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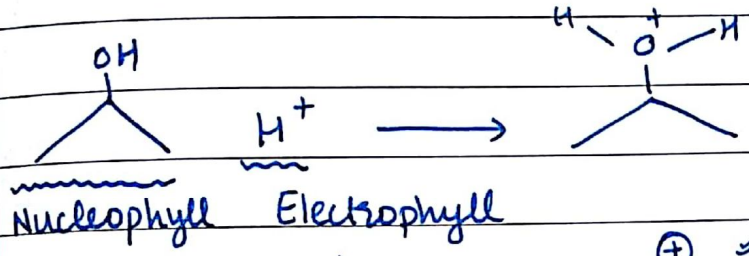
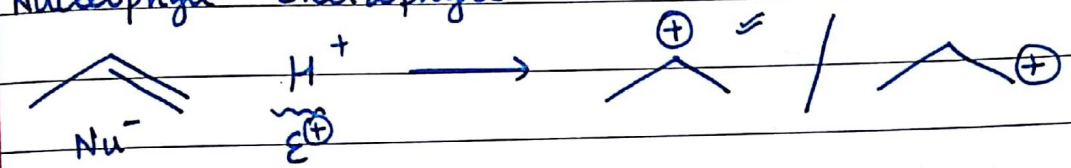
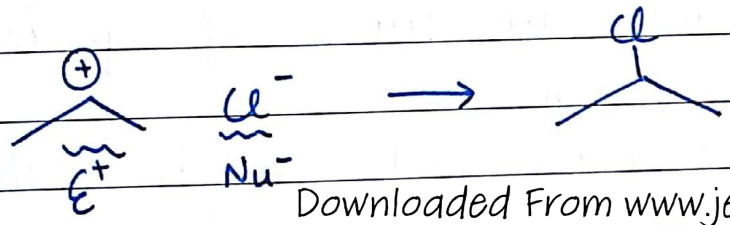
16/5/18

Basics of Organic Chemistry Mechanisms

- In this topic you will be provided with the tools to understand rxn mechanisms.

⇒ 

⇒ 

⇒ 

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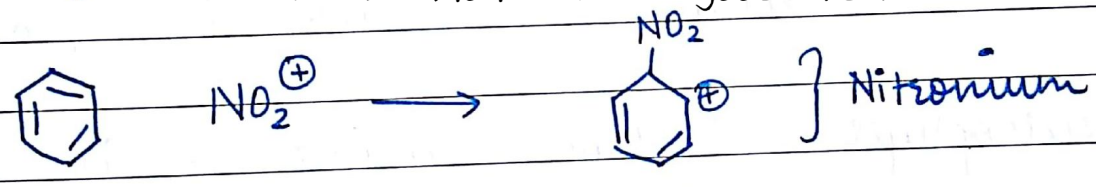
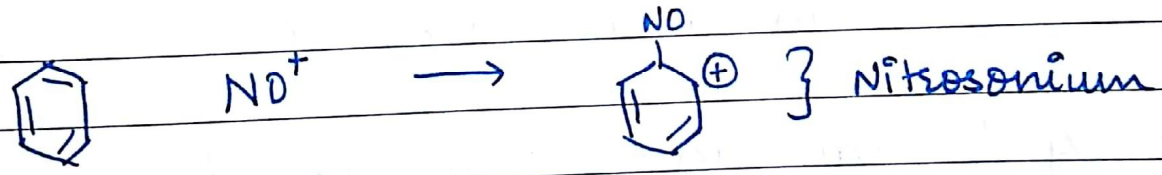
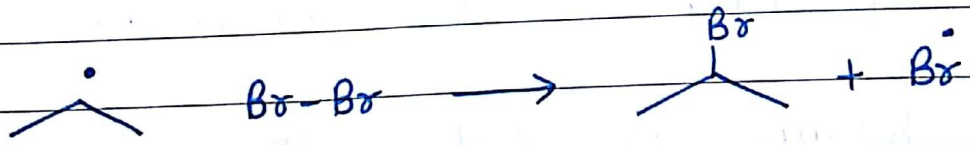
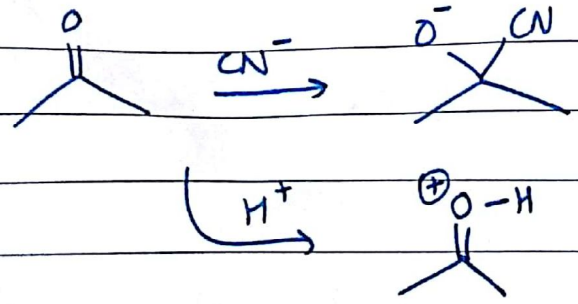
⇒ 

⇒ 

⇒ 

⇒ Cl − Cl ⟶ 2Cl

⇒ 

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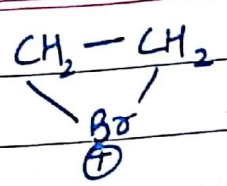
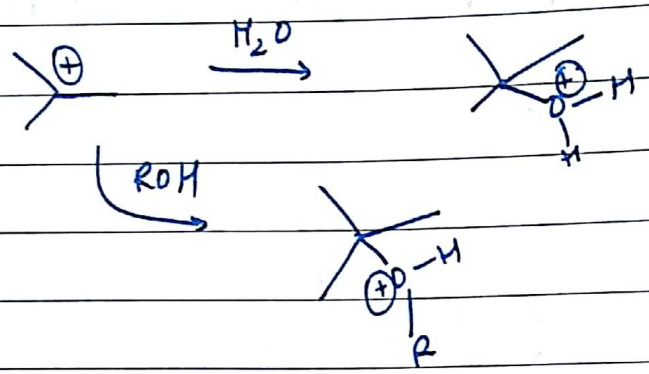
⇒ $CH_2 = CH_2 \xrightarrow{Br_2}$ 

⇒ 

- In most of the rxns two types of specie will exist in each step.
  i] Nucleophyll - electron rich specie which donates e^- pair (l.p. / b.p.)

  ii] electrophyll - electron deficient specie which can accept pair of e^-.

- Few specie can act as nucleophyll or electrophyll depending on the conditions.

- Few specie behave as electrophyll by using its LUMO.

- In free radical rxns focus on homolysis & e^- pairing.

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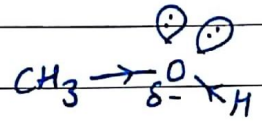
* Nucleophile :-

Types

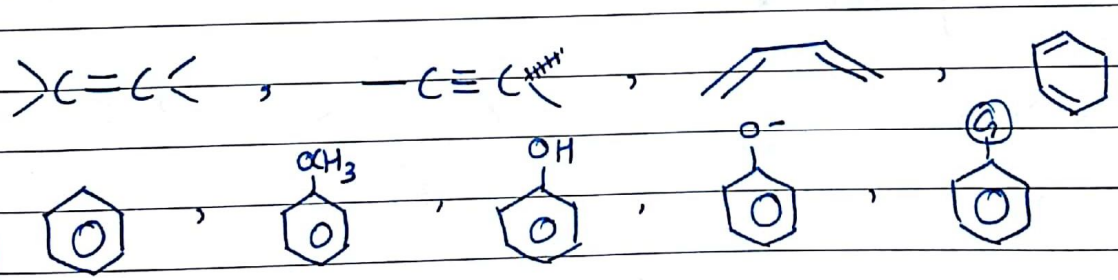
1) l.p. containing nucleophylls

OH^-, CN^-, CH_3COO^-, SH^-, PhS^-, NH_2^-, RO^-, CH_3O^-, , , $R\ddot{O}H$, H_2O,

NH_3, PH_3, RNH_2, RSH, R_3N, ,

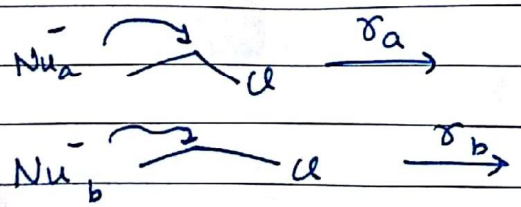
, 

2) π-e^- containing nucleophiles



- Nucleophilicity :

- Tendency of a nucleophile to donate e^-.
- A strong nucleophile is able to donate e^- rapidly.



If $r_b > r_a$

$\Rightarrow Nu_b^- > Nu_a^-$.

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- How to compare nucleophilicity :

1. -vely charge nu⁻ are stronger than corr. neutral nu⁻

$OH^- > H_2O$

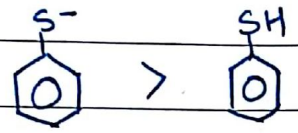
$RO^- > ROH$

$CH_3O^- > CH_3OH$

$PhO^- > PhOH$

$AcO^- > AcOH$

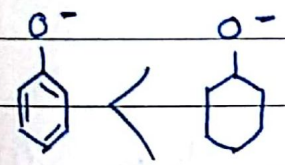
$RS^- > RSH$



$H-O-O^- > H-O-O-H$

$NH_2-NH^- > NH_2NH_2$

Q.
a)



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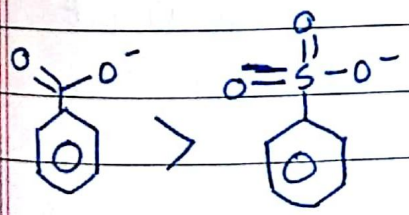
b) PhO^- AcO^- CH_3O^-) c>a>b

c)



2. Within the same pd. major factor is EN. less EN atom will donate e⁻ more readily.

$CH_3^- > NH_2^- > OH^- > F^-$

$RO^- < R\bar{N}H$

$H_2O < NH_3$

$ROH < RNH_2$

$CH_3OH < CH_3NH_2$

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$SiH_3^- > PH_2^- > SH^- >$

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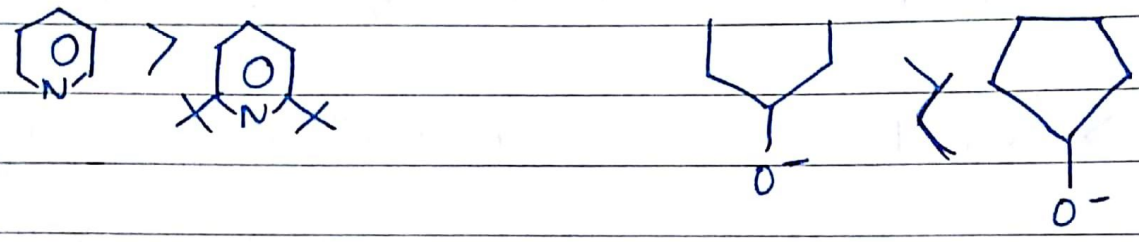
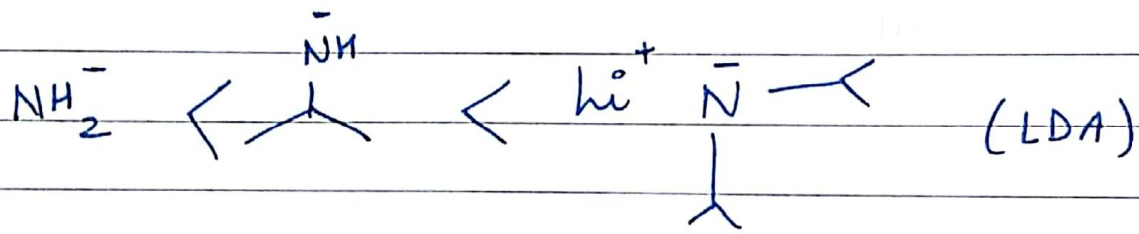
$H_2S < PH_3$ $\qquad$ $RSH < RPH_2$

As steric factor ↑ ; Nu^- ↓





(LDA)

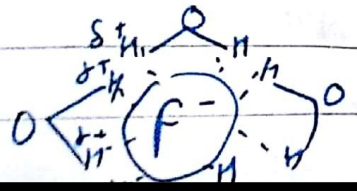
Consider the effect of solvent when donor atom belongs to diff. pd.
Polar protic solvent ↓ the nu^- by solvating the anion. But polar aprotic solvent ↑ Nu^- due to repulsive interaction with anion.

$F^- \quad Cl^- \quad Br^- \quad I^-$

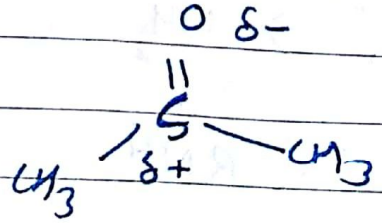
$\xrightarrow{\text{size} \uparrow}$

In H_2O,

$F^- < Cl^- < Br^- < I^-$



In DMSO,



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Q. Compare Nu^- in water

i) $\bar{O}H < \bar{S}H$

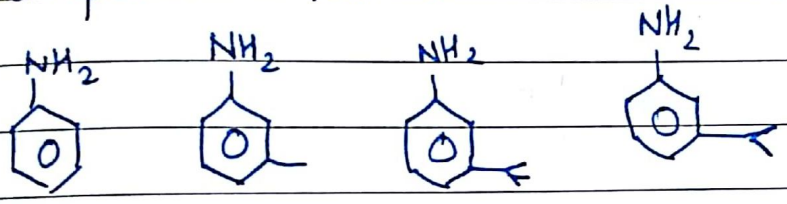
ii) $CH_3O^- < CH_3S^-$

iii) $NH_3 < PH_3$

iv) $RNH_2 < RPH_2$

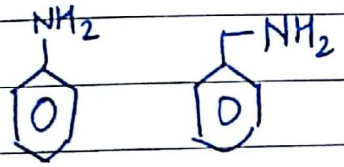
Q. Compare Nu^- :→

i)



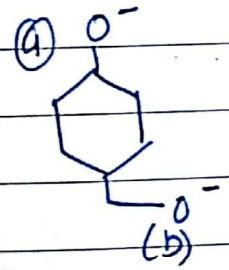
c > d > b > a

ii)



b > a

iii)

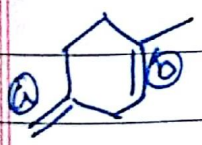


b > a

iv) $CH_2 = CH_2$

b > c > a

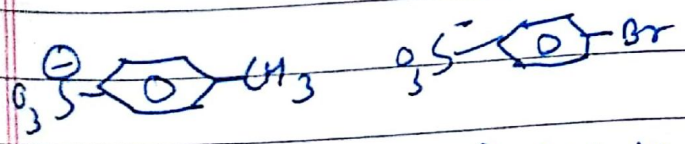
v)



a > b

vi) $CH_2 = CH_2$, $H-C\equiv C-H$ a > b

vii)



a > b

Tosylate
$\bar{O}Ts$

Brosylate
$\bar{O}Br$

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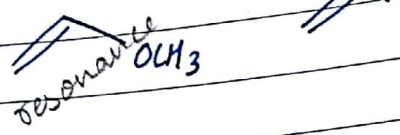
* viii) 

a>b

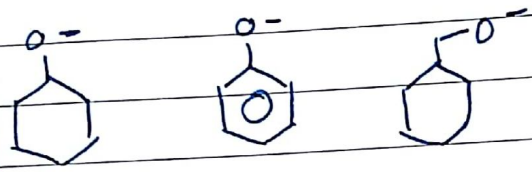
ix)

$CH_2=CH_2$ b>a

x)

a>b

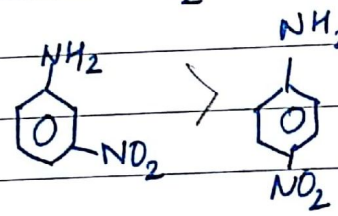
xi) $HC\equiv C^- < CH_2=CH^- < CH_3CH_2^-$

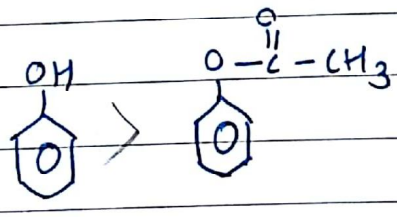
xii) 

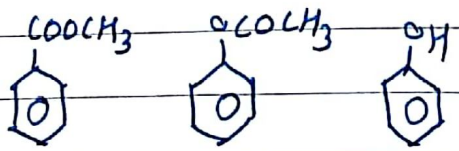
c>a>b

* xiii)

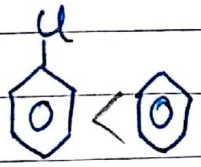
b>a

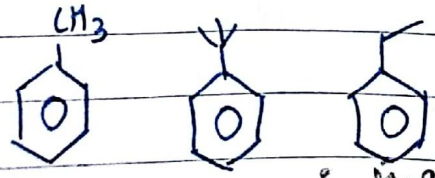
xiv) 

xv) 

xvi) * 

c>b>a

xvii) 

xviii) 

b<c<a

(+H dominating)

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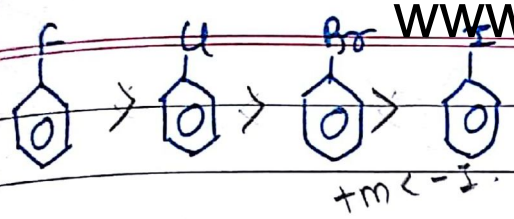
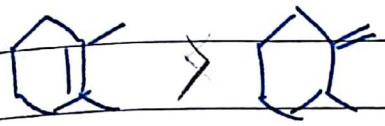
xxix) 

(better +m in F (2p-2p interact))

xx) 

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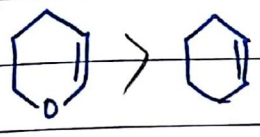
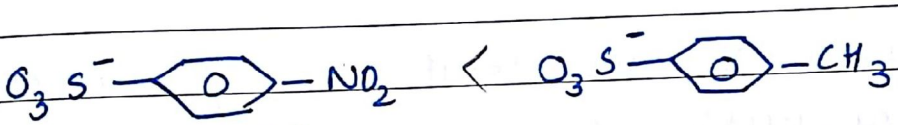
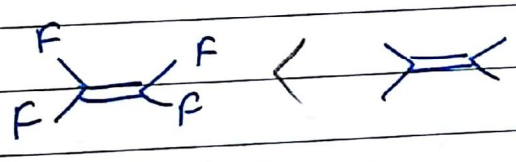
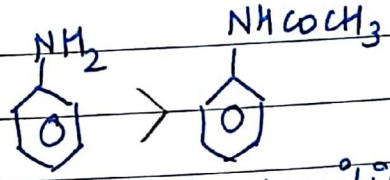
xxii) 

xxiii) 

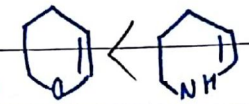
(Nosylate)

xxiv) $CH_3-SO_3^-$ > $CF_3-SO_3^-$ (triflate)

xxv) 

xxvi) 

(Acetanilide)

xxvii) 

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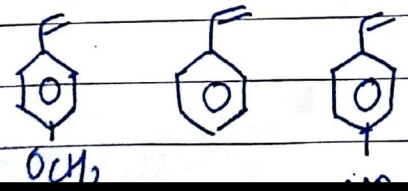
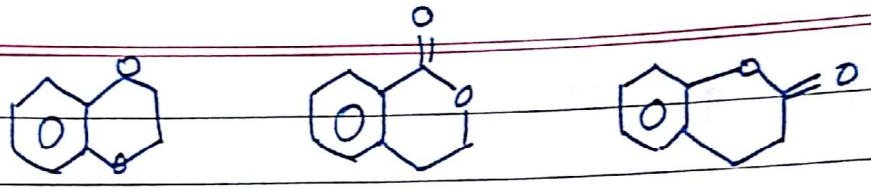
xxix) 

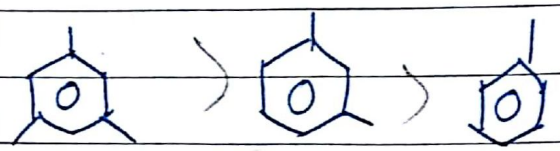
a>b>c

★ xxx) good

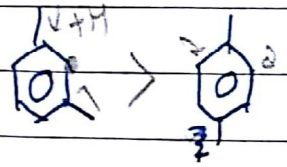


c > a > b

~~xxxi)~~



~~xxxii)~~ ~~good~~



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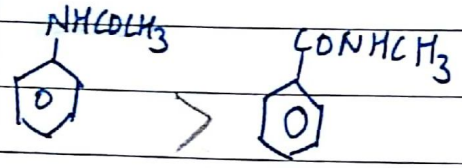
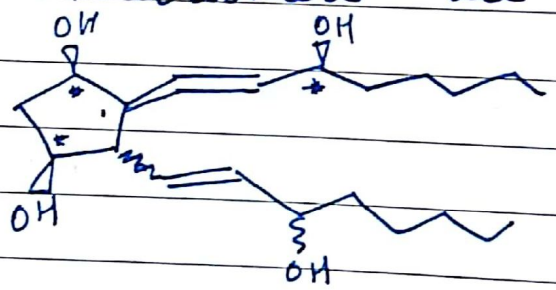


Q. For the cmpd X the total no. of optically active stereoisomers are



① +2+2

▽ → this type of bond indicates that the conf^n at the specific C & geometry of double bond is fixed.

〰 → — " — not fixed.

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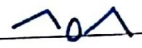
Date
Page

Solvent

Non-polar ($\mu = 0$)

- Benzene
- CCl_4
- CS_2

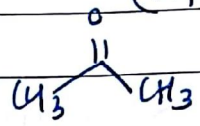
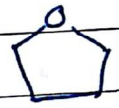
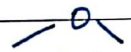
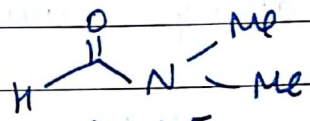
Polar

- $H-O-H$
- $CH_3-C(=O)-CH_3$
- 

H – FON → (Protic)

H * FON → (Aprotic)

H_2O, CH_3OH, NH_3, $R-NH_2$, $HCOOH$, HF

- 
  Acetone
- 
  T.H.F
- $CH_3-C\equiv N$
  Acetonitrile
- 
  D.M.E
- 
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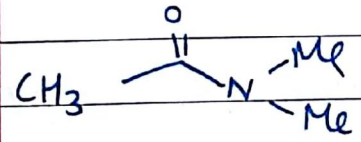
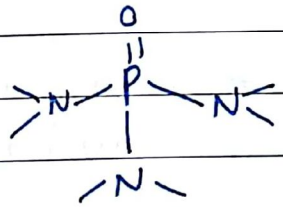
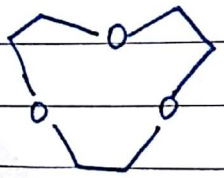
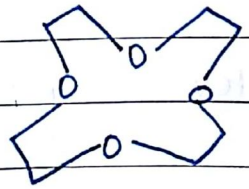
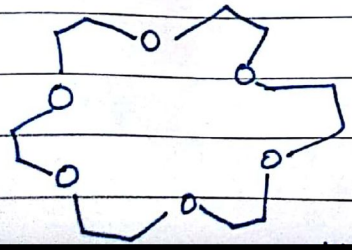
- 
  D.M.A
- 
  H.M.P.A (Hexamethyl Phosphoramide)
- 
  9-crown-3-ether
- 
  12-crown-4 ether
- 

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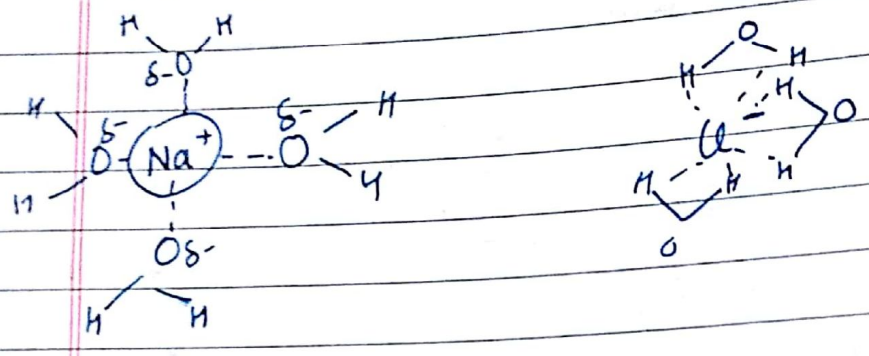
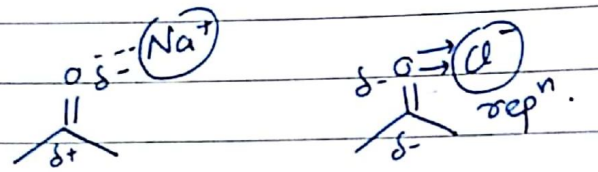
- P.P.S → solvates cation as well as anion



- P.A.S. → solvates only cation or anion.



* Leaving group:

- Nucleophilic subs. rxn (S_N rxn):

  - The group or an atom which is replaced in a rxn is leaving group.

  - A good l.g. is one which is removed in the form of stable ion or molecule.

Q. Compare better l.g :→

1) $F^- < Cl^- < Br^- < I^-$ check stability of anions after leaving

2) $OH^- < H_2O$

3) $R-NH_2 < R-\overset{+}{N}H_3$

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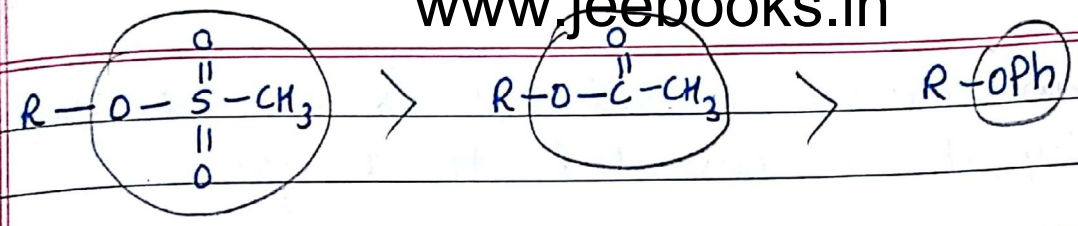
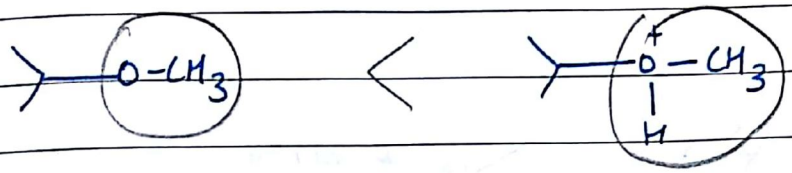
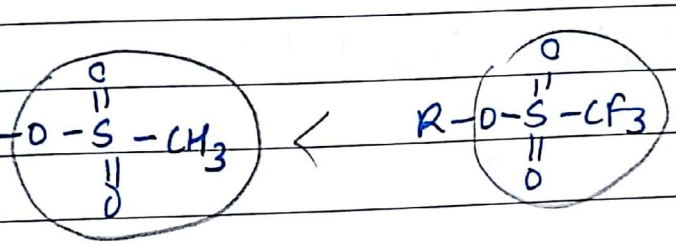
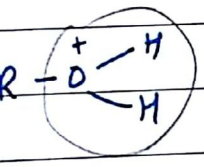
4) 

5) 

6) R–OTs < R–OBs < R–ONs

7) $OH^- < SH^-$

8) 

9)  < $R-\overset{+}{N}\equiv N$ Gases are better leaving groups (Le chatelier's principle)

one of the best leaving grps

10) $OH^- < Cl^-$

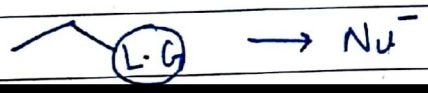
} conjugate acid acid str ↑ L.g. ↑

11) CH_3COO^- CH_3O^- Cl^-

c > a > b

- Feaseability of the rxn :

- For feaseable rxn nucleophilicity of Nu^- > LG^-
- leaving ability LG^- > Nu^-



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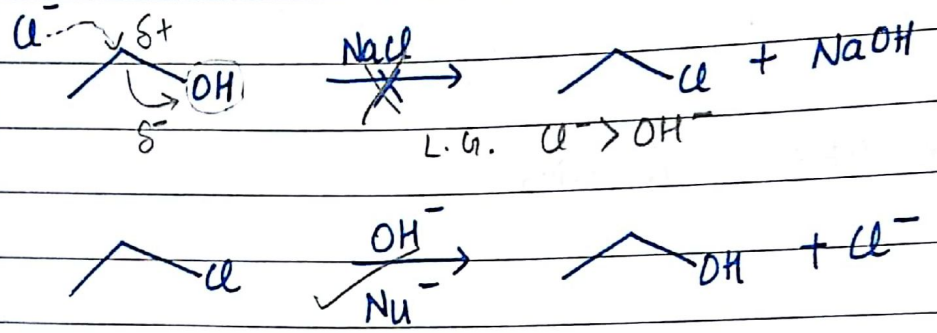
- In few rxns if bad L.G is present then initially it is converted to a good L.G.

*



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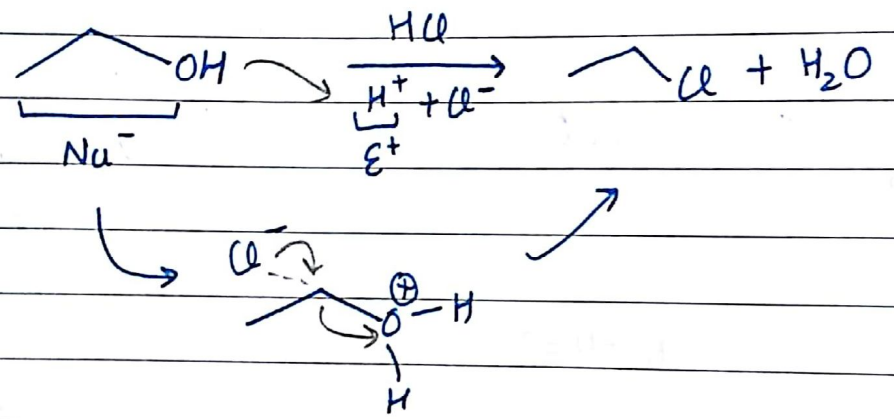

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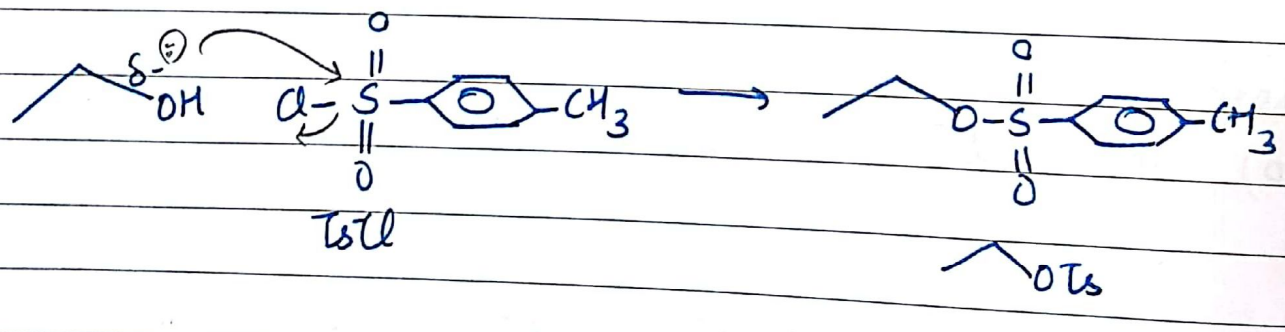
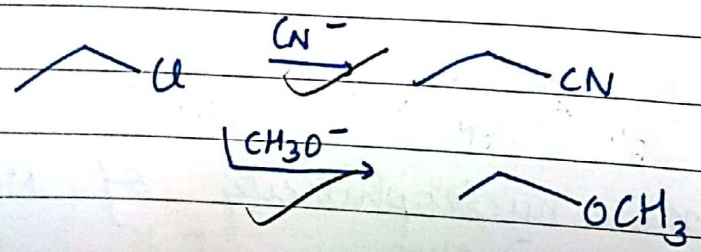


Q. Check feaseability of rxn:

a)



LG: $Cl^- > CN^-$

LG: $Cl^- > CH_3O^-$

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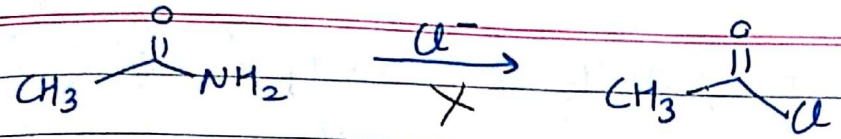
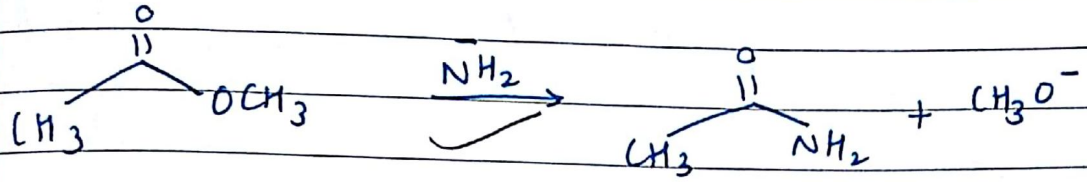
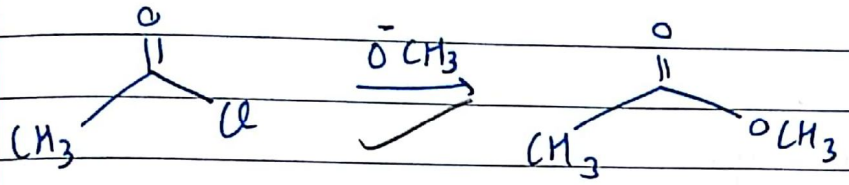
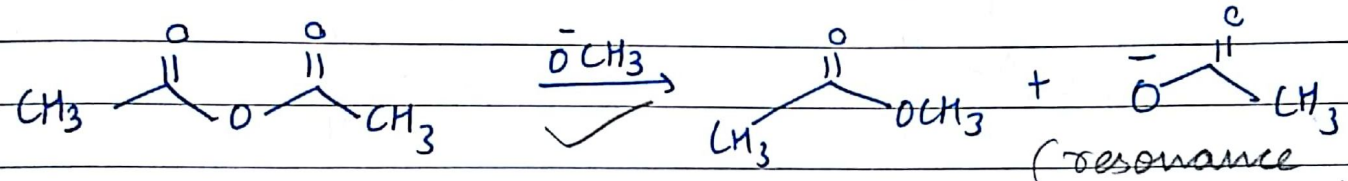
b) 

L.G : $Cl^- > NH_2^-$

c) 

LG : $\bar{O}CH_3 > NH_2^-$

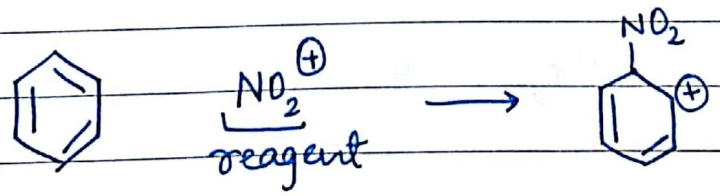
d) 

e) 

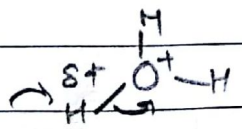
(resonance stabalisat^n)

* ELECTROPHILE :

- An electrophile is a reagent that forms a bond to its ran partner (Nu^-) by accepting both es$^-$ from it



Types,

- Charged : H^+ / NO_2^+ (Nitronium) / NO^+ (Nitrosonium) / $R-\overset{+}{C}=O$ (Acylium) / $CH_3-\overset{+}{C}=O$ /
R^+ / / H_3O^+ 

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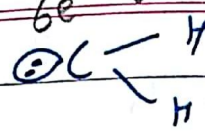
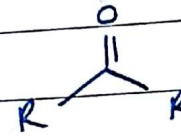
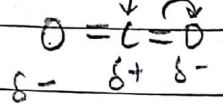
- **Neutral** : BF_3 / $AlCl_3$ / $FeBr_3$ / 

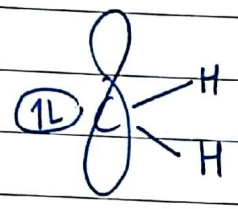
CO_2 / SO_3 /  / PCl_5 / $SbCl_5$



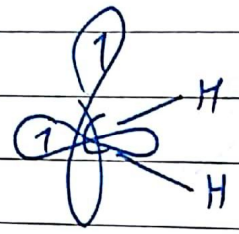
Lewis acid → adduct.

* **Carbenes** :
are of two types,

(multiplicity) M = 2S+1

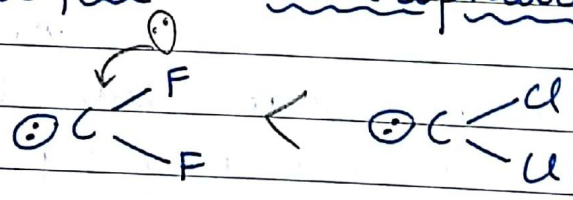


Singlet



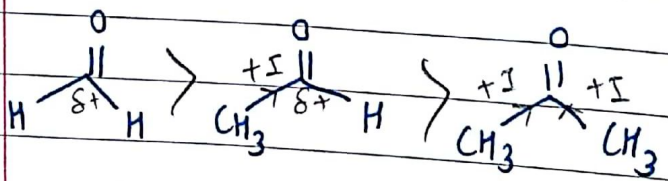
Triplet

Q. **Compare Electrophilicity** :

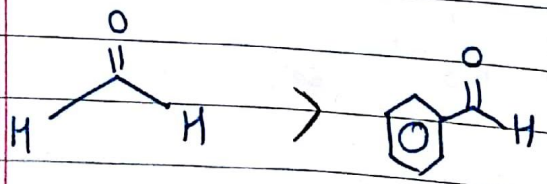
* 1. 

(Backbonding 2p–2p better than 2p–3p)

* 2. $BF_3 < BCl_3 < BBr_3 < BI_3$

3. 

