

Solvent:

2 types of solvent are present.

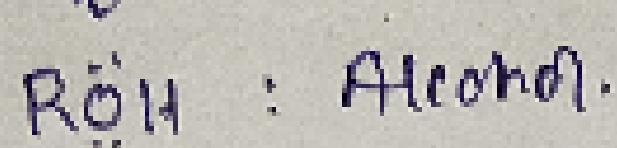
(i)

a) Protic Solvent b) Aprotic Solvent.

Protic solvent: Solvent which furnishes H^+ . [If H is attached with highly electronegative element]



$NH_3 \cdot Cl$: Ammonia attached with highly electronegative element



$C_2H_5CO_2H$: Acetic Acid

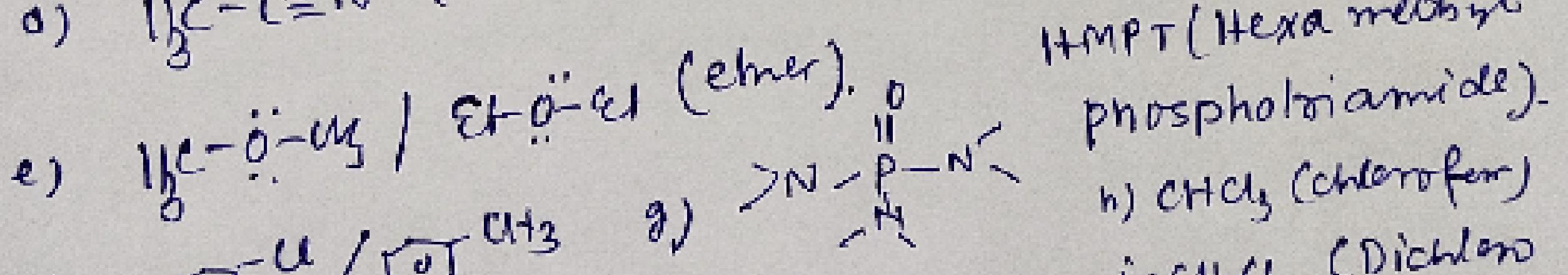
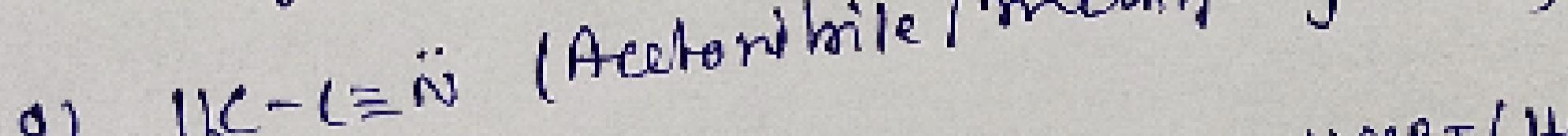
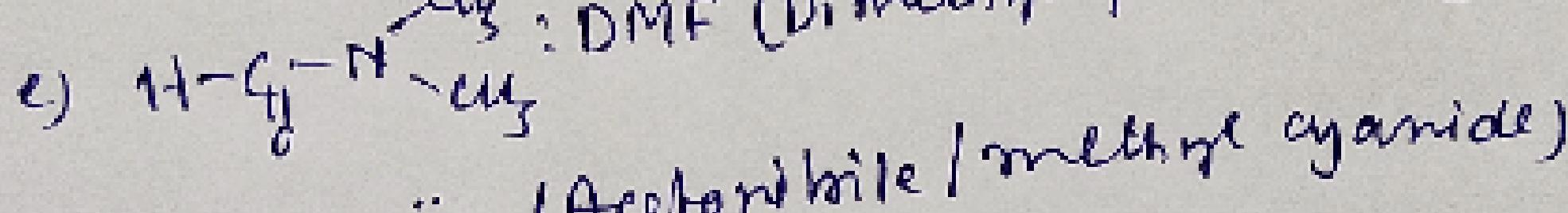
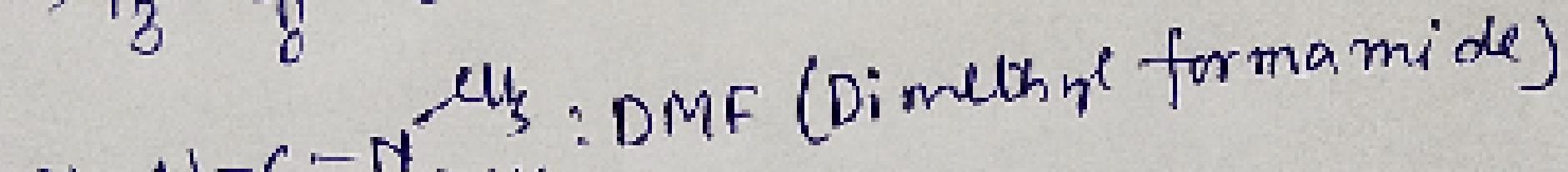
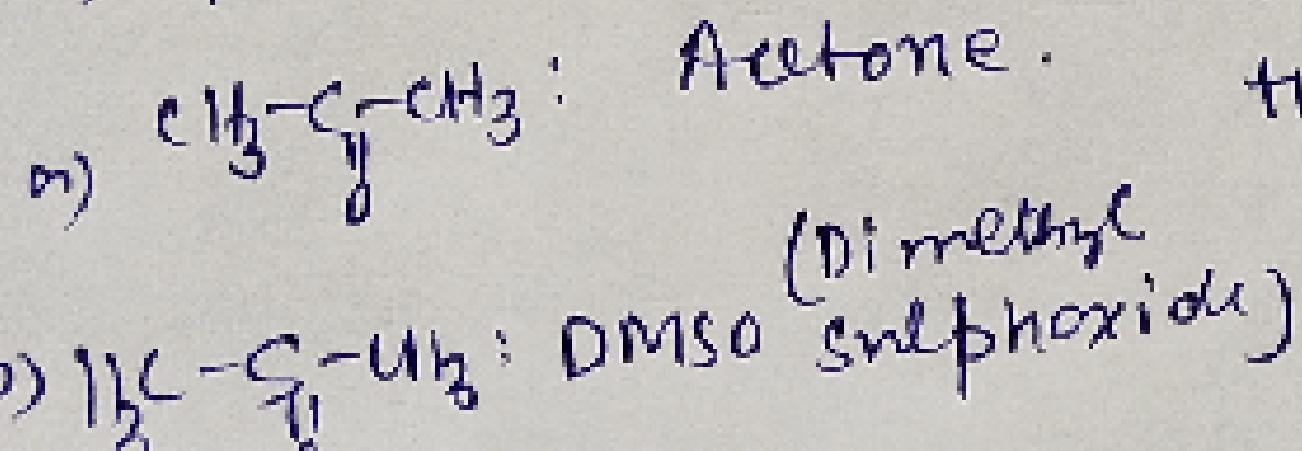


Protic solvent are generally polar in nature.

b) Aprotic solvent. These are further classified in 2 parts

a) Aprotic Polar solvent: If H attached with sp^2 / sp carbon

then it can not give H^+ So they are example of Aprotic solvent.



f) $C_2H_5-O-C_2H_5$ / CH_3Cl (Chloroform)

g) $>N-P(=O)(C_2H_5)_2-N<$ $i, C_2H_5Cl_2$ (Dichloro methane)

h) $TiCl_4$ (Tetrachloro titanium)

i) CH_3SiCl_3 (Trichloromethylsilane)

j) $TiCl_3$ (Tetrachloro titanocene)

k) $LiAlD_4$ (Lithium aluminium deuteride)

l) $LiAlH_4$ (Lithium aluminium hydride)

m) $LiAlCl_4$ (Lithium aluminium chloride)

n) $LiAlD_4$ (Lithium aluminium deuteride)

o) $LiAlH_4$ (Lithium aluminium hydride)

p) $LiAlCl_4$ (Lithium aluminium chloride)

q) $LiAlD_4$ (Lithium aluminium deuteride)

r) $LiAlH_4$ (Lithium aluminium hydride)

s) $LiAlCl_4$ (Lithium aluminium chloride)

t) $LiAlD_4$ (Lithium aluminium deuteride)

u) $LiAlH_4$ (Lithium aluminium hydride)

v) $LiAlCl_4$ (Lithium aluminium chloride)

w) $LiAlD_4$ (Lithium aluminium deuteride)

