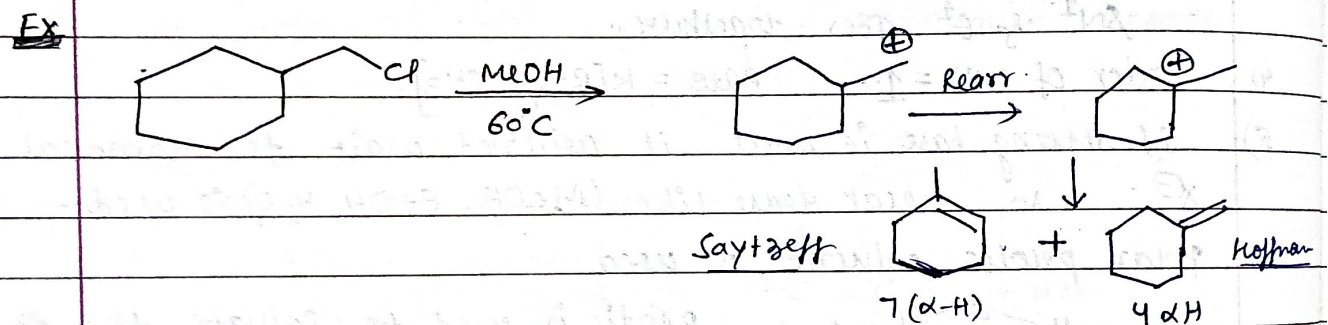
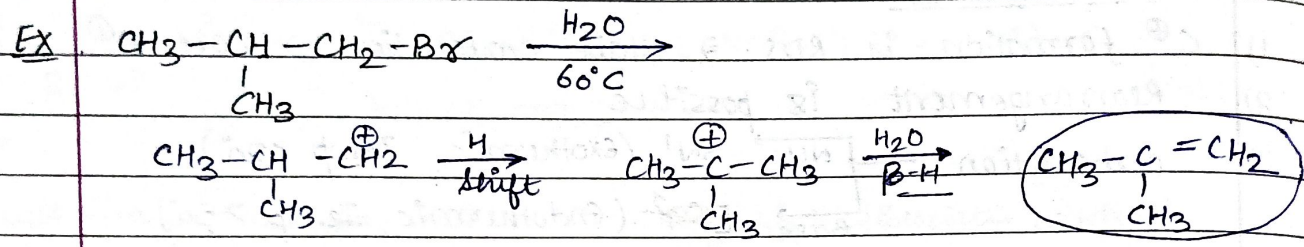
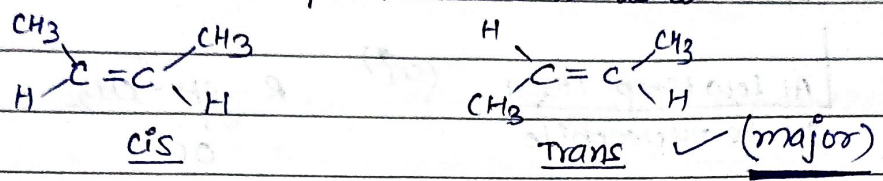
protic is used to solvate the leaving group.

7) Rate of E¹ & ability to leave.

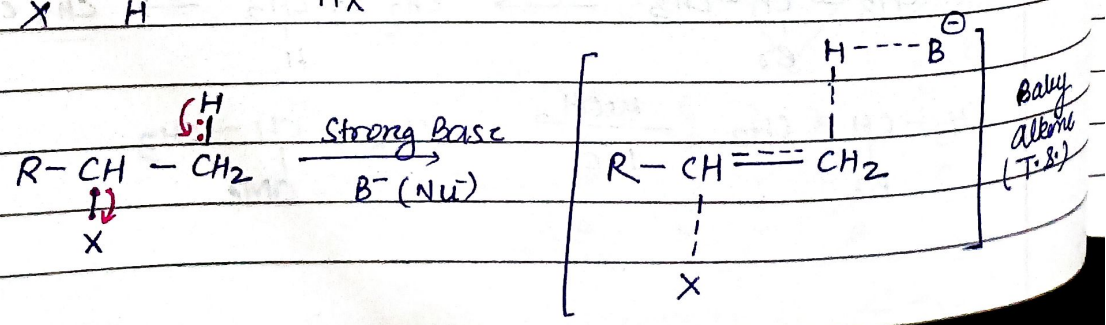




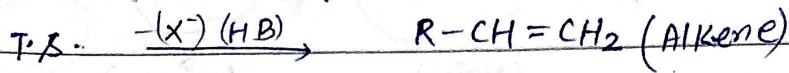
SAYTZEFF RULE: More stable alkene is the major product when small base is used.



Mechanism:



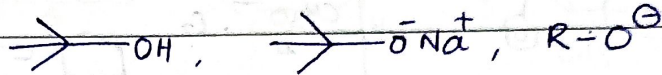
As Base attacks from other side, it is called "Anti Elimination".



characteristics: 1) single step. no C^\oplus formation, no rearrangement

2) E^2 : Bimolecular. Rate = $k[R-X][Base]$. order = 2

3) Strong Base: Alcoholic KOH Alcoholic NaOH | $NaNH_2$ | NH_3 |



4) More stable T.S. \Rightarrow More is the rate of $E^2 \uparrow$

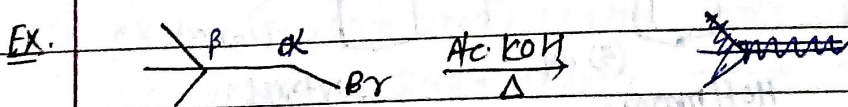
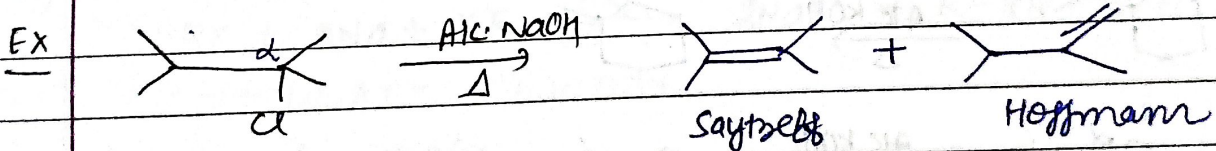
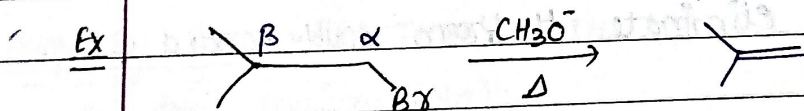
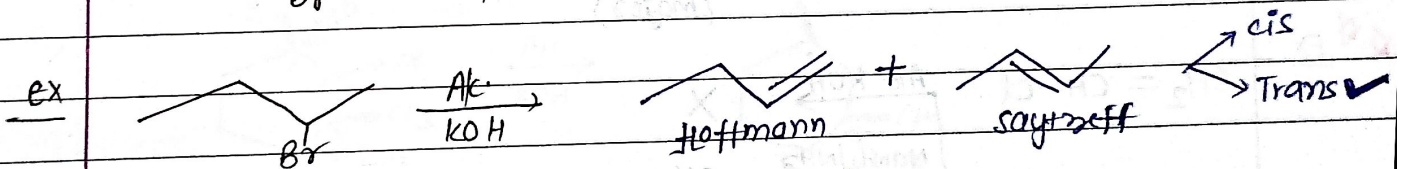
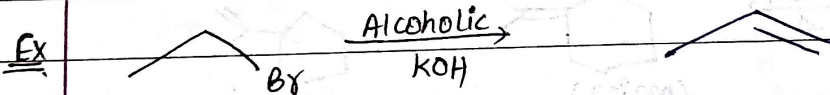


5) Anti-Elimination

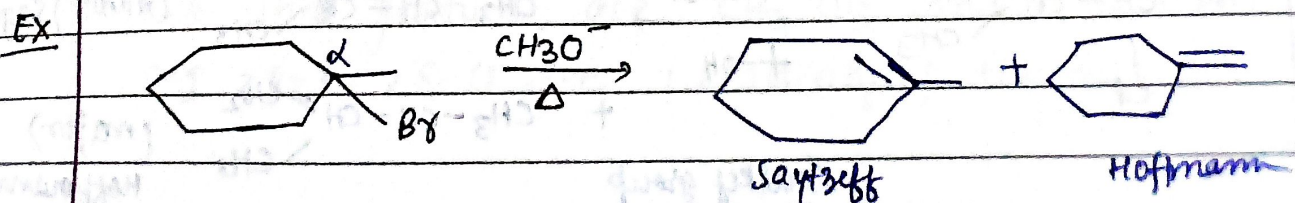
6) Solvent: Polar Aprotic. If it is protic, it solvates B^- . So, polar Aprotic solvent is needed.