{Check δ+ on 'C' containing 'O'}

4. 

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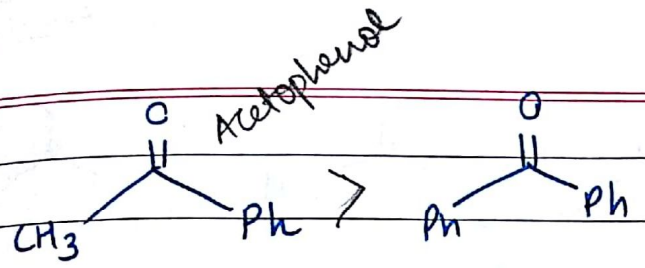
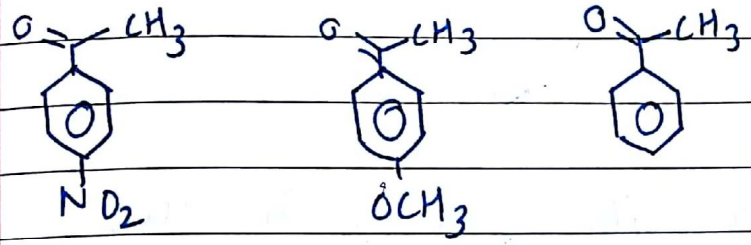
5. 

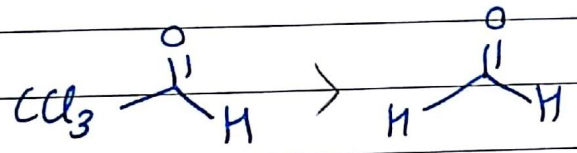
6. 

(+m)

a > c > b

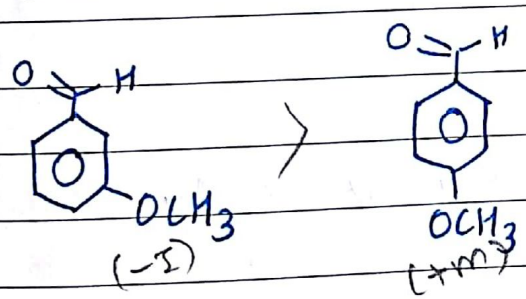
7.

c > a > b

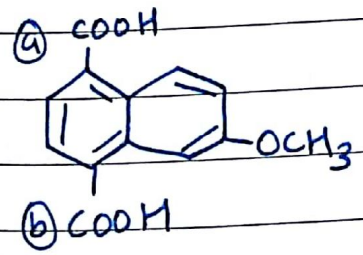
8. 

(−I)

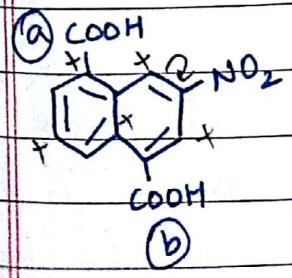
Chloral

9. 

{better donation due to presence on para.}

10. 

a > b

11. 

a > b

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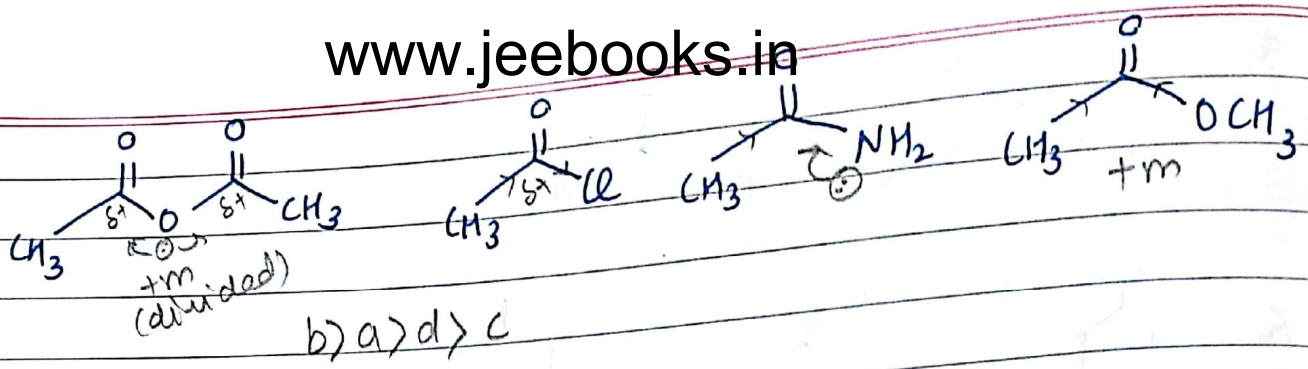
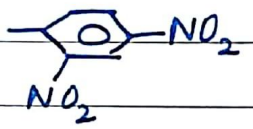
12. 

b > a > d > c

Q. Identify the donor site (major) in the following reagents.

1. $\overset{*}{N}H_2OH$ } hydroxy amine

2. $NH_2NHCONH_2 \rightarrow H_2\overset{*}{N}-NH-\overset{O}{\overset{\|}{C}}-NH_2$ } semicarbazide

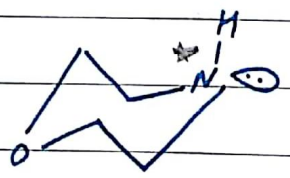
3. $\overset{*}{N}H_2-NH$  } Brady's Reagent

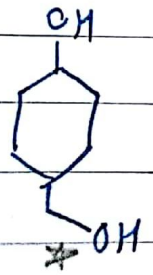
(2,4-DNPhydrazine)

4. $\overset{*}{C}N^-$

5. $Ag\ \overset{*}{N}O_2$ $\quad Ag-O-\overset{*}{N}=O$

6. $\overset{*}{N}H_2-NH-Ph$ } Phenyl hydrazine

7. 

8. 

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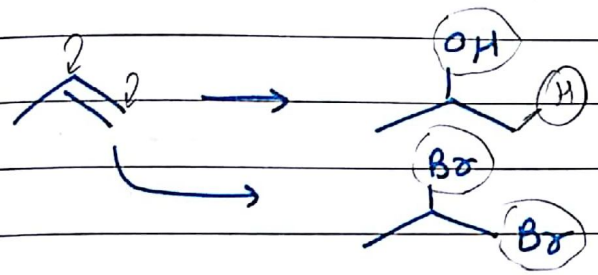
* Types of Reaction :

1] Addition Reaction :

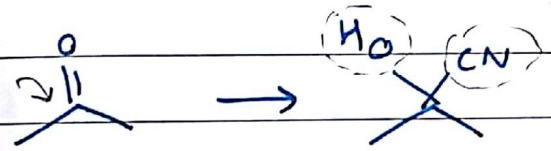
Reagent is added on the substrate containing π-bond

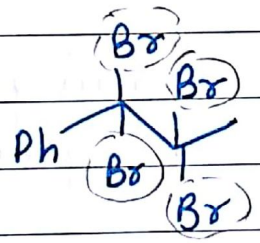
$$\underset{\text{Substrate}}{A = B} \xrightarrow[\text{Reagent}]{X-Y} A(X)-B(Y)$$

- 

} Hydroxination
} Bromination

☆ Only incoming no outgoing

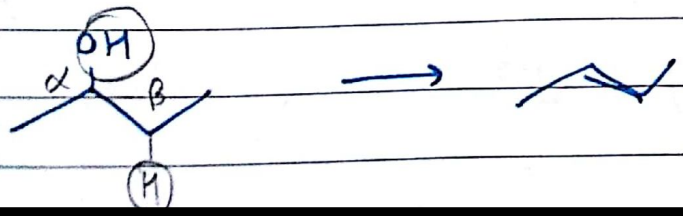
- 

- $Ph-C\equiv C-CH_3 \longrightarrow$ 

2] Elimination Reaction :

- It is reverse of addⁿ rxn.
- In most of elimination rxns, π bond is formed.

- $A(X)-B(Y) \xrightarrow{-XY} A \overset{\pi}{=} B$

- 

) β/(1,2) elimination

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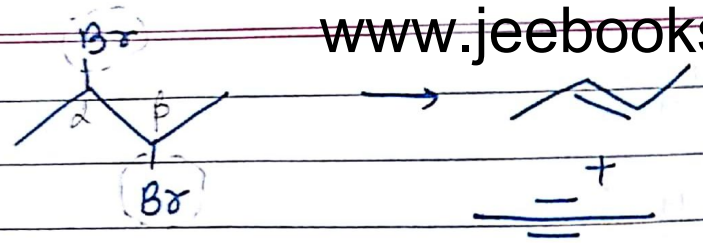
- 

-

- $CHCl_3 \xrightarrow[\Delta]{KOH} :CCl_2 + HCl + H_2O$

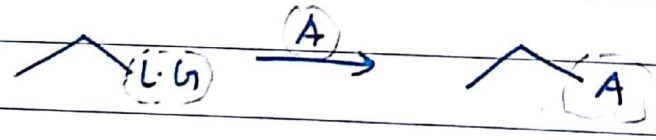
- $CHFClBr \xrightarrow[\Delta]{KOH} :CFCl$

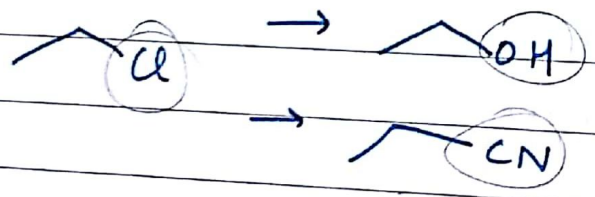
- $CH_2ClBr \xrightarrow[\Delta]{t\text{-}BuOK} :CCl_2$

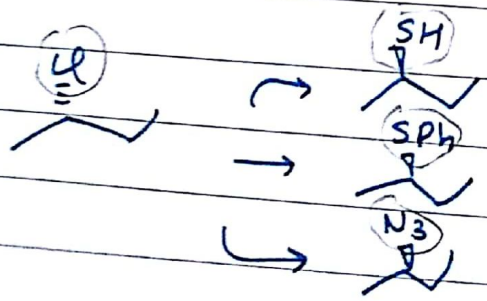
α (1,1) elimination (carbenes are formed)

3] Substitution (Replacement) Reactions :→

- In these rxns, leaving grp is replaced by another atom or group of atoms.



- 

- 

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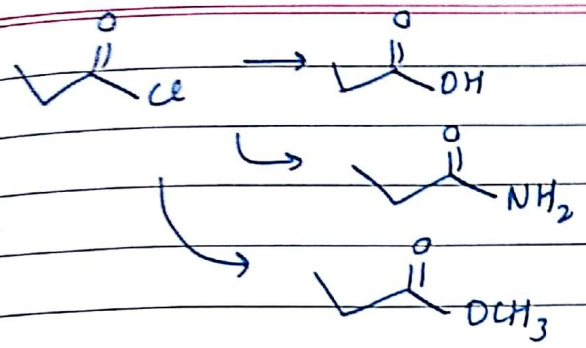
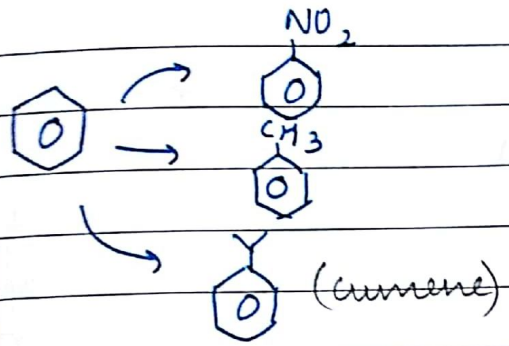
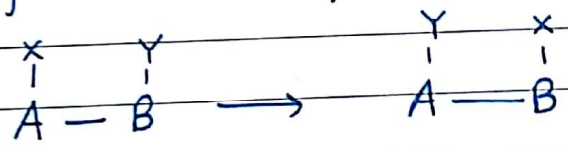
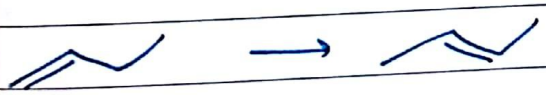
- 

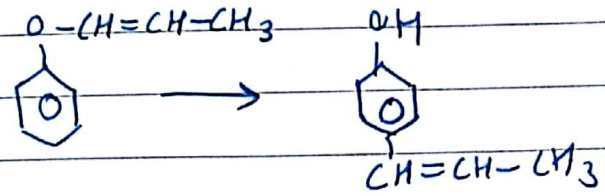
- 

4] Rearrangement Reactions :→

- One isomer converts to other and thermodynamically more favourable form is formed.



- 

- 

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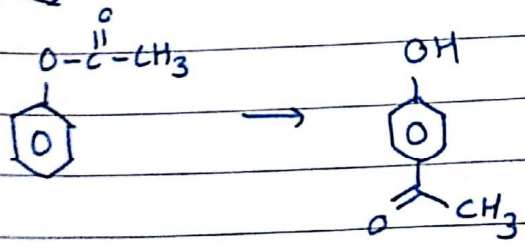
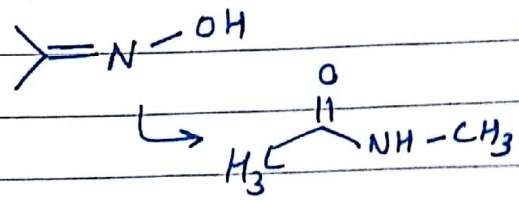
* MF must be same i.e. should be structural isomers.

- 

[oxime]

- 

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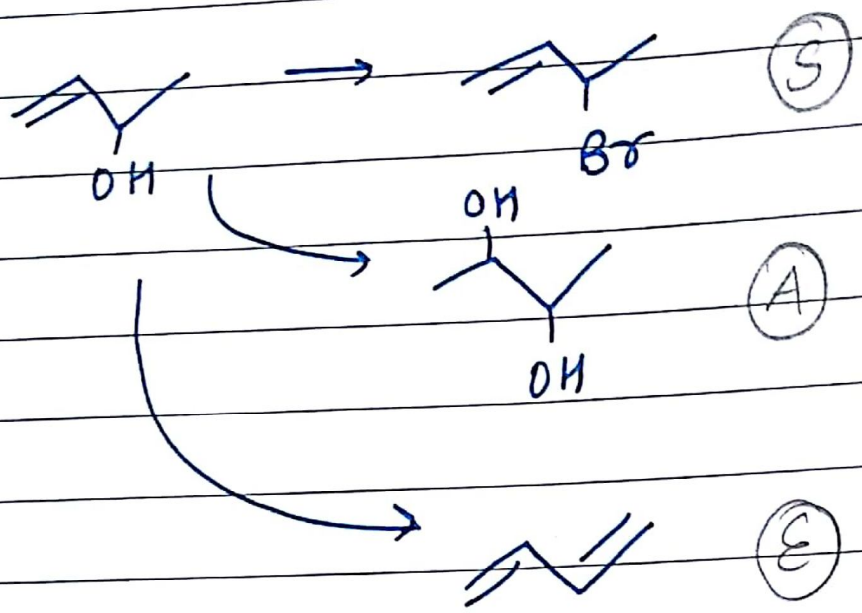
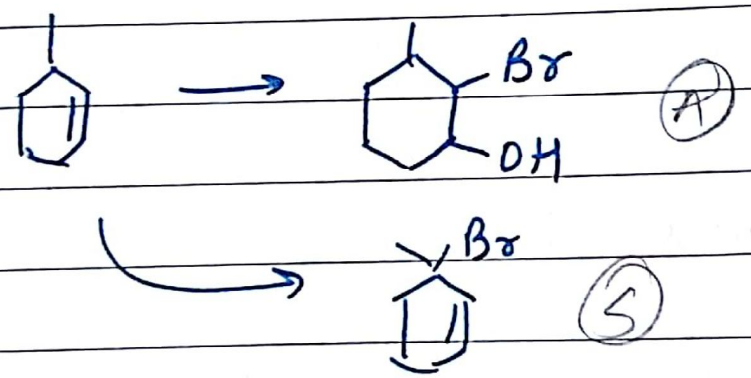
S → substitution
A → Addition
E → Elimination
R → Rearrang

Identify T.O.R.





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* FREE RADICALS & REACTIONS :

Eg, $\dot{Cl}$, $R\dot{O}$, $\dot{Br}$, $\dot{I}$, $\dot{O}H$, $\dot{H}$, $\dot{N}O$

- species containing one unpaired e^-.

• Generation :→

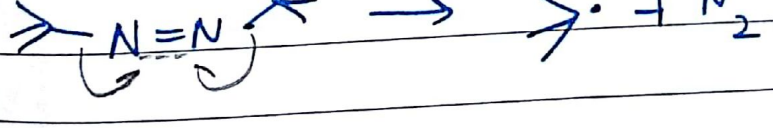
- It takes place in presence of heat / light
- It is favourable in presence of gas phase / non polar solvent
- By homolysis of weak bonds.

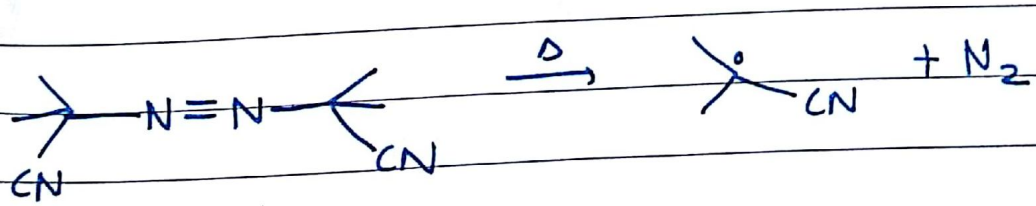
• $Br-Br \xrightarrow[\Delta]{h\nu} 2\dot{Br}$

• $Cl-Cl \xrightarrow[\Delta]{h\nu} 2\dot{Cl}$

• $R-\ddot{O}-\ddot{O}-R \longrightarrow 2R\dot{O}$

• $O=N-\ddot{Cl} \longrightarrow \dot{N}O + \dot{Cl}$

• 

• 

AIBN

Azo bis Isobutyl nitrile

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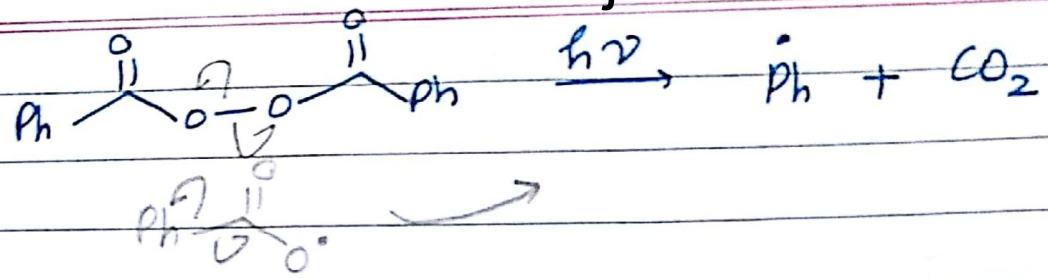
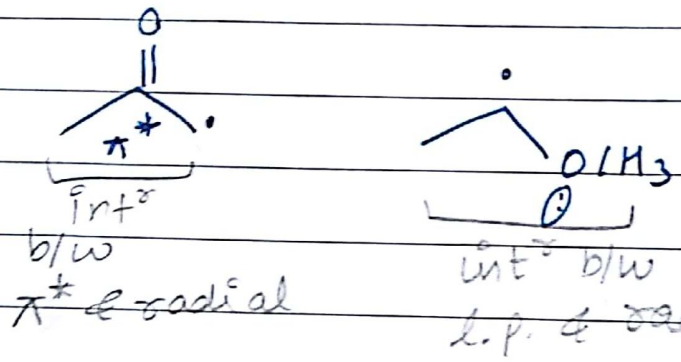
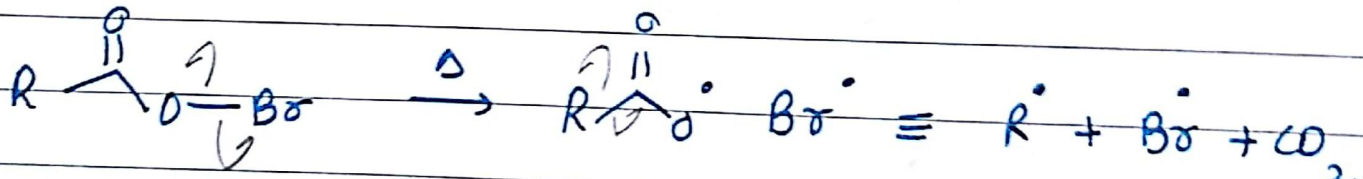
- 

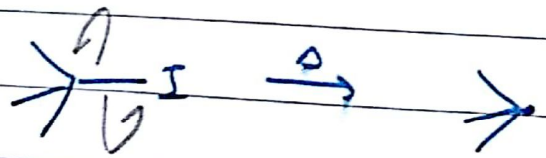
Dibenzoyl peroxide

- Any group which is e^- withdrawing or donor will stabalize free radical.





$NOBr \xrightarrow{\Delta} \dot{N}O \quad \dot{B}r$



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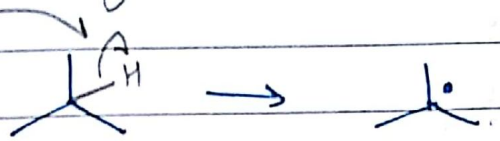
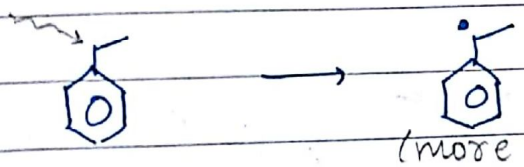
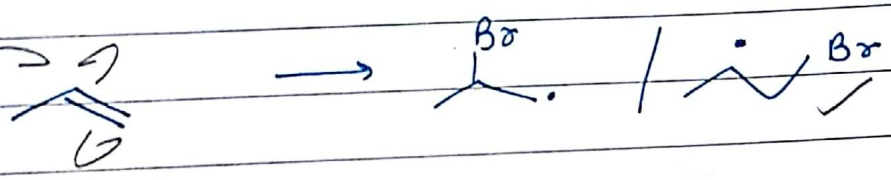
30/5/18

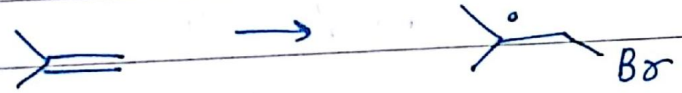
- In presence of radicals, new radicals can be generated.
  It can be due to H- abstraction or addition on π bonds.

- $RO^{\bullet} \cdots H-Br \longrightarrow ROH + Br^{\bullet}$

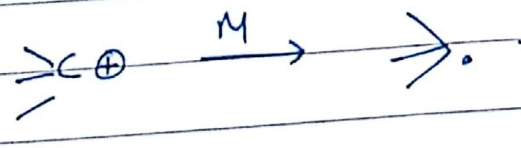
- $Cl^{\bullet}$  + HCl

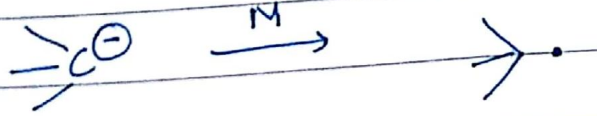
- $Br^{\bullet}$  + HBr
  (more stable)

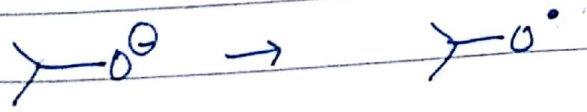
- $Br^{\bullet}$ 

- $Br^{\bullet}$ 

- From Metals,
  It can take place in presence of metals. Redox rans take place.

- 

- 

- 

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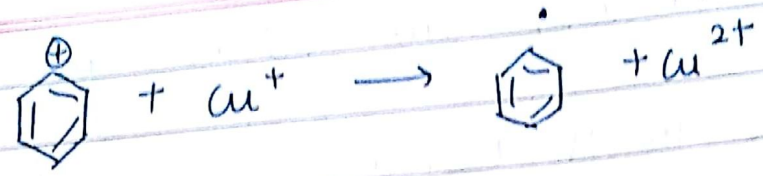
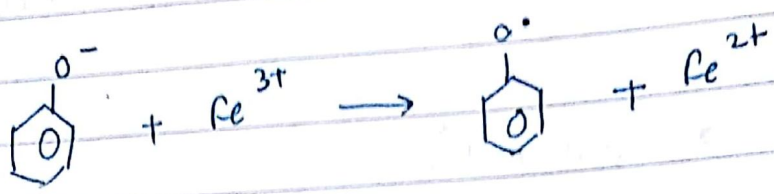
- 

- 

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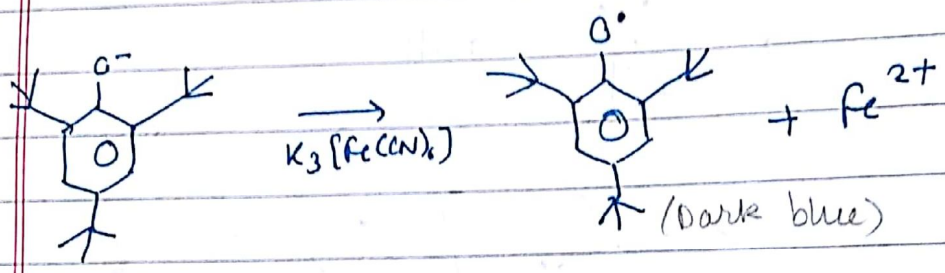
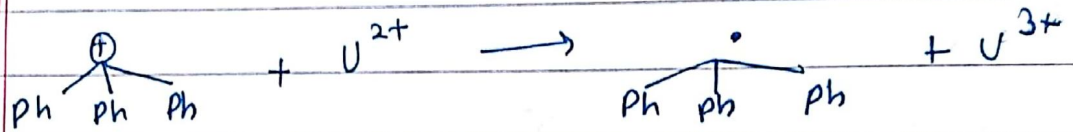
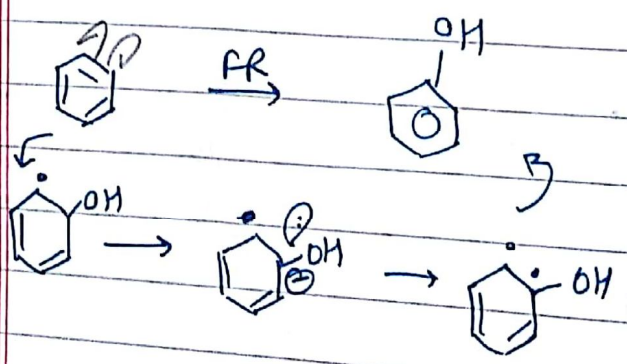
- 

- 

(N.I.S) - Fenton's Reagent → It will act as an oxidising agent

$$Fe^{2+} + \underbrace{H-O-O-H}_{F.R.} \longrightarrow Fe^{3+} + \dot{O}H + \bar{O}H$$

- 

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* General rxns of Radical :→

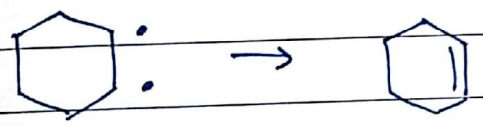
1] Combination :

- $\dot{Cl} + \dot{Cl} \longrightarrow Cl-Cl$

- $\dot{R} + \dot{R} \longrightarrow R-R$

- $\dot{R} + \dot{I} \longrightarrow R-I + R-R + I-I$ (2)

- $\dot{Me} + \dot{Et} + \dot{Pr} \longrightarrow Me-Me + Me-Et + Me-Pr + Et-Pr + Pr-Pr + Et-Et$ (5)

- 

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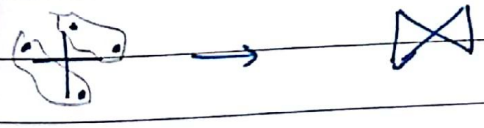
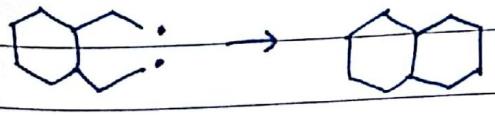
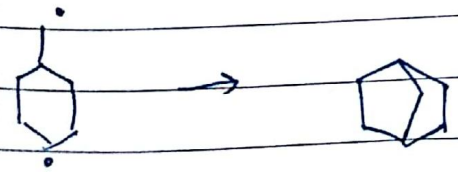
} In diradical intramolecular is better

Q.

1) 

2)

3)  decalin

4) 

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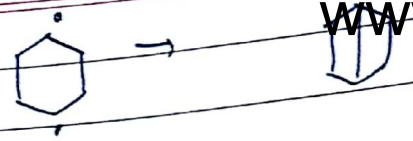
6) 

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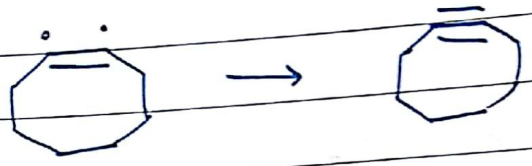
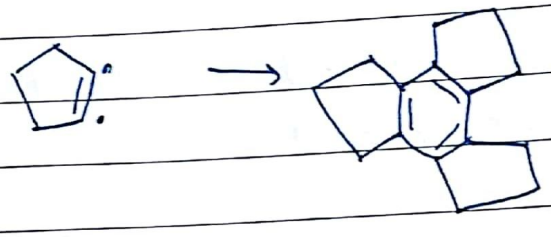
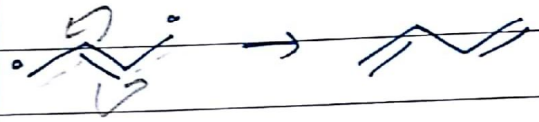
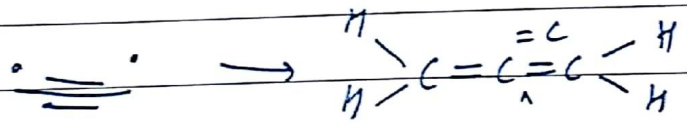
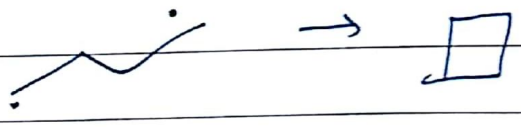
8) 

Dimerisation

9) 

10) 

11) 

12) 

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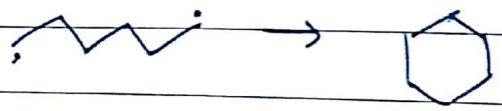
14) 

Polymerisation

15) $\rightarrow -(CH_2)_n-$

$-(CH_2)_n-$

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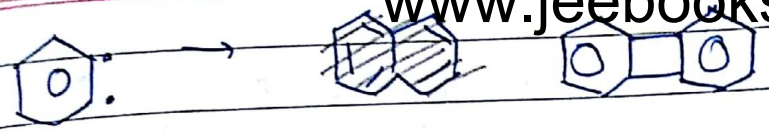
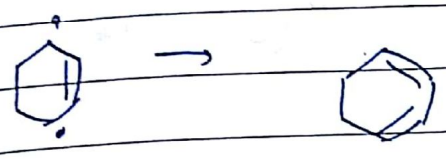
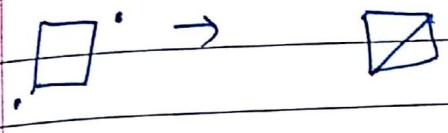
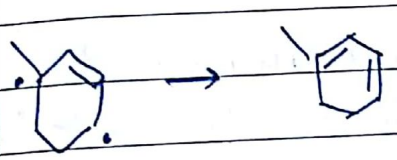
16) 

17) 

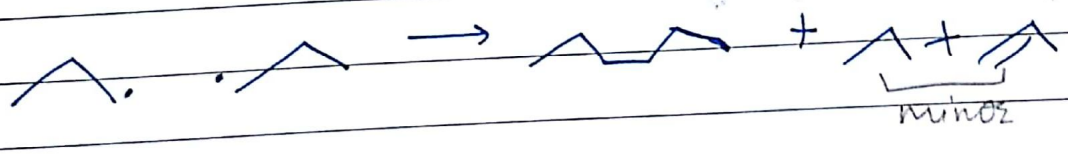
18) 

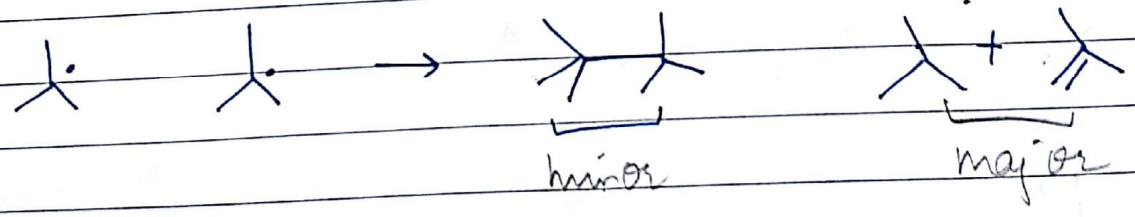
19) 

2] <u>Disproportionation</u> :→

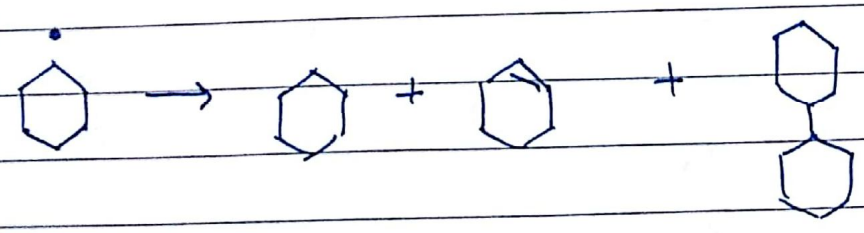
-

i/2° → Dimer
3° → Dis p.

- 

- 

Q.

1) 

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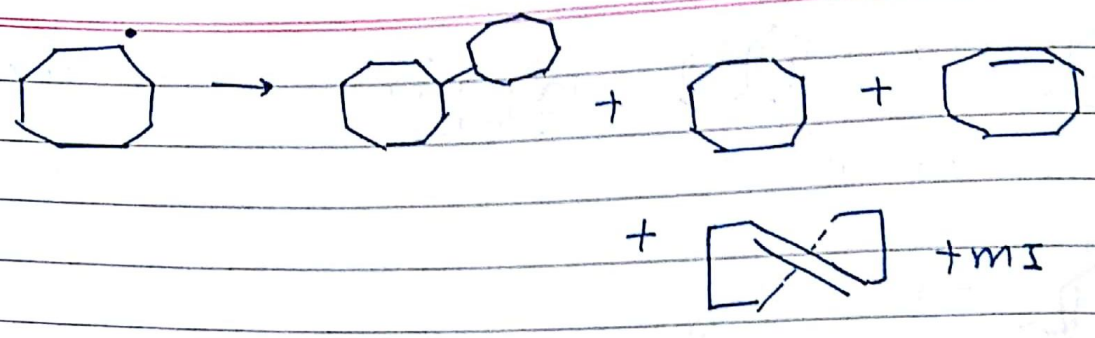
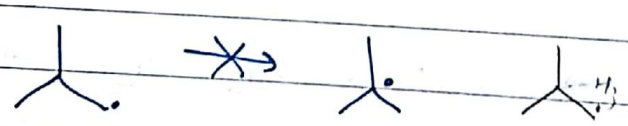
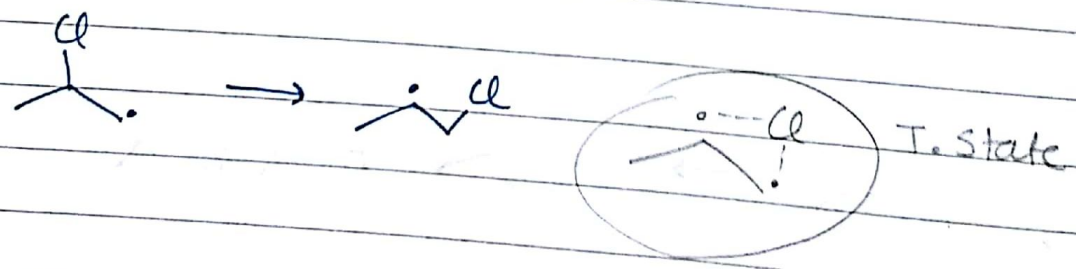
2) 

3] <u>Rearrangement</u> :→

- Radicals fail to undergo rearrangement coz of high energy requirements but it is possible when transition state is stabalised.

eg,

- 

- 

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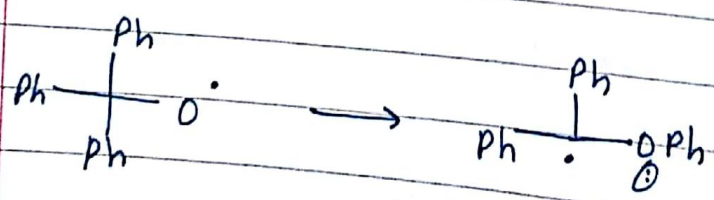
- 

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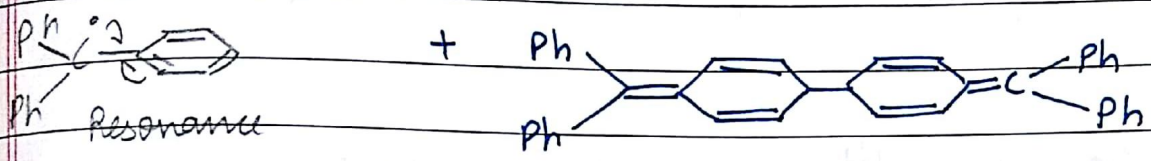
Q. Observe the rxn & write down the mechanism.