x) $LiAlH_4$ (Lithium aluminium hydride)

y) $LiAlCl_4$ (Lithium aluminium chloride)

z) $LiAlD_4$ (Lithium aluminium deuteride)

aa) $LiAlH_4$ (Lithium aluminium hydride)

bb) $LiAlCl_4$ (Lithium aluminium chloride)

cc) $LiAlD_4$ (Lithium aluminium deuteride)

dd) $LiAlH_4$ (Lithium aluminium hydride)

ee) $LiAlCl_4$ (Lithium aluminium chloride)

ff) $LiAlD_4$ (Lithium aluminium deuteride)

gg) $LiAlH_4$ (Lithium aluminium hydride)

hh) $LiAlCl_4$ (Lithium aluminium chloride)

ii) $LiAlD_4$ (Lithium aluminium deuteride)

jj) $LiAlH_4$ (Lithium aluminium hydride)

kk) $LiAlCl_4$ (Lithium aluminium chloride)

ll) $LiAlD_4$ (Lithium aluminium deuteride)

mm) $LiAlH_4$ (Lithium aluminium hydride)

nn) $LiAlCl_4$ (Lithium aluminium chloride)

oo) $LiAlD_4$ (Lithium aluminium deuteride)

pp) $LiAlH_4$ (Lithium aluminium hydride)

qq) $LiAlCl_4$ (Lithium aluminium chloride)

rr) $LiAlD_4$ (Lithium aluminium deuteride)

ss) $LiAlH_4$ (Lithium aluminium hydride)

tt) $LiAlCl_4$ (Lithium aluminium chloride)

uu) $LiAlD_4$ (Lithium aluminium deuteride)

vv) $LiAlH_4$ (Lithium aluminium hydride)

ww) $LiAlCl_4$ (Lithium aluminium chloride)

xx) $LiAlD_4$ (Lithium aluminium deuteride)

yy) $LiAlH_4$ (Lithium aluminium hydride)

zz) $LiAlCl_4$ (Lithium aluminium chloride)

aa) $LiAlD_4$ (Lithium aluminium deuteride)

bb) $LiAlH_4$ (Lithium aluminium hydride)

cc) $LiAlCl_4$ (Lithium aluminium chloride)

dd) $LiAlD_4$ (Lithium aluminium deuteride)

ee) $LiAlH_4$ (Lithium aluminium hydride)

ff) $LiAlCl_4$ (Lithium aluminium chloride)

gg) $LiAlD_4$ (Lithium aluminium deuteride)

hh) $LiAlH_4$ (Lithium aluminium hydride)

ii) $LiAlCl_4$ (Lithium aluminium chloride)

jj) $LiAlD_4$ (Lithium aluminium deuteride)

kk) $LiAlH_4$ (Lithium aluminium hydride)

ll) $LiAlCl_4$ (Lithium aluminium chloride)

mm) $LiAlD_4$ (Lithium aluminium deuteride)

nn) $LiAlH_4$ (Lithium aluminium hydride)

oo) $LiAlCl_4$ (Lithium aluminium chloride)

pp) $LiAlD_4$ (Lithium aluminium deuteride)

qq) $LiAlH_4$ (Lithium aluminium hydride)

rr) $LiAlCl_4$ (Lithium aluminium chloride)

ss) $LiAlD_4$ (Lithium aluminium deuteride)

tt) $LiAlH_4$ (Lithium aluminium hydride)

uu) $LiAlCl_4$ (Lithium aluminium chloride)

vv) $LiAlD_4$ (Lithium aluminium deuteride)

ww) $LiAlH_4$ (Lithium aluminium hydride)

xx) $LiAlCl_4$ (Lithium aluminium chloride)

yy) $LiAlD_4$ (Lithium aluminium deuteride)

zz) $LiAlH_4$ (Lithium aluminium hydride)

aa) $LiAlCl_4$ (Lithium aluminium chloride)

bb) $LiAlD_4$ (Lithium aluminium deuteride)

cc) $LiAlH_4$ (Lithium aluminium hydride)

dd) $LiAlCl_4$ (Lithium aluminium chloride)

ee) $LiAlD_4$ (Lithium aluminium deuteride)

ff) $LiAlH_4$ (Lithium aluminium hydride)

gg) $LiAlCl_4$ (Lithium aluminium chloride)

hh) $LiAlD_4$ (Lithium aluminium deuteride)

ii) $LiAlH_4$ (Lithium aluminium hydride)

jj) $LiAlCl_4$ (Lithium aluminium chloride)

kk) $LiAlD_4$ (Lithium aluminium deuteride)

ll) $LiAlH_4$ (Lithium aluminium hydride)

mm) $LiAlCl_4$ (Lithium aluminium chloride)

nn) $LiAlD_4$ (Lithium aluminium deuteride)

oo) $LiAlH_4$ (Lithium aluminium hydride)

pp) $LiAlCl_4$ (Lithium aluminium chloride)

qq) $LiAlD_4$ (Lithium aluminium deuteride)

rr) $LiAlH_4$ (Lithium aluminium hydride)

ss) $LiAlCl_4$ (Lithium aluminium chloride)

tt) $LiAlD_4$ (Lithium aluminium deuteride)

uu) $LiAlH_4$ (Lithium aluminium hydride)

vv) $LiAlCl_4$ (Lithium aluminium chloride)

ww) $LiAlD_4$ (Lithium aluminium deuteride)

xx) $LiAlH_4$ (Lithium aluminium hydride)

yy) $LiAlCl_4$ (Lithium aluminium chloride)

zz) $LiAlD_4$ (Lithium aluminium deuteride)

aa) $LiAlH_4$ (Lithium aluminium hydride)

bb) $LiAlCl_4$ (Lithium aluminium chloride)

cc) $LiAlD_4$ (Lithium aluminium deuteride)

dd) $LiAlH_4$ (Lithium aluminium hydride)

ee) $LiAlCl_4$ (Lithium aluminium chloride)

ff) $LiAlD_4$ (Lithium aluminium deuteride)

gg) $LiAlH_4$ (Lithium aluminium hydride)

hh) $LiAlCl_4$ (Lithium aluminium chloride)

ii) $LiAlD_4$ (Lithium aluminium deuteride)

jj) $LiAlH_4$ (Lithium aluminium hydride)

kk) $LiAlCl_4$ (Lithium aluminium chloride)

ll) $LiAlD_4$ (Lithium aluminium deuteride)

mm) $LiAlH_4$ (Lithium aluminium hydride)

nn) $LiAlCl_4$ (Lithium aluminium chloride)

oo) $LiAlD_4$ (Lithium aluminium deuteride)

pp) $LiAlH_4$ (Lithium aluminium hydride)

qq) $LiAlCl_4$ (Lithium aluminium chloride)

rr) $LiAlD_4$ (Lithium aluminium deuteride)

ss) $LiAlH_4$ (Lithium aluminium hydride)

tt) $LiAlCl_4$ (Lithium aluminium chloride)

uu) $LiAlD_4$ (Lithium aluminium deuteride)

Role of solvent in reaction mechanism

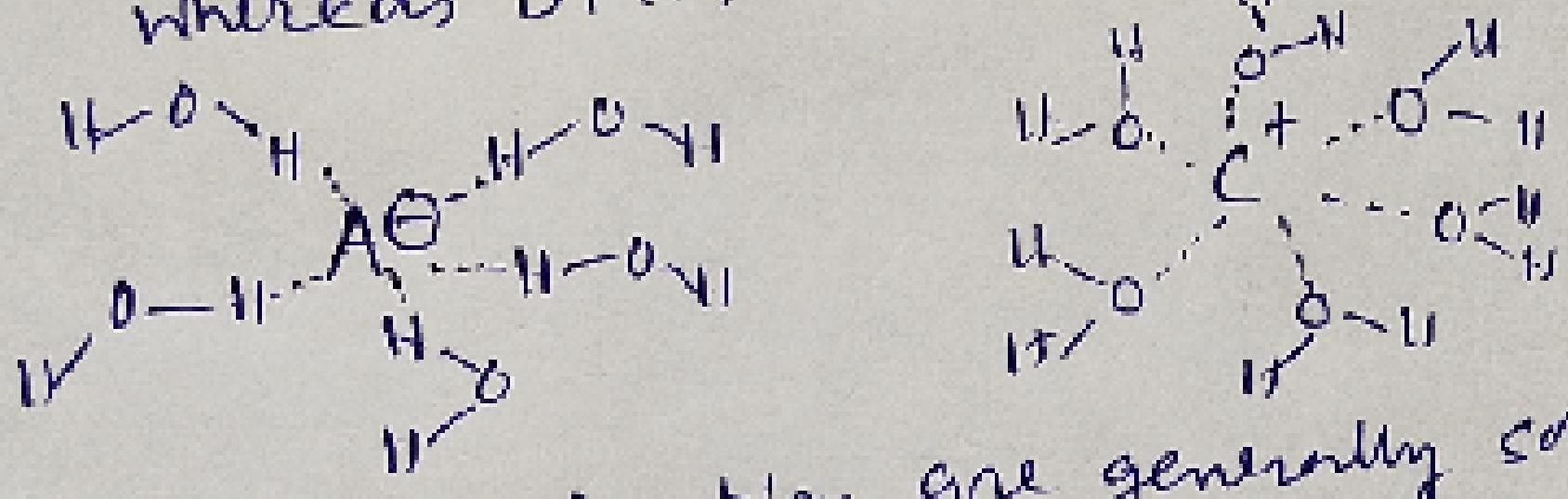
(3)