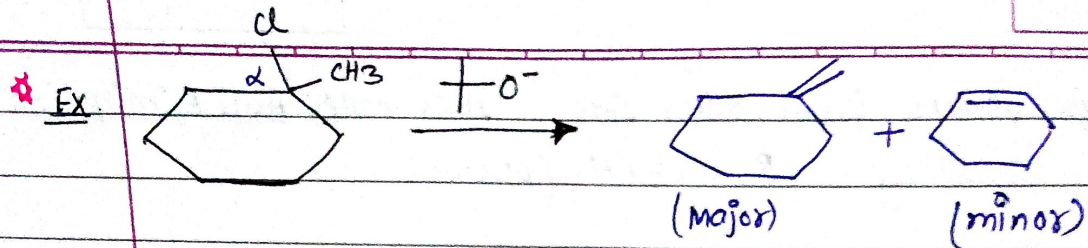
7) leaving Group: More ability to leave \Rightarrow more E^2 rate

8) Endothermic $\Delta H > 0$, favoured at high temperature.

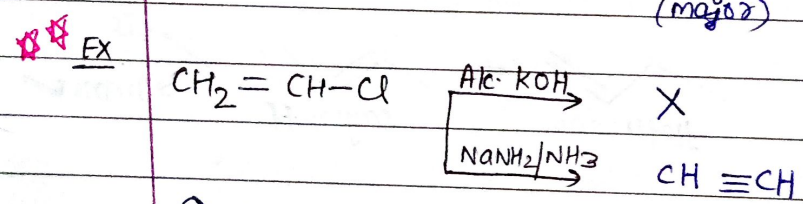
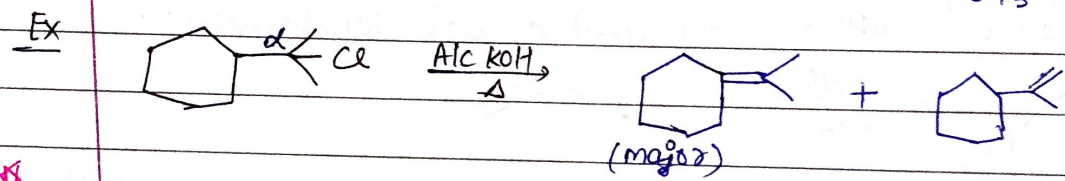
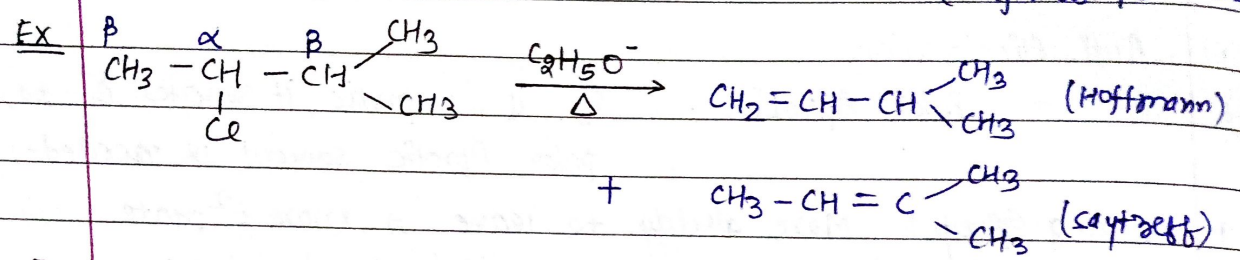
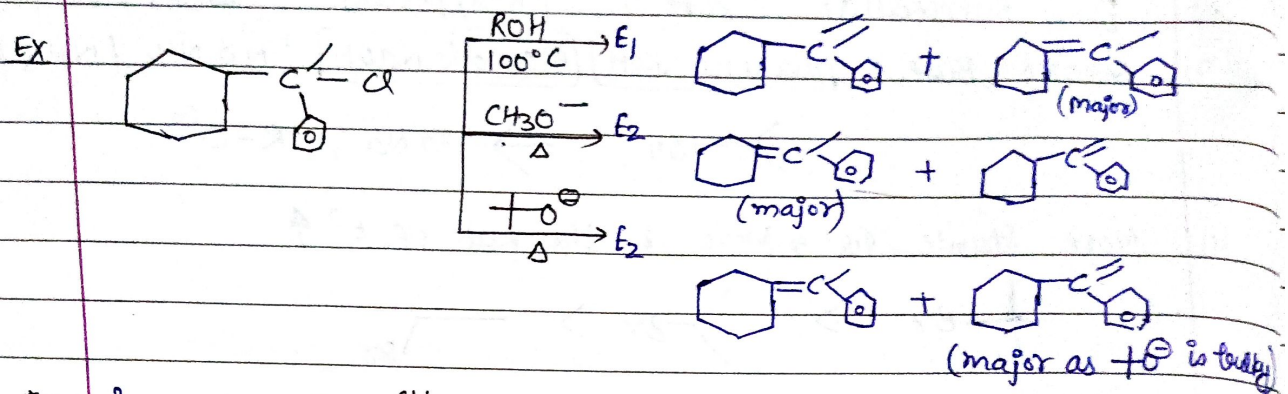


NO β -H. \Rightarrow NO Reaction.

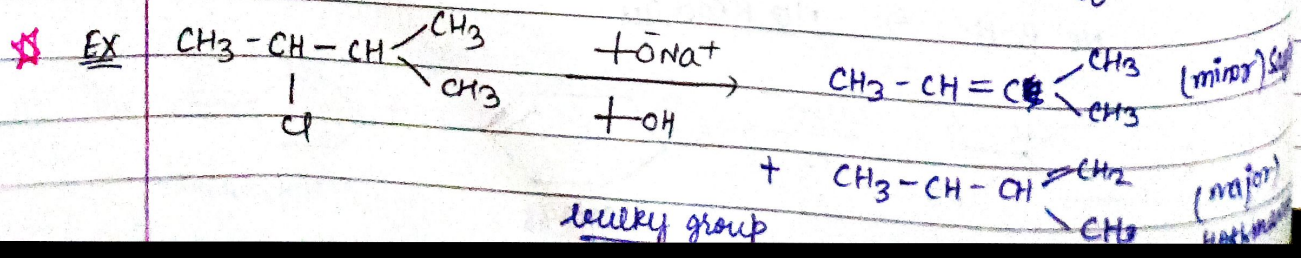
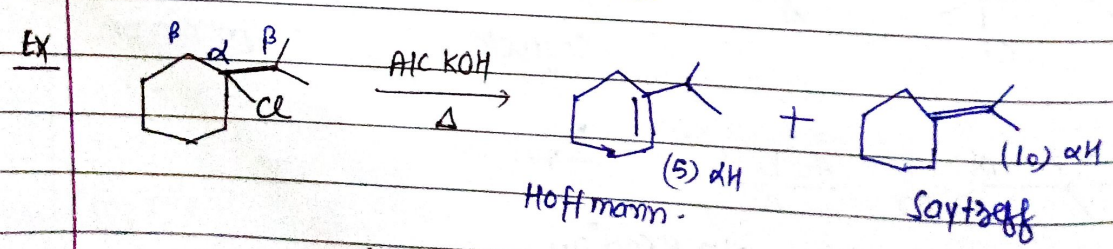
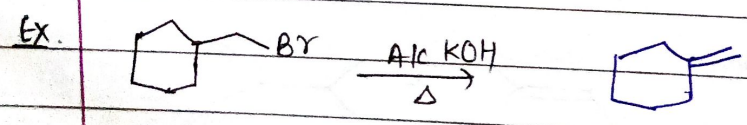


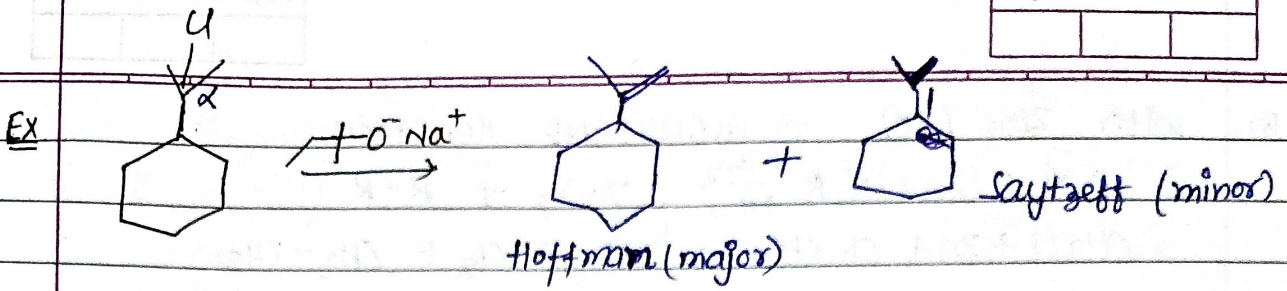


In this case, $t-O^-$ is bulky group so it can't go inside.

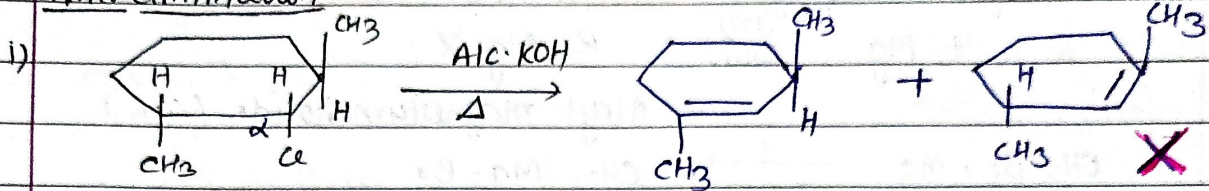


⊕ $NaNH_2/NH_3$ can even eliminate H from double bonded C.