1] $Ph_3\dot{C} \longrightarrow Ph_3C-CPh_3$ (negligible (steric)) + Ph_3C–⟨benzene⟩=C(Ph)(Ph) } Major



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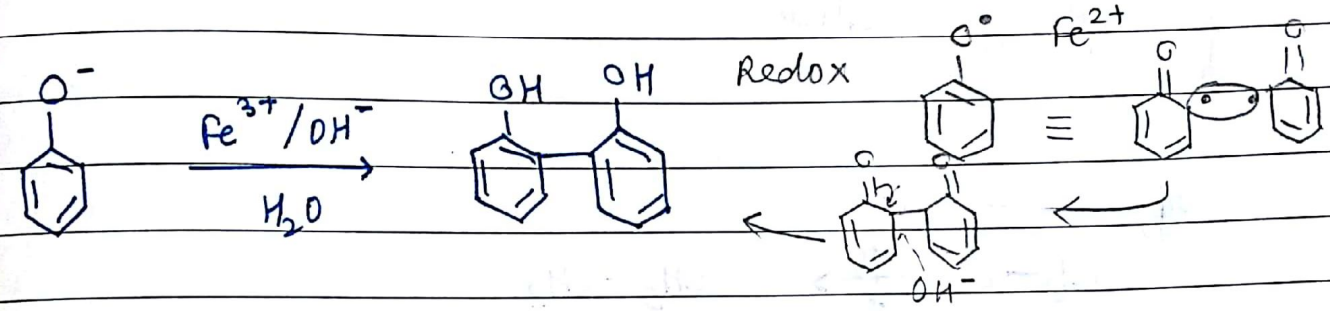

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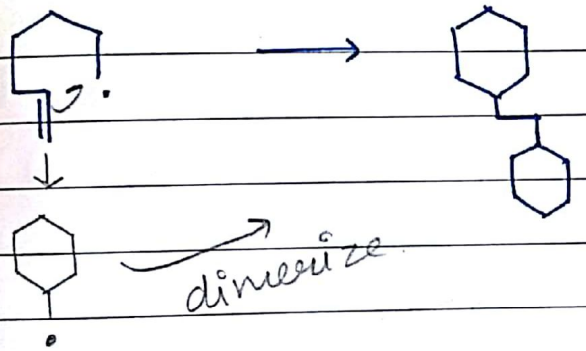

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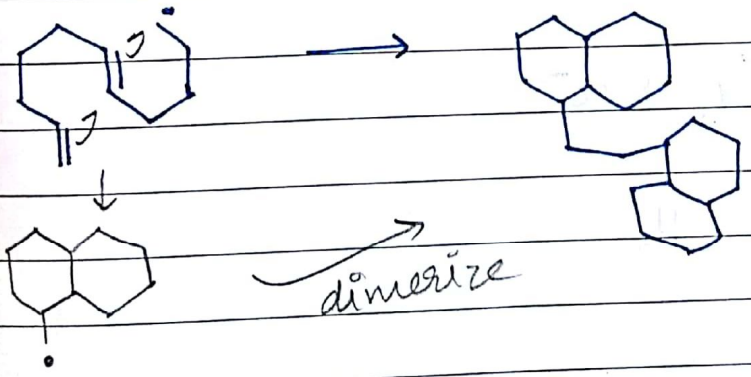

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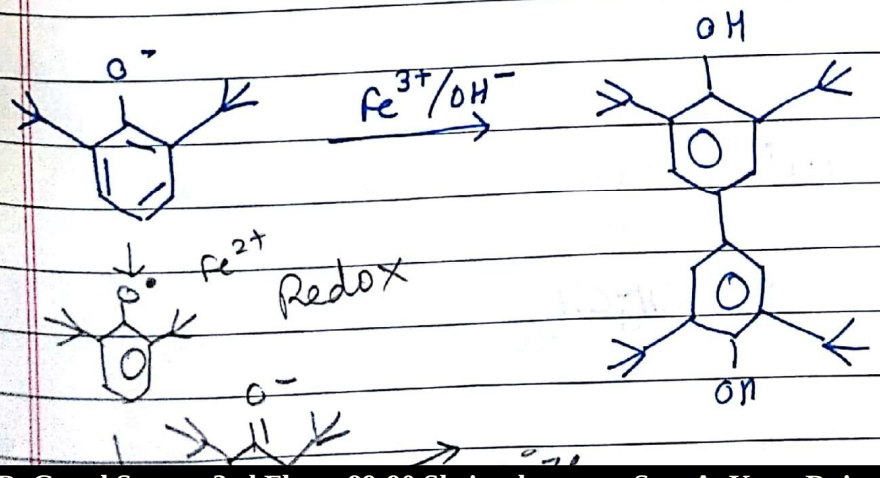

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* WURTZ Reaction :

In this rxn, 2 units of halo alkane combine in the presence of Na metal to produce alkane.

$$2(R-X) \xrightarrow[\text{Dry Ether}]{Na} R-R + NaX$$

alkyl halide → symme. alkane (dimer); NaX: (solution)

eg,

$$CH_3-Cl \xrightarrow[\text{(anhy.)}]{Na} CH_3-CH_3$$

Mechanism

1] Free Radical

$$Na \longrightarrow Na^+ + e^-$$

$$e^- \rightarrow \overset{\delta+}{C}H_3-\overset{\delta-}{Cl} \longrightarrow \dot{C}H_3 + Cl^-$$

(σ^*)

$$\dot{C}H_3 \curvearrowright \dot{C}H_3 \longrightarrow C_2H_6$$

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2] Ionic

$$\dot{C}H_3 \xrightarrow{e^-} CH_3^- \; Na^+ \quad \text{(organo metallic)}$$

$$\underset{Na^-}{CH_3^-} \rightarrow \underset{E^+}{CH_3-Cl} \longrightarrow CH_3-CH_3$$

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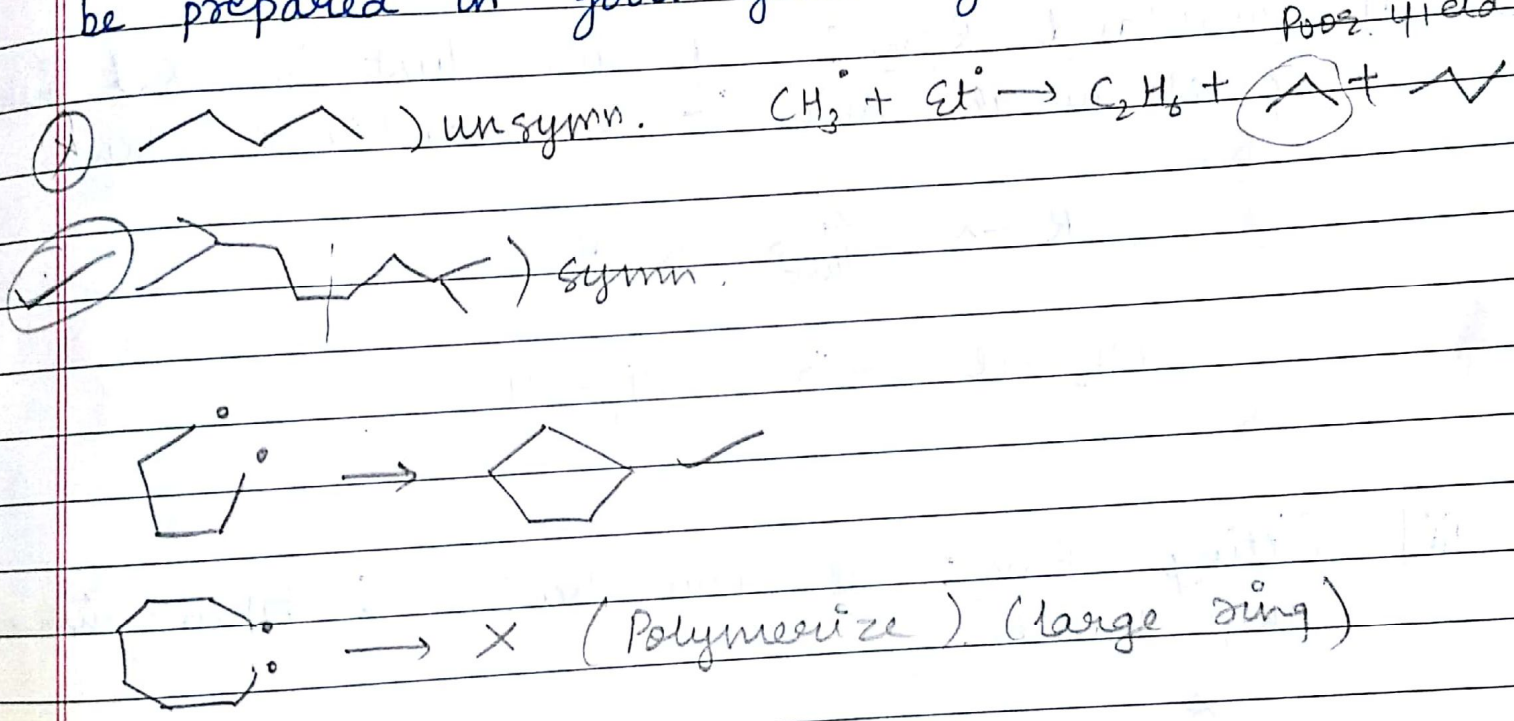
- **Characteristics :**

i) CH_4 cannot be prepared by this method.

ii) Rate of Wurtz rxn,

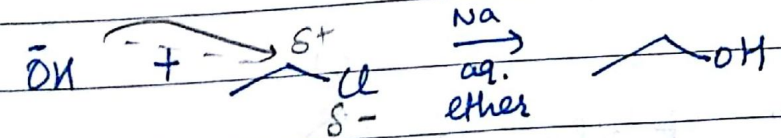
$$R\text{-}I > R\text{-}Br > R\text{-}Cl > R\text{-}F$$

iii) Alkane having even carbon (symmetrical) can be prepared in good yield by wurtz rxn.



iv) In case aq. sol^n is taken then following rxn will take place

$$H_2O + Na \longrightarrow \bar{O}H + \frac{1}{2} H_2\uparrow$$



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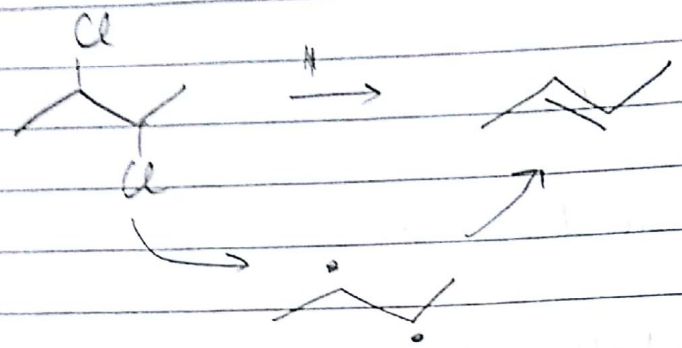
[v] in case dihalide is present, intramolecular rxn will take place.

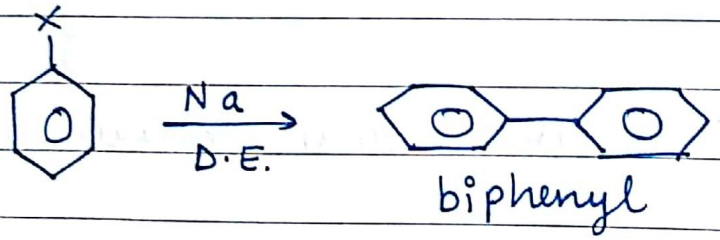


vi] Frankland Rxn: If zinc dust is used instead of Na metal then it is frankland rxn.

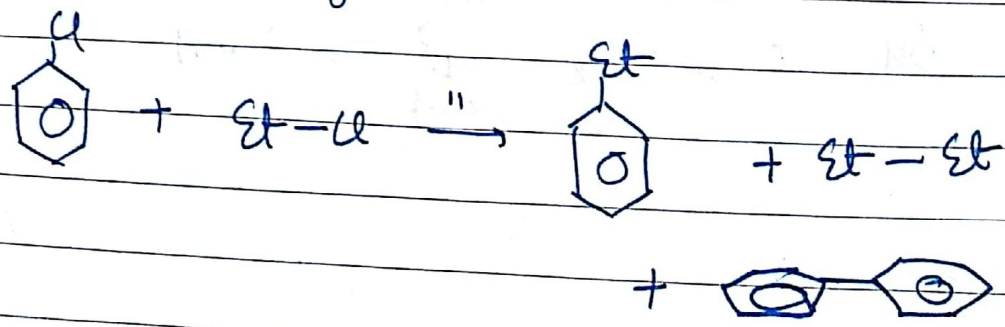
$$R-X \xrightarrow[\text{dust}]{Zn} R-R$$

$$CH_3-Cl \longrightarrow CH_3-CH_3$$

vii] Fitting Rxn: If aryl halide is taken instead of alkyl halide.



viii] Wurtz-Fitting Rxn: If one is aryl halide and other is alkyl halide



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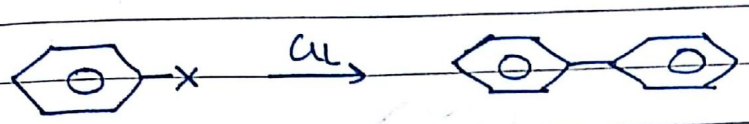
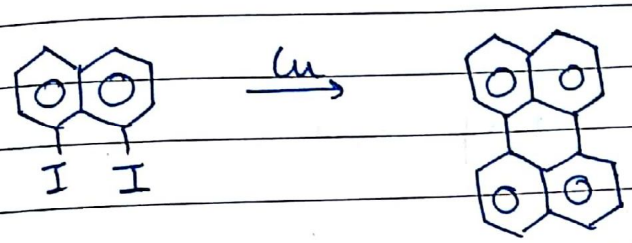
ix] Ullmann rxn : If aryl halides are coupled in presence of Cu then it is Ullmann rxn.



Q.

1)



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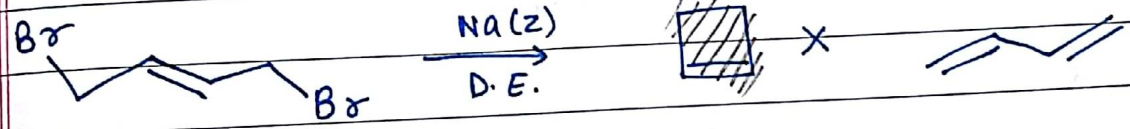

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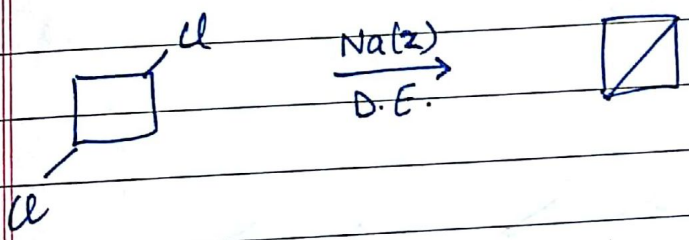

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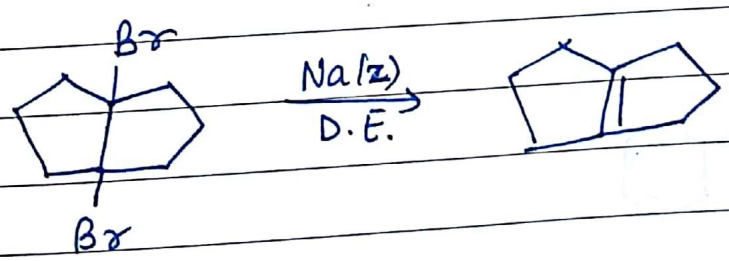

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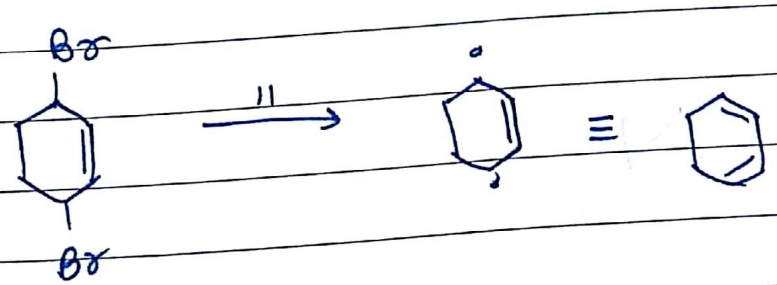

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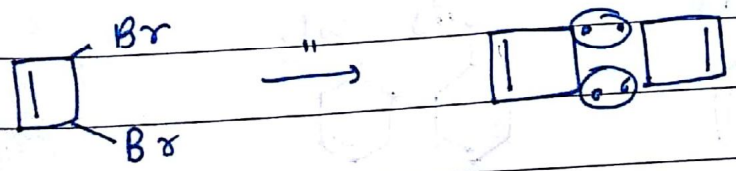

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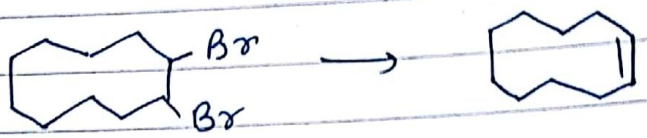
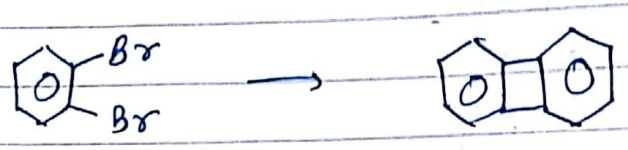
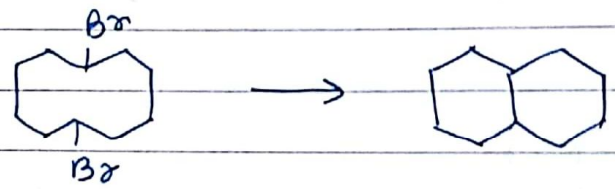
7)

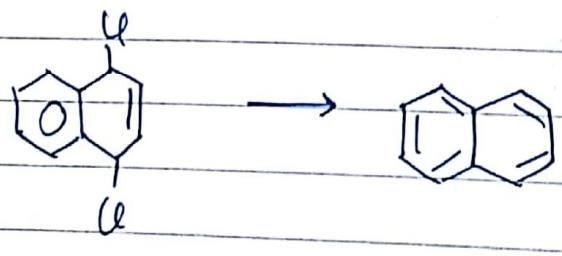
8) 

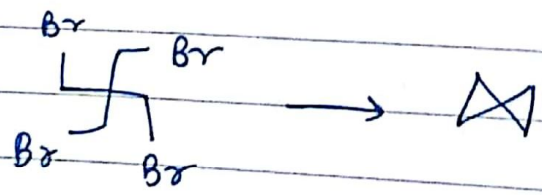
9)  biphenylene

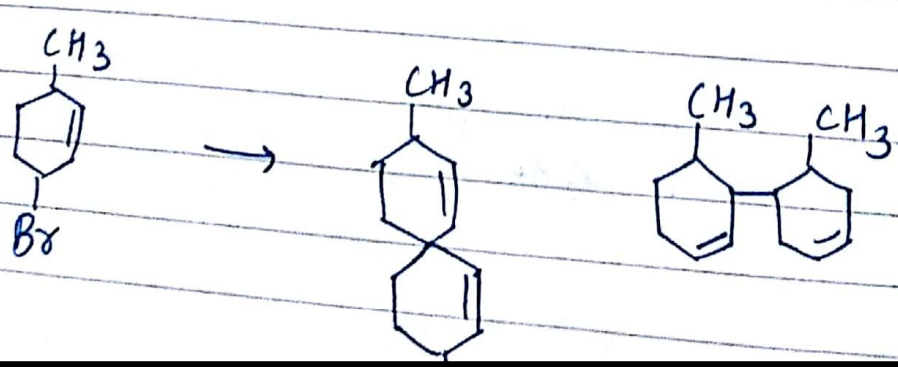
10) $CHCl_3 \xrightarrow{6Ag} CH \equiv CH$

11) 

12)

13)  naphthalene

14) 

15) 

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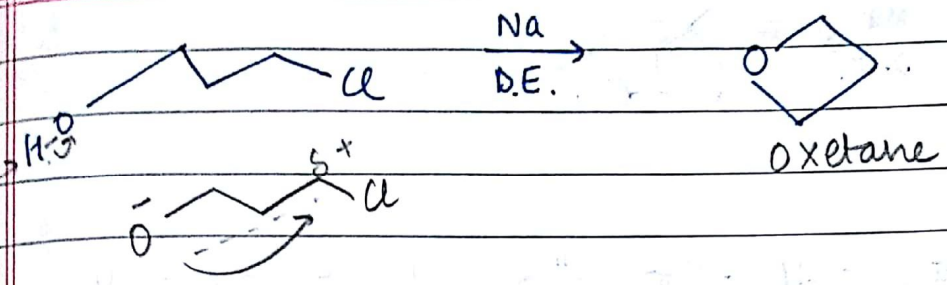
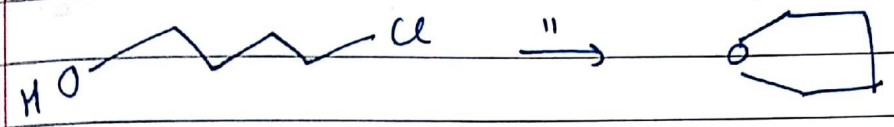
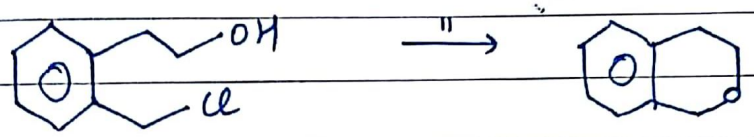
16) 

Intramolecular NP Substitution
OR
N.G.P (Neighbouring group Participation)

17) 

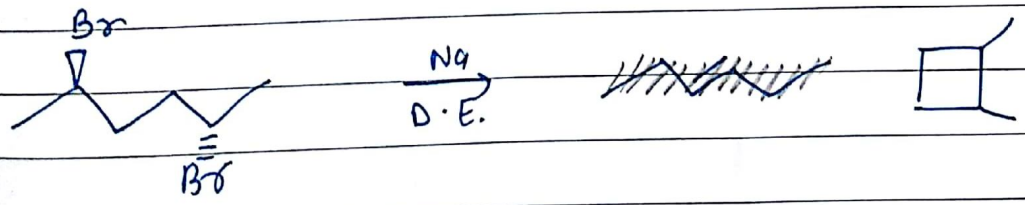
18) 

19) $CH_3-Cl + Mg \xrightarrow{''} CH_3-MgCl$ (Grignard Reagent)

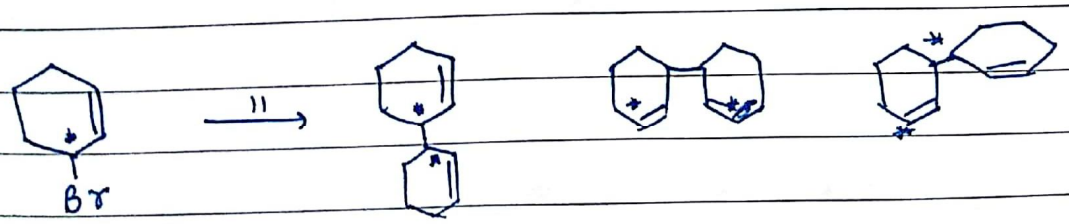
R-Mg X.

organo magnesium cmpd is formed.

20) $2CH_3-Cl + Mg \xrightarrow{''} CH_3-CH_3$

21) 

(T.S.I. = 3)

22) 

- Acidic 'H' should not be present in substrate

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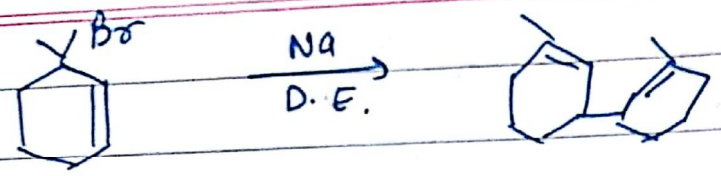
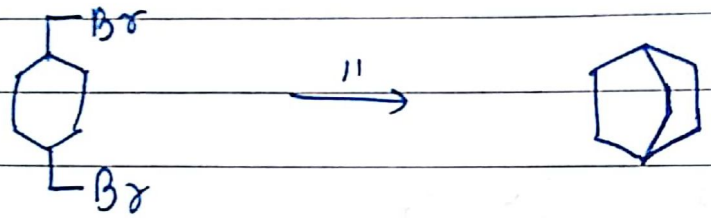
23) 

24) $BrH_2C-C\equiv C-CH_2-Br \xrightarrow{''} H_2C=C=C=CH_2$

25) 

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* KOLBE'S Electrolytic Synthesis :

$$R-COO^- Na^+ / K^+ \xrightarrow{\text{Electrolysis}} \underbrace{R-R}_{\text{Alkane}} + CO_2(\uparrow) + H_2(\uparrow)$$

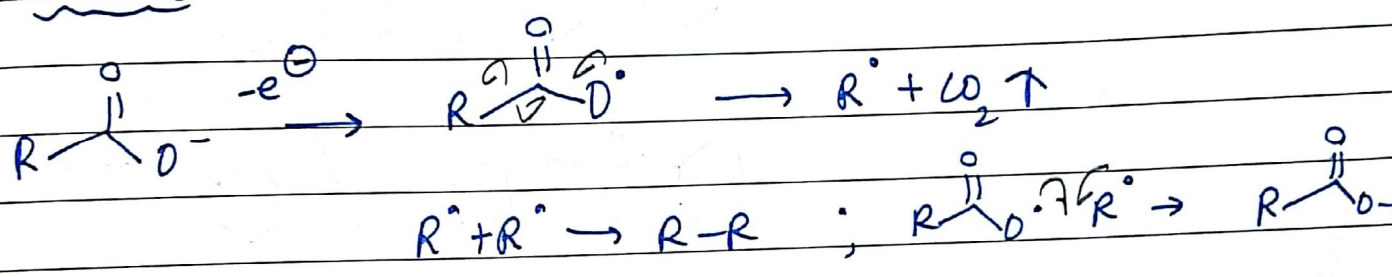
(aq. salt) / acid salt

$$+ \; R-\overset{O}{\overset{\|}{C}}-O-R$$

(minor)

Electrolysis,

At Anode



At Cathode

$$e^- \curvearrowright H-O-H \longrightarrow H^+ + {}^-OH \uparrow \quad (pH \text{ increases})$$

- CO_2 is released at anode. H_2 is released at cathode
- pH ↑ gradually in the reaction.
- CH_4 cannot be prepared in good yield.
- If salt of dicarboxylic acid is used then intramolecular product is ~~increasing~~ major

Q.

1) $CH_3COONa \longrightarrow C_2H_6 + CO_2\uparrow + H_2\uparrow + CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3$

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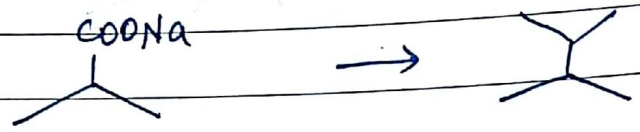
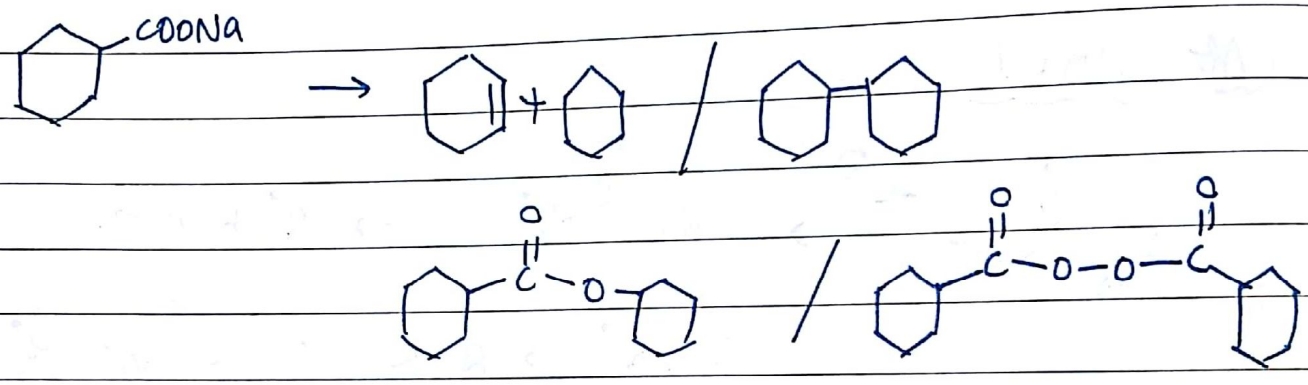
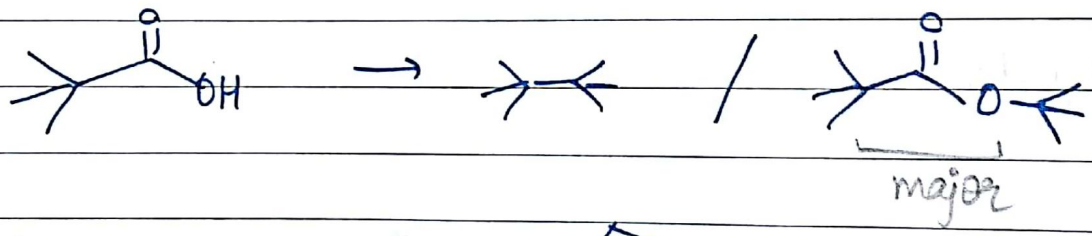
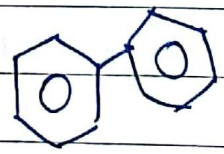
2) $EtCOONa \longrightarrow Et-Et$

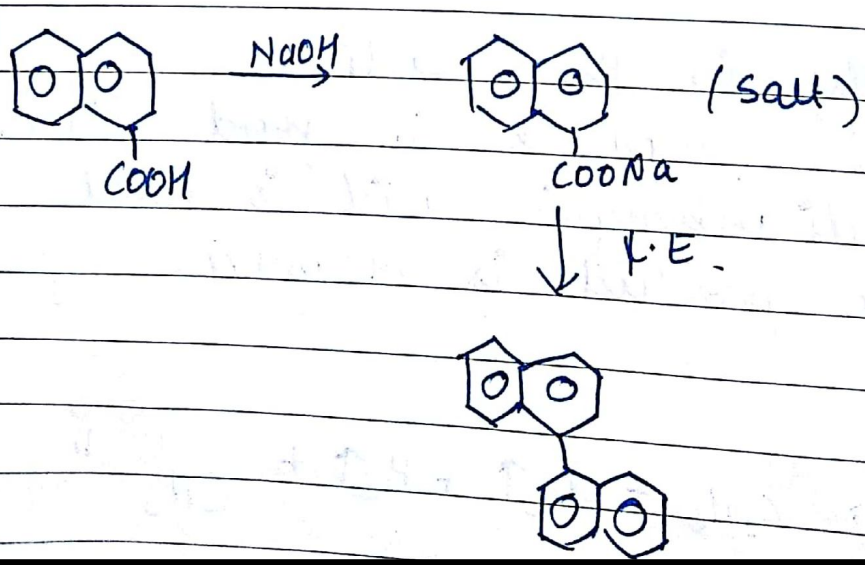
3) CH_3COONa + $\longrightarrow CH_3-CH_3 + Et-Et + Et-CH_3$

4) 

all 5) 

6) 

7) $ph-COONa \longrightarrow$ 

8) 

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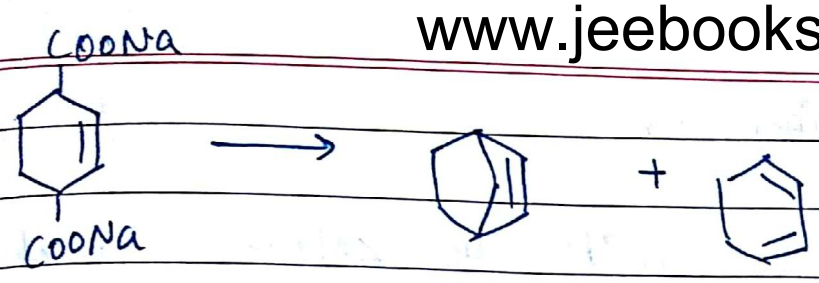
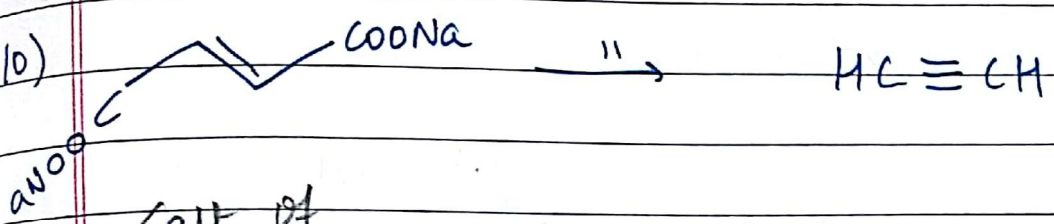
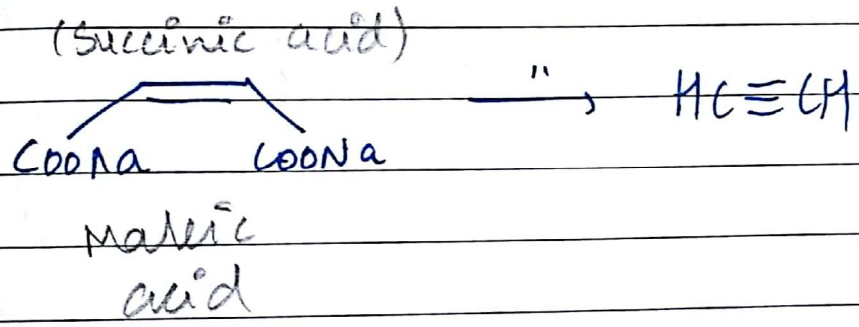
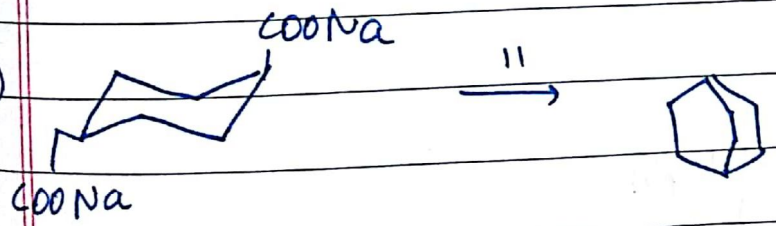
9) 

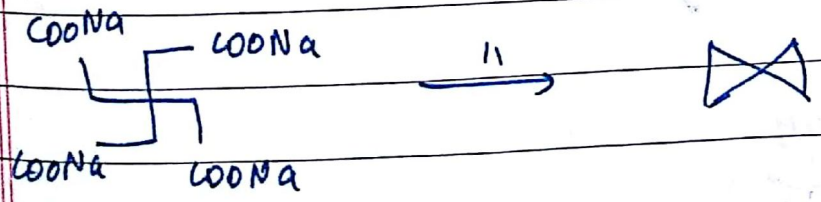
10) 

Salt of Fumaric acid

11) 

12) $HOOC-CH_2-CH_2-COOH \xrightarrow{2Na} A \xrightarrow{KE} CH_2=CH_2$

13) 

14) 

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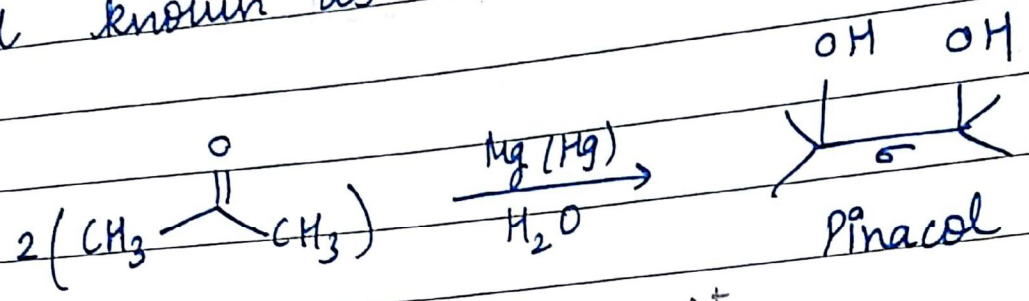
* PINACOL formation

- In this rxn, two units of ketone combine in presence of Mg-Hg Amalgam followed by rxn with protic solvent to give vicinal diol known as Pinacol.