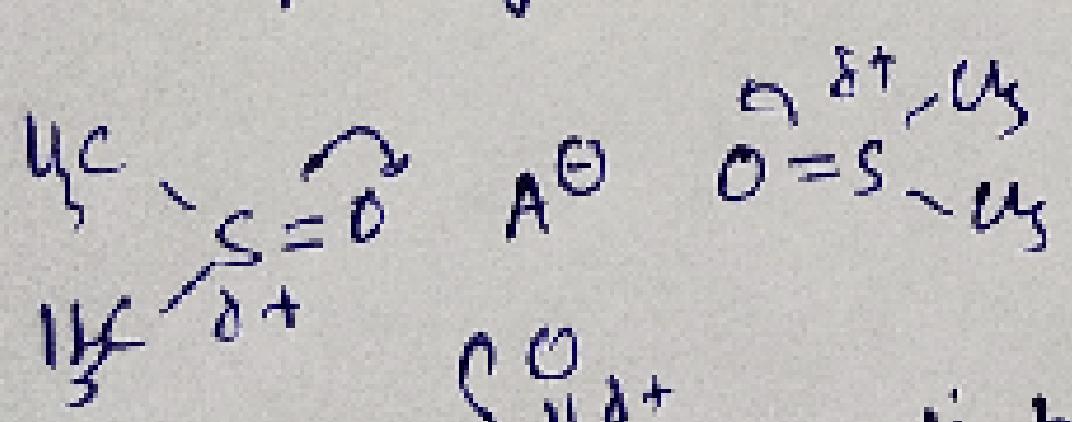
(R = ClB)

Here if we use protic solvent it will solvate the attacking nucleophile by H-bonding thus decreasing the reactivity of nucleophile in nucleophilic substitution. As reaction rate is dependent on attacking nucleophile, so with stabilization of nucleophile by protic solvent by either ion-dipole/H-bonding in reaction.

This reaction rate is increased/favoured in polar aprotic solvent. So H_2O reduces the reaction rate whereas DMF/ DMSO accelerates the reaction rate.



Here anion/cation are generally solvated by protic solvent because both the δ -ve pole is exposed & very high degree of solvation takes place.