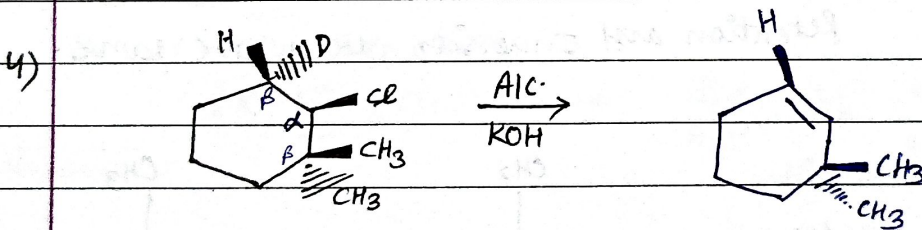
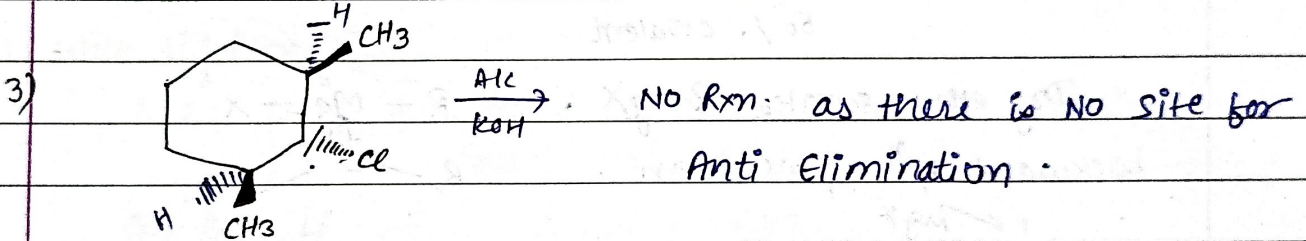
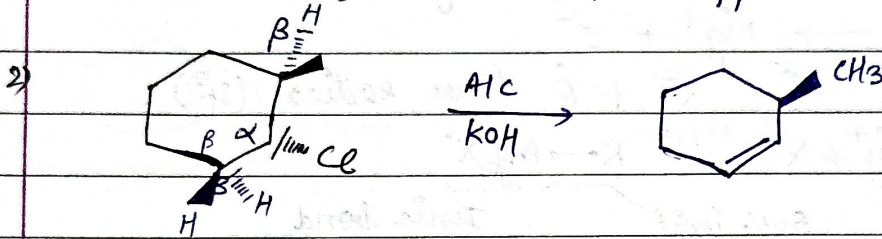




Anti elimination

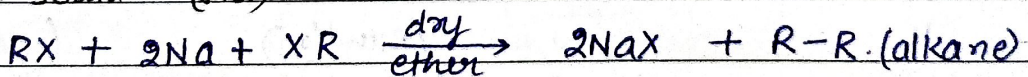


Elimination of H occurs from opposite side when ~~Cl~~ is removed.



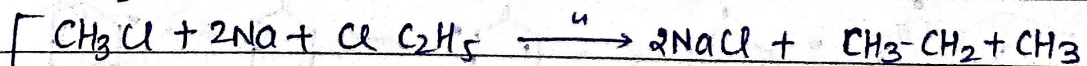
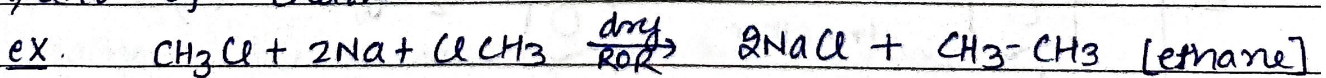
Property (3) REACTION WITH METALS

A) With sodium (Na)



WURTZ REACTION

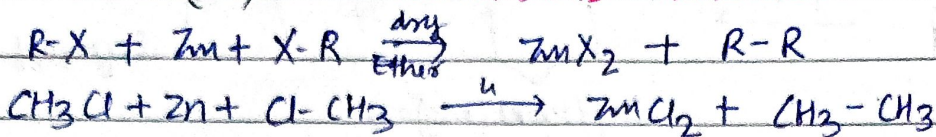
Ascent of chain.



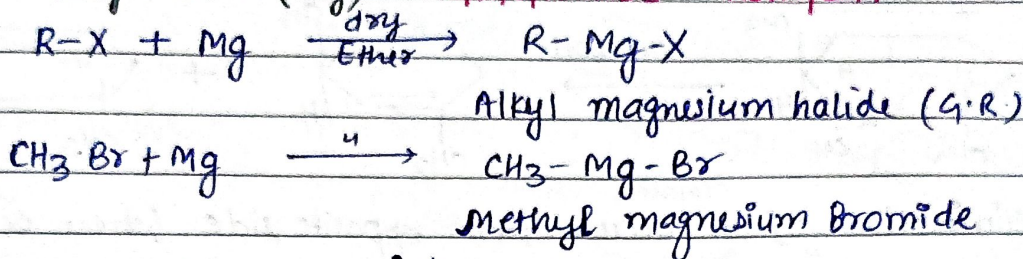
→ other products are CH_3-CH_3 and $C_2H_5-C_2H_5$.

$R-I > R-Br > R-Cl > R-F$ (reactivity of Halides).

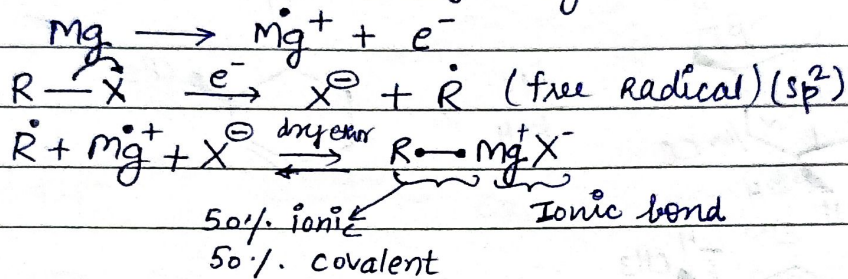
B) with Zinc (Zn) **FRANKLAND REACTION**



C) with Magnesium (Mg) **GRIGNARD'S REAGENT**

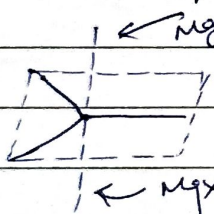


Mechanism:



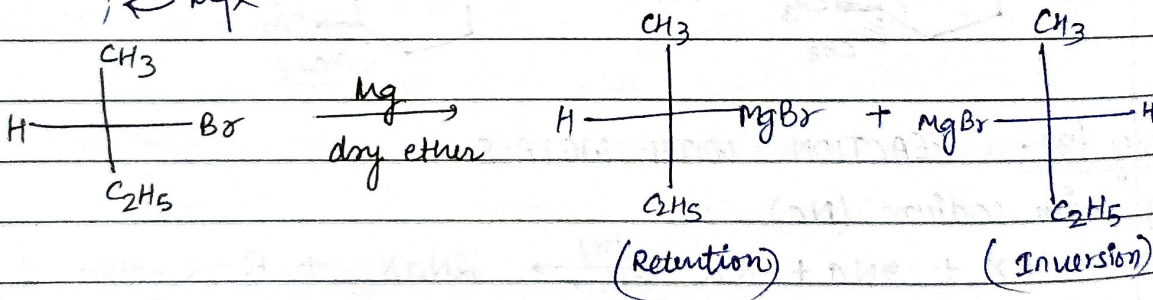
Dry ether solvates $R-MgX$. $R-Mg^{\delta+}-X^{\delta-}$