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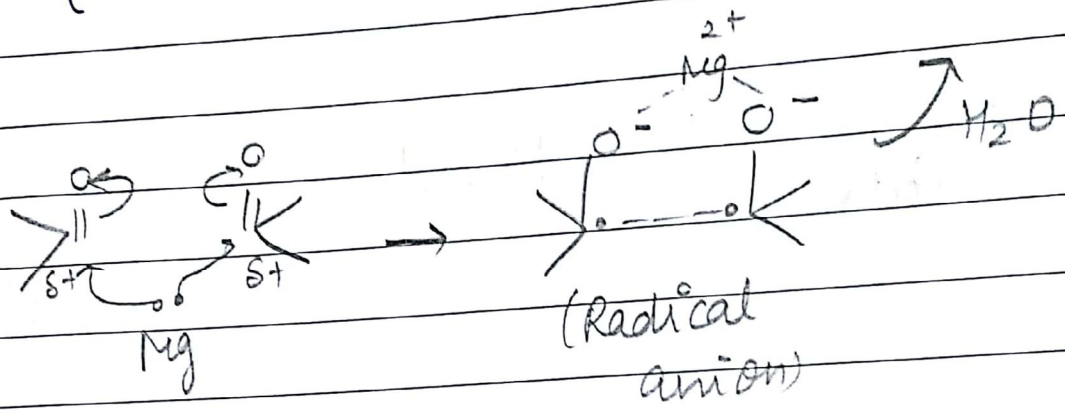

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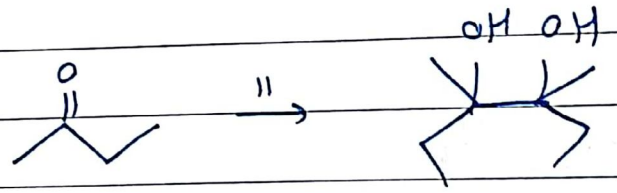

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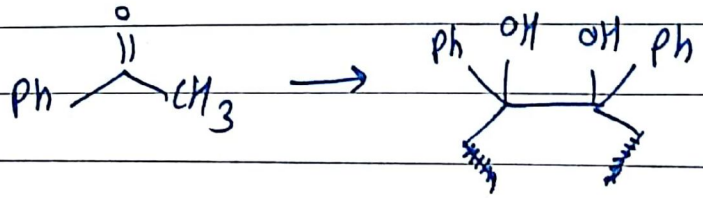

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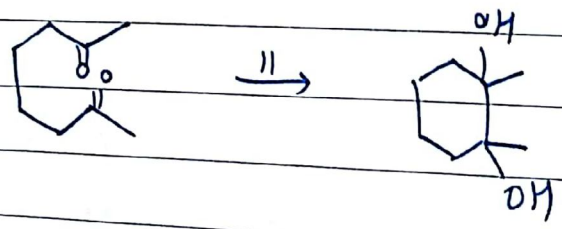

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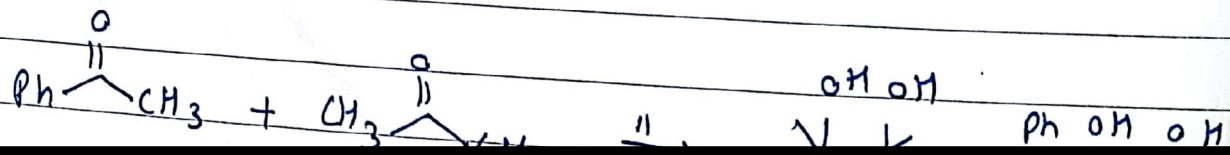

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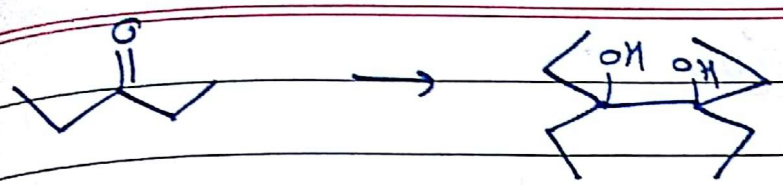
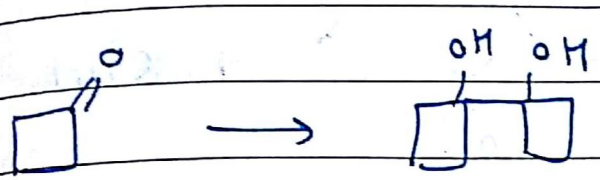
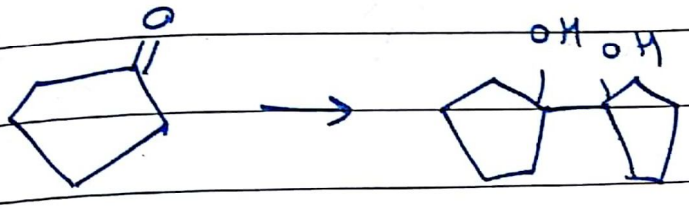
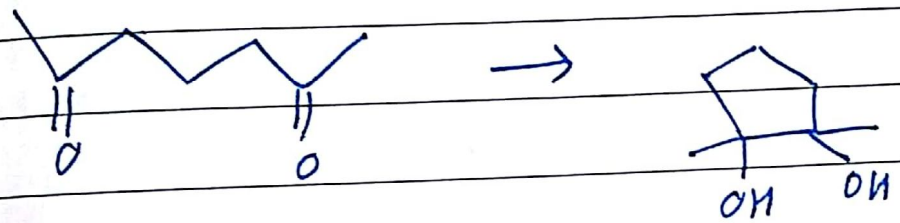
5) 

6) 

7) 

8) 

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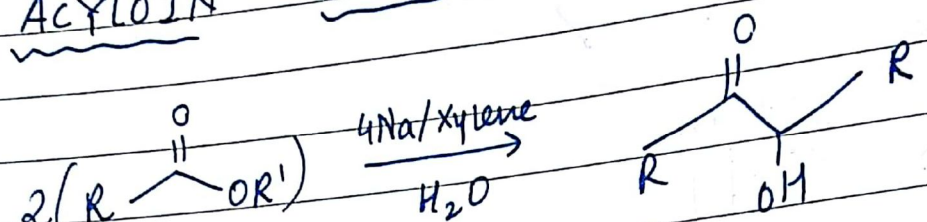
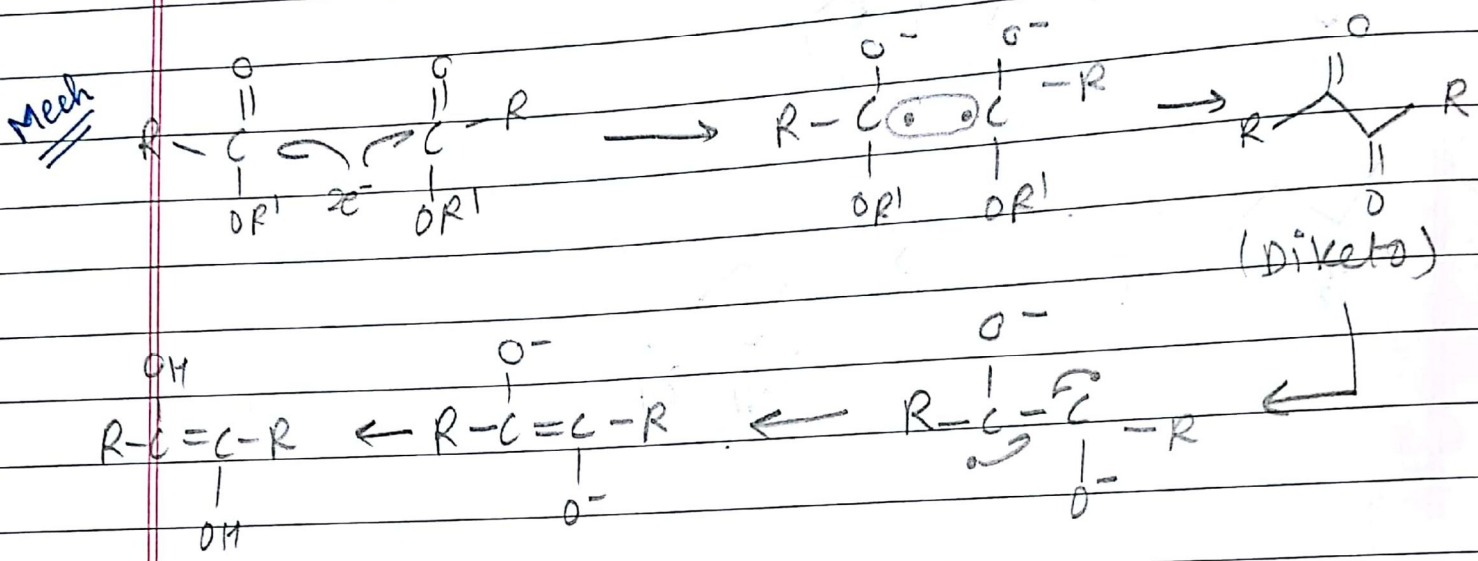
* ACYLOIN Condensation



α-hydroxy Ketone
(Acyloin)

Mech



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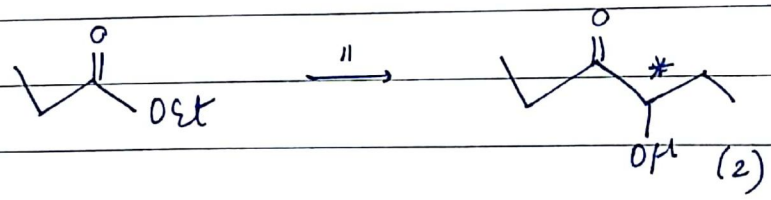

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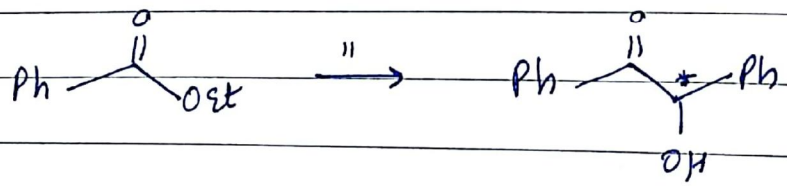

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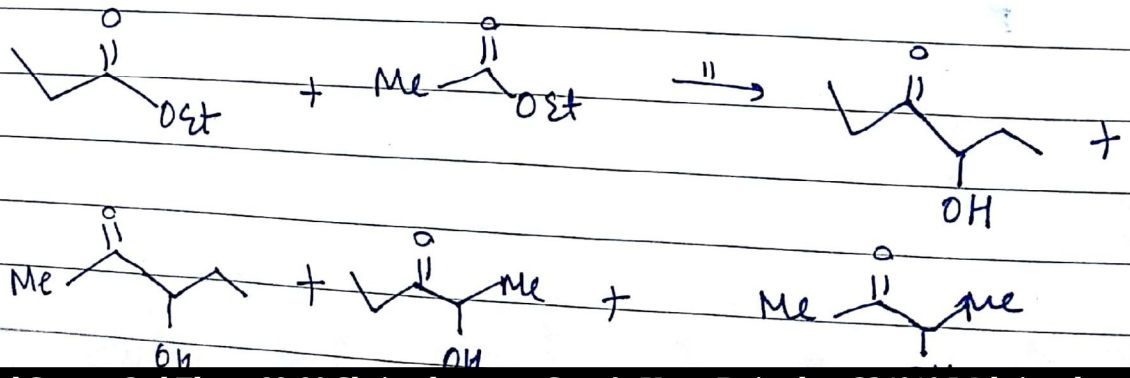

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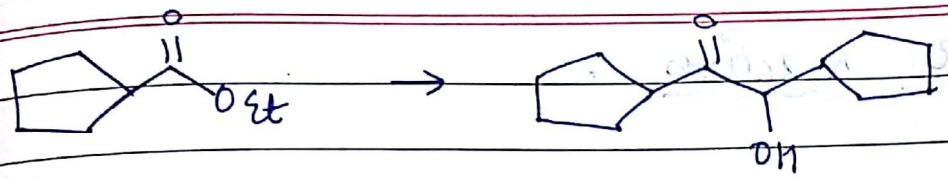
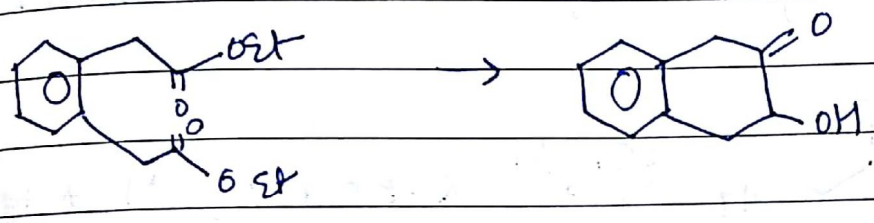
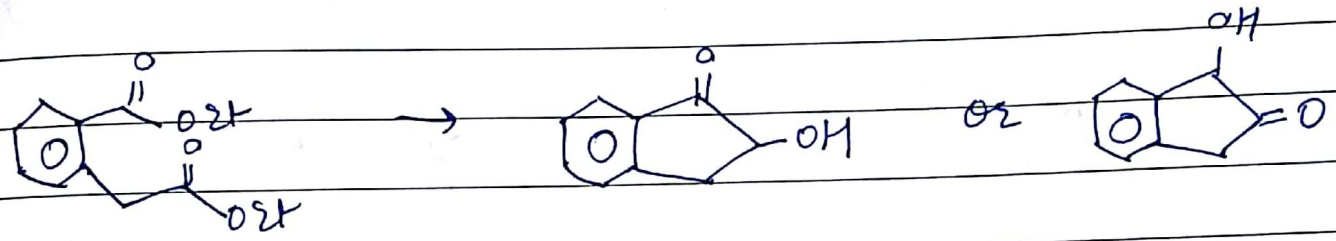
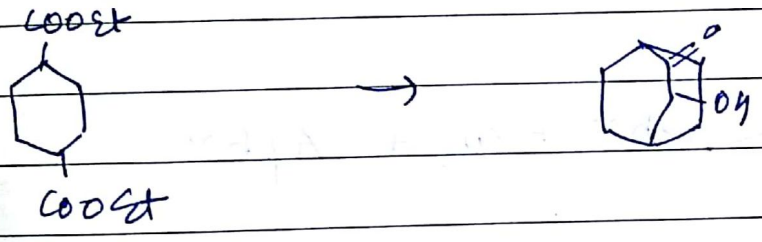
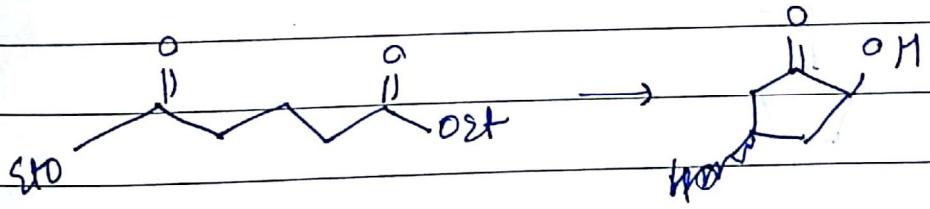
4) 

5) 

6) 

7) 

8) 

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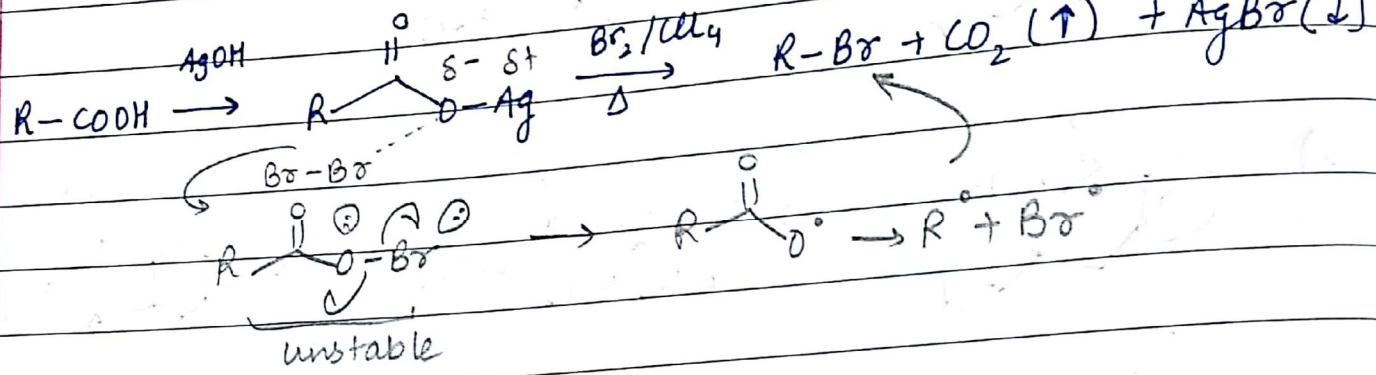
* HUNDSDIECKER Reaction

In this ran Ag salt of carbonylic acid is heated with halogen to produce haloalkane.



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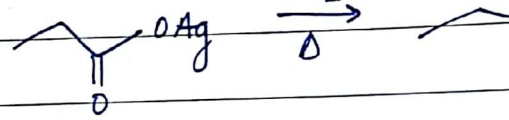
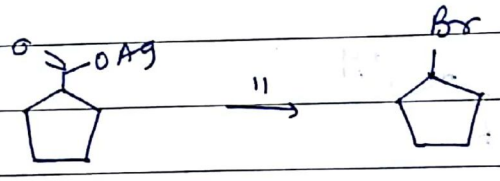
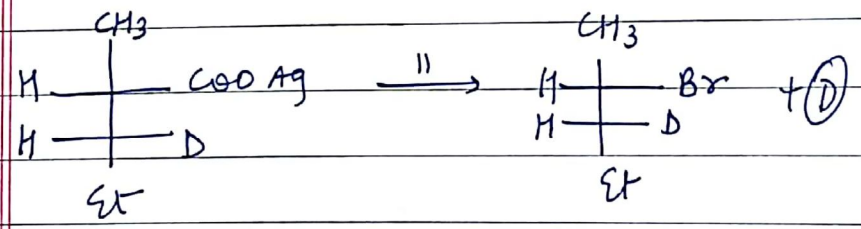
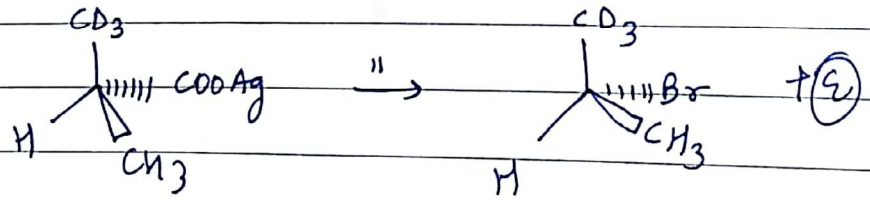
1) 

2) 

3) 

4) 

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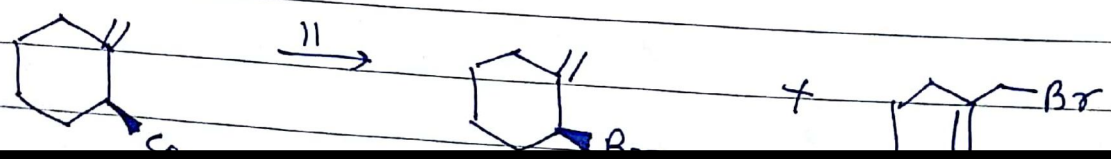
6) 

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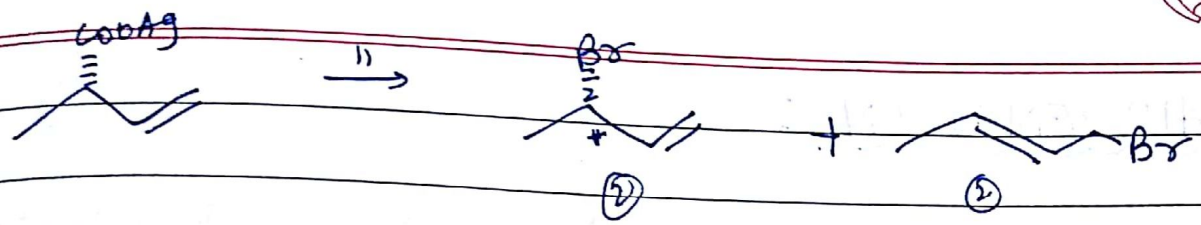
7) 

8)

9) $2CH_3COOAg \xrightarrow{I_2} CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3 + AgI + CO_2 (\uparrow)$

(Simonini reaction) (I_2 is a good l.g.)

- It is modified version of hunsdiecker in which ester is formed

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* PHOTOHALOGENATION :

- When one the hydrogen is replaced by halogen in presence of light then it is monophoto-halogenation.

HELPR It can take place in the presence of high temperature as well.

$$CH_4 \xrightarrow[h\nu/\Delta]{Cl_2} CH_3-Cl \longrightarrow CH_2Cl_2$$

(methane) (monohalogenation)

Mech

- Chain initiation step

$$Cl-Cl \longrightarrow 2\dot{Cl}$$

- Chain propagation step

$$\dot{Cl} + H-CH_3 \longrightarrow \dot{CH_3} + HCl \quad \Big) \; \Delta H = -ve \; \{f_2, Cl_2\}, \; \Delta H = +ve$$

$$\dot{CH_3} \cdots Cl-Cl \longrightarrow CH_3Cl + \dot{Cl} \quad \Big) \; \Delta H = -ve$$

- Chain Terminating step

$$\dot{CH_3} + \dot{CH_3} \longrightarrow C_2H_6$$

$$\dot{Cl} + \dot{Cl} \longrightarrow Cl_2$$

$$\dot{CH_3} + \dot{Cl} \longrightarrow CH_3Cl$$

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- **Characteristics :→**

a) Rate of rxn depends on first chain propagating step.

- $\overset{\text{violent}}{F_2} > Cl_2 > Br_2 > \overset{\text{too slow/ Reversible}}{I_2}$

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI \xrightarrow{HNO_3} I_2$$

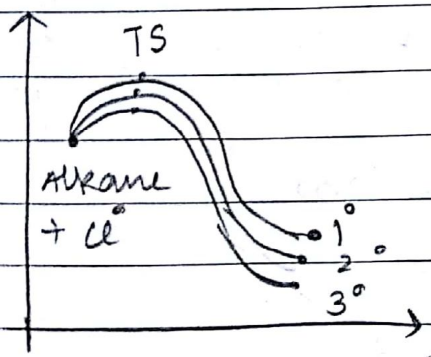
- Rate of H- abstraction,

{due to more stability of }

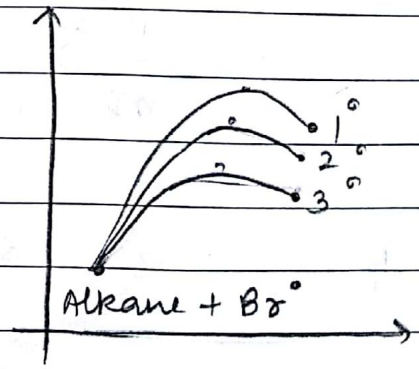
* **Reactivity & Selectivity Principle :→**

Relative rates	1°H	2°H	3°H
Cl_2	1	3.8	5
Br_2	1	82	1600

- More reactive the specie, lesser selective it will be.



TS resembles alkane



TS resembles radical

Endo

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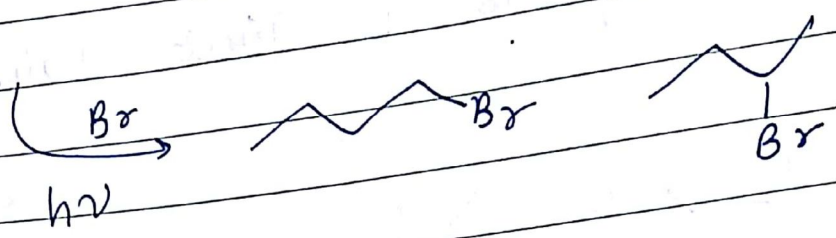
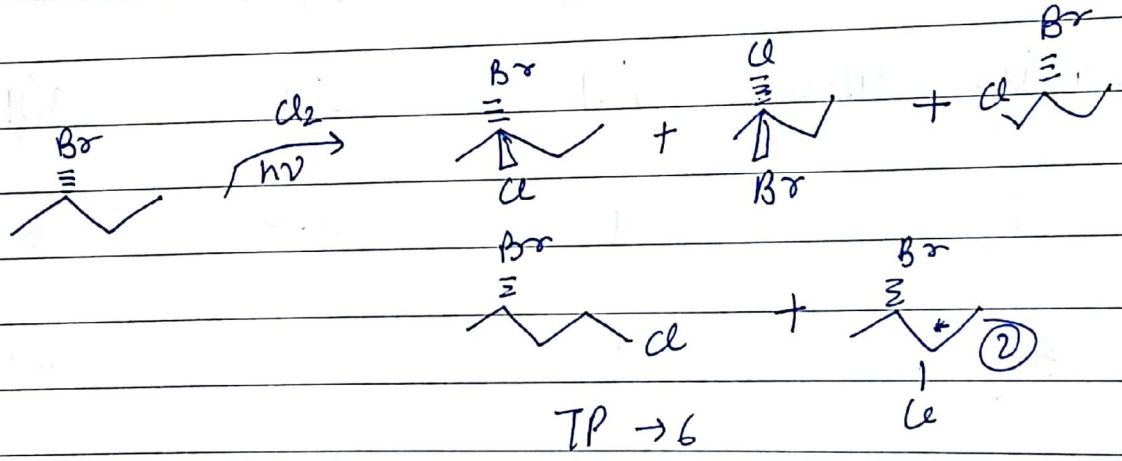
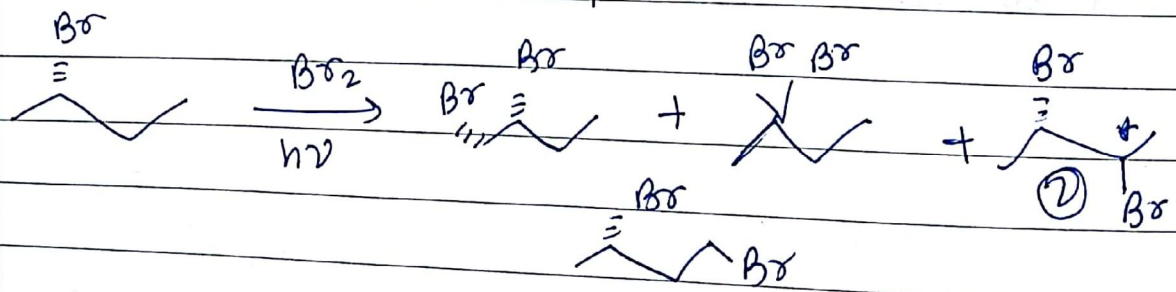


Relative amt.	no. of H	Relative rate	
6 15.2	1°) 6 2°) 4	1 3.8	Cl_2
6 328	1°) 6 2°) 4	1 82	Br_2

Q.
1)



TP → 6
TS → 4
Chiral → 6
Frac^n → 5



TP → 5,
TS → 4

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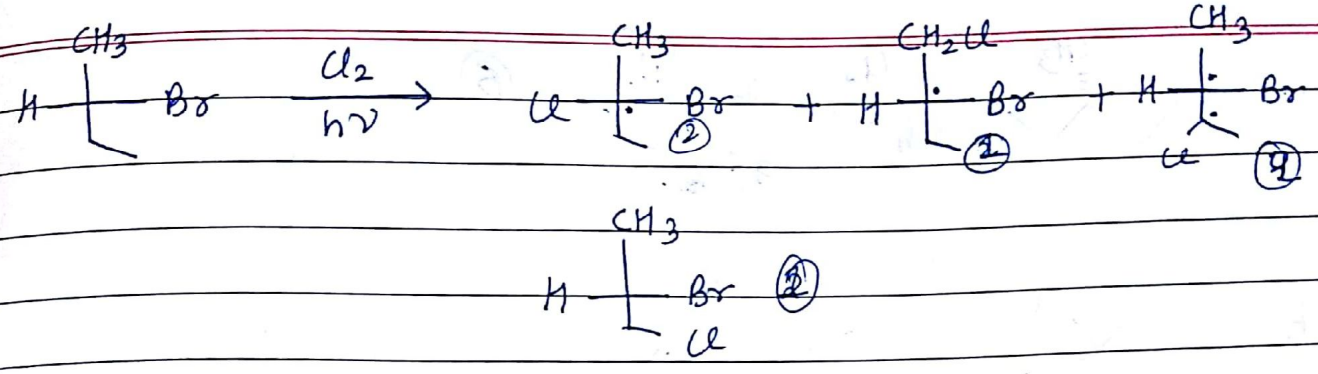
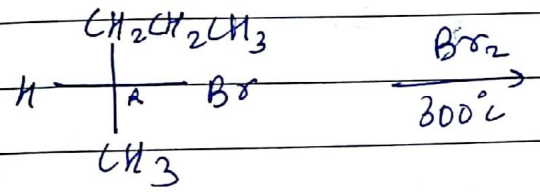
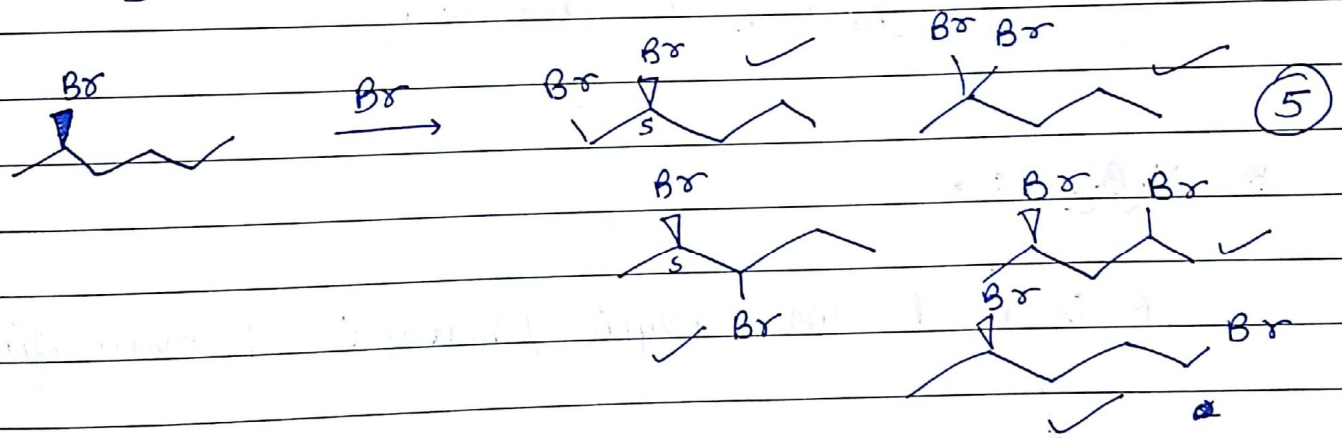
2) 

3) 

How many chiral dibromo products

→ 

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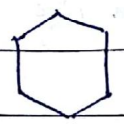
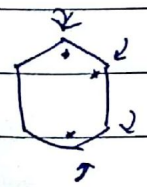
4) 

→ Dibromo products ① ③ ⑤ ②

5) 

→ Tribromo products ② ② ② ⑧ ⑧ ①

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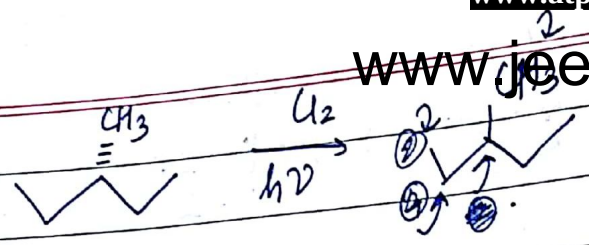
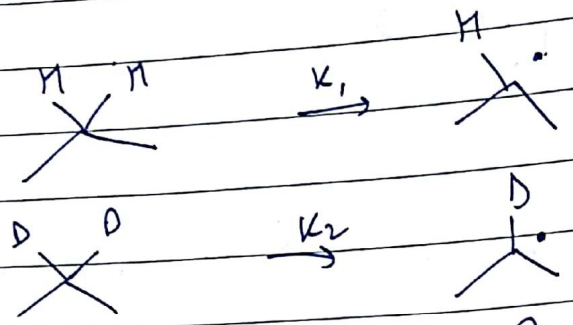
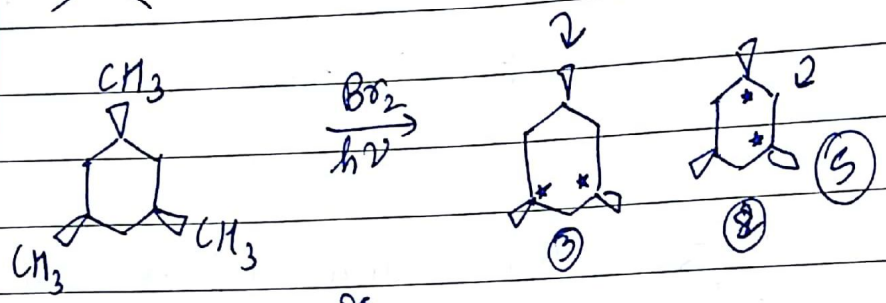
6. 

7. 

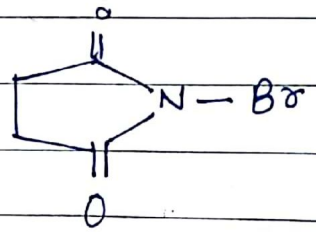
$K_1 > K_2$

8. 

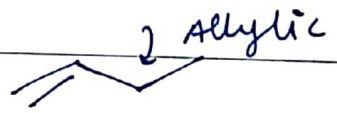
or
$SO_2Cl_2, h\nu$
(performs the same f.n)

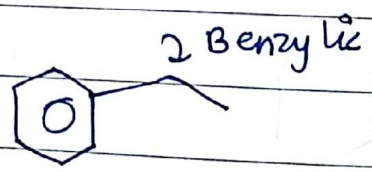
* N.B.S :→

- It is used for allylic / benzylic bromination



N-Bromo succinimide





- $CH_2 = CH - CH_3 \xrightarrow[CCl_4]{NBS, \Delta} CH_2 = CH - \underset{Br}{CH_2}$

It is free radical allylic / benzylic substitution.

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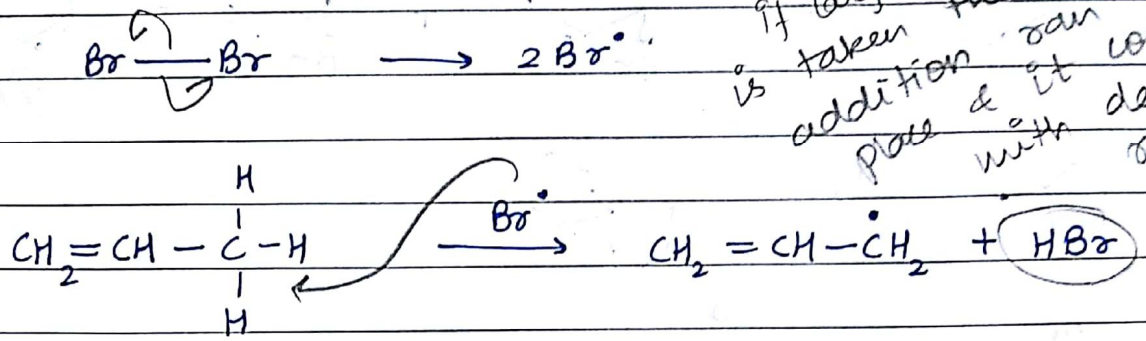
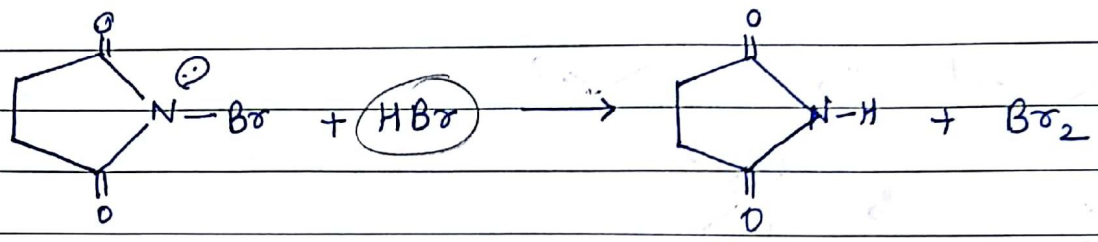
Mech.



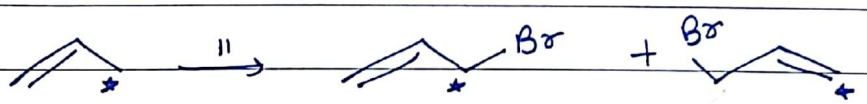
If large qty of Br_2 is taken then parallel addition rxn takes place & it competes with desired rxn.



- NBS is used to supply lesser amount of Br_2 constantly so that substitution dominates.
- For chlorine substitution NCS should be used.

Q.