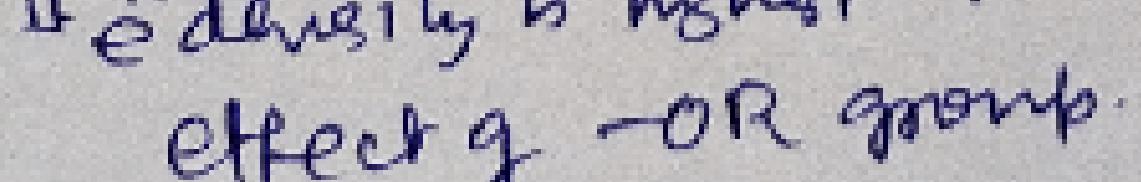
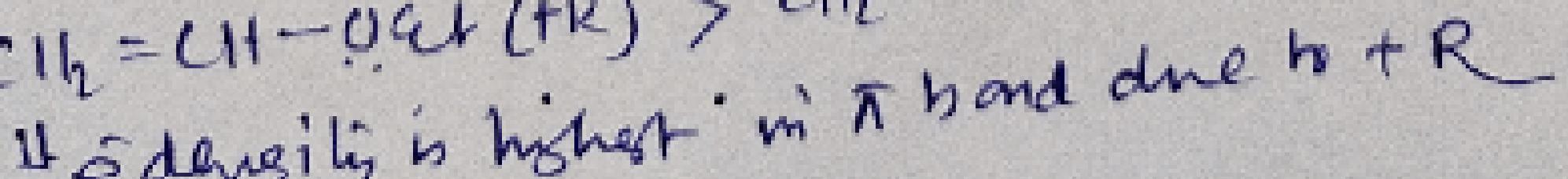
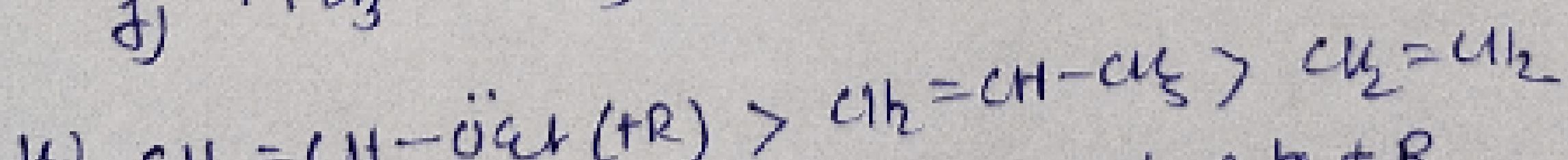
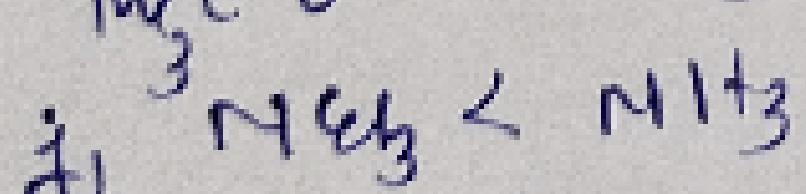
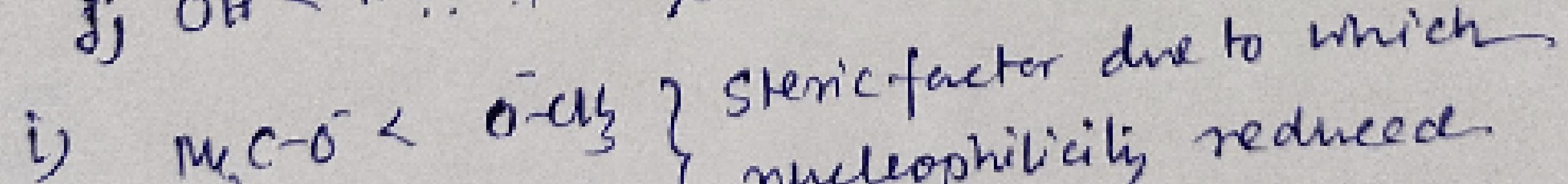
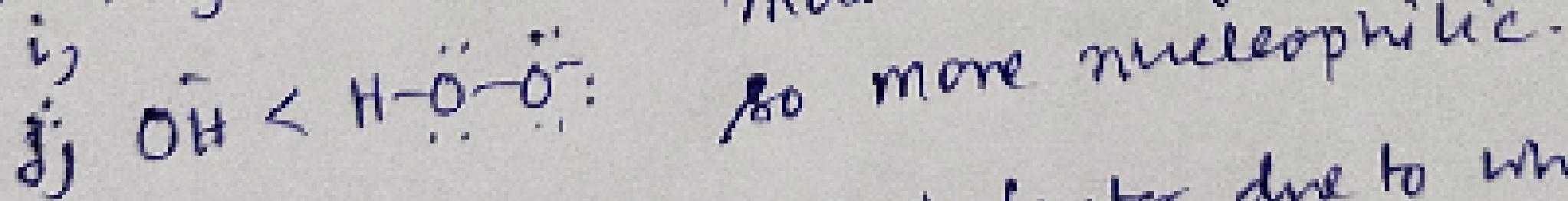
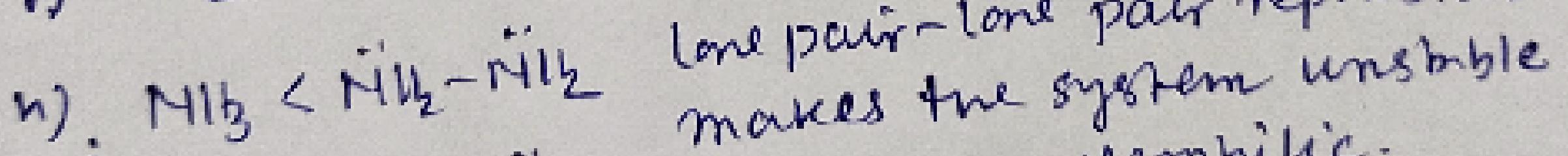
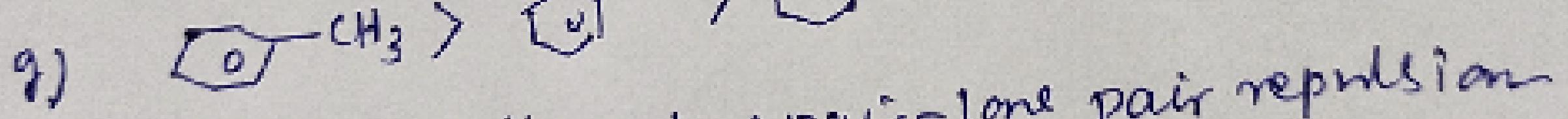
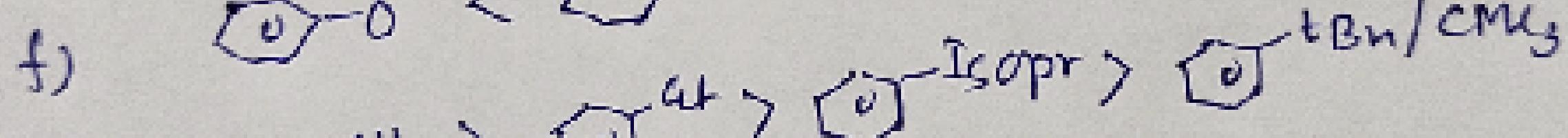
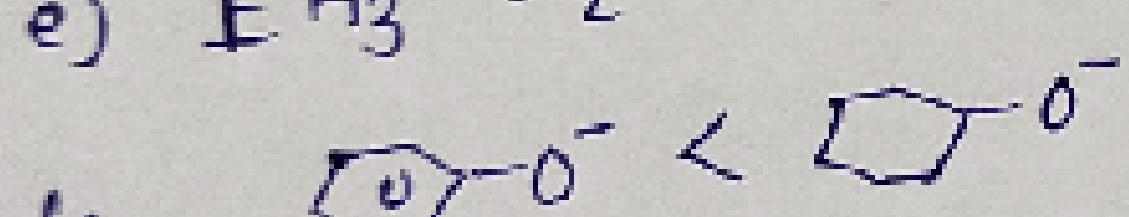
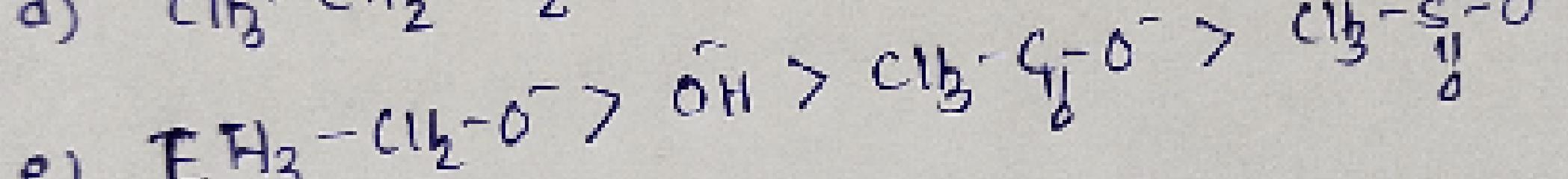
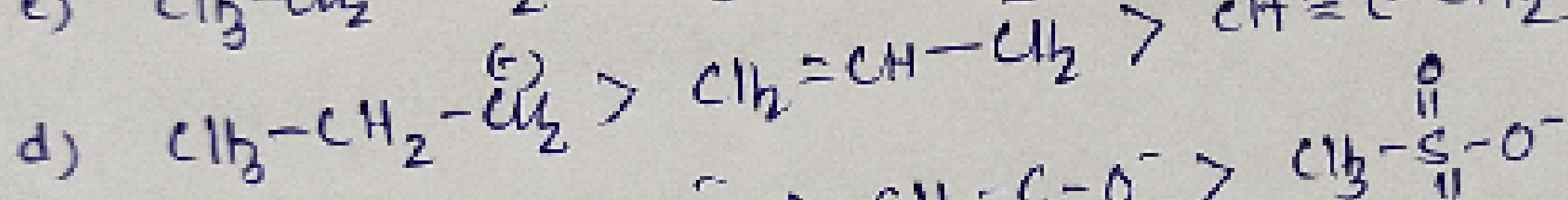
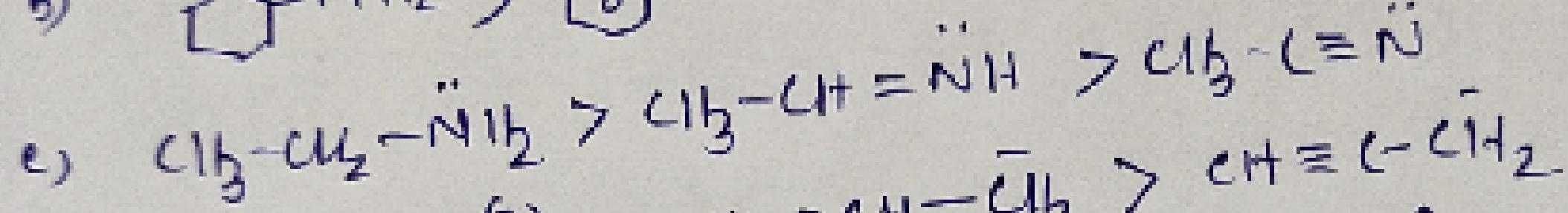
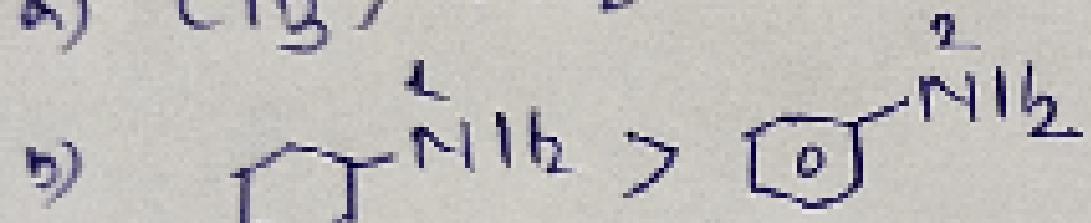
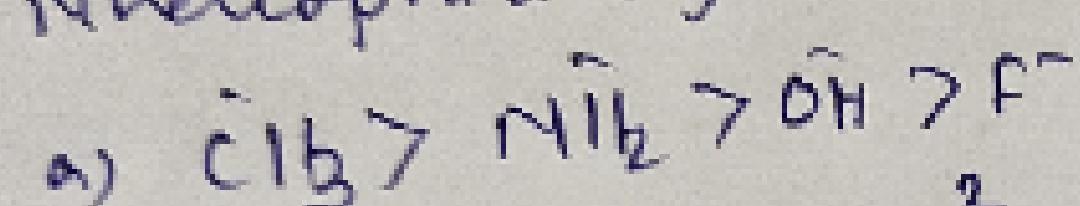