backward rxⁿ slows down. $R-\overset{\ominus}{O}$

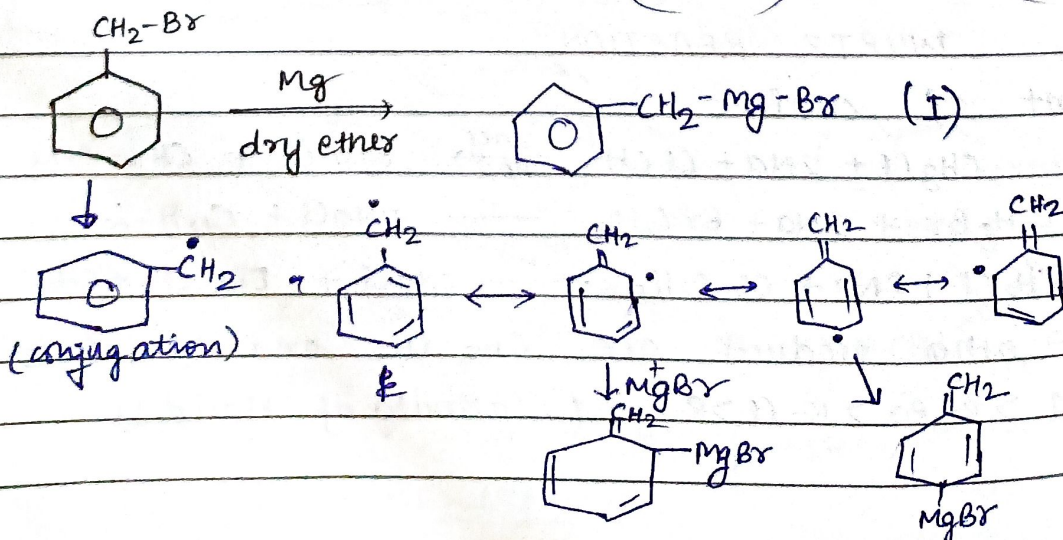


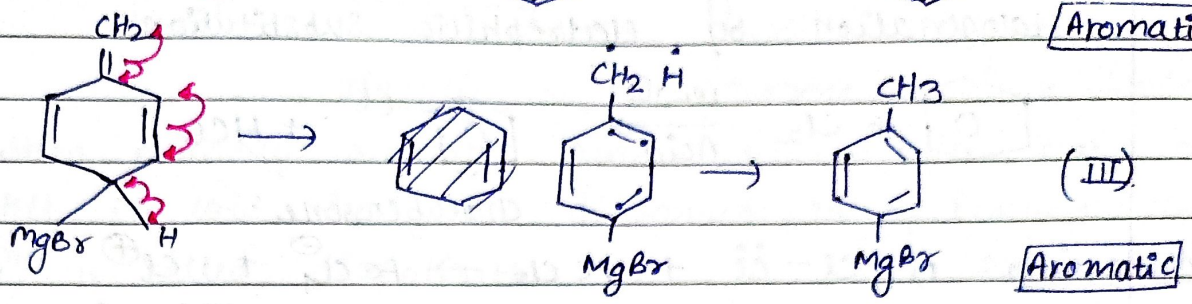
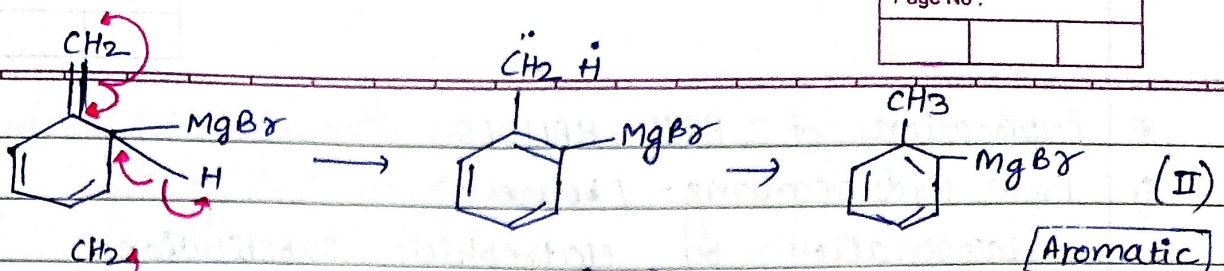
Retention and Inversion both are same.

Ex

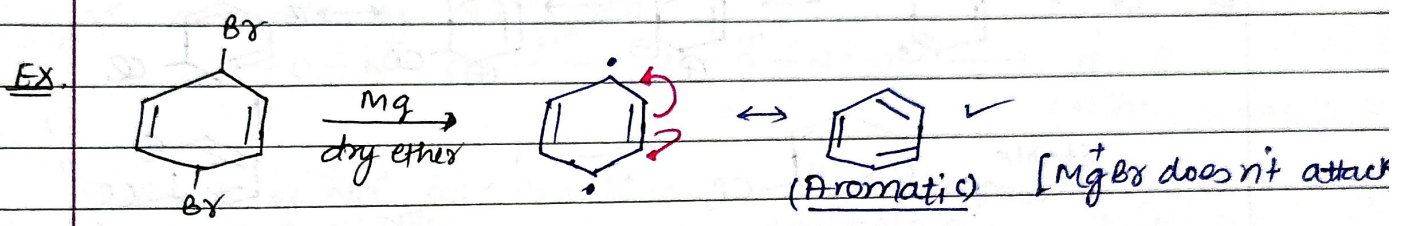


Ex.

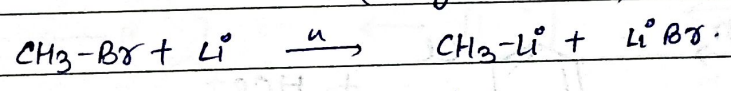
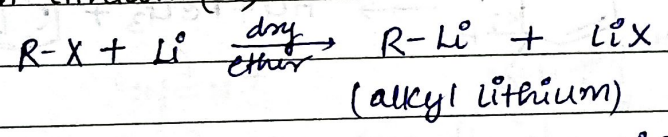




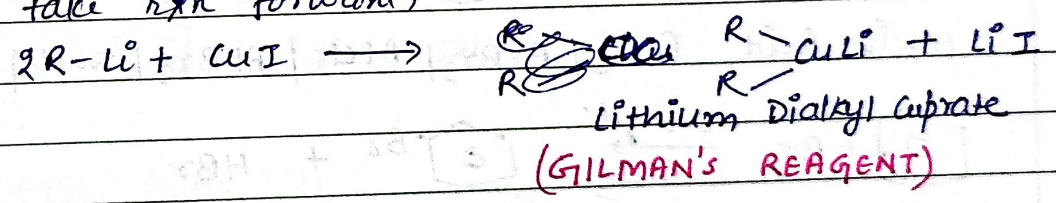
∴ 3 products are formed.



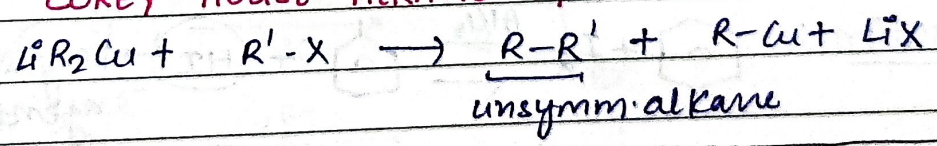
4) with lithium (Li)



If we take rxn forward)

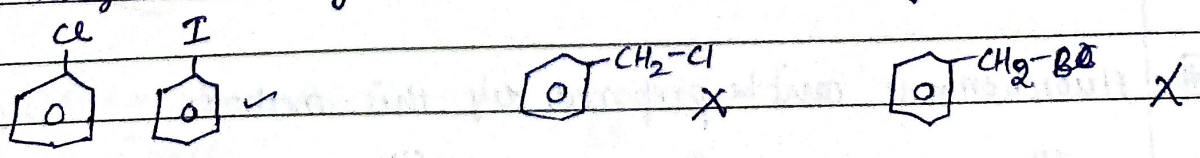


"COREY HOUSE ALKANE SYNTHESIS"



HALOARENES Aryl Halides

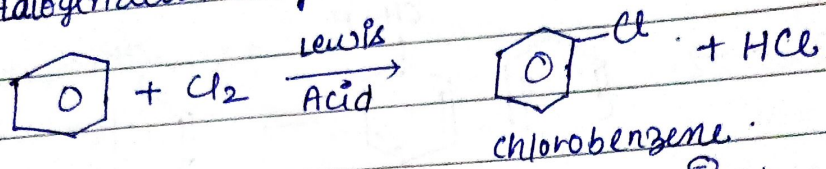
Halogen directly attached to benzene ring.



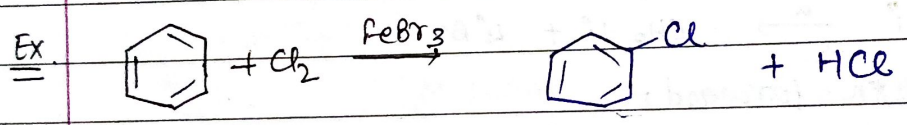
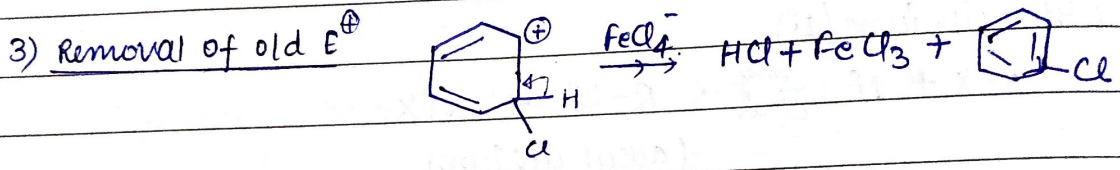
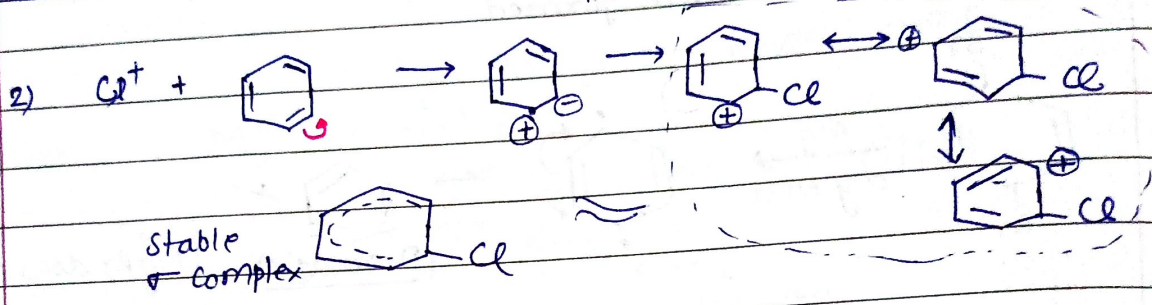
* Preparation of ARYL HALIDES.