1)



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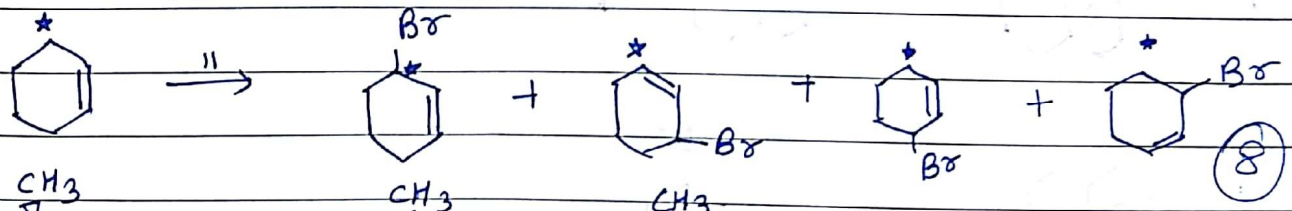

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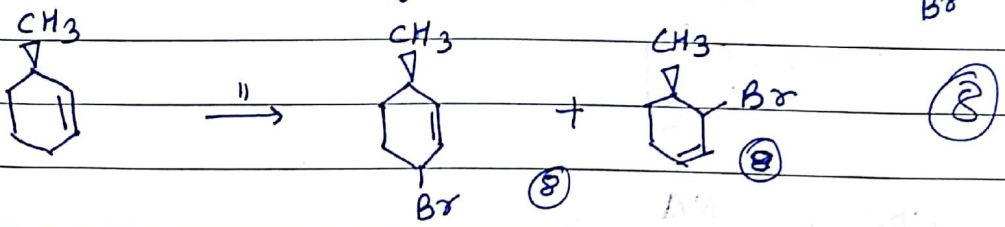

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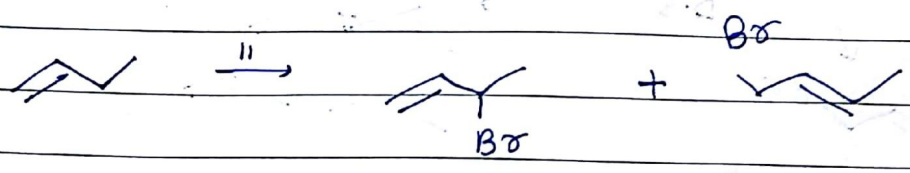

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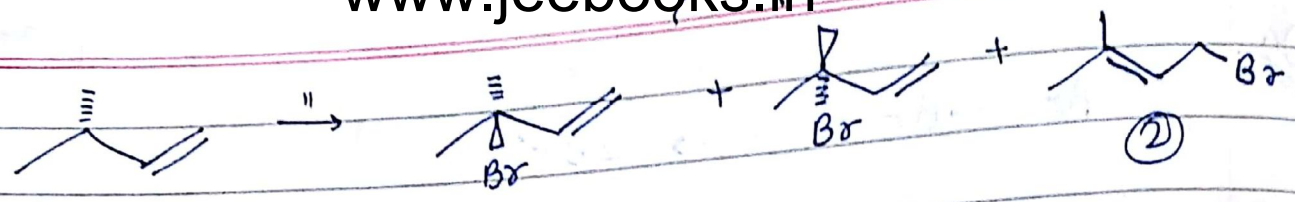
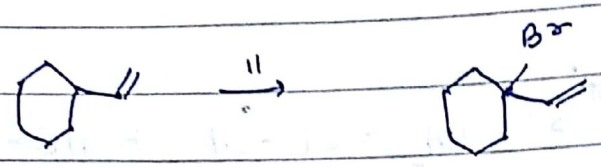
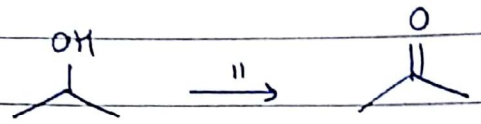
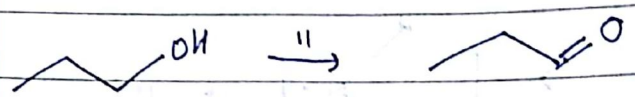
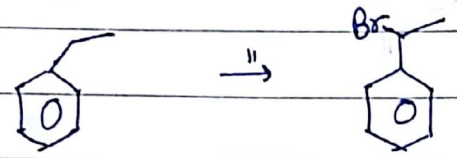
Same

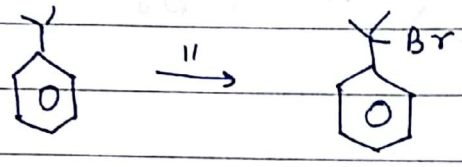
5) 

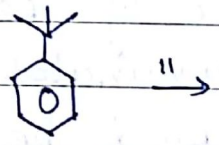
6) 

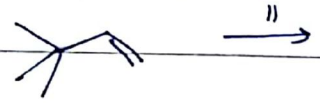
OOS 7) 

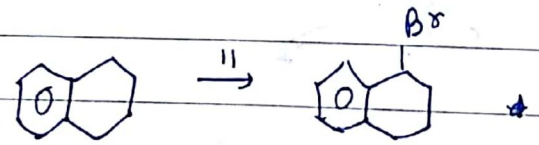
OOS 8) 

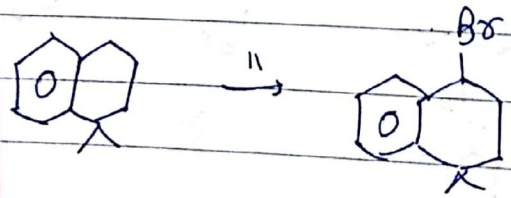
9) 

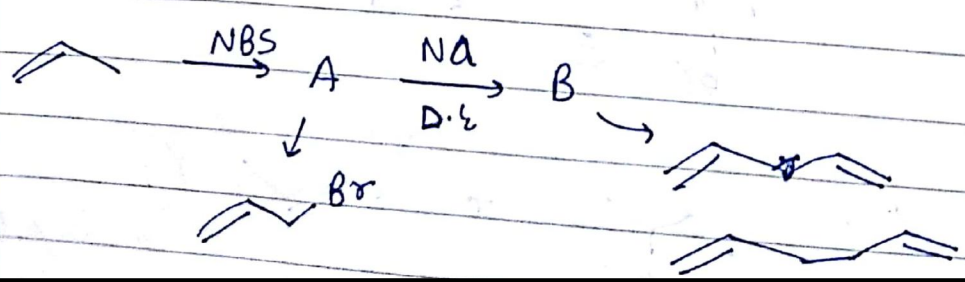
10) 

11) 

12) 

13) 

14) 

15) 

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CARBOCATION

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- **Generation** :→

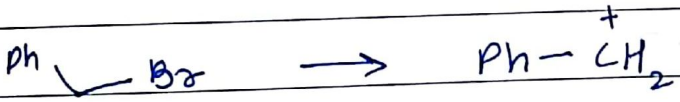
- heterolytic bond breaking

Formation of cation is favoured by,

a) Electron donating groups
b) Polar solvent
c) leaving ability of the group.

$$\overset{\delta+}{R}-\overset{\delta-}{L.G.} \longrightarrow R^+ + (L.G.)^-$$

-

- 

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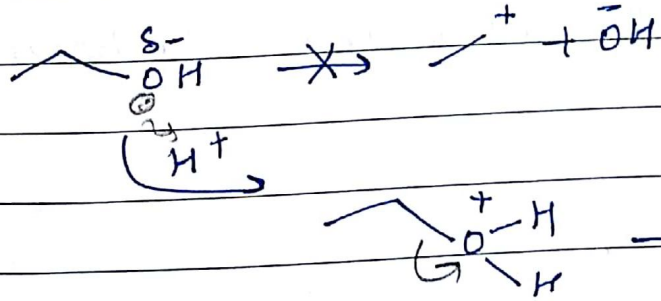
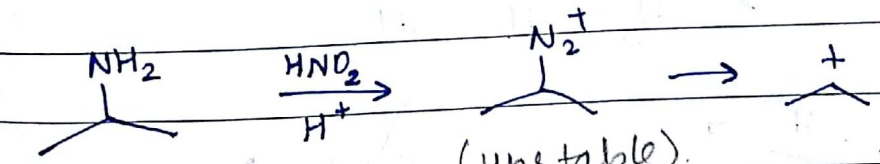
- 

- 
(unstable).

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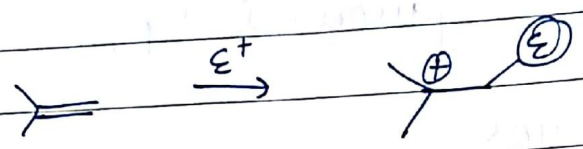
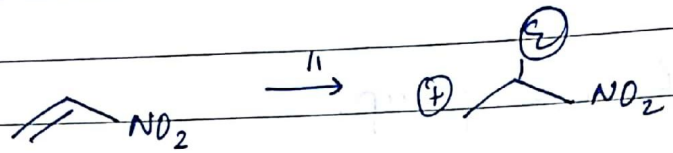
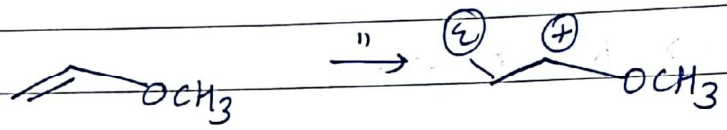
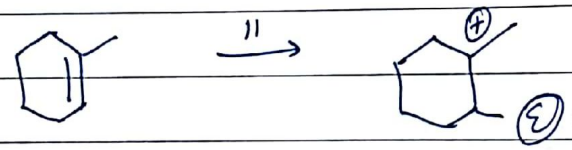
- Interaction of π e^- cloud with electrophile









- Rearrangement of $C^{\oplus}$:→

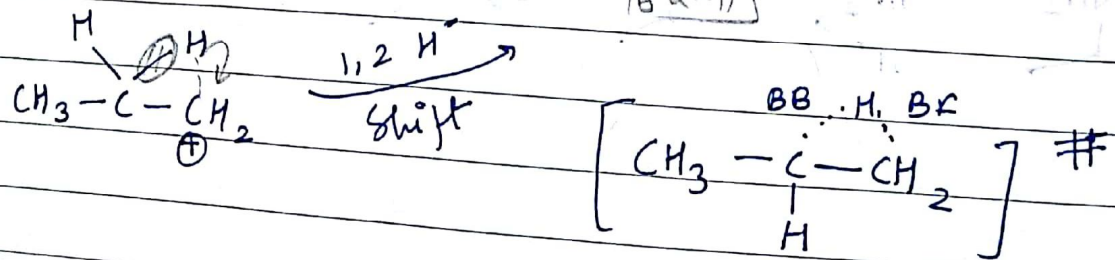
- Check for rearrangement whenever carbocation is formed.

- Shifting is always 1,2.

$$CH_3-CH_2-\overset{\oplus}{C}H_2 \longrightarrow CH_3-\overset{\oplus}{C}H-CH_3$$

[2α-H] [6α-H]

Mech.



T. state

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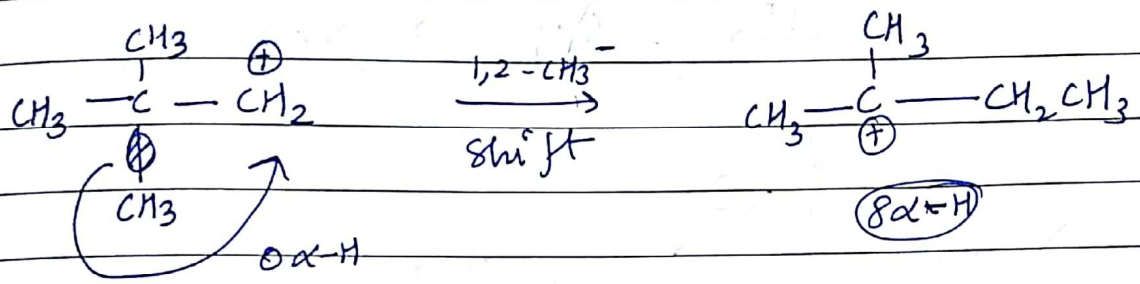
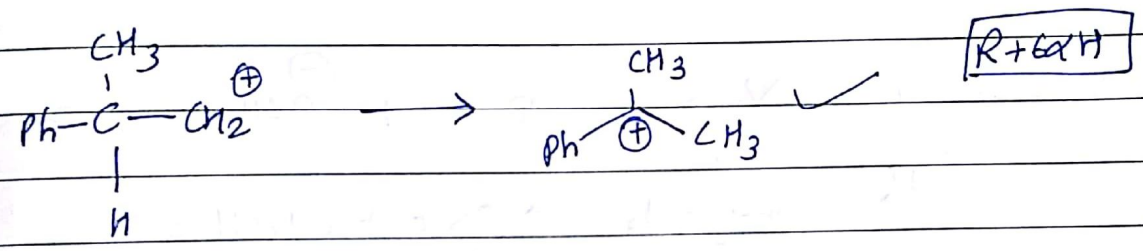
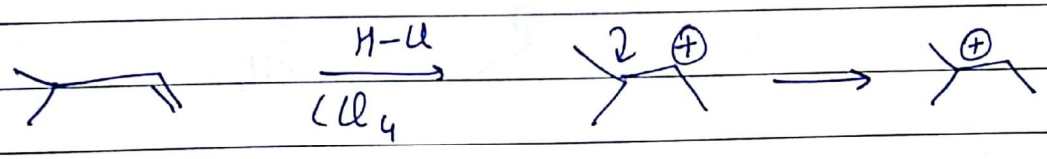
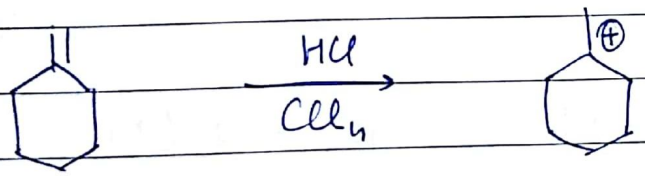
- Shifting is done in such a way that most stable carbocation is formed.

- In case of multiple groups, shifting depends on the formation of stable cation.

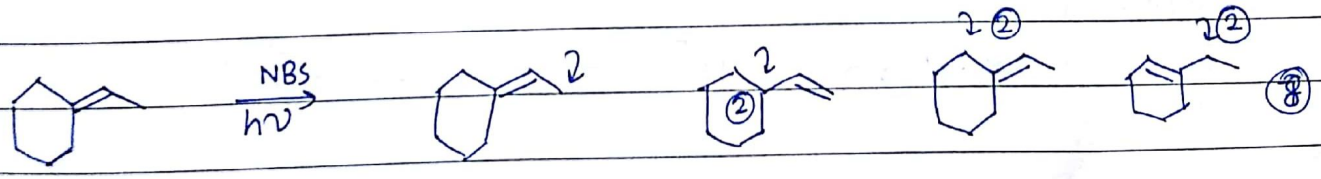
- 

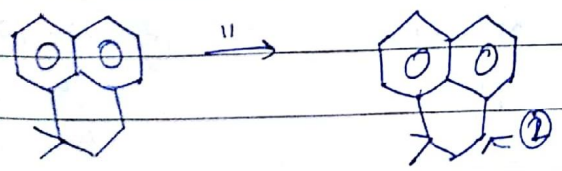
- 

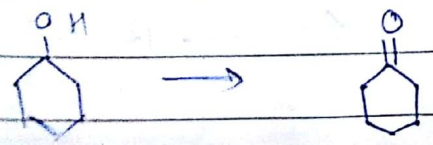
- 

- 

Q.

1) 

2) 

3) 

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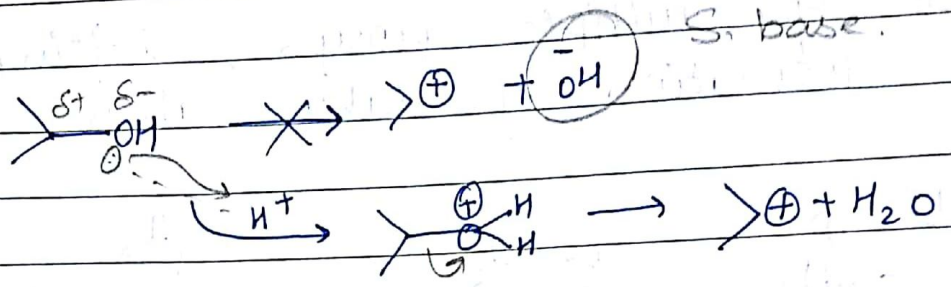
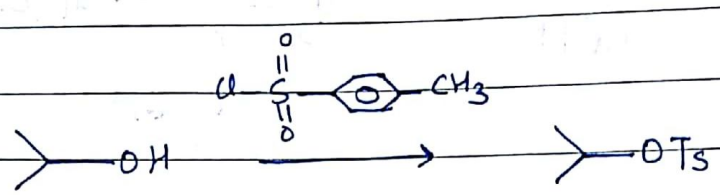
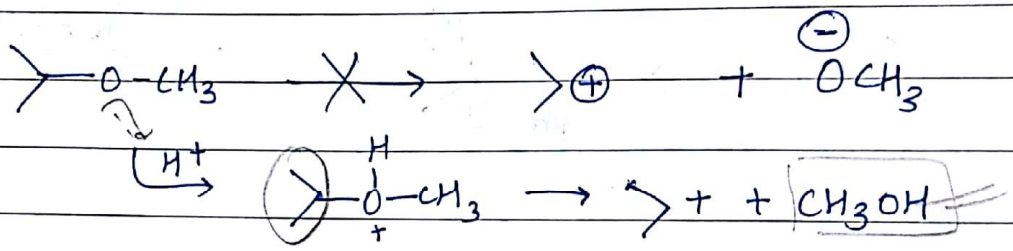
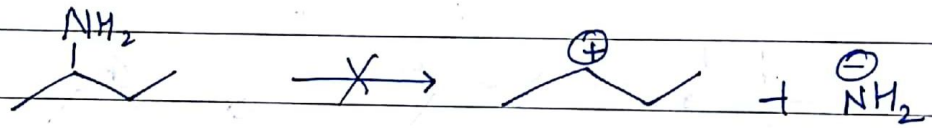
- In case good l.g. is not available it is created thru many reactions.

eg,





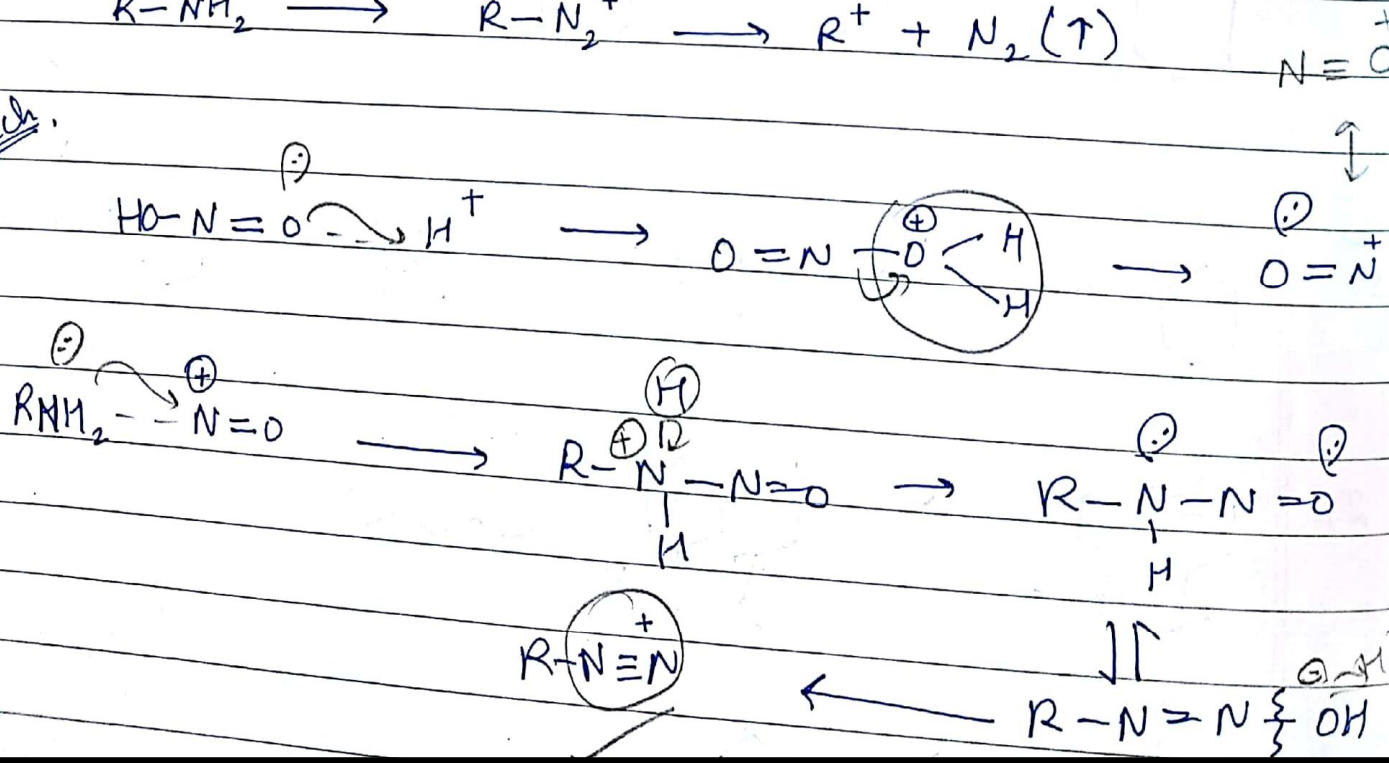




Diazotization

$$R-NH_2 \xrightarrow{NaNO_2 + HCl} R-N_2^+ \longrightarrow R^+ + N_2(\uparrow)$$

Mech.



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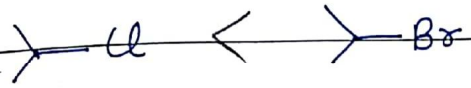
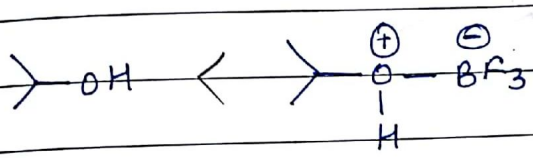
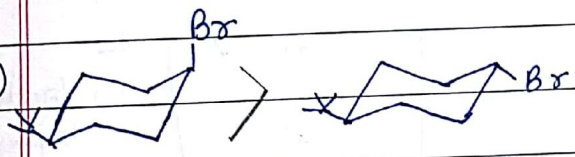
Q. Compare rate of formation of $C^{\oplus}$:→

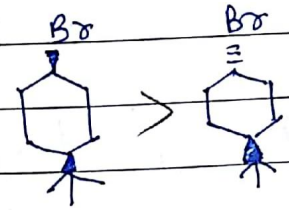
1) (C^+)

2)  (l.g.)

3)  (lewis acid)

4) (l.g.)

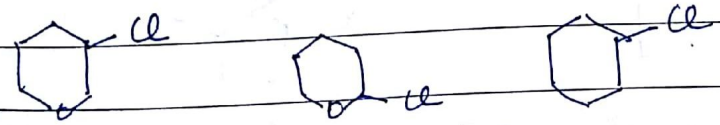
5)  (stability)

6)  (stability)

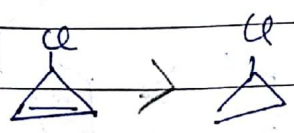
7) (resonance)

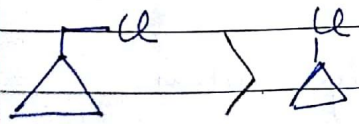
better +m of N than O.

c > b > a

8) 

b > c > a

9)  (aromaticity)

10) 

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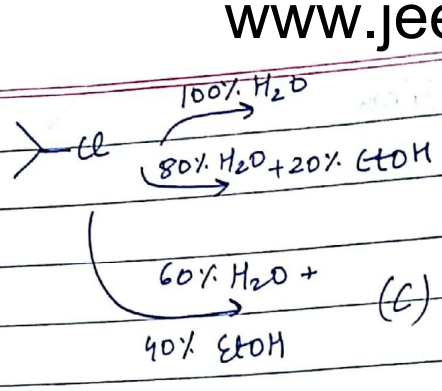
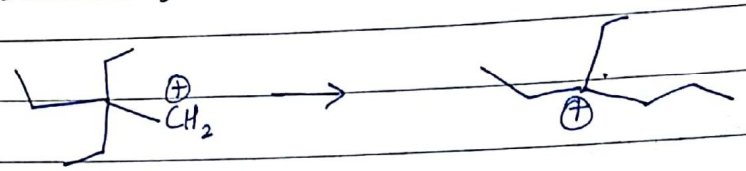
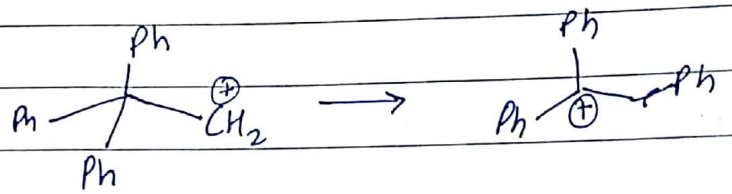
{H-bonding}

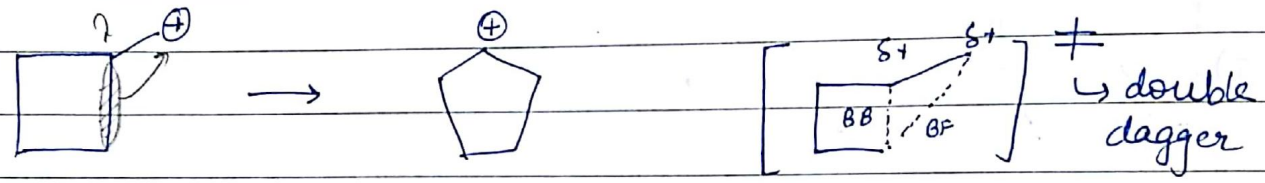
11) 

A > B > C

9. Rearrangement :

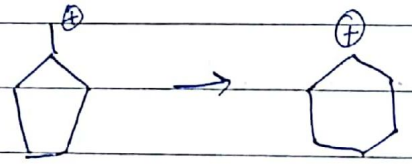
1) 

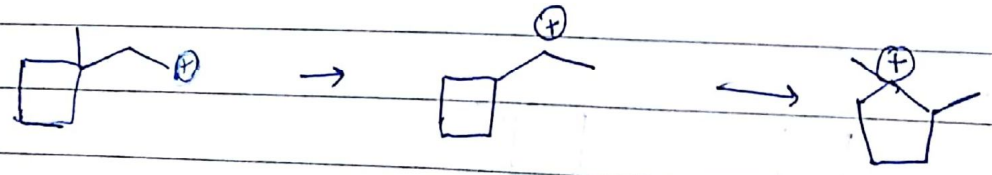
2) 

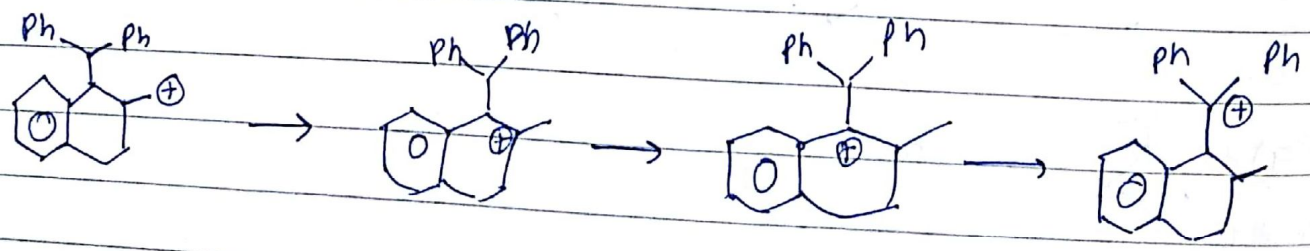
ring exp. 3) 

↳ double dagger

Condition : It is possible in 3, 4, 5 membered rings.
+ve charge must be present on directly attached C-at

4) 

5) 

6) 

Rearrangement can take place (many times) only when stabalization ↑ in each step.

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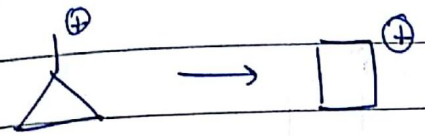
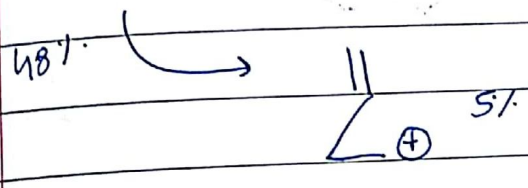
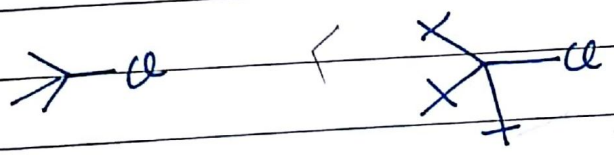
7)

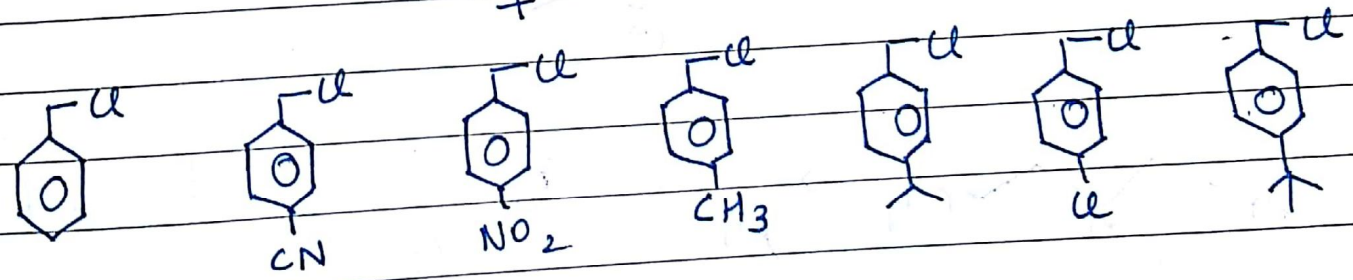
8)

9) 

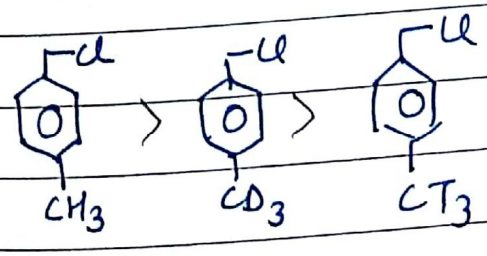


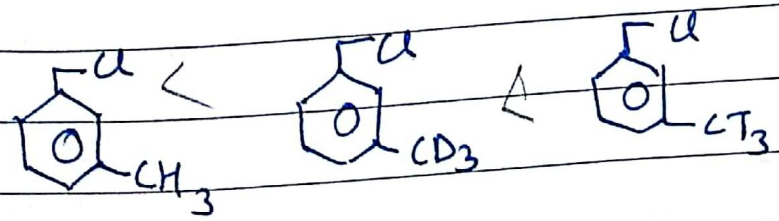
Q. Compare rate of formation of carbocation

1) 
(rep^n b/w b.p.)

2) 

d > e > g > a > f > b > c

3) 

4) 

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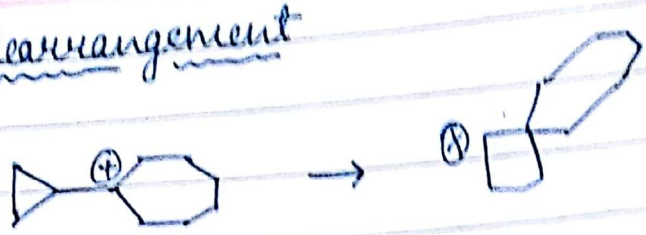
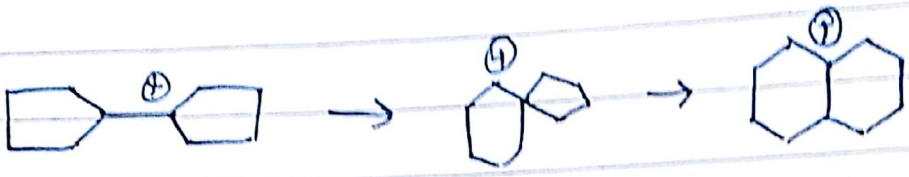
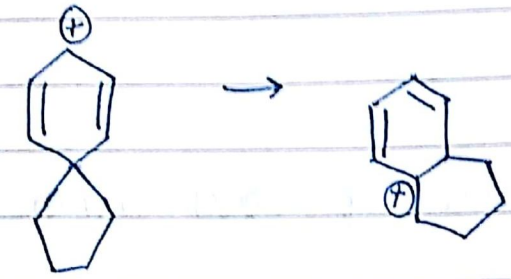
Q. Rearrangement

1) 

2)

Tendency for ring exp is much more in (2) coz there would be charging resonance

3) 

4) 

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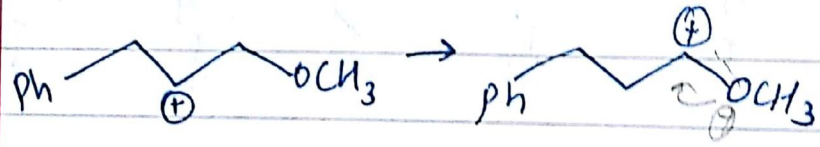
6) 

formation of OCC^+ is highly favourable

7)

8)

9)

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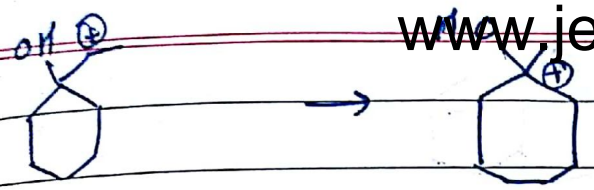
(10)



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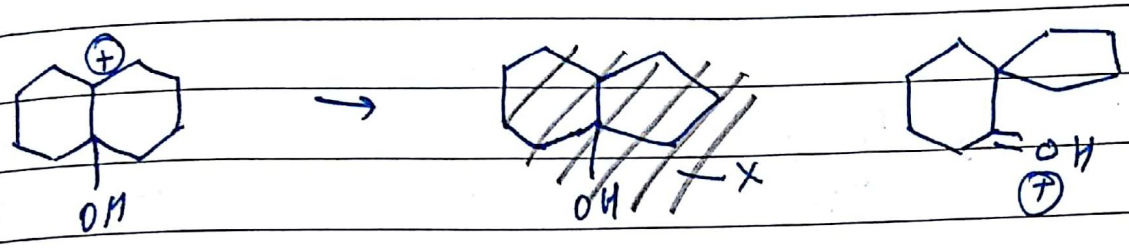

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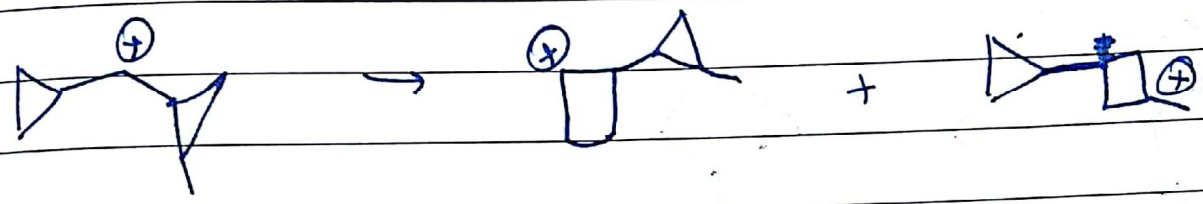

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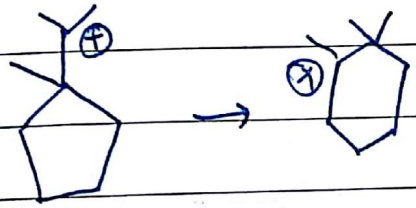

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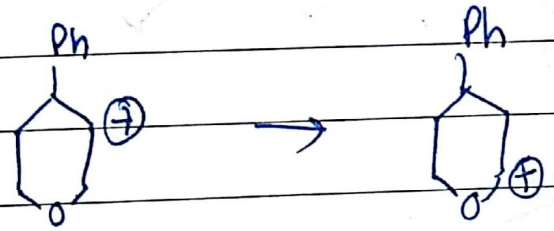

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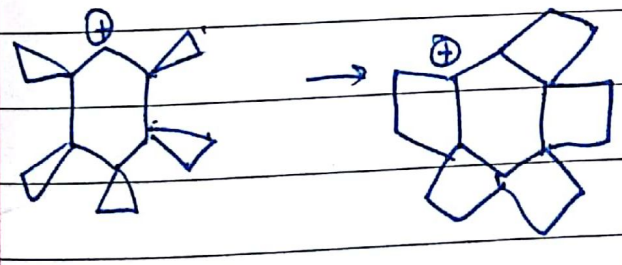

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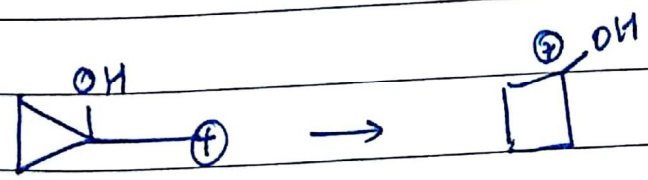

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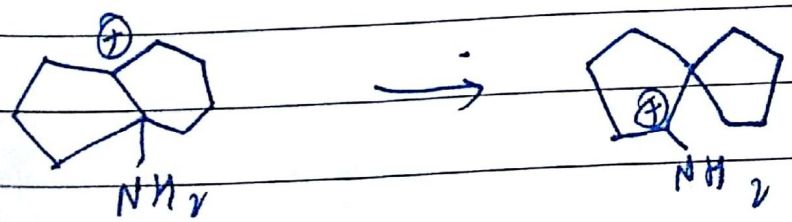

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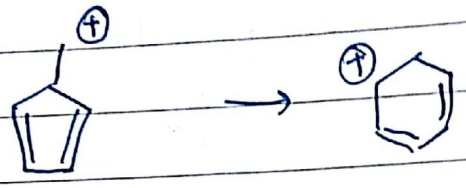
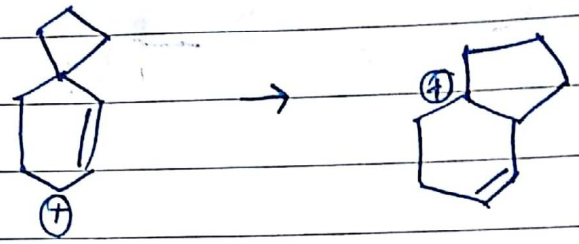
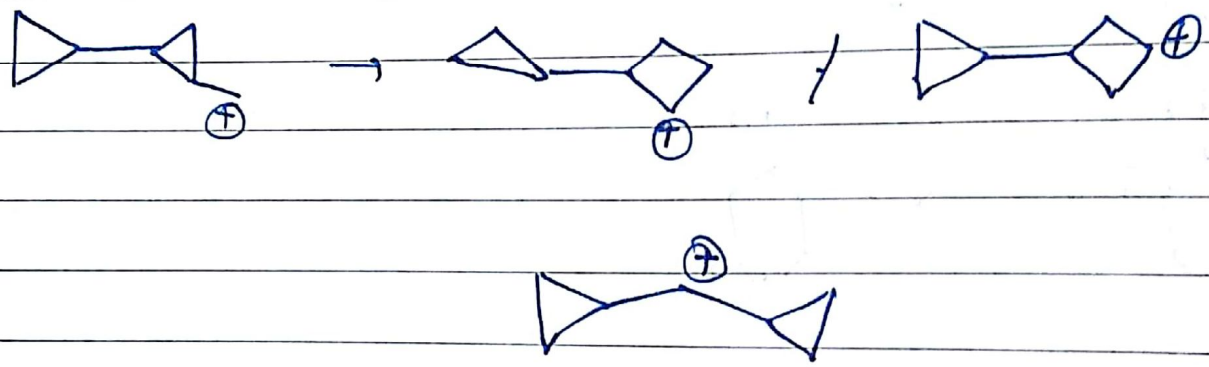
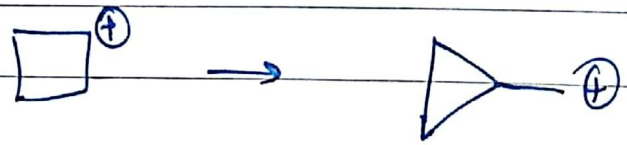
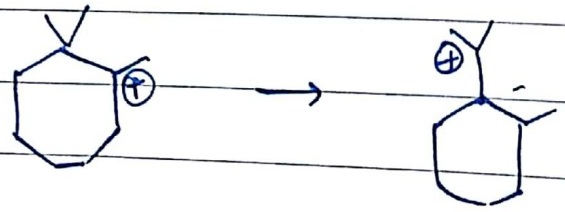
19) 

20) 

21) 

22) 

23) 

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* COMBINATION Reaction :

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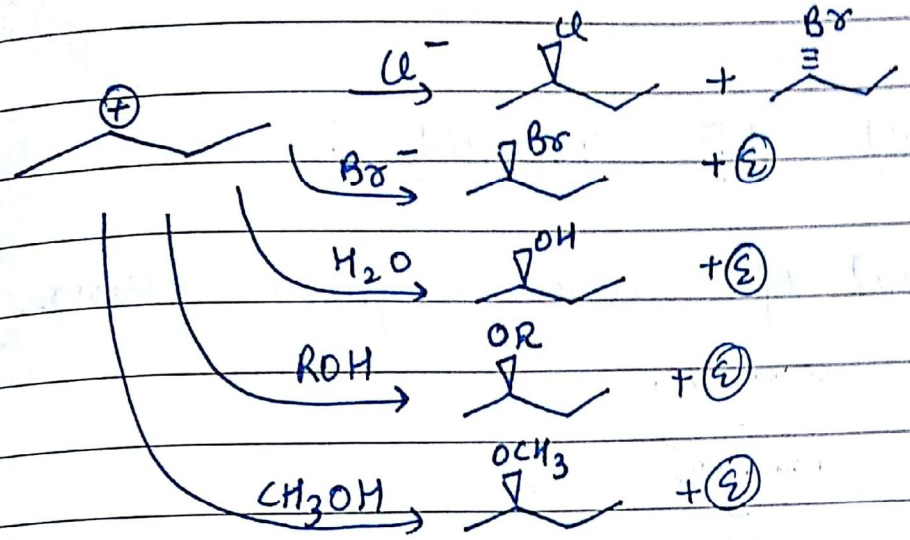
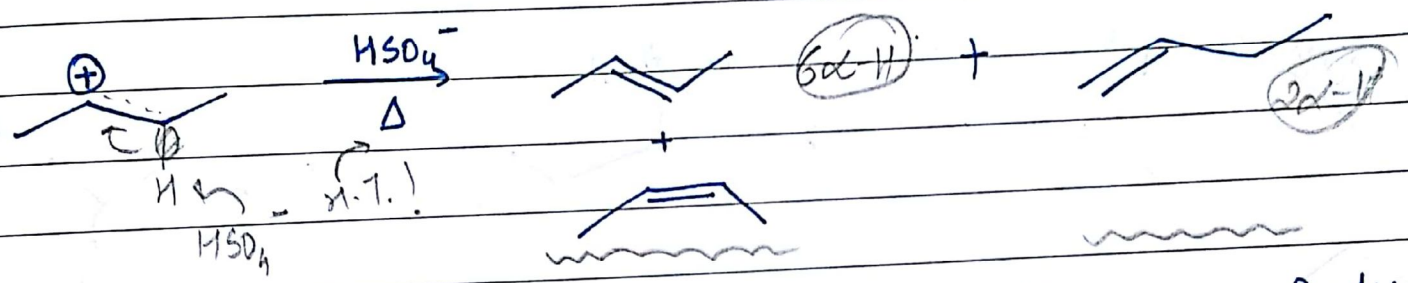


* ELIMINATION Reaction :



Saytzeff Product (Zaitsev) (More Substituted) > Hoffmann Product (less).