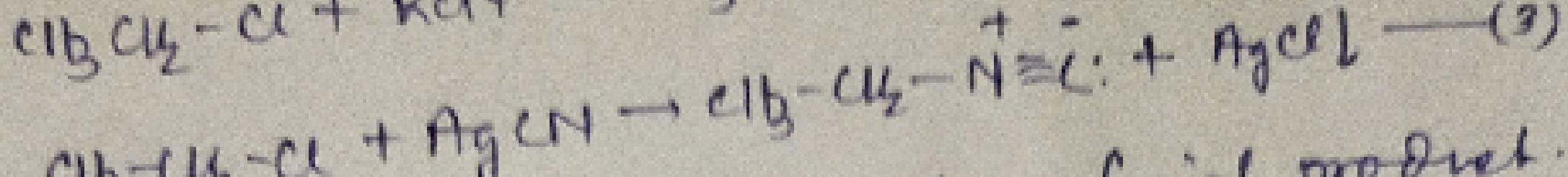
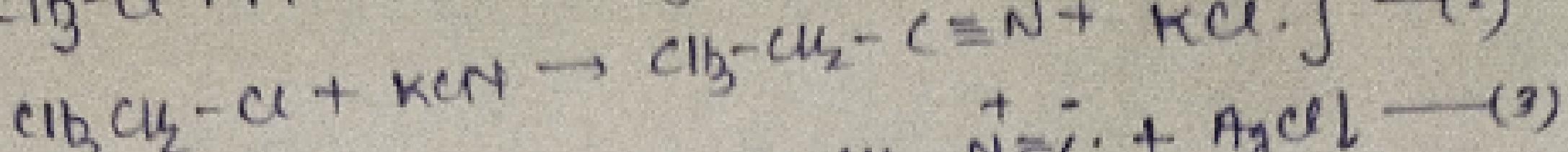
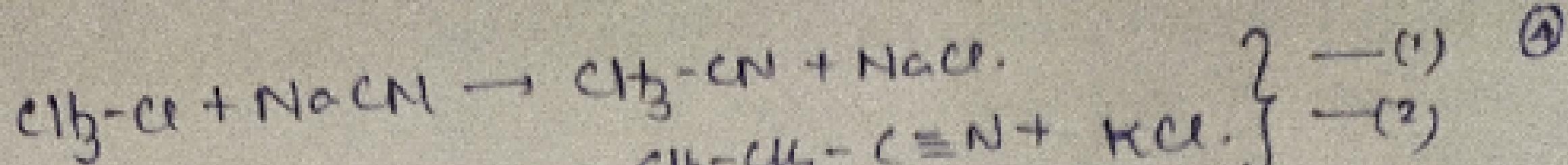
Bt anion solvation in aprotic solvent is very low because δ + charge on aprotic solvent is buried within the molecule (not exposed enough to solvate A^- /anion).

Nucleophilicity order:

- ⇒ Nucleophilicity a) Localised lone pair > delocalised lone pair.
b) C-donor atom > N-donor atom > O-donor atom.
c) sp^3 C-donor atom > sp^2 C-donor atom > sp C-donor atom.
d) i) $\ddot{\text{N}}\text{H}_2 > \text{NH}_3$ [-ve charge is stronger nucleophile w.r.t neutral system].
ii) $\text{O}\bar{\text{H}} > \text{H}_2\text{O}$
iii) $\text{S}\bar{\text{H}} > \text{H}_2\text{S}$

Nucleophilicity order:





In (1) & (2) cyanide is formed as final product.

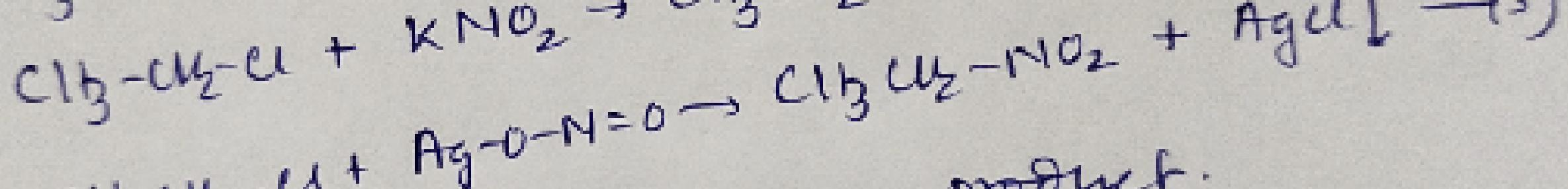
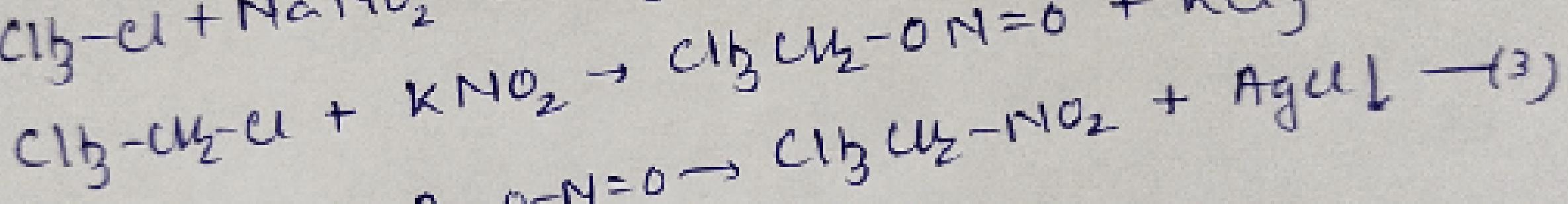
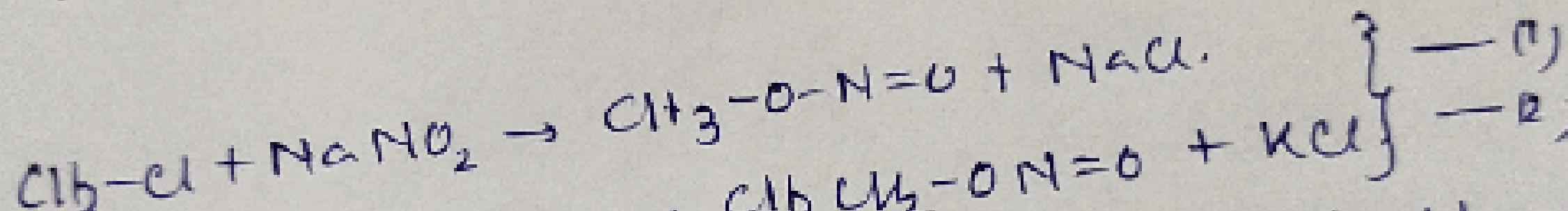
In (3) iso cyanide is formed as final product.

In (4) & (5) N & O can be the donor site.

Other examples: $\begin{matrix} N=O \\ \text{---} \\ \text{O}^{\cdot-} \end{matrix}$

$\text{NaNO}_2 \Rightarrow$ Ionic cpd: $\begin{matrix} N=O \\ \text{---} \\ \text{O}^{\cdot-} \end{matrix}$: oxygen is the donor atom because of -ve charge.

$\text{Ag-O-N=O} \Rightarrow$ Covalent cpd: Nitrogen is the donor atom because it is less en-



$Cl_3-C\ddot{O}-Cl$ is formed as product.

In (1) & (2), nitrite is formed as final product.

In (3), nitroethane is formed as final product.

Q. What is the nucleophilicity of following system?

= $\begin{matrix} + \text{O}^- \text{---} \text{C}\ddot{O}^- \\ \text{Li}^- \text{---} \text{C}\ddot{O}^- \end{matrix}$ LDA (lithium diisopropyl

a) $NH_3 > \text{Li}^+ \text{---} \text{C}\ddot{O}^-$ amide; due to steric factor
amide is order its nucleophilicity is less)

b) $\begin{matrix} + \text{O}^- \text{---} \text{C}\ddot{O}^- \\ \text{Li}^- \text{---} \text{C}\ddot{O}^- \end{matrix}$; Here N⁺ is the donor atom.

because it is localised lone pair, rest are delocalised lone pair.

⑤ If elements are in the same group, then nucleophilicity depends on nature of solvent. In aprotic solvent, -ve charge solvation is very less, so nucleophilicity is decided by charge density. More is the charge density (-ve) more will be nucleophilicity. So in chlorobenzene solvent, more will be nucleophilicity.

- $F^- > Cl^- > Br^- > I^-$ [size factor is the deciding factor.]
- $OH^- > SH^- > SeH^- > TeH^-$ [More will be size, less is e density. So down the grp, nuclicity reduced].
- $RO^- > RS^-$

In protic solvents, solvation is the deciding factor.