1) From hydrocarbons: (benzene)

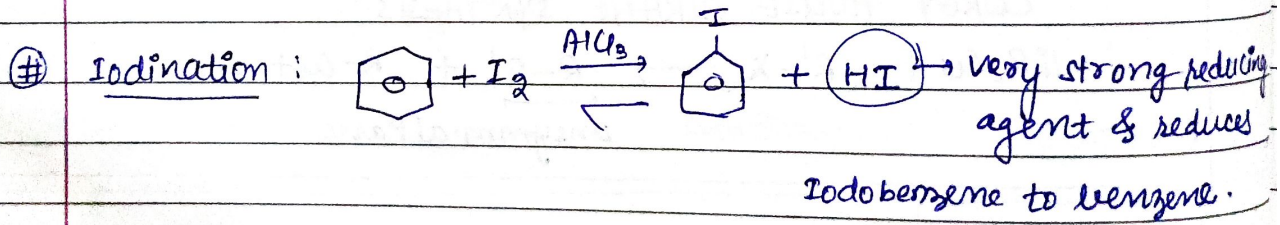
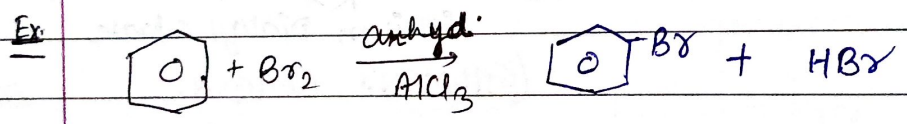
Halogenation by Electrophilic Substitution:



Mechanism: 1) $\text{Cl}-\ddot{\text{Cl}} + \text{FeCl}_3 \rightarrow \text{FeCl}_4^- + \text{Cl}^+$
chloronium ion (E^+)

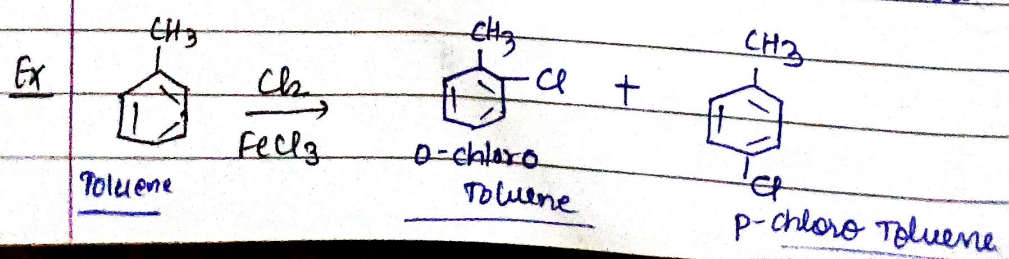


Lewis Acid FeCl_3 | FeBr_3 | AlCl_3 | AlBr_3 | ZnCl_2 | BF_3 | ZnBr_2

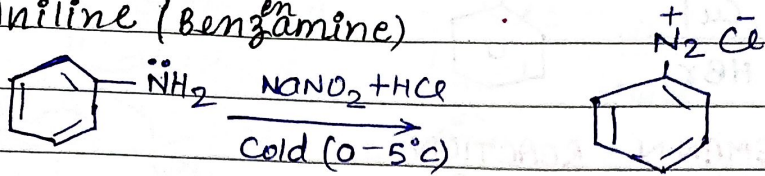


Use strong oxidising Agent like conc. HNO_3 or HIO_4 .
 $2\text{HI} \xrightarrow{\text{HIO}_4} \text{H}_2\text{O} + \text{I}_2$

⊕ Fluorobenzene can't be prepared by this method.



2) From Aniline (Benz^{am}ine)

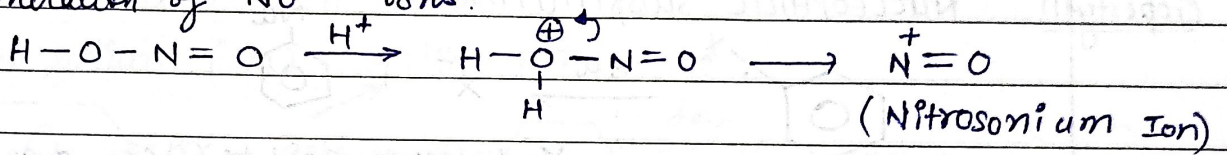


Diazotization (Benzene diazonium chloride)

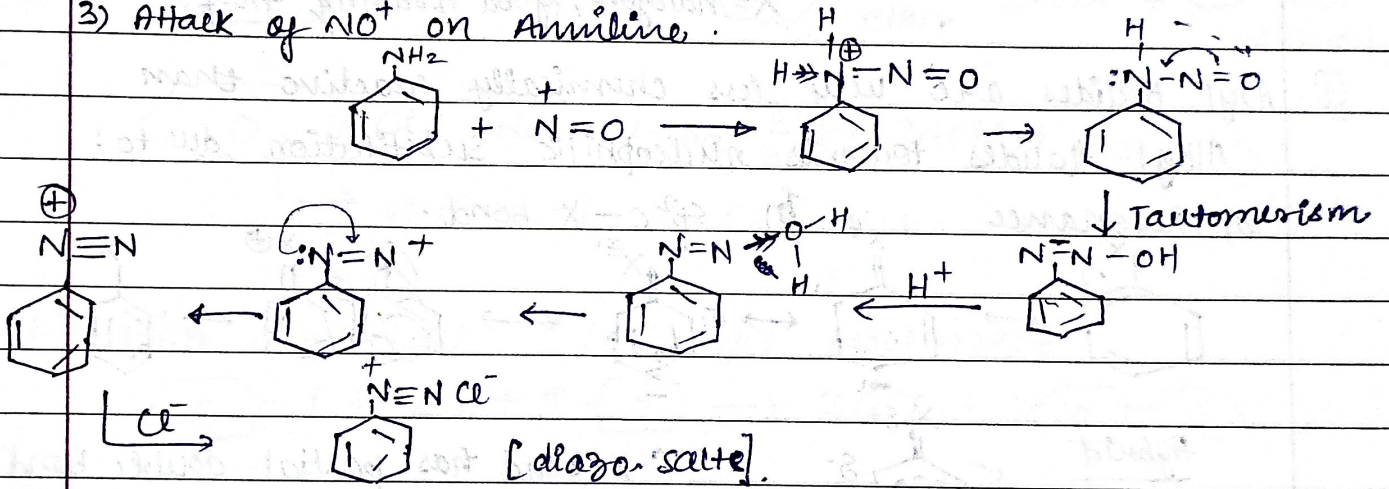
When primary aromatic amine reacts with NaNO_2 and HCl in cold, it forms diazonium salt of benzene. This rxⁿ is called diazotization.

Mechanism: 1) HNO_2 formation: $\text{NaNO}_2 + \text{HCl} \rightarrow \text{NaCl} + \text{HNO}_2$

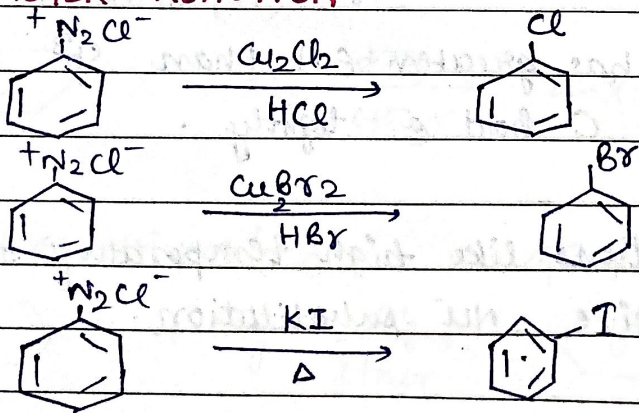
2) generation of NO^+ ions:



3) Attack of NO^+ on Aniline.

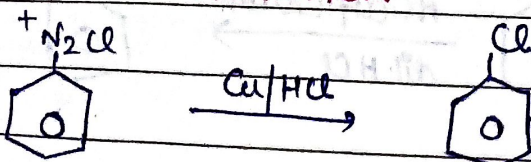


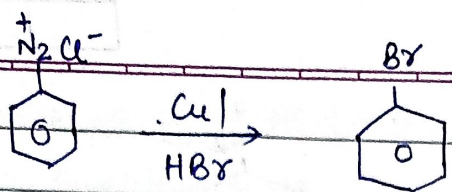
I. SANDMEYER REACTION



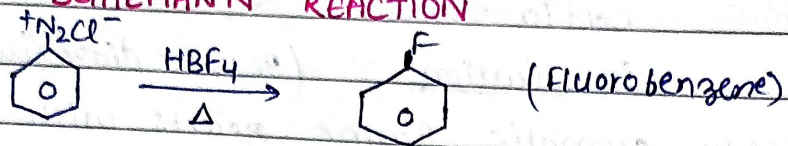
This rxⁿ is not called Sandmeyer's rxⁿ.