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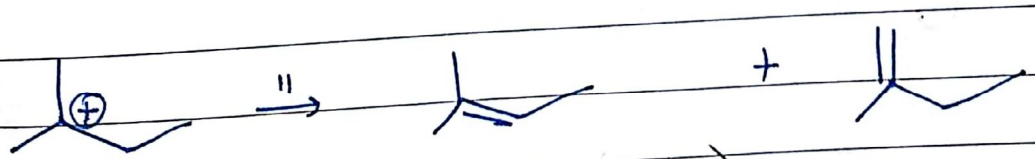
Q.



Saytzeff > Hoff.

- HSO_4^- cannot act as nucleophile
- HSO_4^- will act as a weak base at high temperature.
- More substituted alkene is known as Saytzeff alkene & less substituted is Hoffmann.

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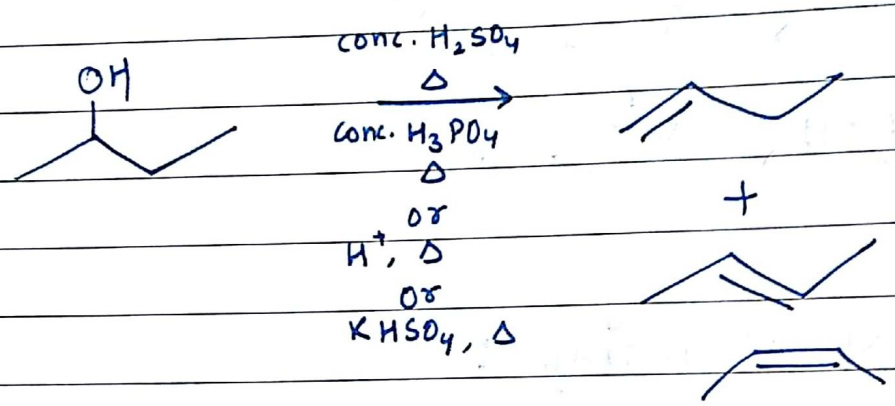
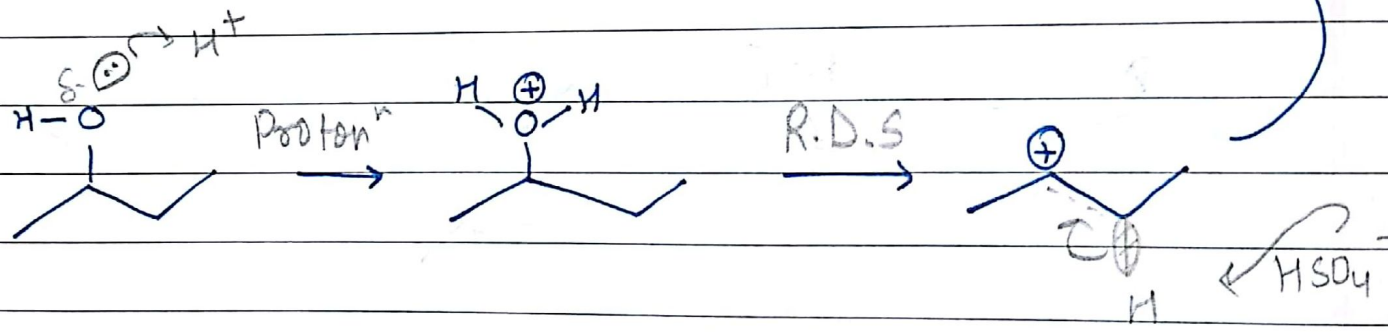
- In general, Zaitsev product dominates.

* DEHYDRATION OF ALCOHOL :

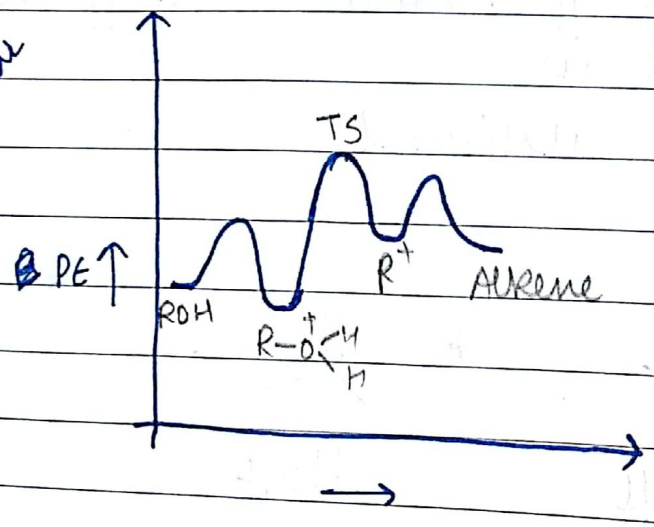
- It is removal of water to form alkene.



Mech.



Unimolecular



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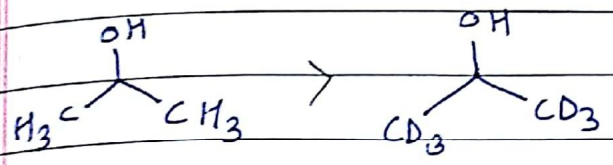
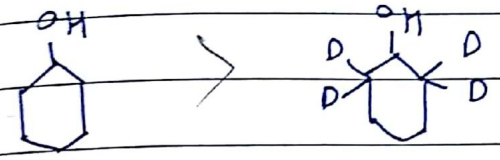
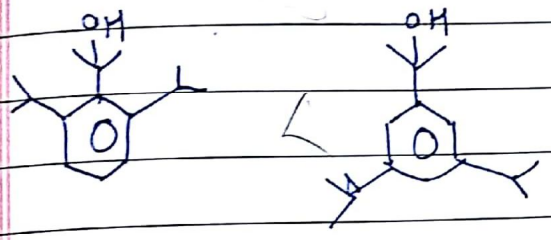
Q. Compare rate of dehydration.

1) 

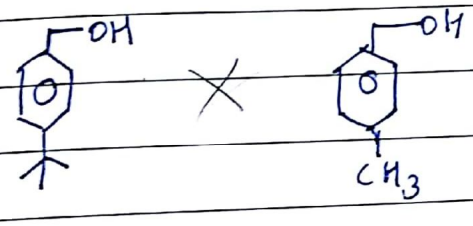
(CD bond is stronger)
isotopic effect.

2) 

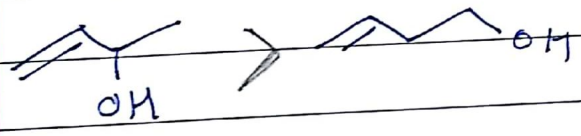
rate of rxn is almost similar.
Primary K.I. will not be obs.
↳ RDS (bond with isotope breaks so formed)

3) 

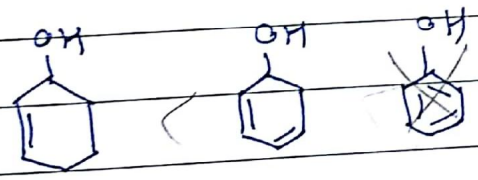
(SIR)

4) 

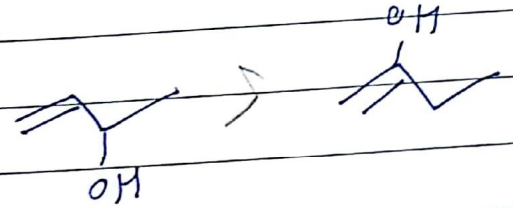
(C–H)
(not possible)

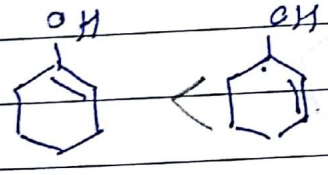
5) 

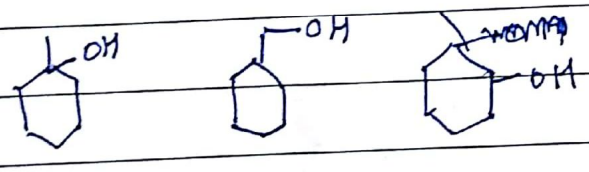
(+ is resonance stabalised)

6) 

{most for cation}

7) 

8) 

9) 

a > c > b

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{ dancing resonance }

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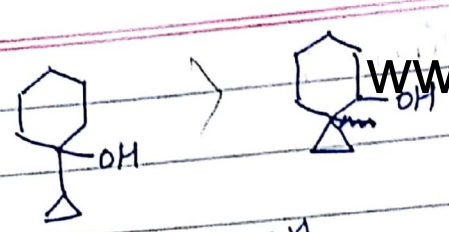
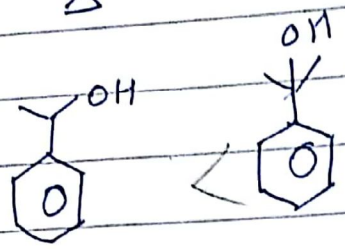
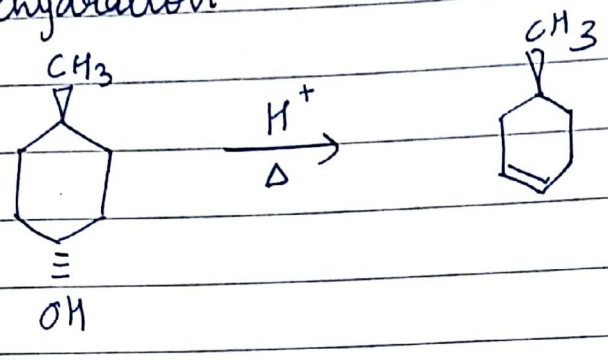
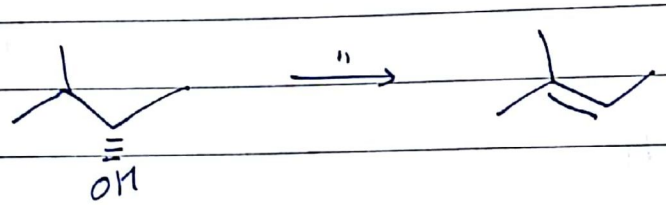
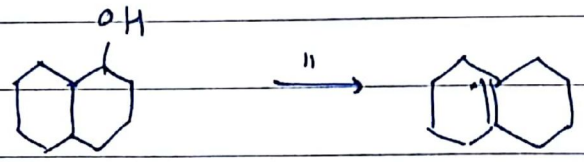
10) 

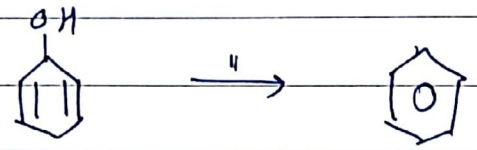
11) 

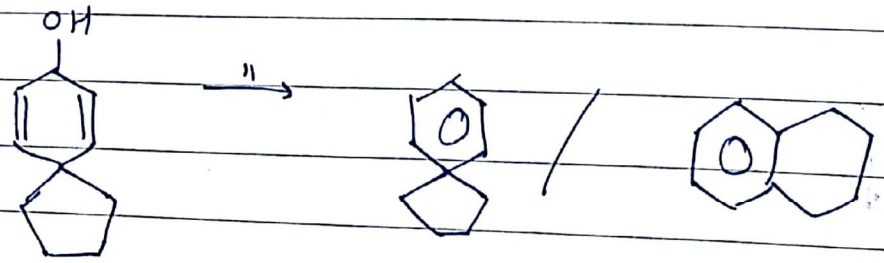
Q. Dehydration

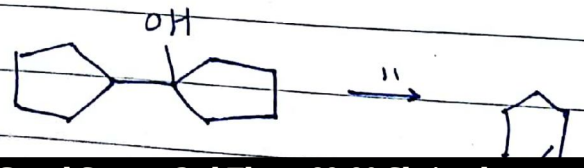
1) 

2) 

3) 

4) 

5) 

6) 

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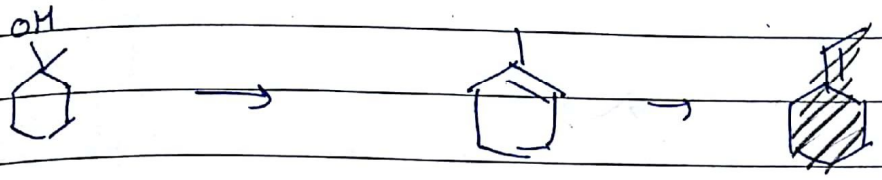
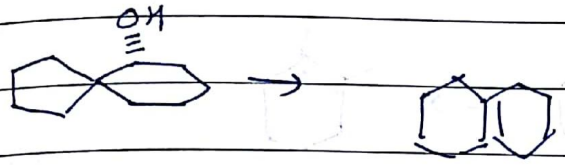
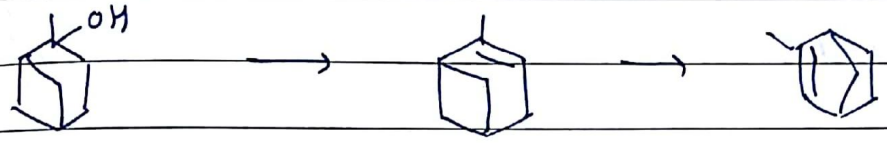
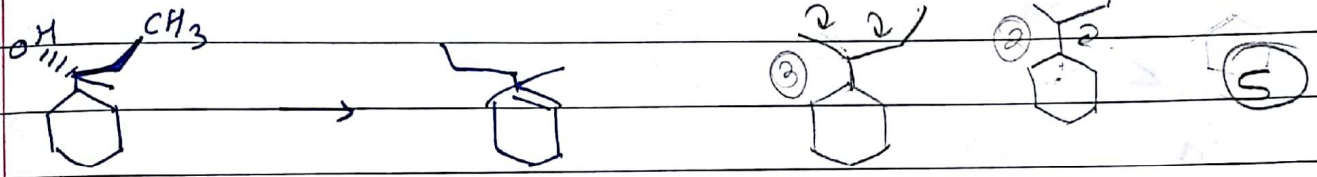
7)

8) 

9) 

* 10) 

11) 

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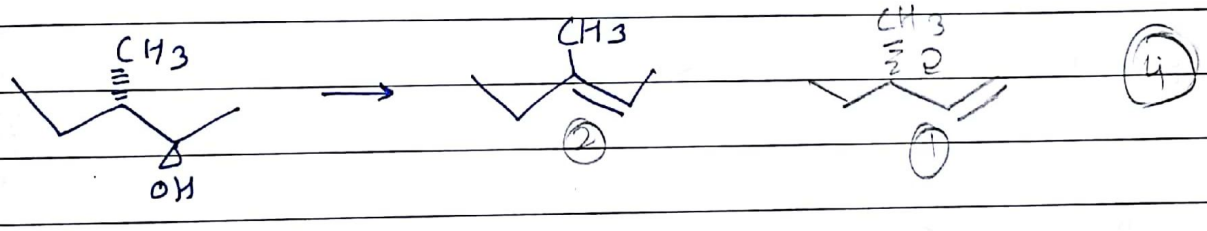
12) 

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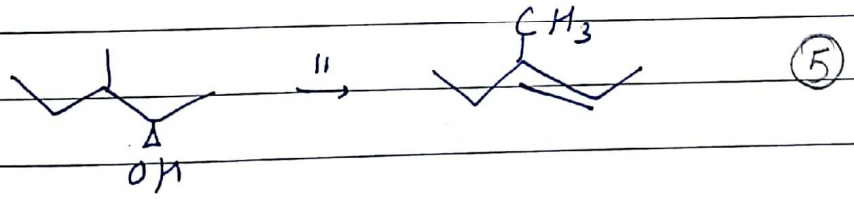
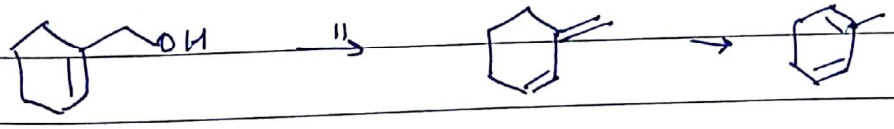
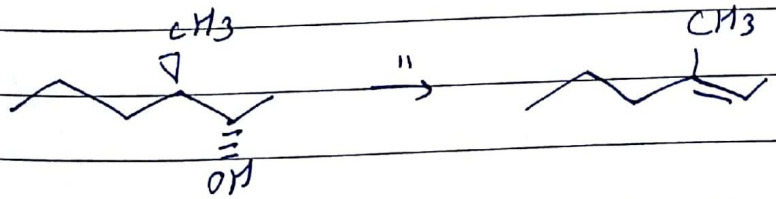
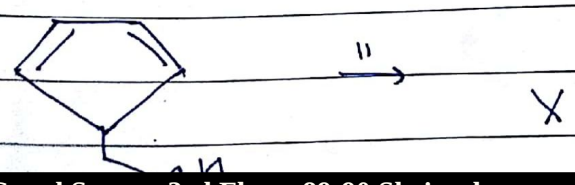
13) 

14) 

15) 

16) 

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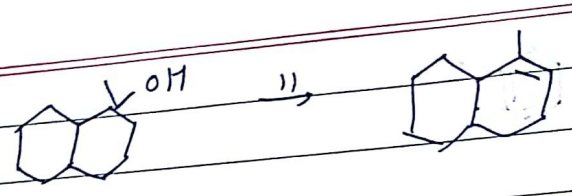
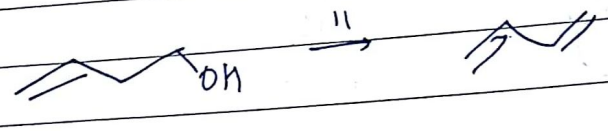
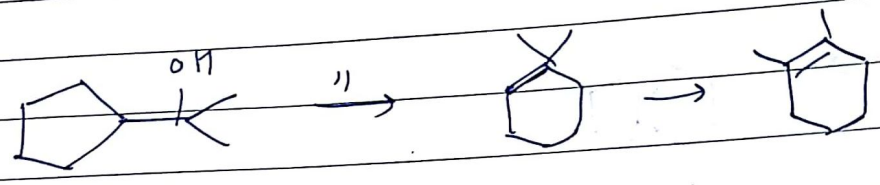
17) 

18) 

19) 

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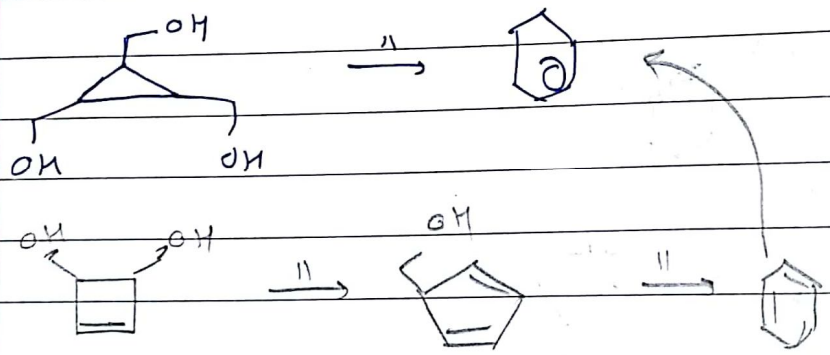
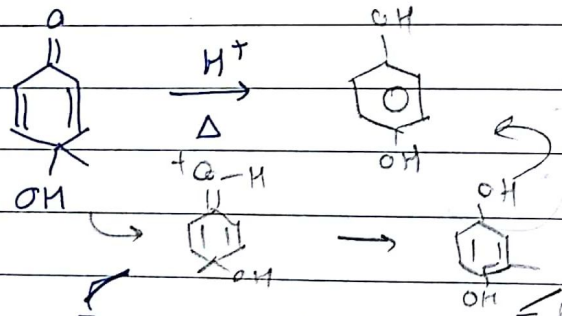
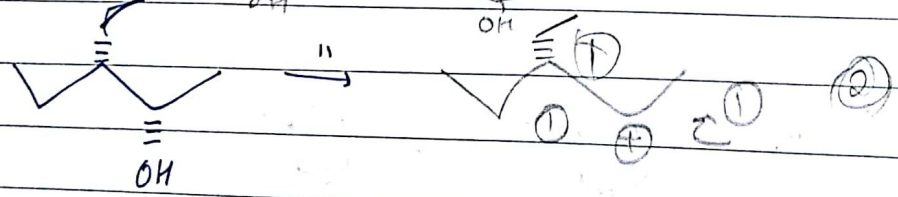
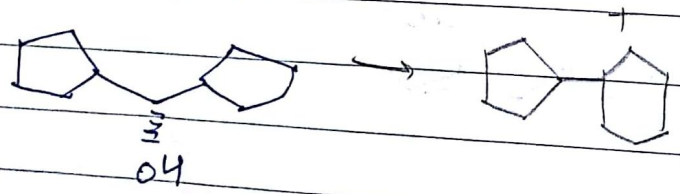


21) 

22) 

23) 

4. 1,2 shifts

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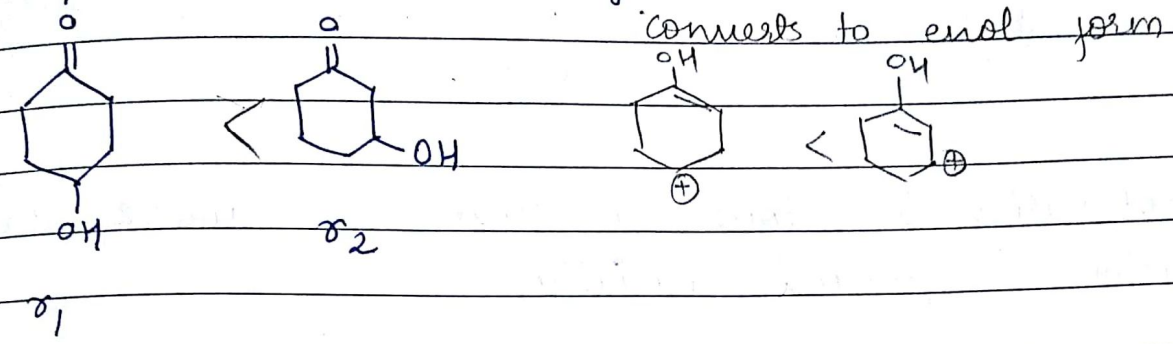
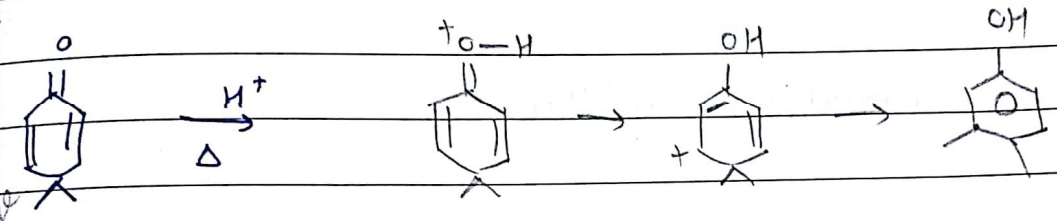
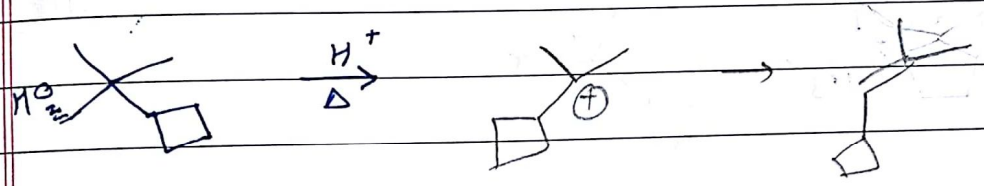
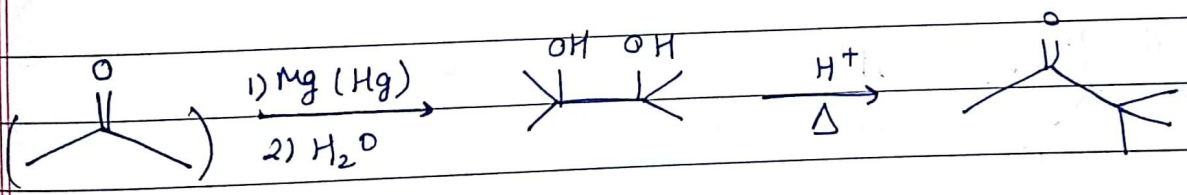
Q. compare rate of dehydration

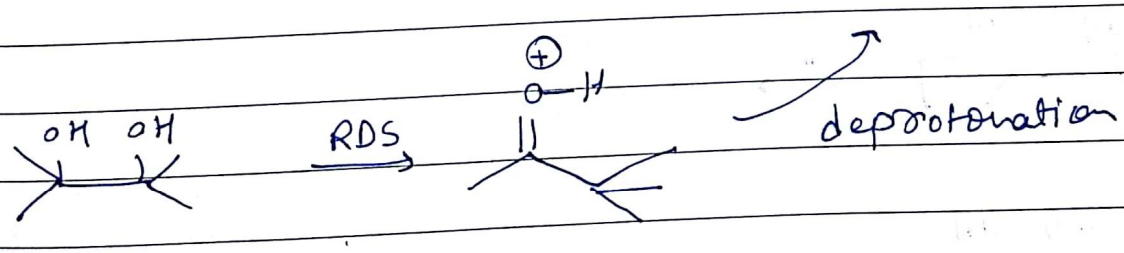
1) 

2) 

3) 

* Pinacol - Pinacolone Rearrangement :

2 

Mech 

• Migratory Aptitude :
(variable)

$-H > -Aryl > -3^\circ / -\langle\ \rangle > -2^\circ / -\prec\ \rangle > -1^\circ / St > -Cl$

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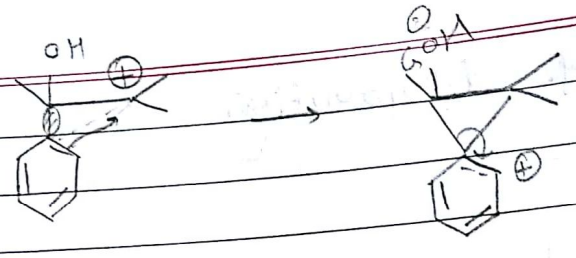
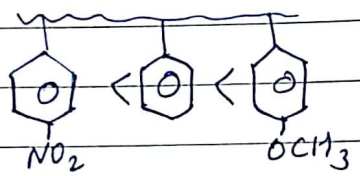
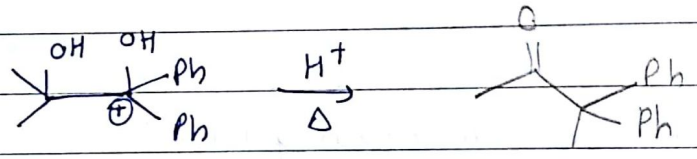


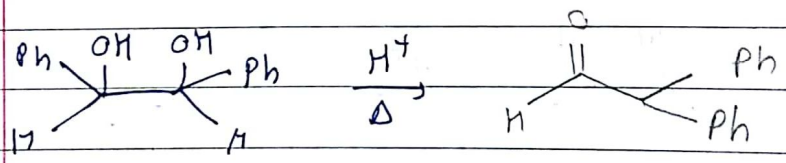
Protonation is done on that site where stable cation is formed initially.

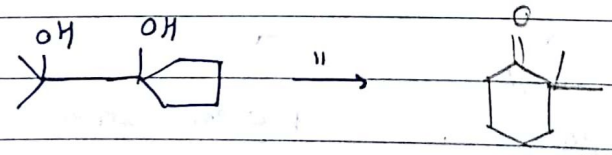
Q. Compare migration aptitude :

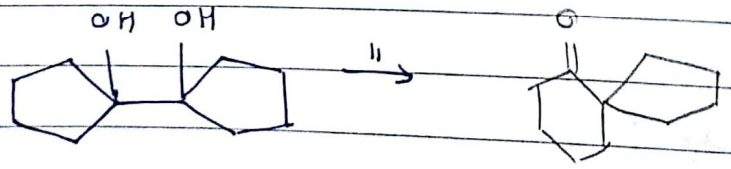
1) 

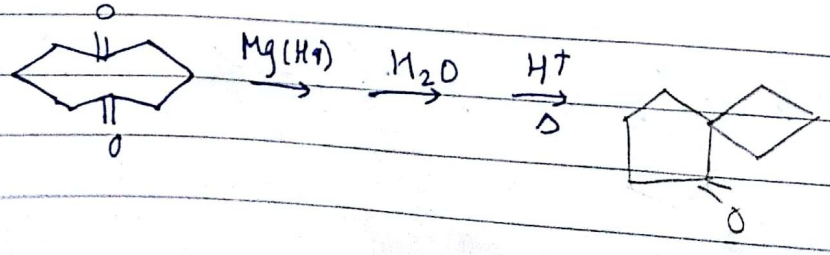
Substitution at ortho will decrease the M. Apt.