- In protic solvents, solvation is the deciding factor.
- $F^- > Cl^- > Br^- > I^-$ [smaller ion extent of solvation]
 - $OH^- > SH^- > SeH^- > TeH^-$ [can be solvated more effectively]
 - $RO^- > RS^-$ [bisty by H_2O].

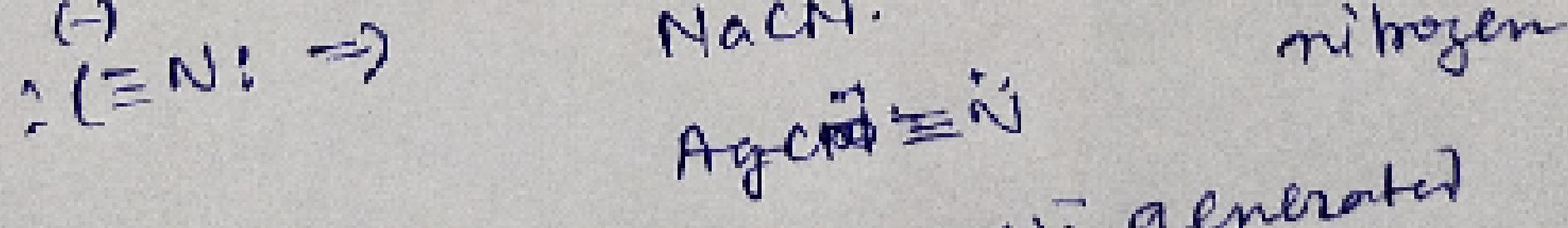
Give order of nucleophilicity: [down the group]

[In H_2O / ROH]

- $F^- < Cl^- < Br^- < I^-$ nucleophilicity increases in protic solvent].
- $OH^- < SH^- < SeH^- < TeH^-$
- $RO^- < RS^-$

: Ambidentate Nucleophile:
If any system having two donor atoms, but during donation it use only one donor atom at a time.
Then it is called Ambidentate Nucleophile.

Source of nucleophile: Donor atom carbon.



$NaCN \Rightarrow$ Ionic cpd; $:\ddot{N}^-$ generated

Carbon is donor atom.

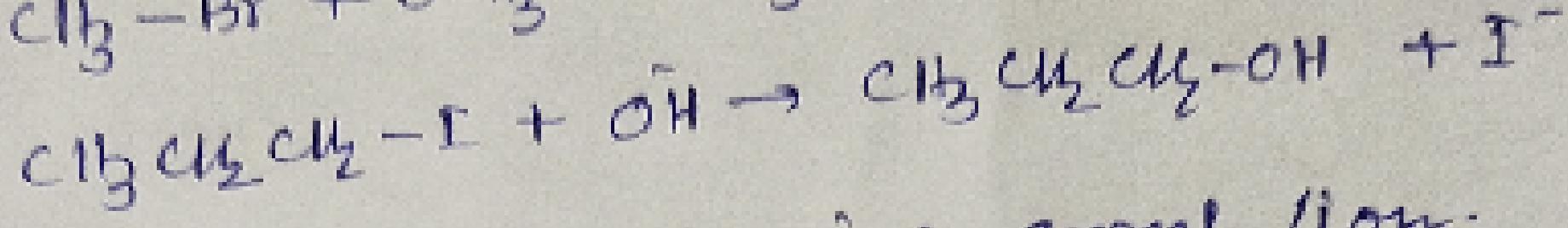
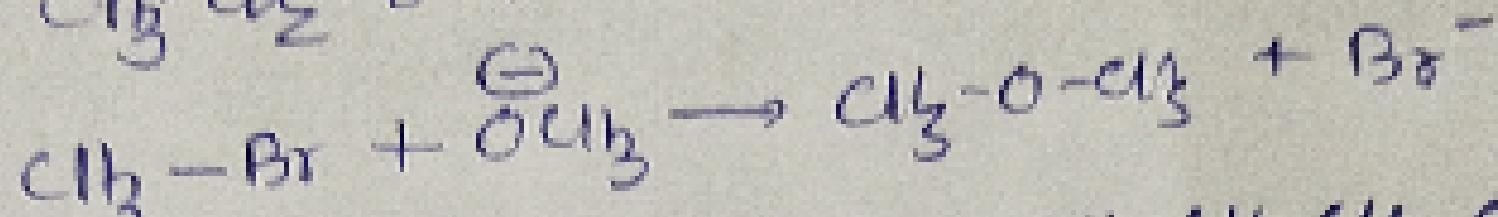
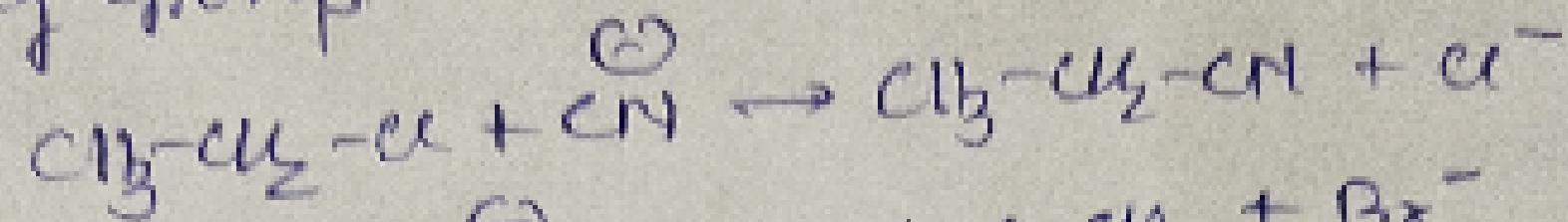
$Ag^+ :\ddot{N}^- \Rightarrow$ lone pair on N

$Ag(CN) \Rightarrow$ covalent cpd! Ag- (\ddot{N}) is available; N donor atom.

Leaving group:

(6)

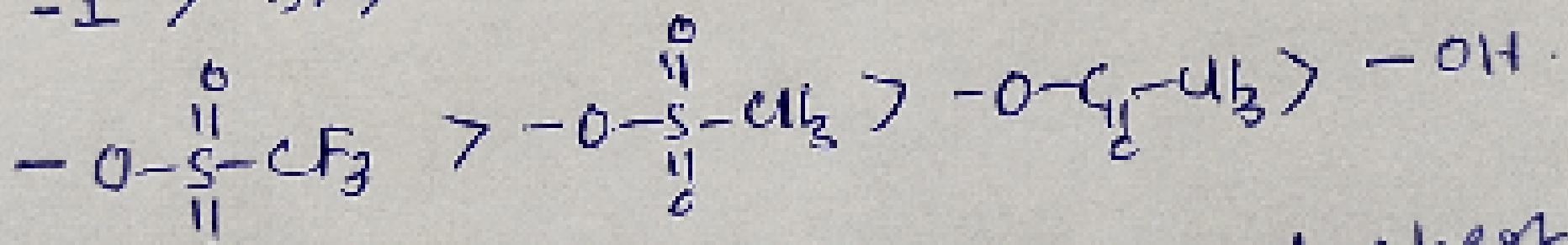
In a nucleophilic substitution reaction, the atom/group which is left from reactant is called leaving group.



Here Cl^- , Br^- , I^- acts as leaving group/ion.
 More is the stability of X^- , better is the leaving group. So leaving group ability: $\text{F}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$

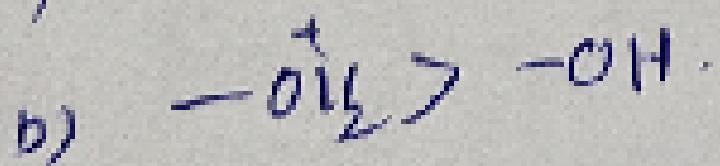
Leaving group ability:

for better leaving group of the system, its conjugate acid should be strong acid.



$-\text{O}-\overset{\text{O}}{\underset{\parallel}{\text{S}}}(\text{CF}_3)_2$ (Triflate ion) is one of the best leaving group, because its conjugate acid is example of strong acid.

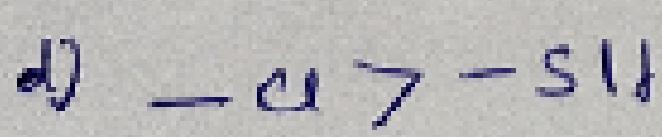
$-\text{OH}^-$, $-\text{OR}^-$, $-\text{NHR}^-$ all are examples of bad/poor leaving group because their conjugate acid is strong acid.