II. GATTERMANN REACTION





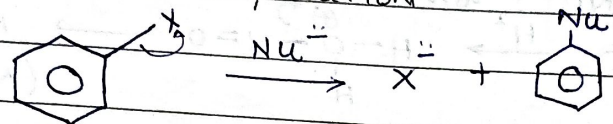
III. BALZ-SCHIEMANN REACTION



*** PROPERTIES OF HALOARENES**

S_N , reaction with metals, E.S.

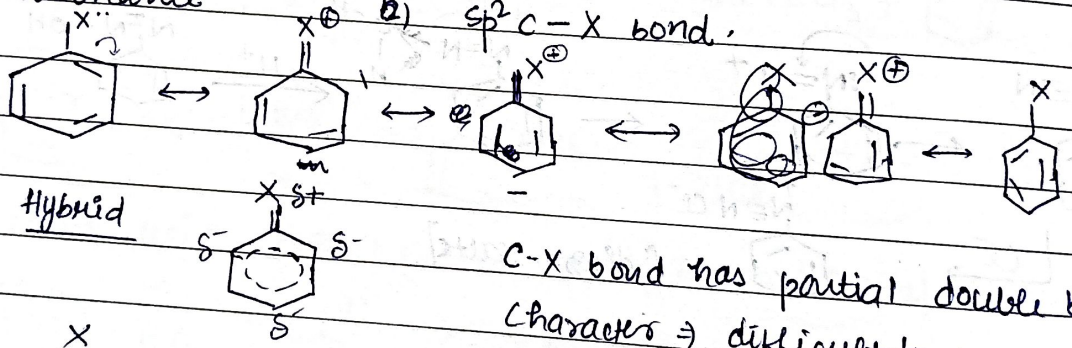
Property (1) NUCLEOPHILIC SUBSTITUTION



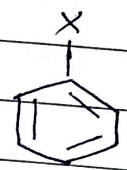
X = halogen, good leaving group.

⊛. Aryl halides are very less chemically reactive than Alkyl halides towards nucleophilic substitution due to:

- a) Resonance
- b) $sp^2 C-X$ bond.



C-X bond has partial double bond character \Rightarrow difficult to remove X from Aryl Halide.

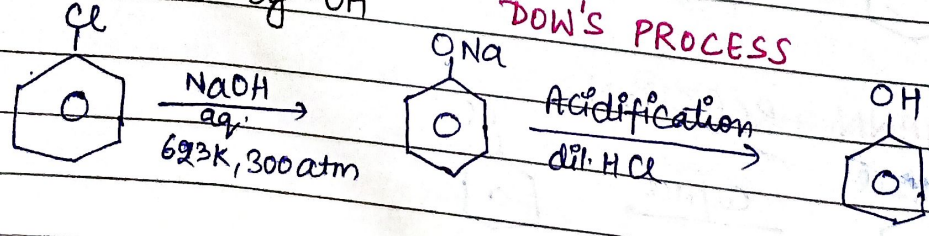


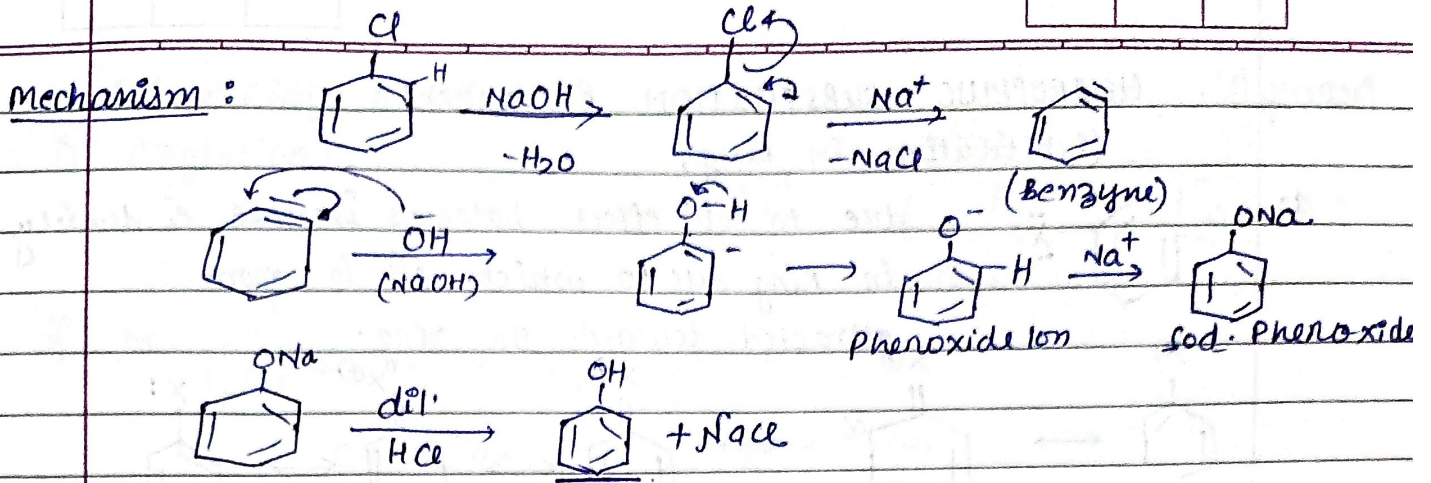
$sp^2 C$ has greater E.N. than sp^3 mus, C hold e^- tightly.

Under drastic conditions like high temperature or pressure, haloarenes may give Nu^- substitution.

A) Substitution by -OH

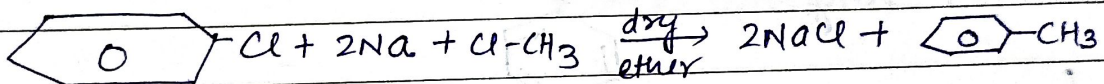
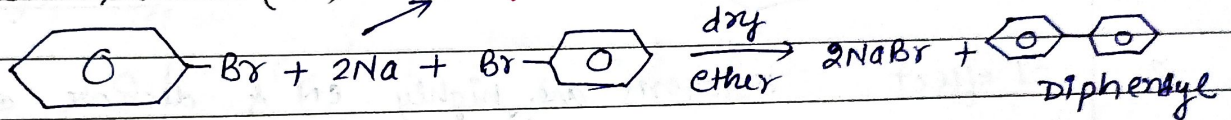
DOW'S PROCESS





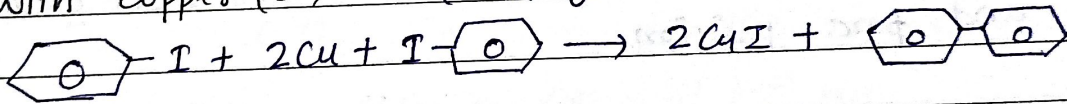
Property (2) Reaction with Metals

A) with sodium (Na) **FITTIQ REACTION**



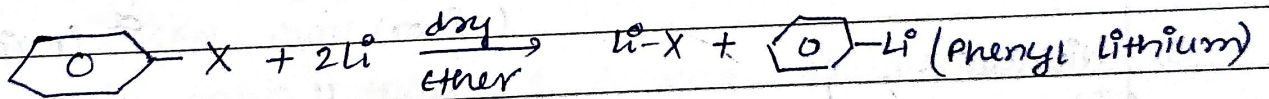
↳ **WURTZ-FITTIQ REACTION**

B) with Copper (Cu) (only for iodobenzene)



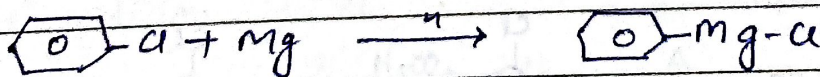
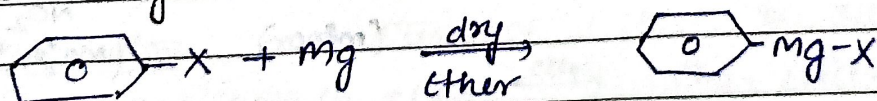
ULMANN REACTION

C) with lithium (Li)



D) with magnesium (Mg)

GRIGNARD REAGENT

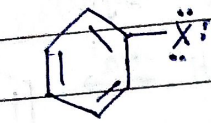


Phenyl magnesium hal

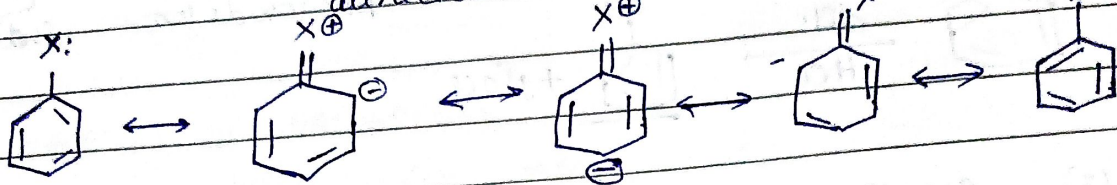
PROPERTY (3). ELECTROPHILIC SUBSTITUTION REACTIONS

(Substitution in Ring)

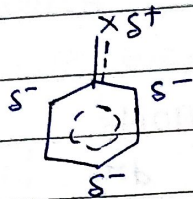
1.



due to +M effect, halogens increase e^- density in ring due to which E^+ is more attracted towards the ring.



Hybrid:



2.

-I effect.