2) 

3) 

4) 

5) 

6) 

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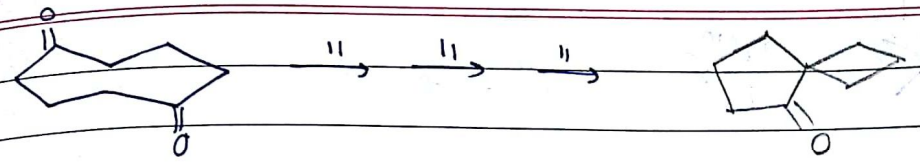
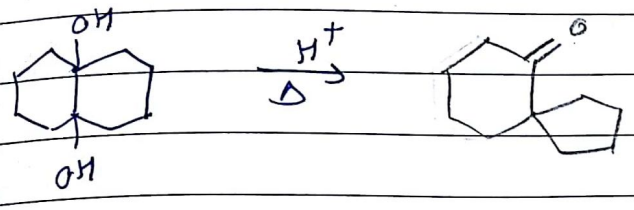
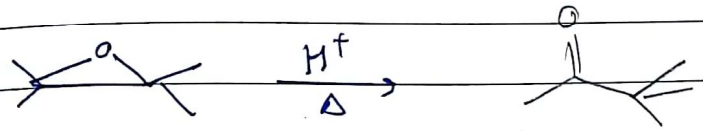
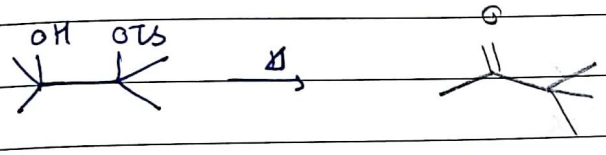
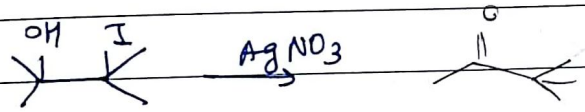
7) 

8) 

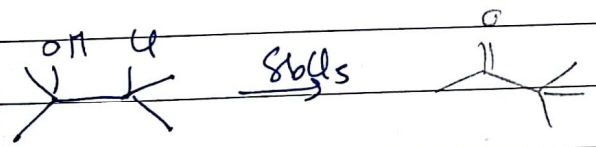
9) 

10) 

{ Semi pinacol }

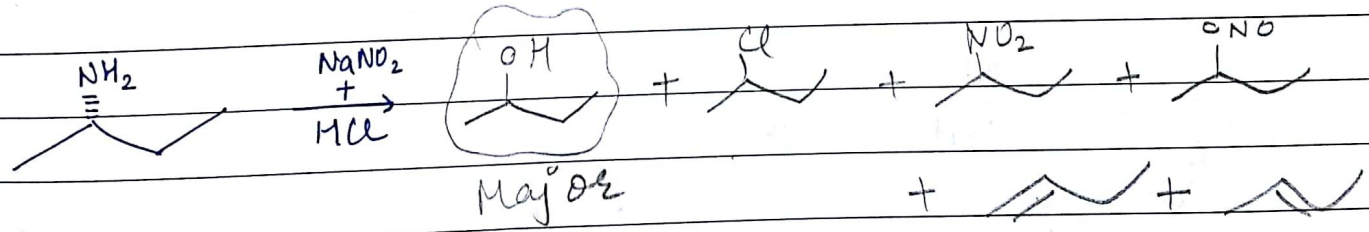
11) 

+ AgI ↓

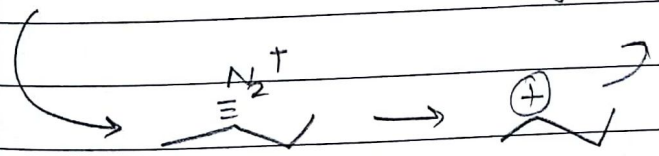
13) 

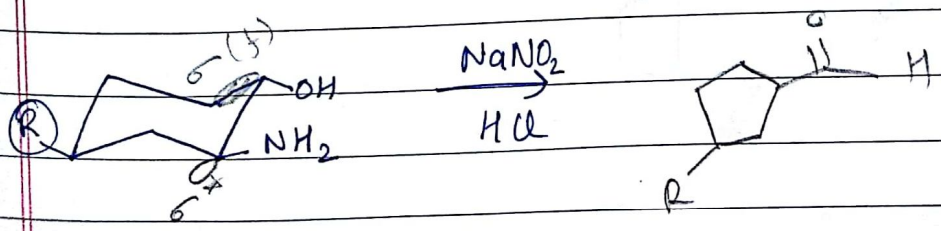
+ $SbCl_6^-$ ↓

Gazotsar

14) 

Maj OR



15) 

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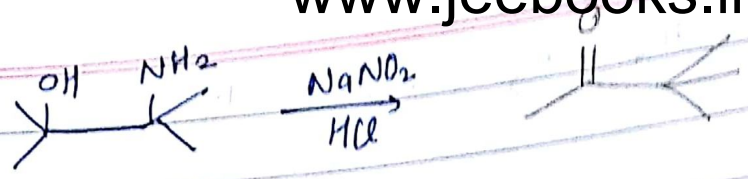
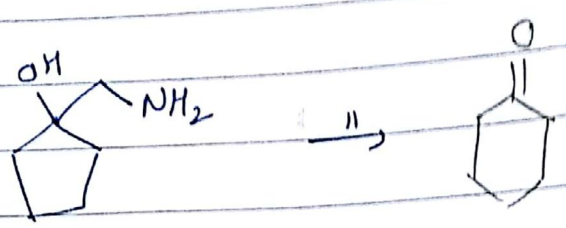
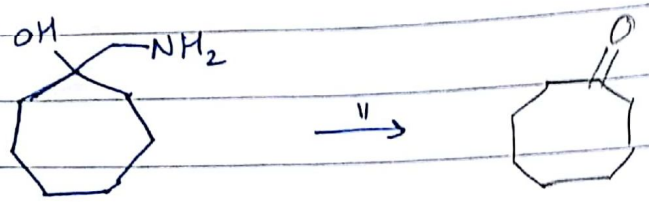
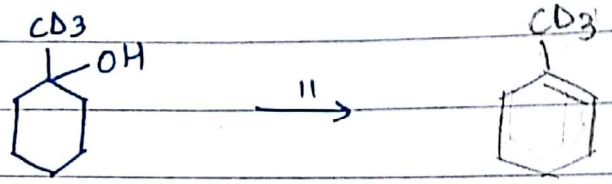
16) 

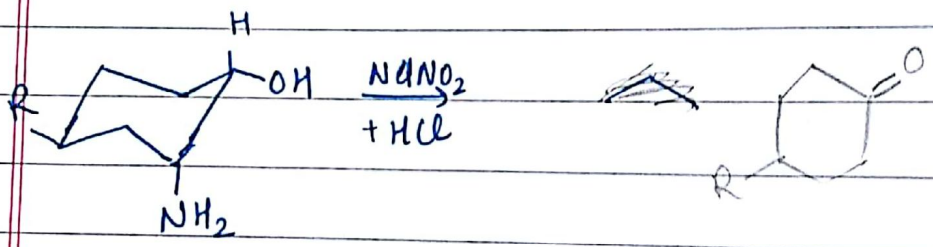
Tiffeneau-Demjanov

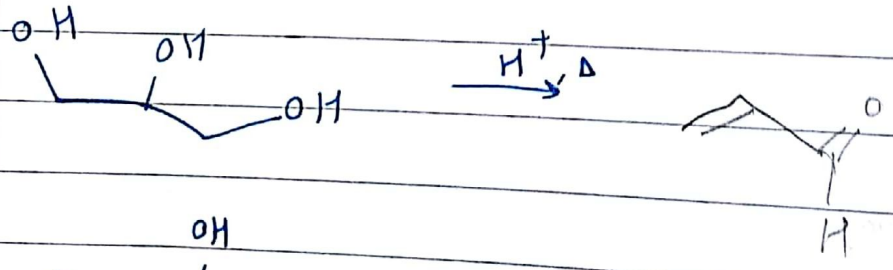
1 - 1.5 ⇒ Secondary
> 1.5 ⇒ Primary

17) 

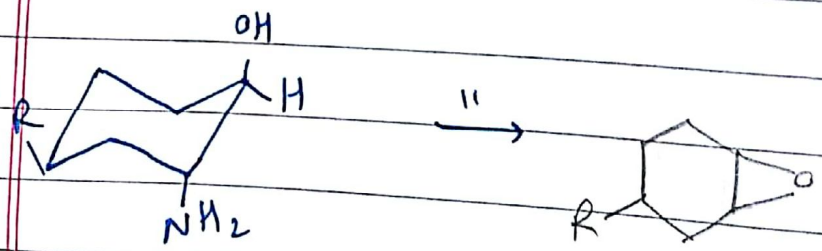
18) 

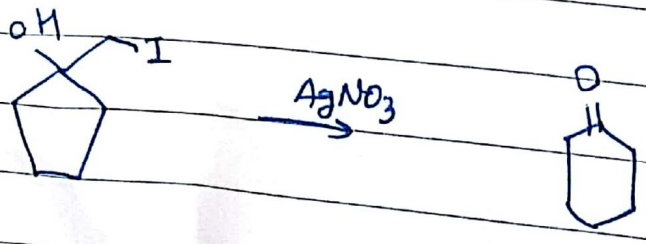
19) 

20) 

21) 

Acrolein
Pinacol + Dehydration

22) 

23) 

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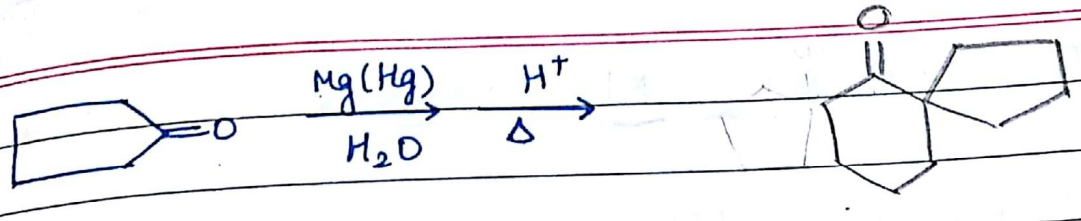
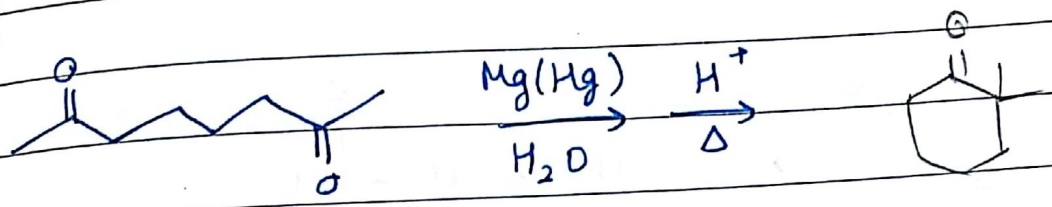
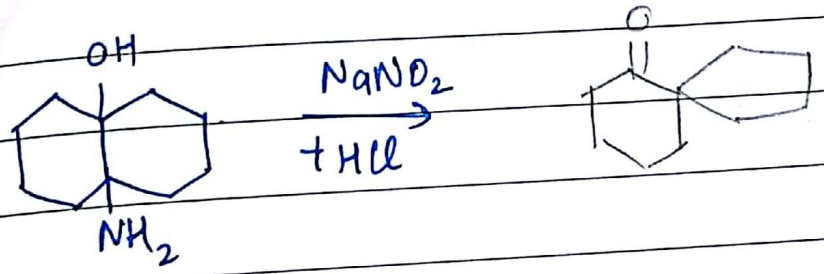
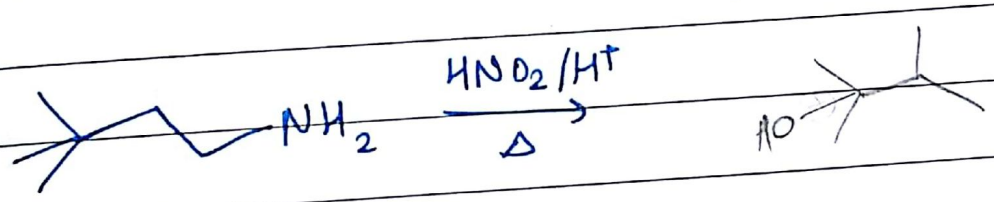
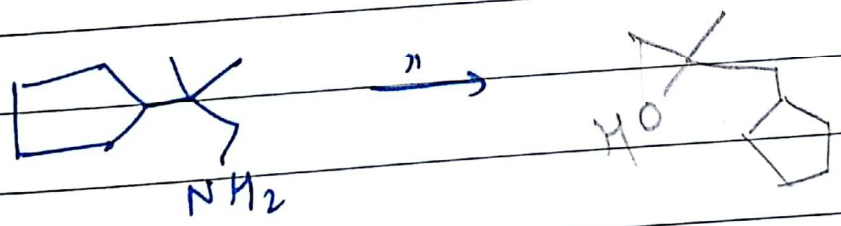
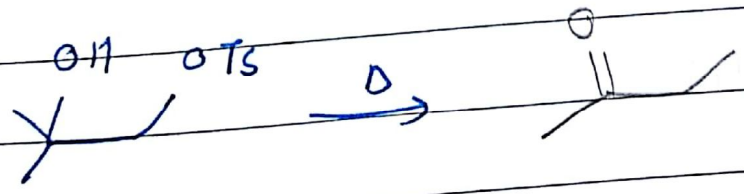
24) 

25) 

26) 

27) 

28) 

29) 

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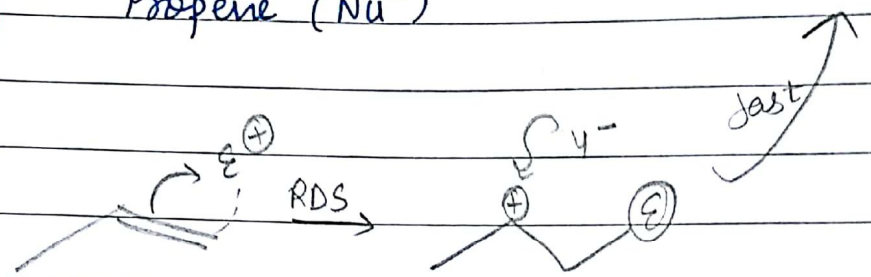
* ELECTROPHILIC ADDITION Rxns :

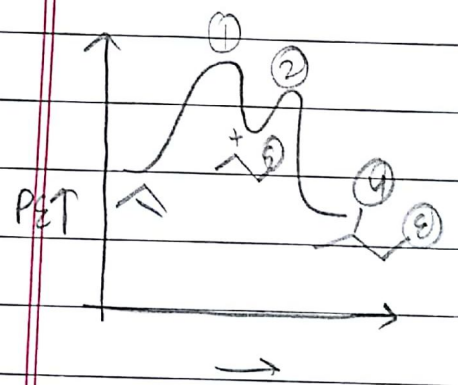
Rxns of alkenes/ynes/diene

$$CH_3-CH=CH_2 \xrightarrow{E^{\oplus}Y^{\ominus}} CH_3-\overset{Y}{\overset{|}{CH}}-\overset{E}{\overset{|}{CH_2}}$$

Propene (Nu^-)

Mech



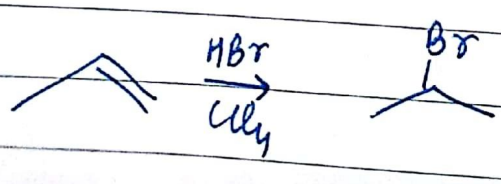


R ∝ Stab. of $C^{\oplus}$

- Formation of C^+ is RDS

- Markovnikov (M.K) Rule :

Electrophile is added to the 'C' having more no. of hydrogens.



(M.K. product)

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Q. Compare rate of electrophilic addⁿ

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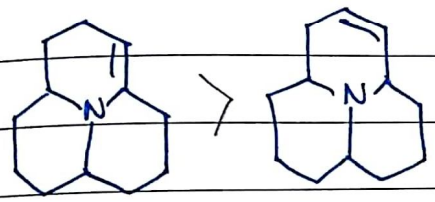
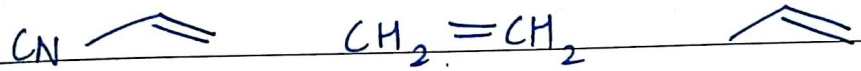
1) $CH_2 = CH_2$

a > c > b > d

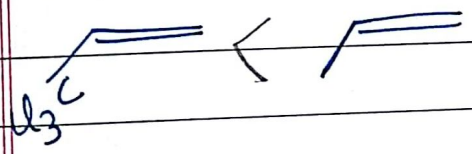
2) $CH_2 = CH_2$ $CH_2 = CH - CH_3$ $CH_3 = CH - Cl$ $CH_2 = CH - OCH_3$

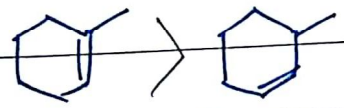
d > b > a > c

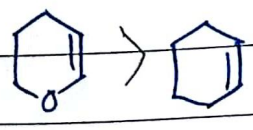
3) 

4) 

* c > b > a

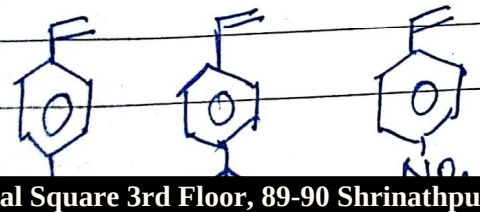
5) 

6) 

7) 

8) $CH_2 = CH_2 > H - C \equiv C - H$

9)

10) 

a > b > c

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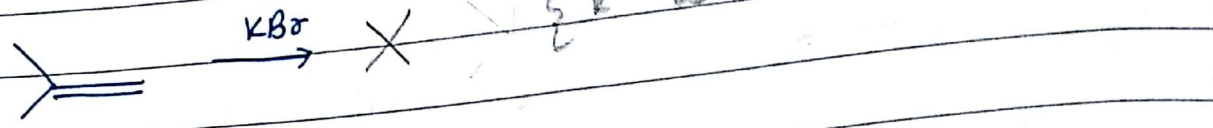
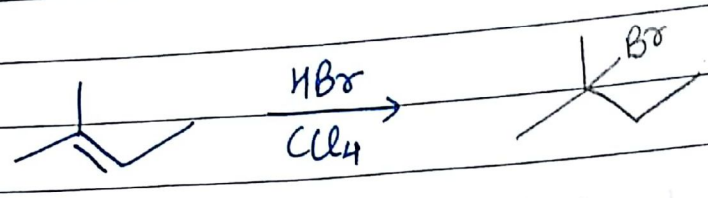
1.) 

{K^+ is not electrophile}

2) 

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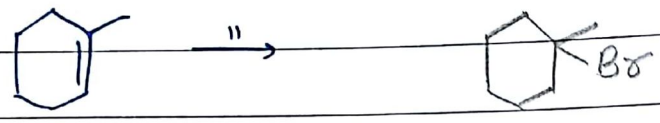
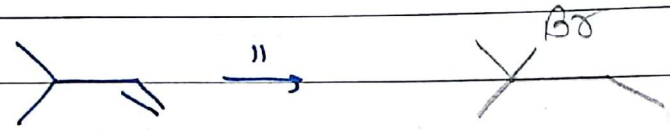
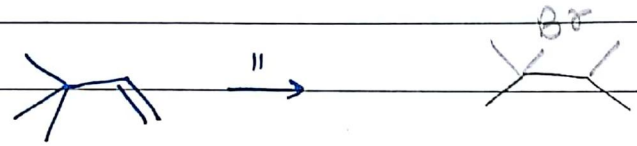
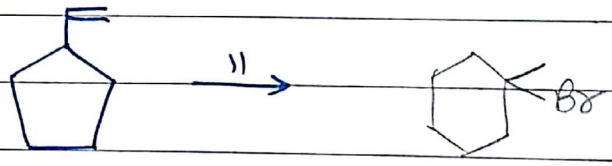
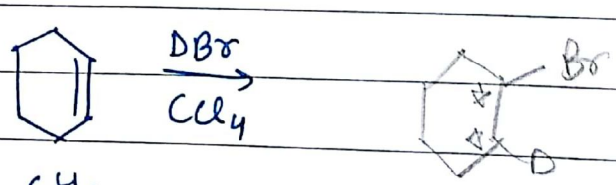
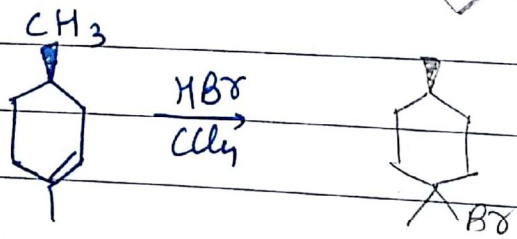
4) 

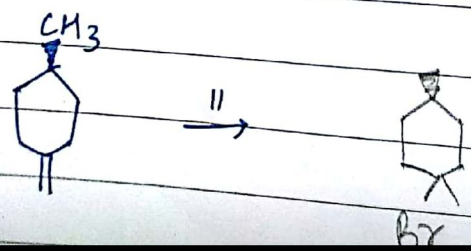
5) 

6) 

7) 

8) 

9) 

10) 

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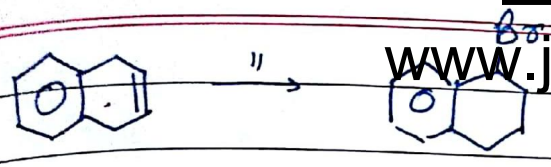
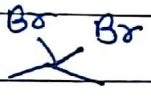
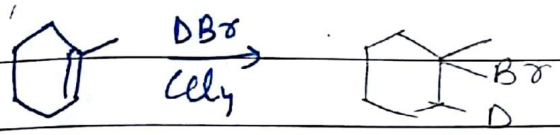
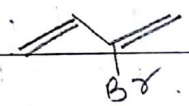
11) 

12) $CH_3-\underset{\underset{Br}{|}}{C}=CH_2 \xrightarrow[CCl_4]{HBr}$

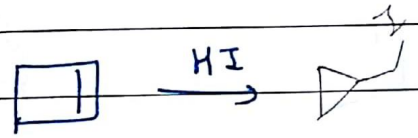
13) $CH_3-C\equiv CH \xrightarrow[CCl_4]{HBr}$ 

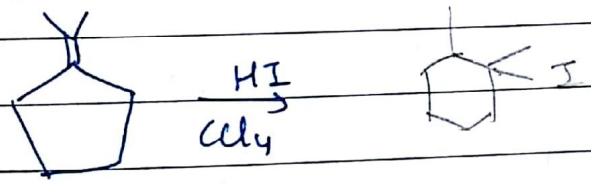
14) 

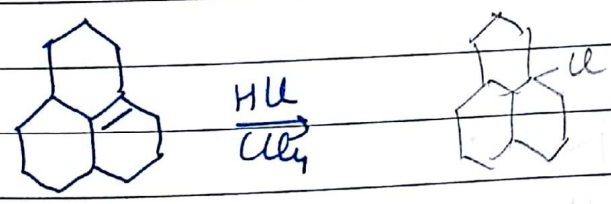
★ 15) $H_2C=CH-C\equiv CH \longrightarrow$ 

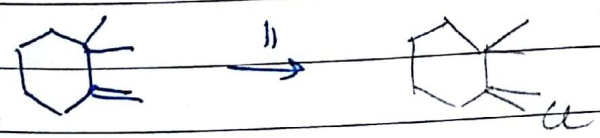
(When alkene & alkyne are in conj. attack will take place on alkyne)

16) $H_2C=CH-CH_2-C\equiv C-H \longrightarrow H_3C-\underset{\underset{Br}{|}}{CH}-CH_2-C\equiv C-H$

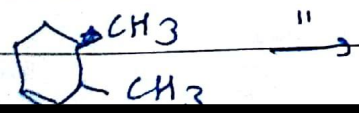
✕ 17) 

18) 

19) 

20) 

21) $O_2N-CH=CH_2 \xrightarrow{\parallel} O_2N-CH_2-CH_2Br$

22) 

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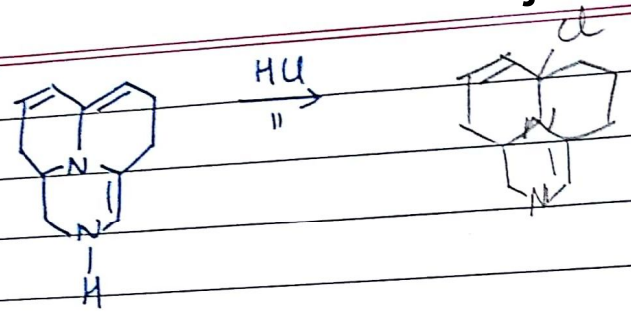
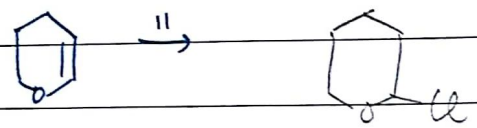
23) 

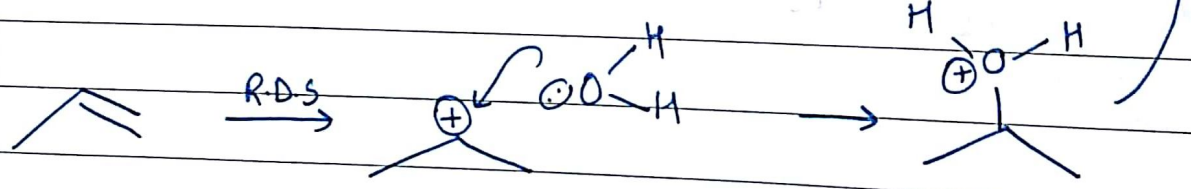
24) $CH_3-O-CH=CH_2 \xrightarrow[CCl_4]{HCl} CH_3-O-\underset{}{\overset{Cl}{CH}}-CH_3$

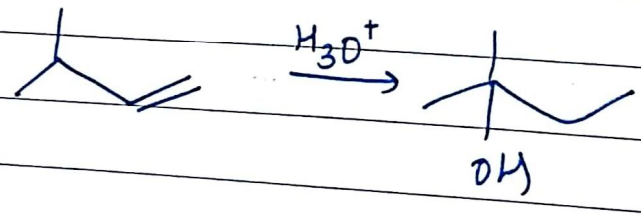
25) 

* Acid Catalysed Hydration :

$$CH_3-CH=CH_2 \xrightarrow[\text{dil. } H_2SO_4 \text{ or } H^+/H_2O]{H_2O} \text{OH}$$

Mech.





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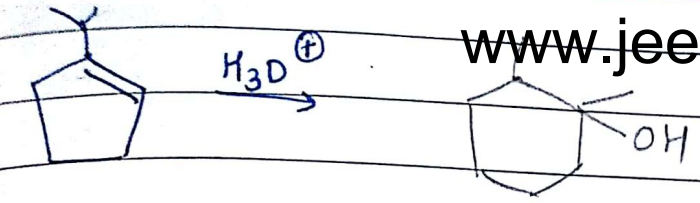
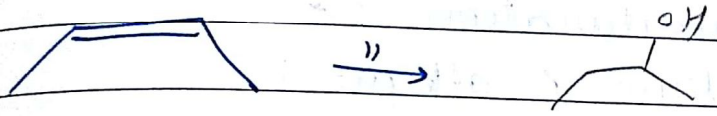
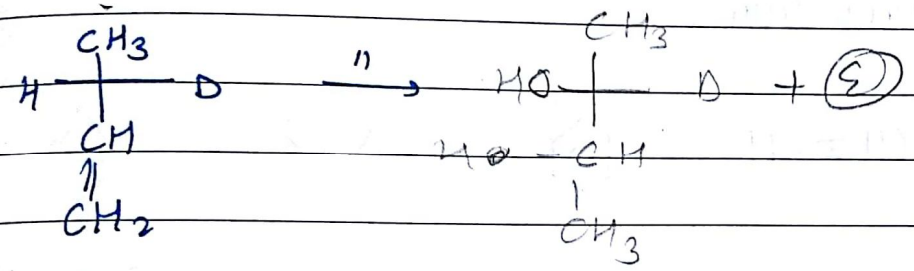
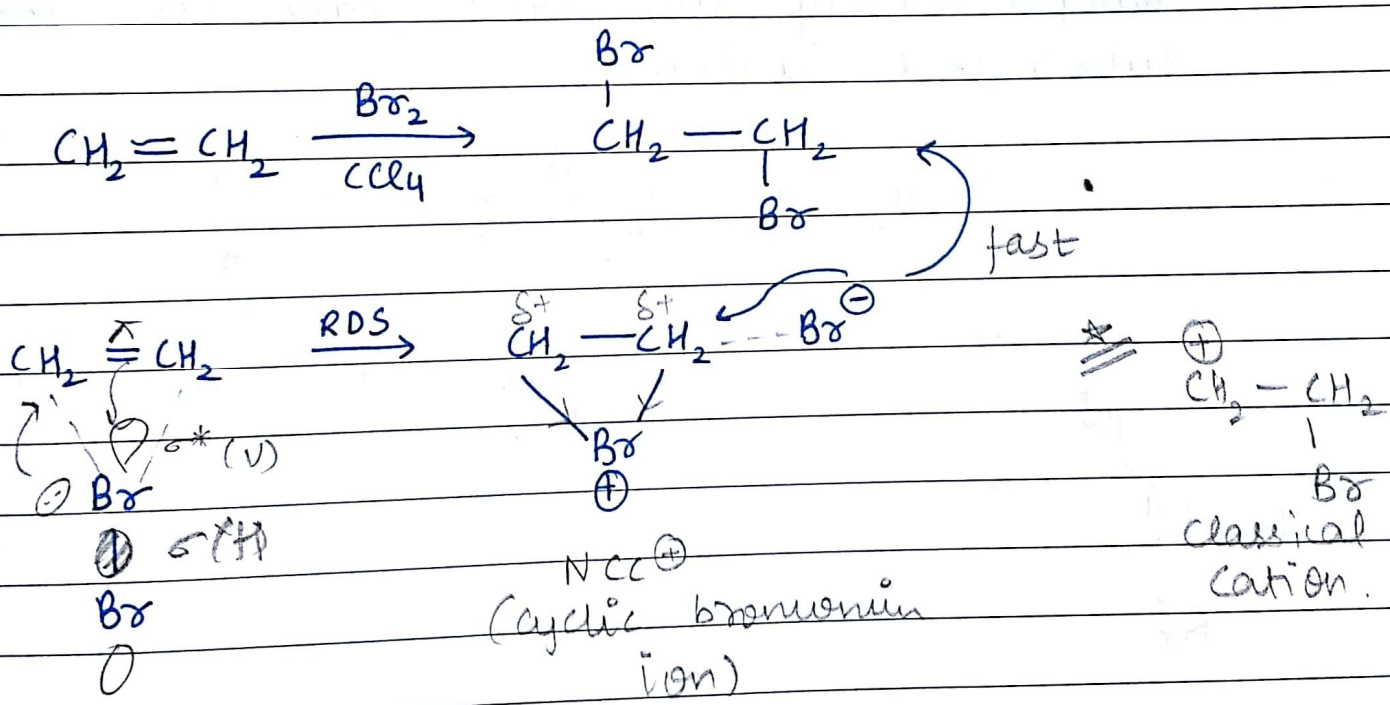
1) 

2) 

cis-2-butene

3) 

* <u>Addition of Br_2 on alkene / alkyne</u> :



- In this rxn, non classical cation is formed particularly cyclic halonium ion.
- It is more stable than classical cation coz o completed octet & formation of new σ bond.
- Br^- will attack from the opp. side of the cyclic halonium ion in order to minimise rep

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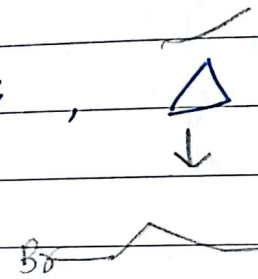
- Rate of halogenation,

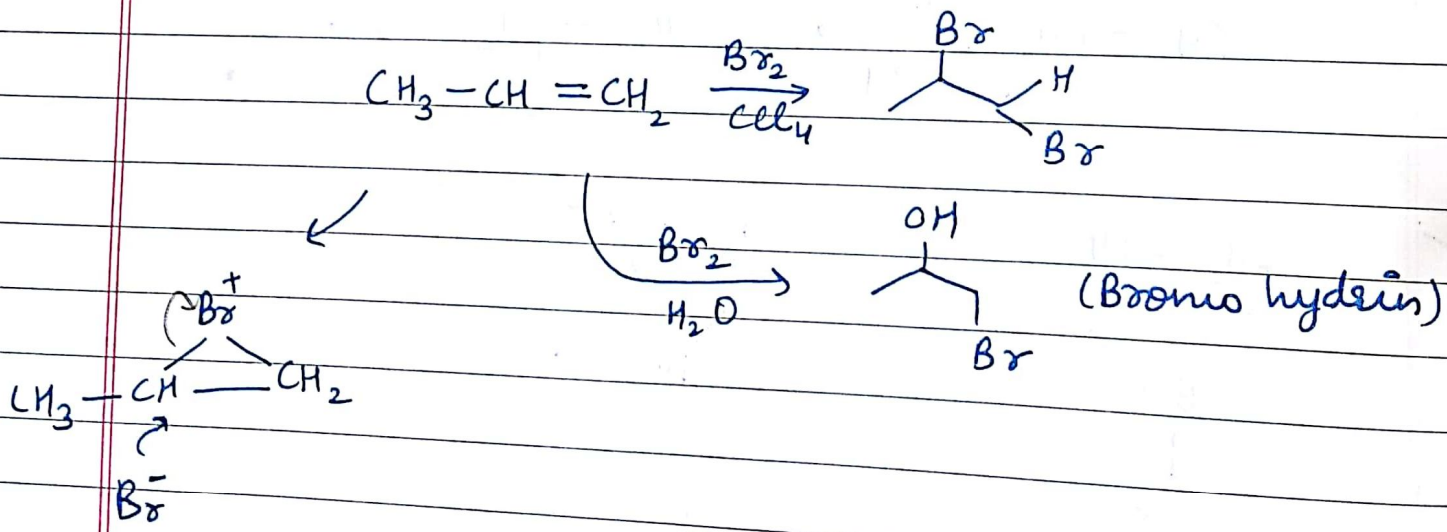
$Cl_2 > Br_2 > I_2$

- It is a test for unsaturation (alkene & alkyne)

Obs : Brown colour of the sol^n disappears (Decolourisation)

$CH_2 = CH_2$, $CH \equiv CH$, , , 

- In case of unsymmetrical attack of -vely charged entity will take place on more substituted carbon.



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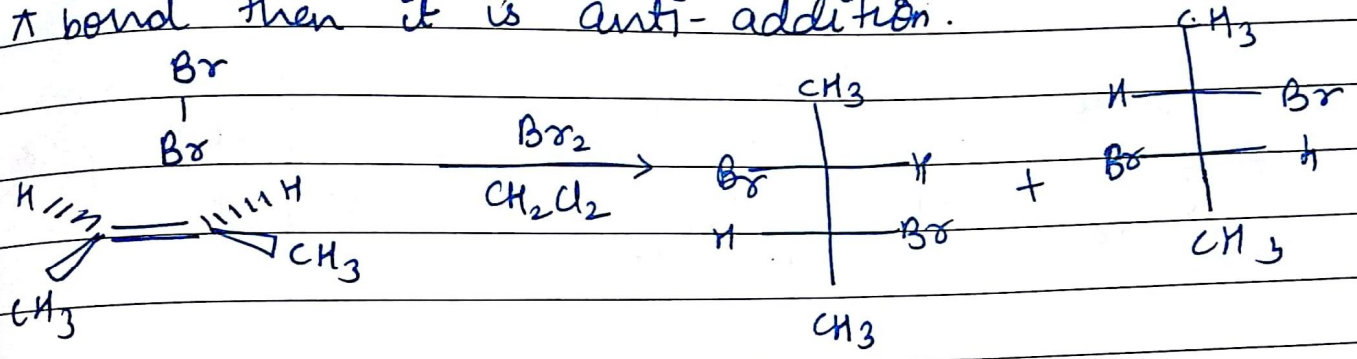
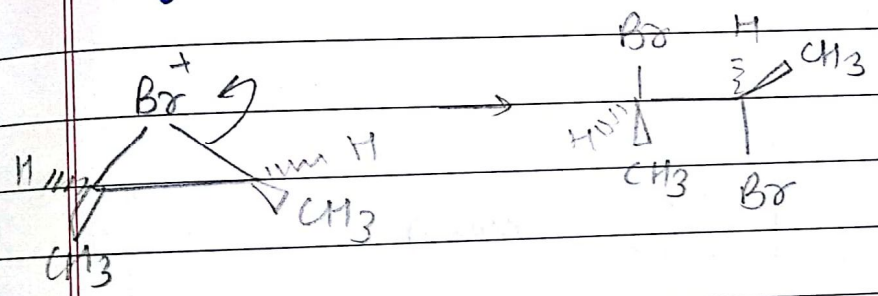
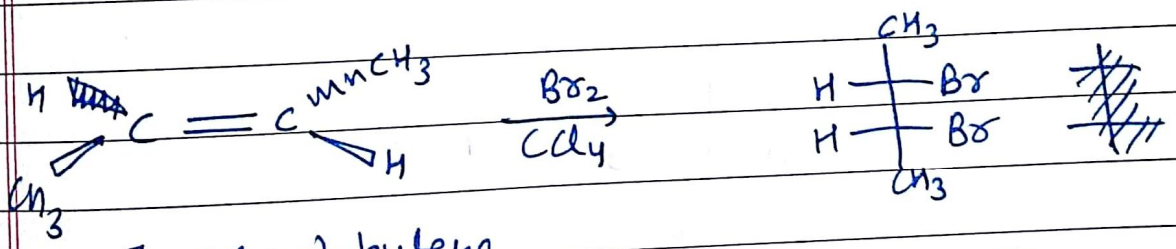
* Anti - Addition :→

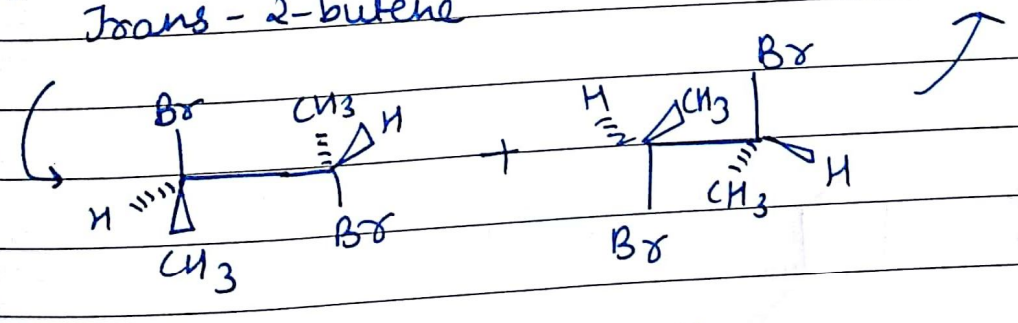
When atoms are added on the opp. sides of π bond then it is anti-addition.

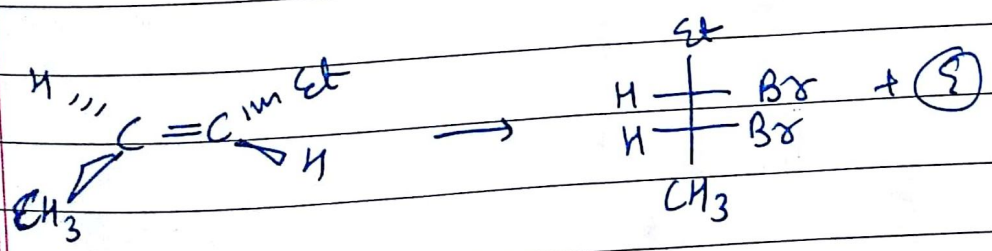




• 

Trans - 2-butene



• 

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em! • Short trick :

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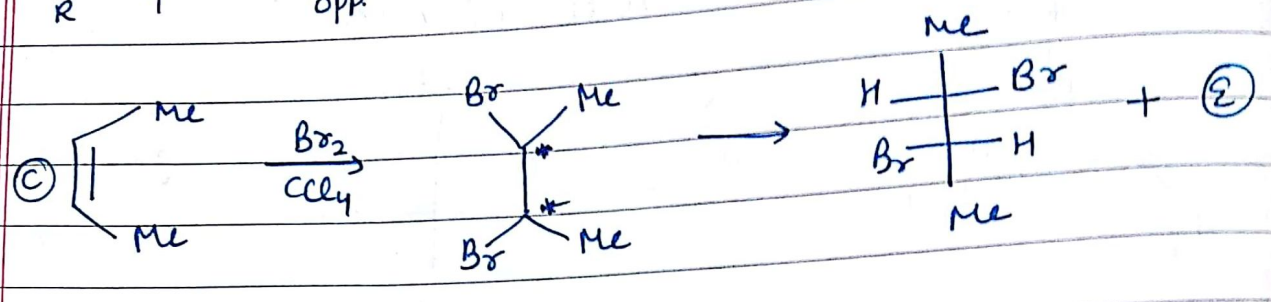
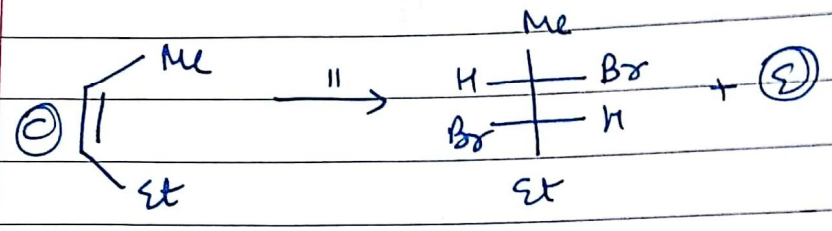
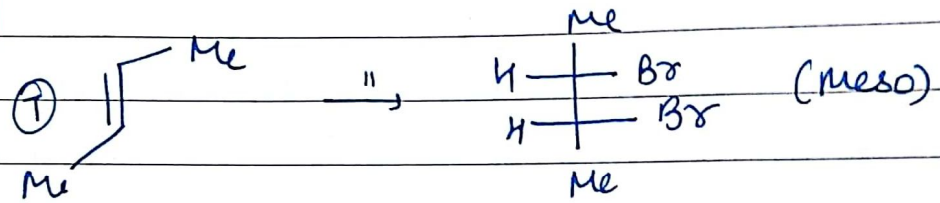
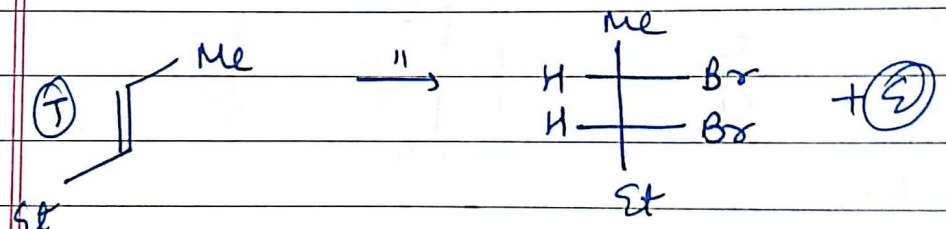
R T opp.