$-\text{R}^-$, $-\text{H}^-$ can not act as leaving group because

their conjugate acid is extremely weak acid

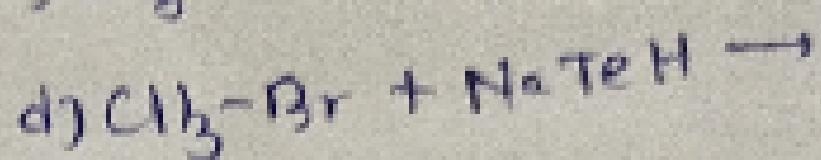
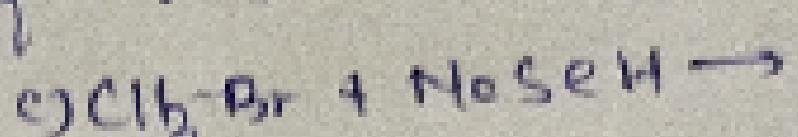
$\text{RH}/\text{H}_2\text{S}$



- Q. Which reaction is fastest?
- $R-F + OH^- \rightarrow R-OH + F^-$
 - $R-Cl + OH^- \rightarrow R-OH + Cl^-$
 - $R-Br + OH^- \rightarrow R-OH + Br^-$ (f)
 - $R-I + OH^- \rightarrow R-OH + I^-$

Q. Which reaction is slowest in aqueous medium.

- $CH_3-Br + NaOH \rightarrow$
- $CH_3-Br + NaSH \rightarrow$

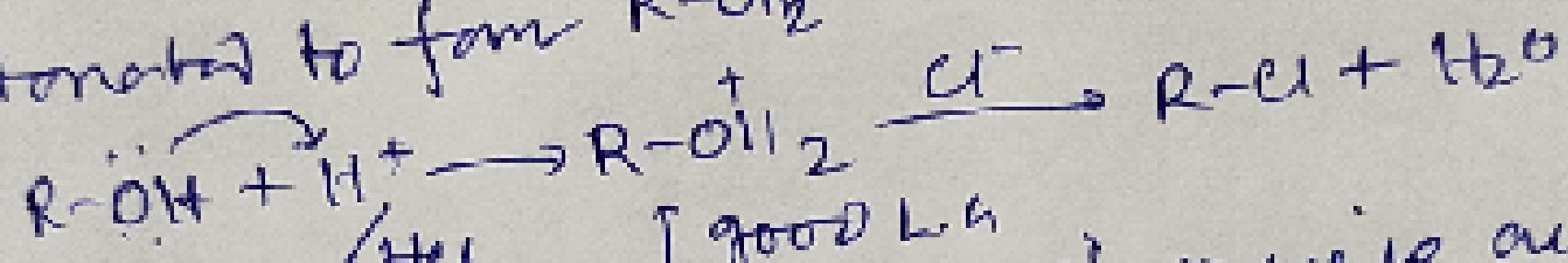


Q. What is the role of H^+ to ~~make~~ convert $-OH$ (bad/poor L.G.) into good leaving group.

But on addition of

H^+ (in HCl), ROH is

protonated to form $R-OH_2^+$ & it becomes good leaving group.



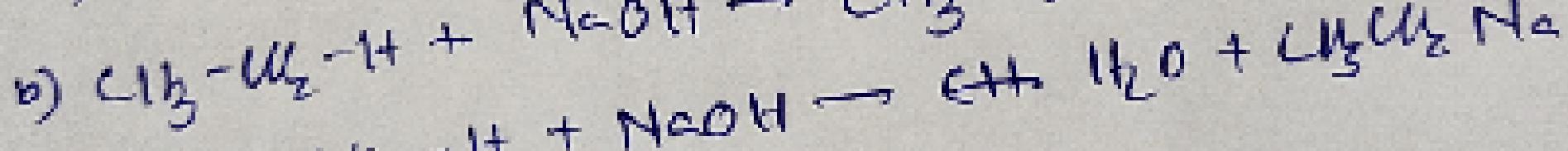
[good L.G.]

because its conjugate acid

H_3O^+ is example of my acid].

Q. Which reaction is feasible?

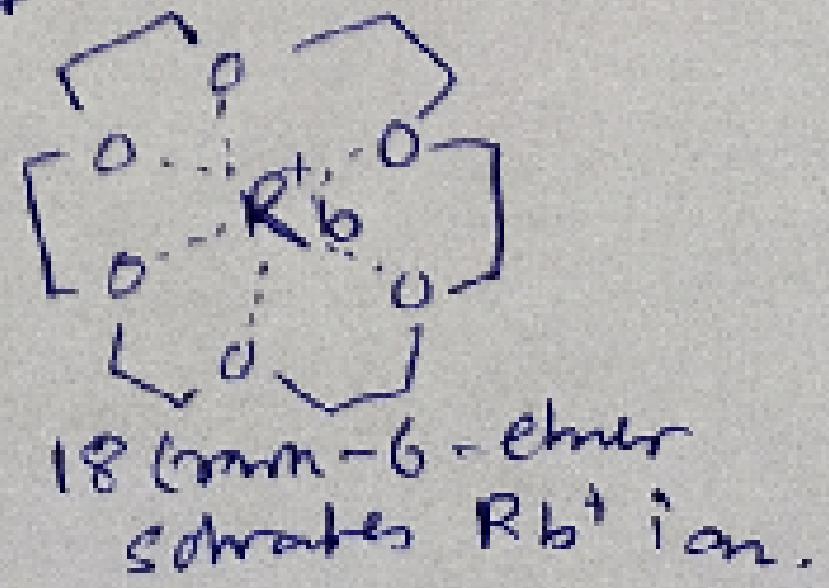
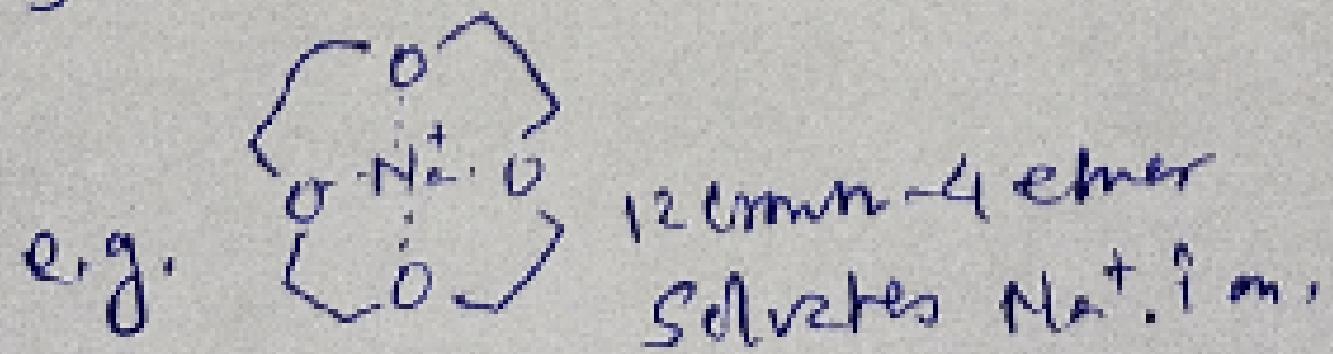
- $R-OH + NaCl \rightarrow R-Cl + NaOH$