Halogens are highly EN & decrease e^- density in ring.

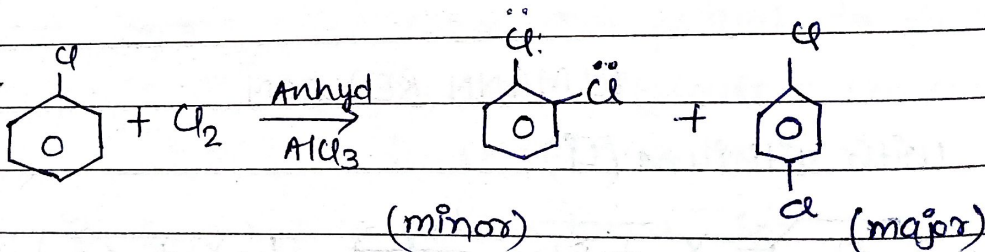


In case of Halogen

{ As -I dominates +M, overall e^- density decreases and X deactivates ring for ESR.

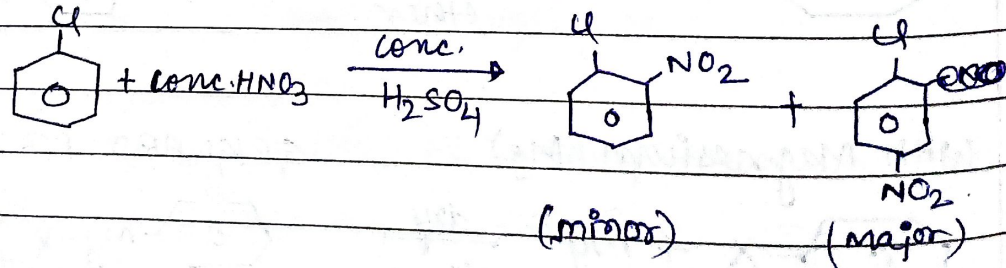
but if somehow ESR is forced, it will occur at ortho and para position.

A) Chlorination

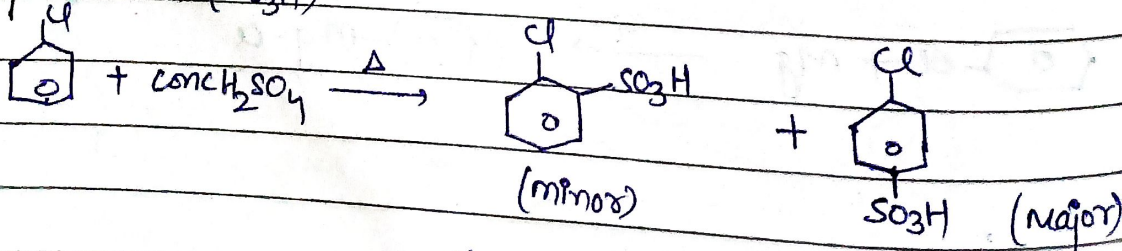


B) Nitration

(NO₂⁺)



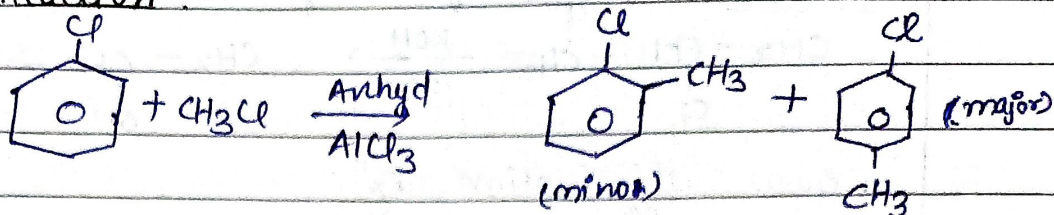
C) Sulphonation (SO₃H⁺)



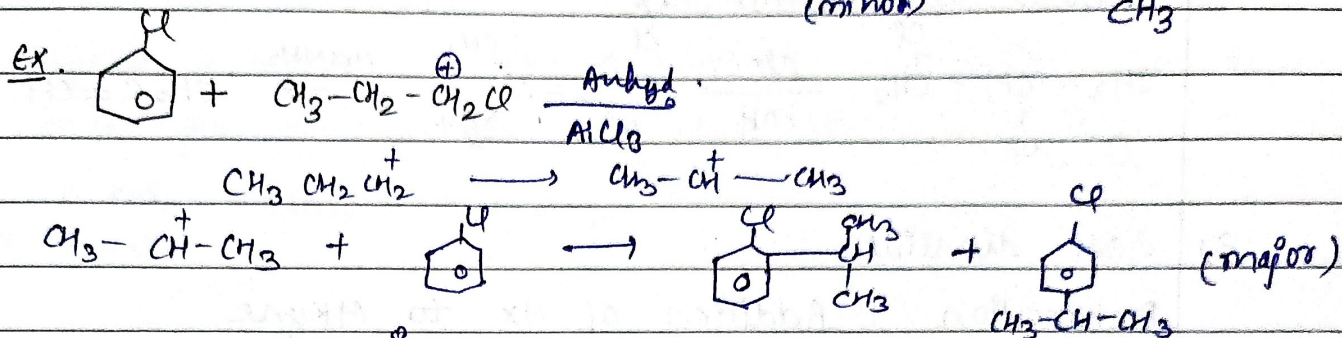
Chloro benzene sulphonic acids

D) Friedel Craft Reaction

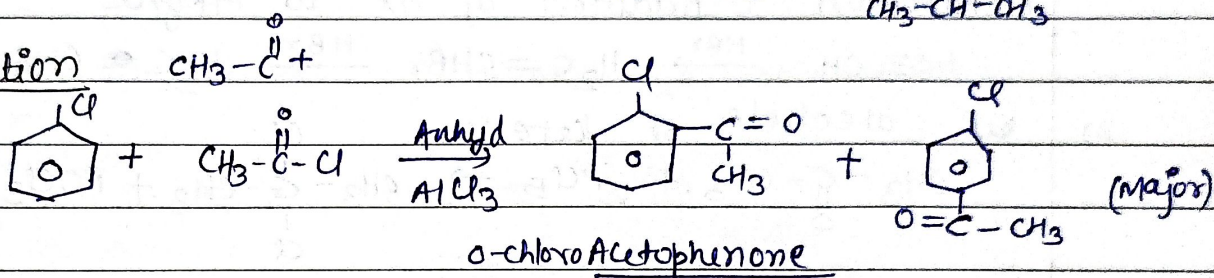
i) Alkylation



eg

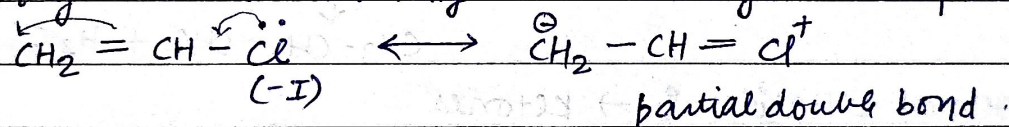


ii) Acylation

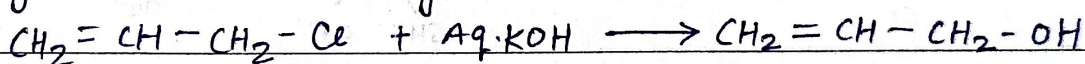


* REACTION OF VINYL HALIDES AND ALLYL HALIDES

→ Vinyl Halides normally don't undergo Nucleophilic Substitution.



→ Allyl halides undergo SN¹ and SN² both.



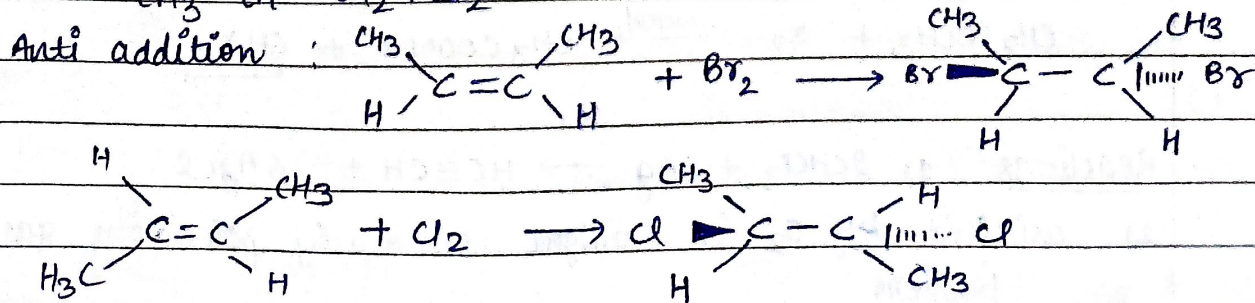
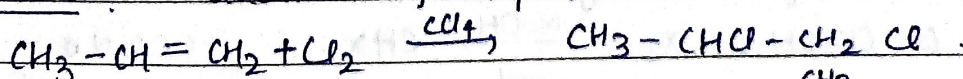
* POLYHALOGEN COMPOUNDS

contain more than 1 halogen atom.

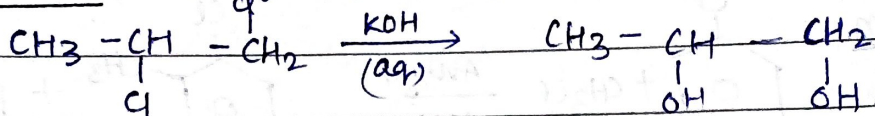
1) DIHALIDES

A) Vicinal dihalides: adjacent Carbon has halogens.

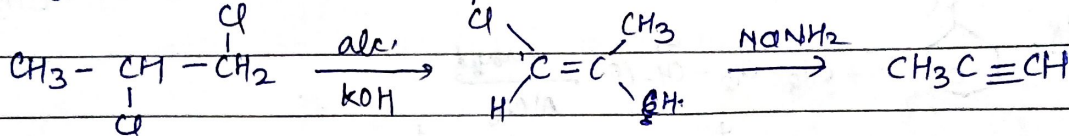
Preparation: addition of Cl₂/Br₂ to alkenes.



Reactions: 1) Hydrolysed by alkali to vicinal diols.

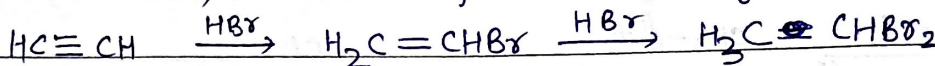


2) show elimination rxn.

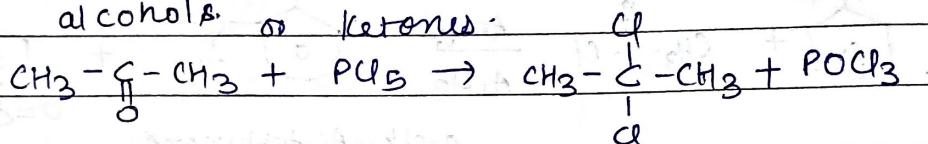


B) Gem dihalides.

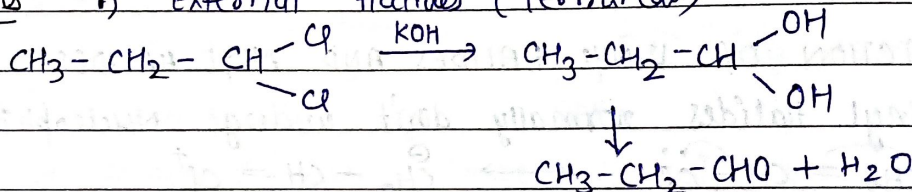
Preparation: 1) Addition of HX to Alkyne



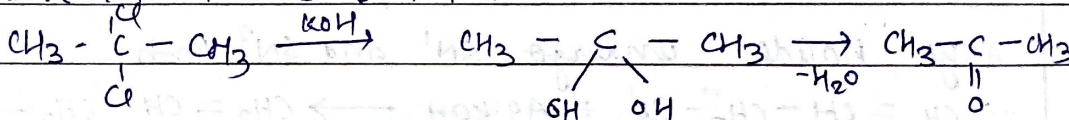
2) by alcohols or ketones.



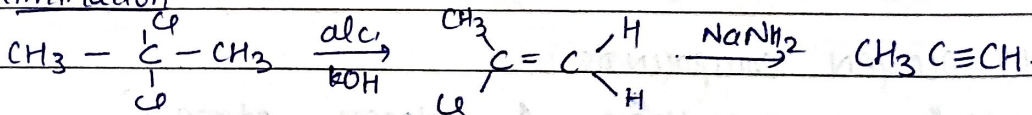
Reactions 1) External Halides (Terminal) \rightarrow Aldehydes



2) Internal Halides \rightarrow Ketones

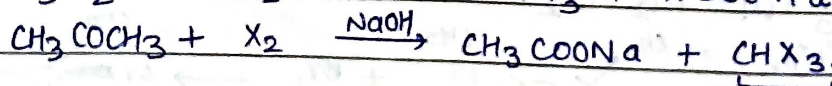
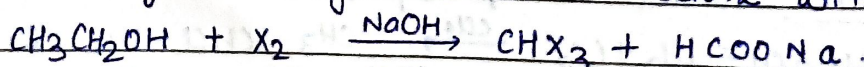


3) Elimination.



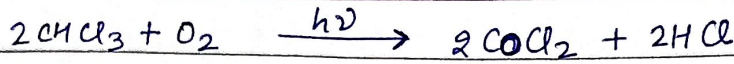
2) TRIHALIDES. Haloforms. CHCl_3 , CHBr_3 , CHI_3 .

Prepared by heating Ethanol or Acetone with X_2 .

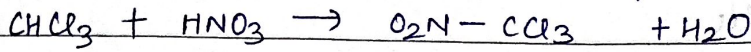


Reactions: 1) $2\text{CHCl}_3 + 6\text{Ag} \rightarrow \text{HC}\equiv\text{CH} + 6\text{AgCl}$

2) oxidised by O_2 in sunlight to deadly poisonous gas phosgene.

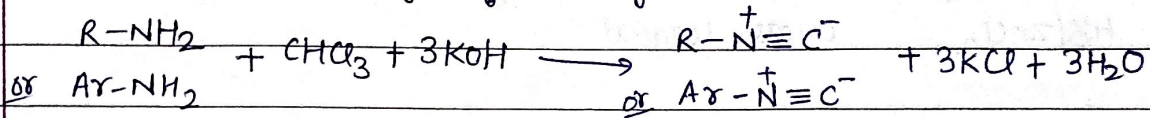


3) with conc. HNO_3 , it gives chloropicrin (CCl_3NO_2)

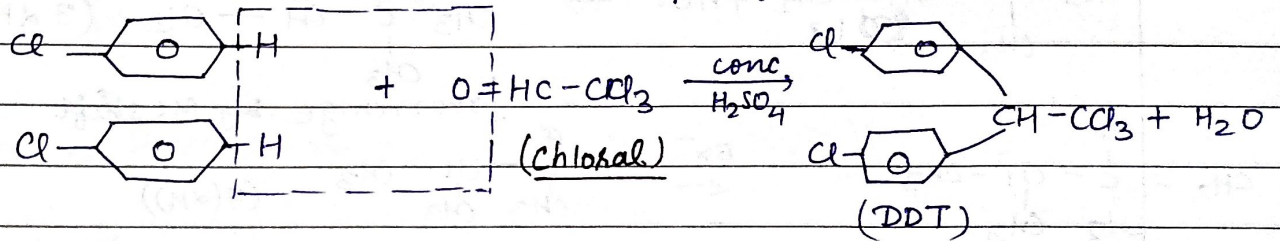


CCl_3-NO_2 is insecticide (crying gas)

4) Aliphatic & Aromatic primary amines react with CHCl_3 to form foul smelling ~~gas~~ isocyanide. This is "CARBYLAMINE TEST"

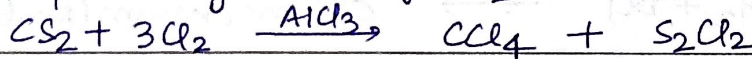


5) formation of DDT (p,p' - dichlorodiphenyl trichloroethane)



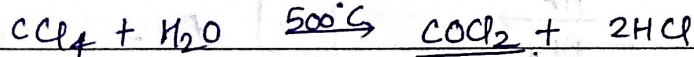
3) TETRAHALIDES.

CCl_4 prepared by action of Cl_2 on CS_2 .

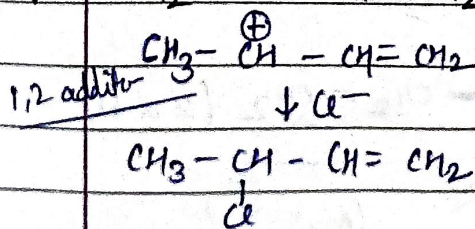
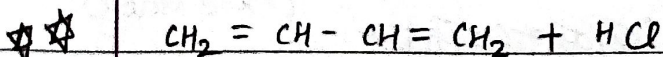
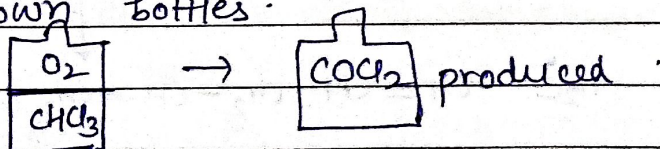


CCl_4 is insoluble in H_2O but soluble in ethanol or ether.

CCl_4 reacts with $\text{H}_2\text{O}(\text{g})$ at 500°C to form phosgene.

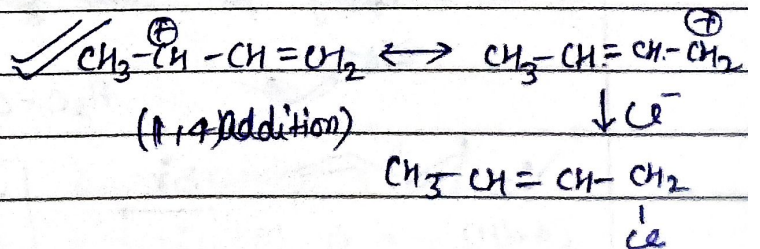


⊕ CHCl_3 can't be stored half filled as it forms COCl_2 . It is stored in brown bottles.



(kinetically controlled)

(at low temp.)



Thermodynamically controlled

(at high temp.)