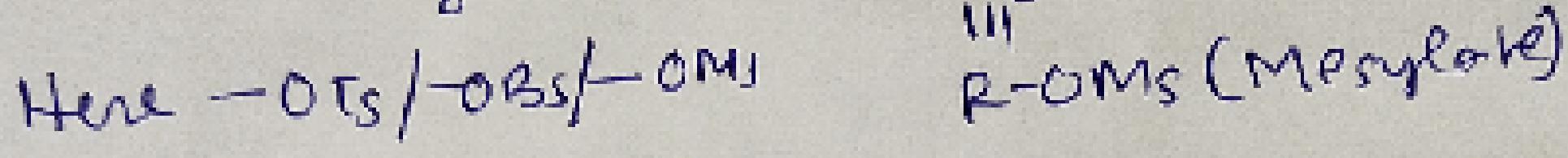
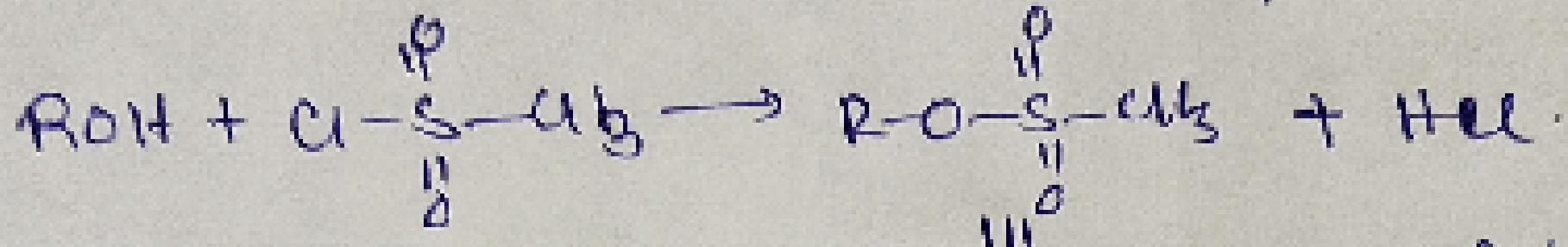
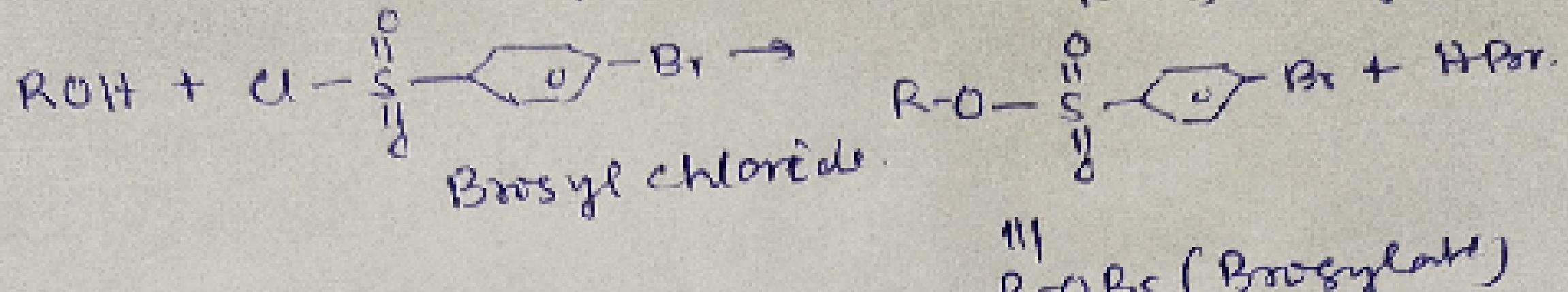
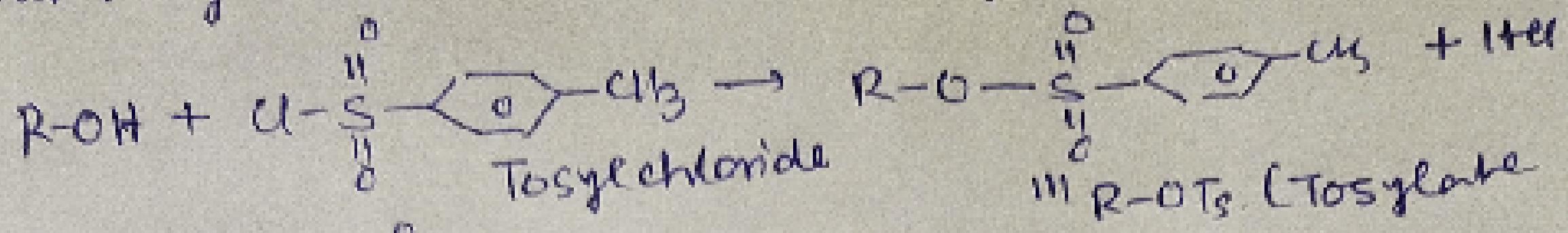
- ✓ d) $R-OH + HCl \rightarrow R-Cl + H_2O$

Q. What is the purpose of crown ethers?

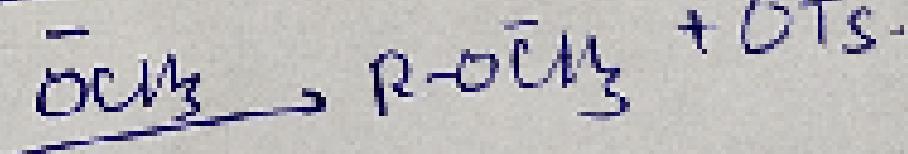
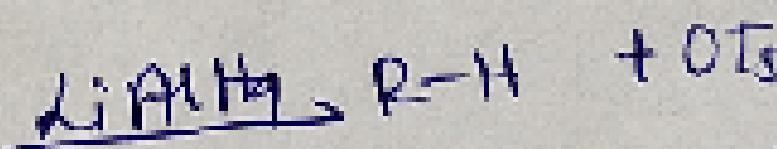
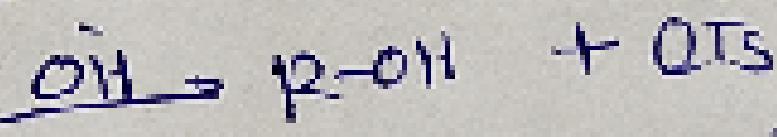
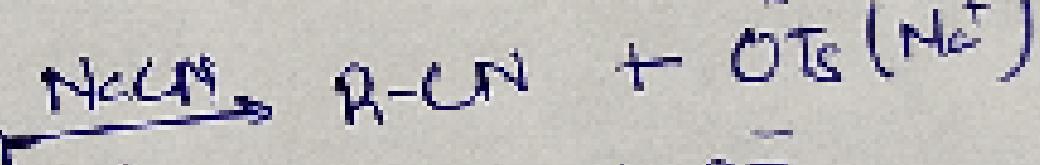
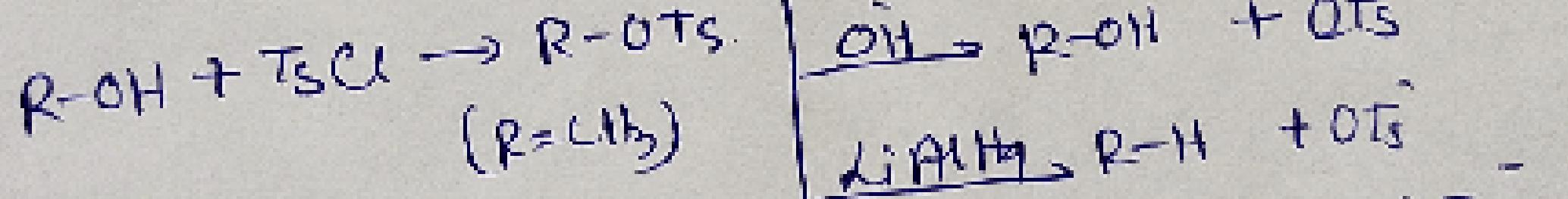
Crown ether is used to solvate different metal ions, depending on the size of cavity, different sized metal ions are solvated, but



Other way to make bad L.G. with good L.B.: G



are example of very good leaving group where acidic strength of conjugate acid is very much increased (Sulphonic acids are example very strong acid). So they be removed very easily, this can undergo reaction via S_N mechanism with them ($S_N \Rightarrow$ Nucleophilic substitution).

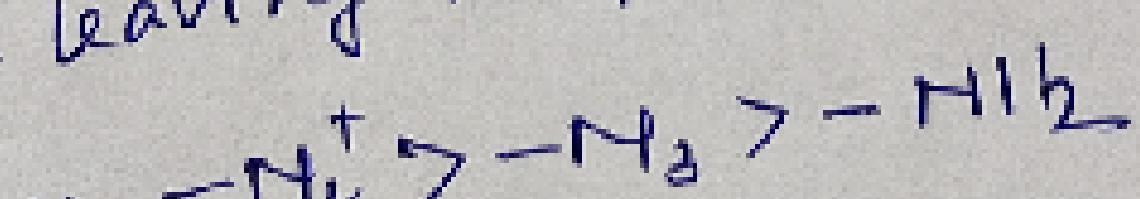


$-OBs$ is even better leaving group than $-OTs$.

$-OTf$ (triflate ion) is one of the best leaving group.

(short form)

Q. Leaving group ability order:



\Rightarrow Na⁺ is the pKa of HA,
better is the leaving group -A.

H_2^+ diazonium ion is one of the best L.G.

because after removal it becomes very stable.