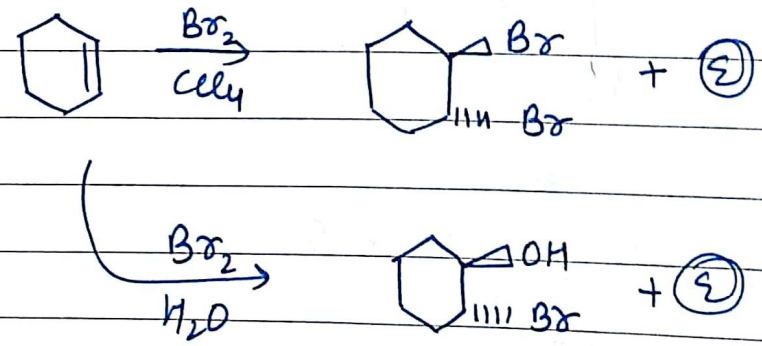








1)



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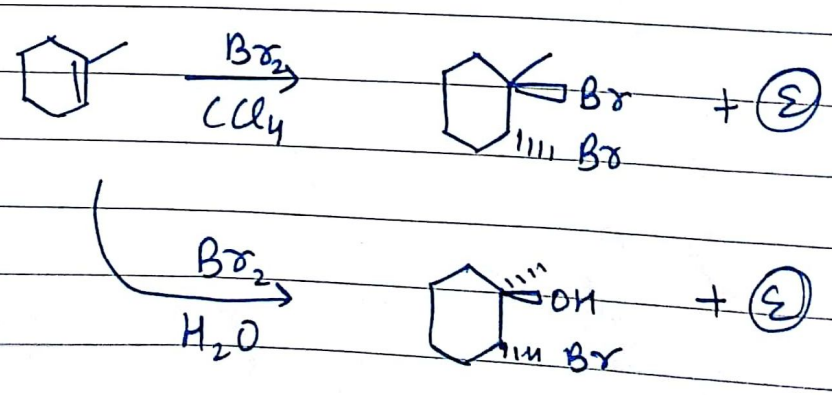

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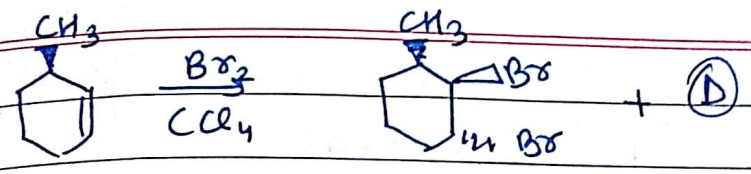
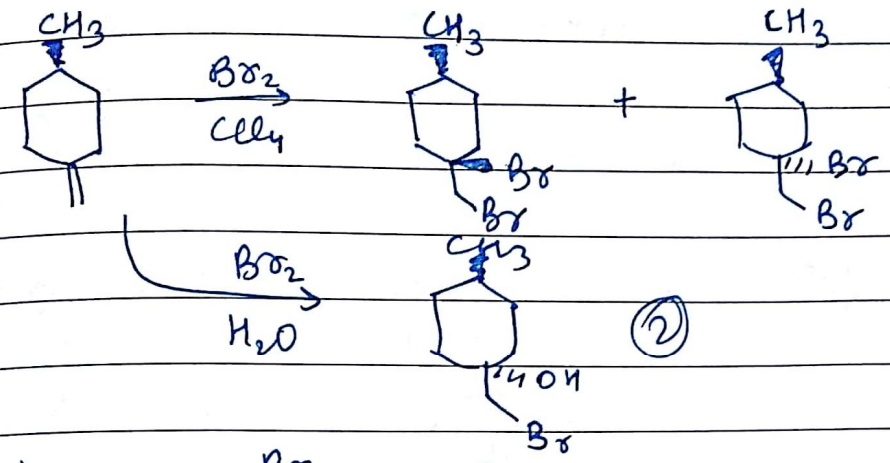
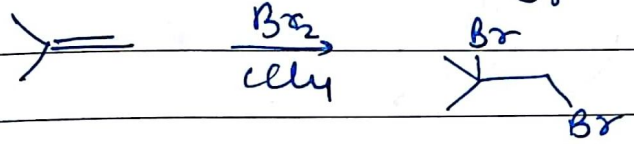
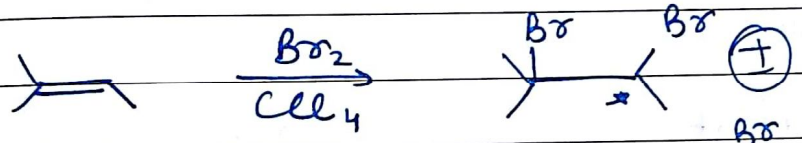
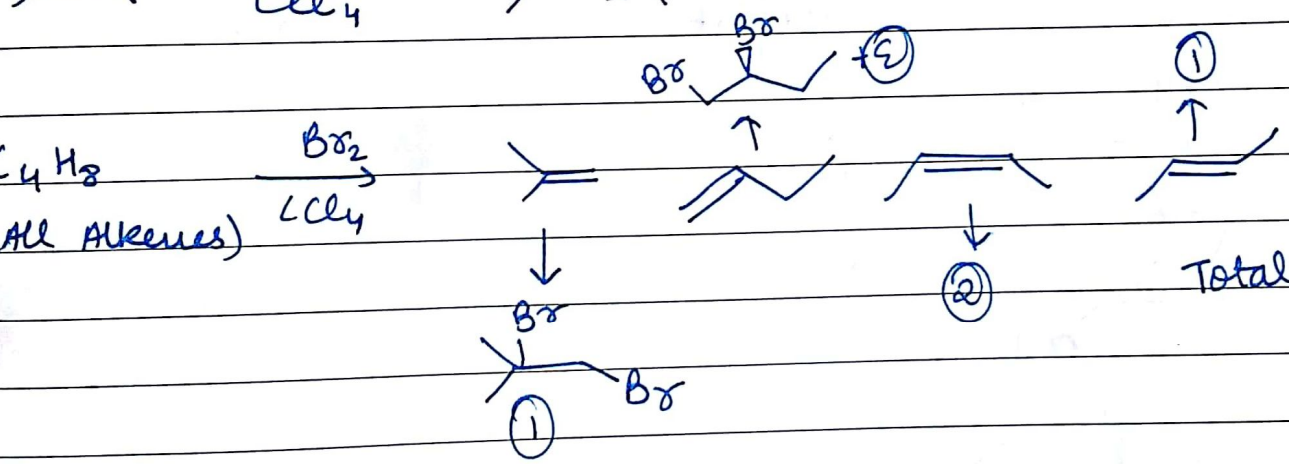
CPP #3
11 to 23
DPP #21 (2,3x)

3) 

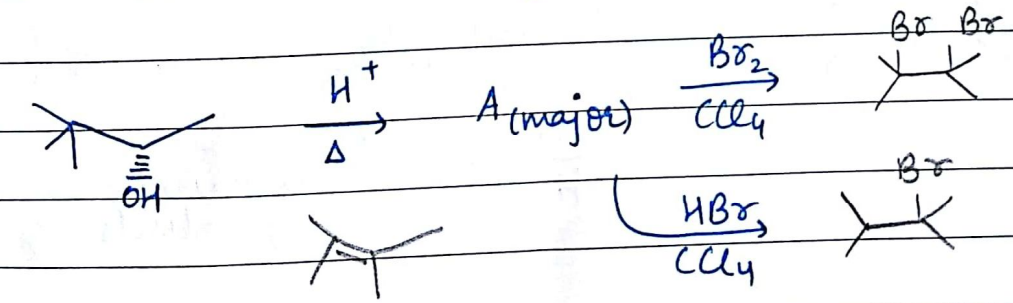
4) 

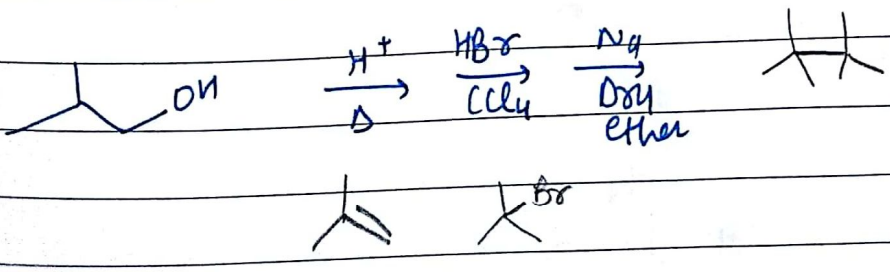
5) 

6) 

7) C_4H_8 (All Alkenes) 

Total = 6

8) 

9) 

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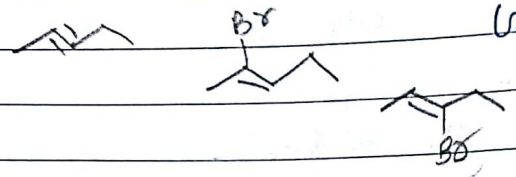
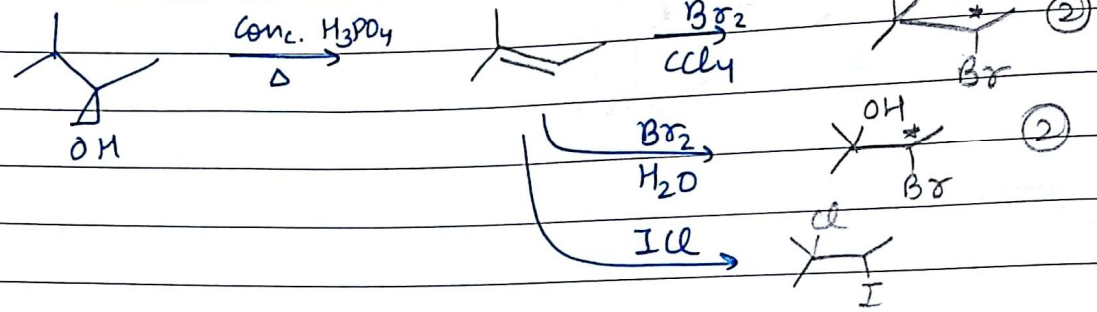
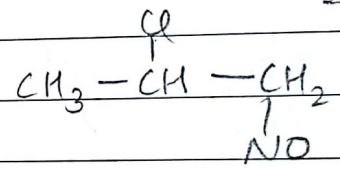
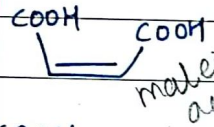
10) 2-Pentyne $\xrightarrow[CCl_4]{HBr\,(1eq)}$ "X" Long^n Isomers (2) + (2)
"Y" Structural (1) + (1)
(X+Y) ? (6)

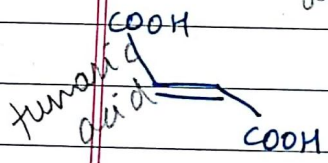


11) 

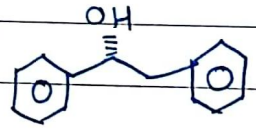
12) $CH_3-CH=CH_2 \xrightarrow[\text{Tilden's reagent}]{NOCl}$ 

13) 

$\xrightarrow[CCl_4]{Br_2}$ (2)



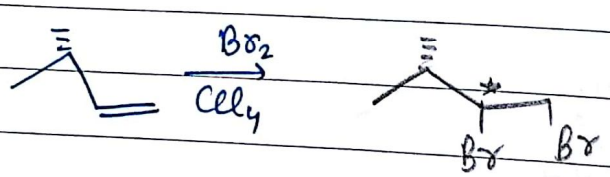
$\xrightarrow{''}$ (1)

14) 

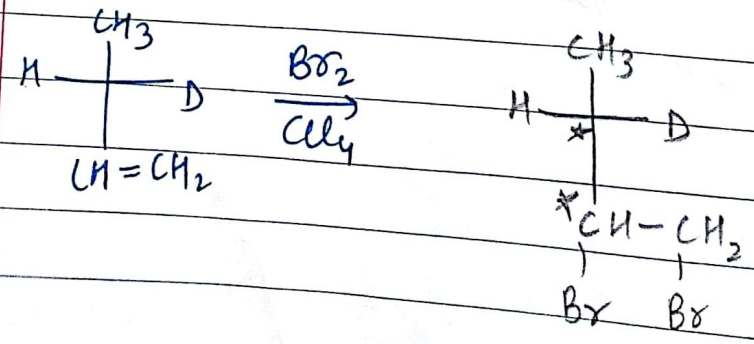
$\xrightarrow[\Delta]{Conc\ H_2SO_4}$ "X" Isomeric products (2)

$\xrightarrow[H_2O]{Br_2}$ "Y" isomeric products (3)

$\boxed{5}$

15) 

(2)

16) 

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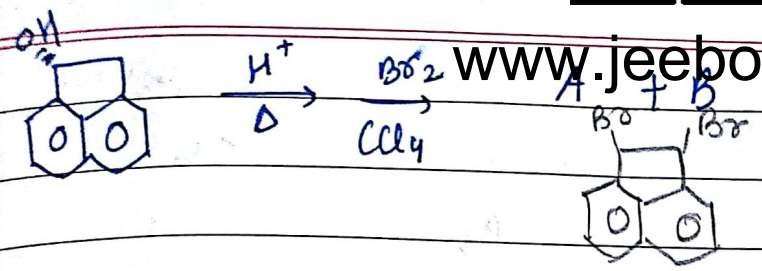
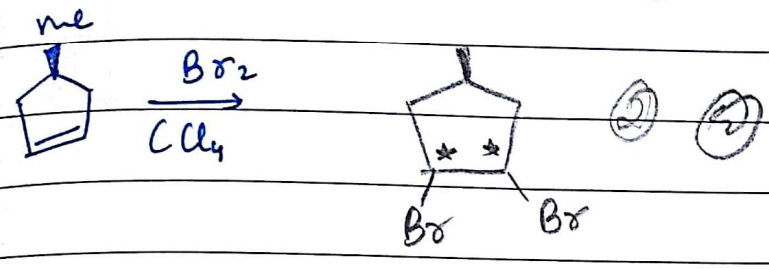
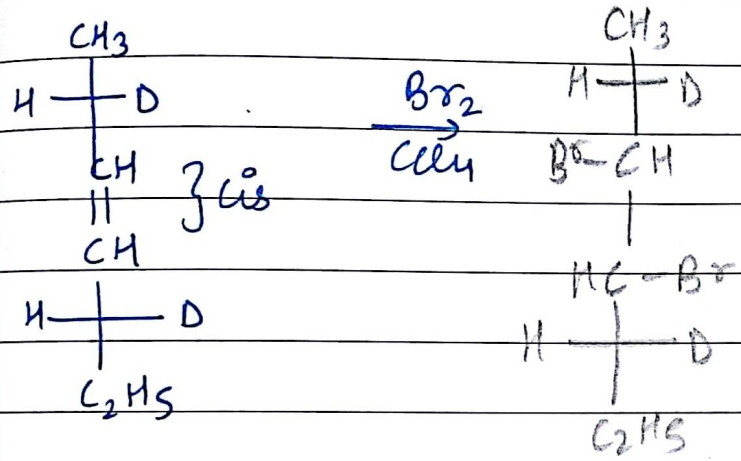
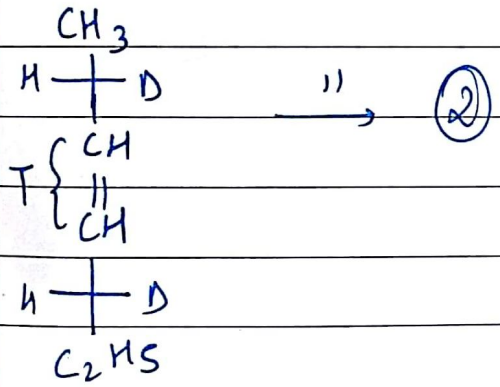
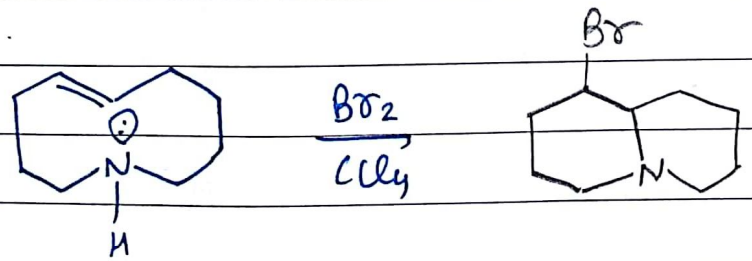
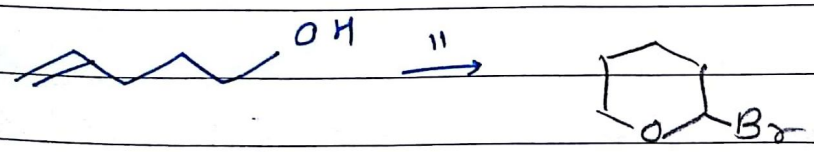
17) 

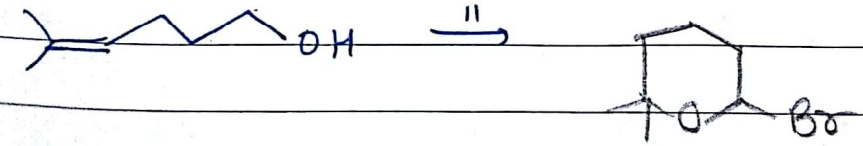
18) 

19) 

20) 

21) 

22) 

23) 

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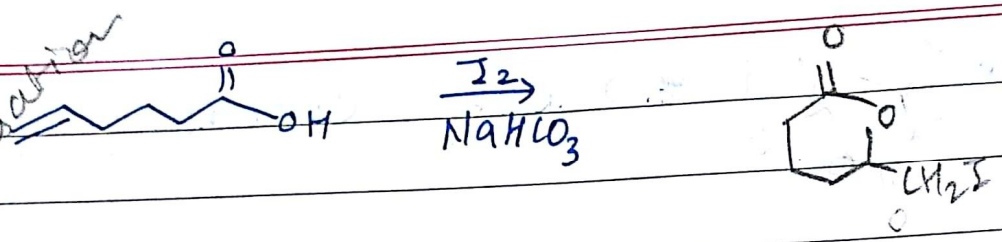
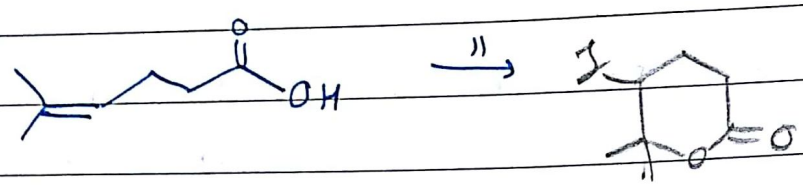
24) Iodo halogenation



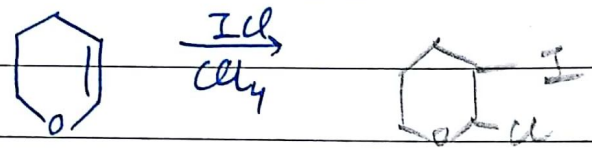
Lactonisation
formation of ester

25)



26) $O_2N-CH=CH_2 \xrightarrow[CCl_4]{IBr} O_2N-\underset{I}{CH}-\underset{Br}{CH_2}$

27)



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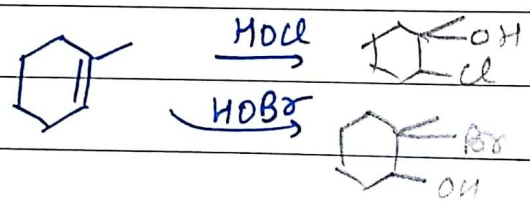

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* PEROXIDE EFFET / A.M.K Rule / Kharasch Effect :→

- When HBr is added to alkene in presence of peroxide then anti markonikov product is major.

$$CH_3-CH=CH_2 \xrightarrow[\text{Peroxide}]{HBr} CH_3-CH_2-CH_2-Br.$$

Alkene

(R_2O_2)

$(Ph-\overset{O}{\overset{\|}{C}}-O_2)$ | Benzoyl Peroxide

(R)

MECH

Radical initiator $\{ R-O-O-R \longrightarrow 2(R-O^{\bullet})$

$$RO^{\bullet} + H-Br \longrightarrow ROH + Br^{\bullet}$$

$$CH_3-CH=CH_2 + Br^{\bullet} \longrightarrow CH_3-\dot{C}H-CH_2-Br$$

2° (5 α H)

$$CH_3-CH(Br)-\dot{C}H_2$$

1° (1 α H)

$$CH_3-\dot{C}H-CH_2-Br \longrightarrow CH_3CH_2-CH_2-Br + Br^{\bullet}$$

- Anti Markonikov addⁿ will take place in order to form a stable free radical.

- It is free radical addition

- Rearrangement is not possible.

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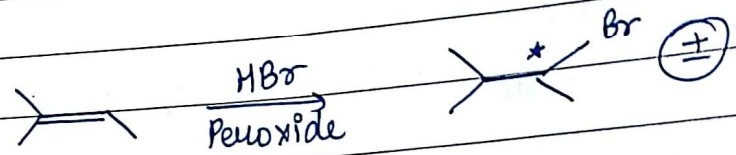
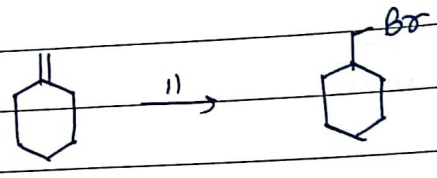
DPP.

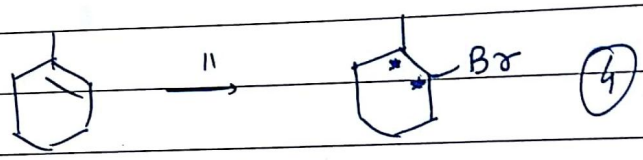
It is applicable only for HBr. In case of HCl, HI markonikov add^n takes place even in the presence of peroxide. In HCl, HI one of the step is endothermic in each case.

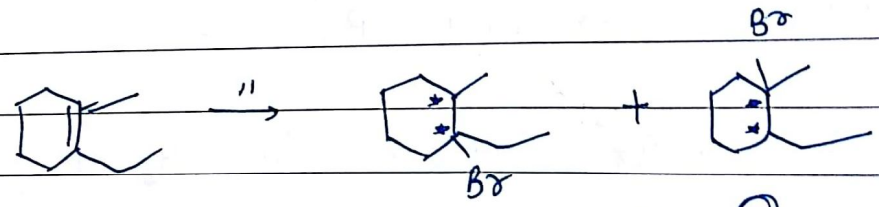
Termination also completed

Q.

1) 

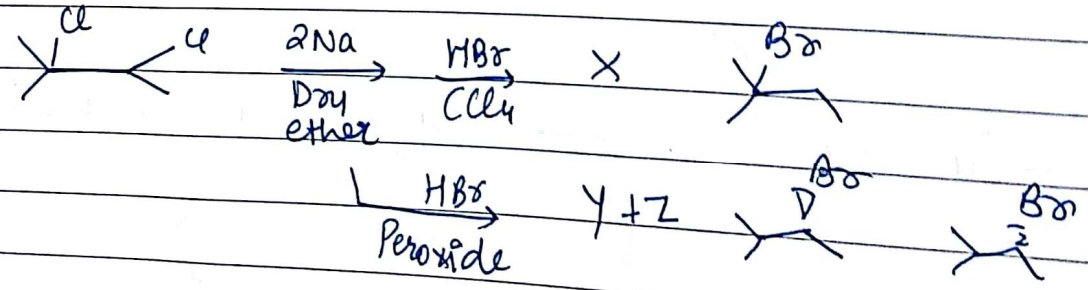
2) 

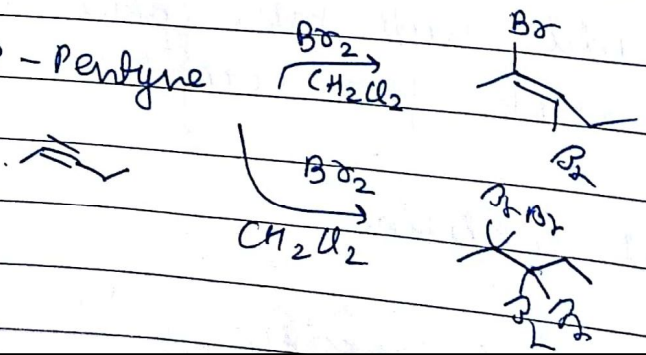
3) 

4) 

SI = 2

CI = 8

5) 

6) 2 - Pentyne 

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7) $H-C\equiv C-H \xrightarrow{HOCl} H-\overset{O}{\overset{\|}{C}}-CH_2Cl$

$\xrightarrow{HOCl(2)} H-\overset{O}{\overset{\|}{C}}-CHCl_2$

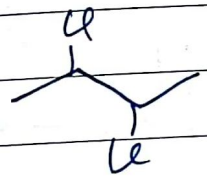
$\xrightarrow{HOCl(xs)} HO-\overset{O}{\overset{\|}{C}}-CCl_2$

* HOCl will oxidise aldehyde to carboxylic acid

8) $CH_3-C\equiv C-H \xrightarrow{HOCl} CH_3-\overset{O}{\overset{\|}{C}}-CH_2Cl$

$\xrightarrow{HOCl(2)} CH_3-\overset{O}{\overset{\|}{C}}-CHCl_2$

$\xrightarrow{HOCl\ (xs)} -\overset{O}{\overset{\|}{C}}-CHCl_2$

9) 

$\xrightarrow[\text{Boil}]{2Na}$ $\xrightarrow{Br_2/H_2O}$ (4)

$\xrightarrow{Br_2/CCl_4}$ (3)

9

10)

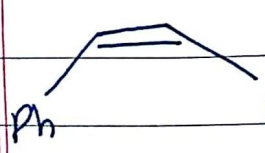
$\xrightarrow[\Delta]{H^+}$ 'X' prod (3)

$\xrightarrow[CCl_4]{Br_2}$ 4 Products (2)

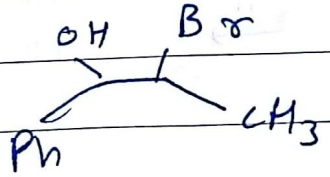
8

11) $CH_2=C=O \xrightarrow{HCl} H-\overset{O}{\overset{\|}{C}}-CH_2Cl$

ketene

12) 

$\xrightarrow{ICl}$

$\xrightarrow{HOBr}$ 

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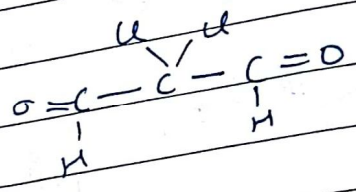
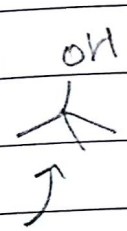
13) $CH_2=C=O \xrightarrow[CH_3OH]{H^+}$

14) $O=C=C=C=O \xrightarrow{HCl(g)}$ 

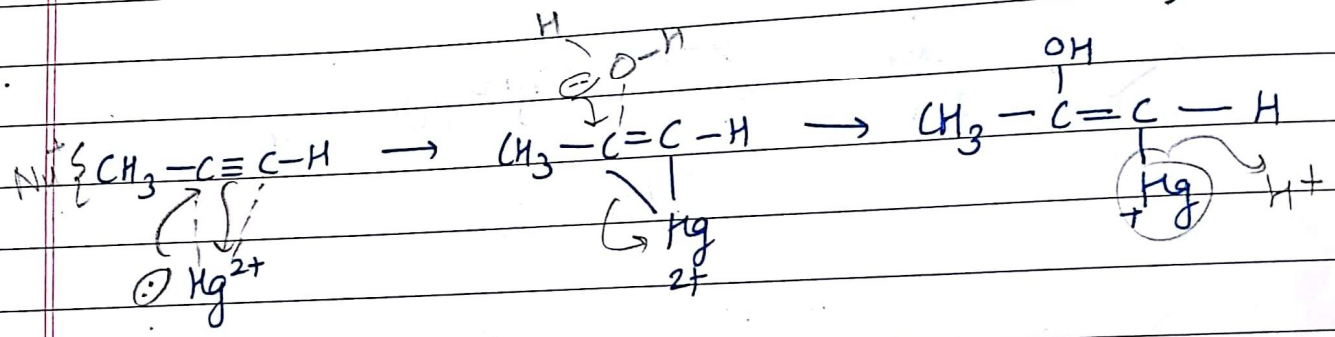
* KUCHEROV'S Rxn :→

(Hydration of Alkynes)

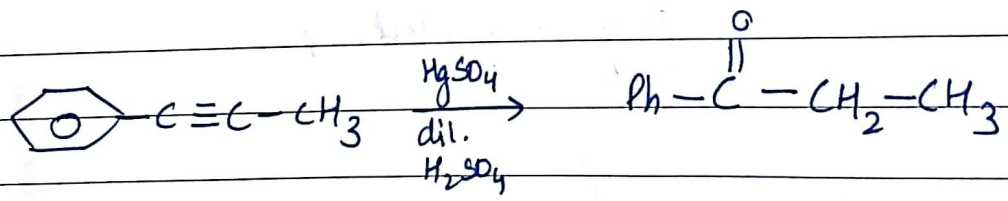
$$CH_3-C\equiv C-H \xrightarrow[C.A.T]{HgSO_4 / dil.\ H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$



Mech.



Q.

1) 

2) $Ph-C\equiv C-Ph \xrightarrow{''} Ph-\overset{O}{\overset{\|}{C}}-CH_2-Ph$

3) $NO_2-C\equiv C-H \xrightarrow{''} NO_2-CH_2-\overset{O}{\overset{\|}{C}}-H$

4) $CH_3-O-C\equiv C-H \xrightarrow{''} CH_3-O-\overset{O}{\overset{\|}{C}}-CH_3$

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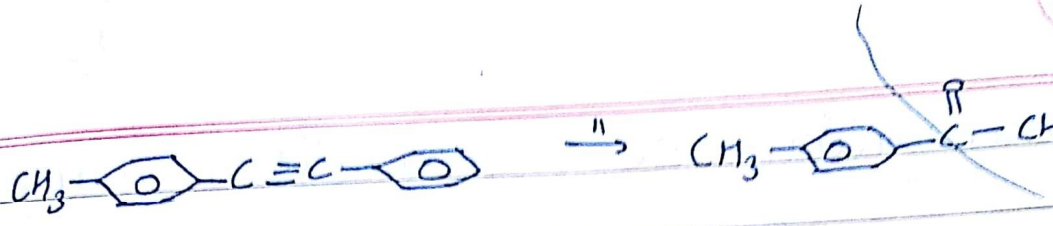
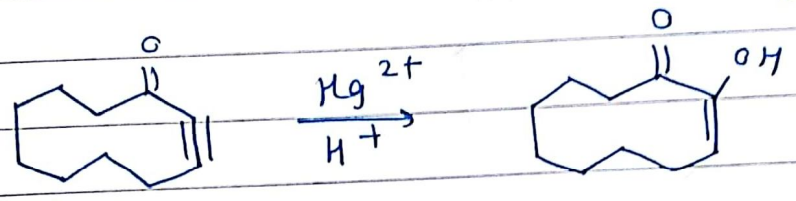
5) 

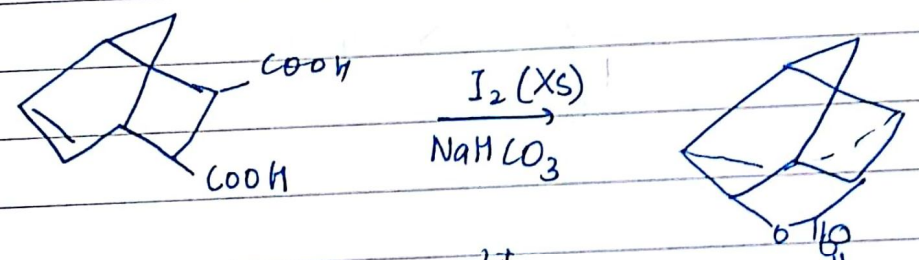
6) $CCl_3-C\equiv C-H \xrightarrow{H^+} CCl_3-CH_2-\overset{O}{\overset{\|}{C}}-H$

Quiz. (MM = 20)

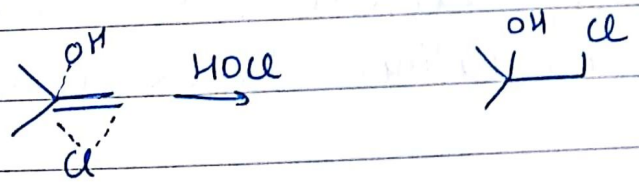
20/20.

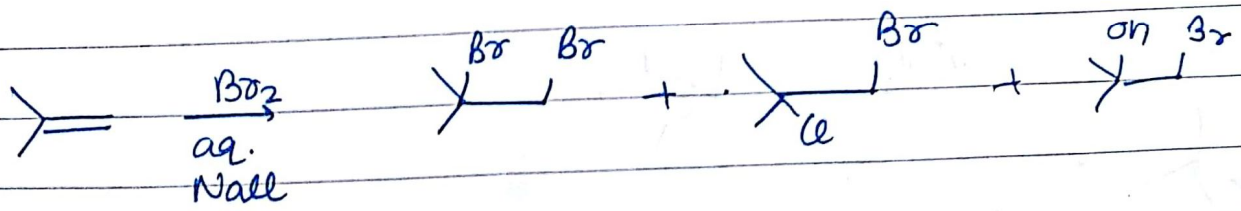
+3 Q.1 $MeO-CH=CH_2 \xrightarrow{NOCl} MeO-\underset{Cl}{CH}-\underset{NO}{CH_2}$

Q.2. +3 

+4 Q3. NCP 

-3 Q4. $CH_3-C\equiv C-D \xrightarrow[H^+]{Hg^{2+}} CH_3-\overset{O}{\overset{\|}{C}}-CD$

mech. Q5. +3 

Q6. +4 

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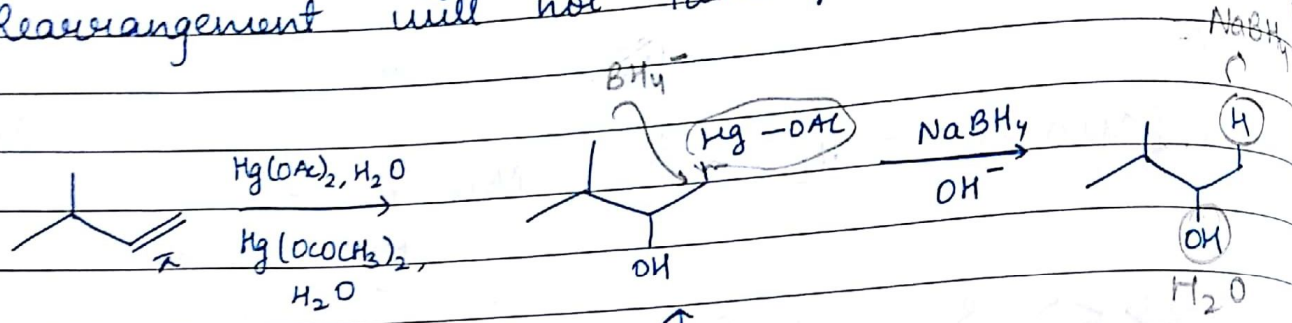
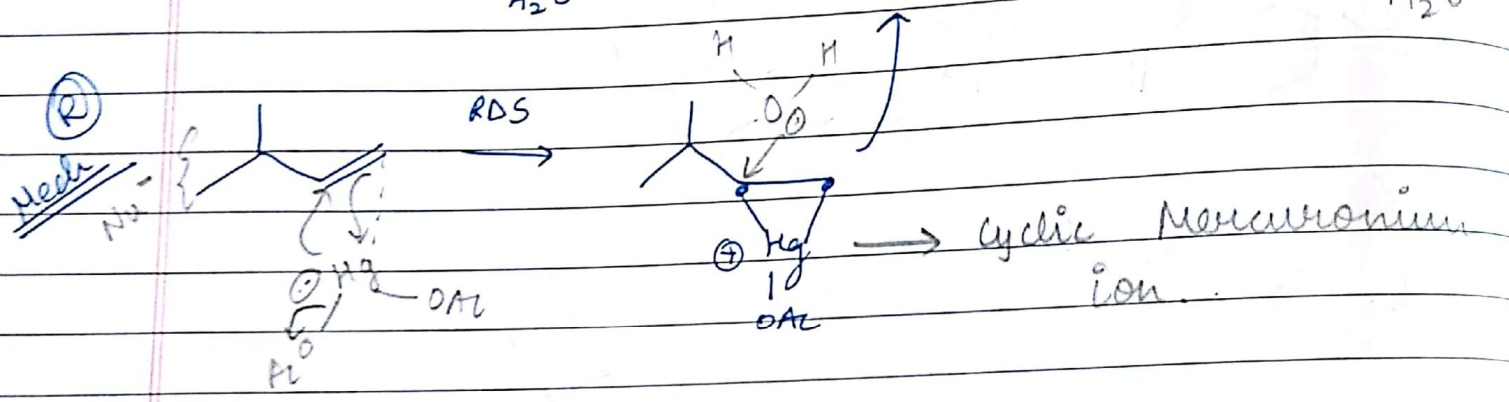
* Oxy Mercuration De-mercuration (O.M.D.M)

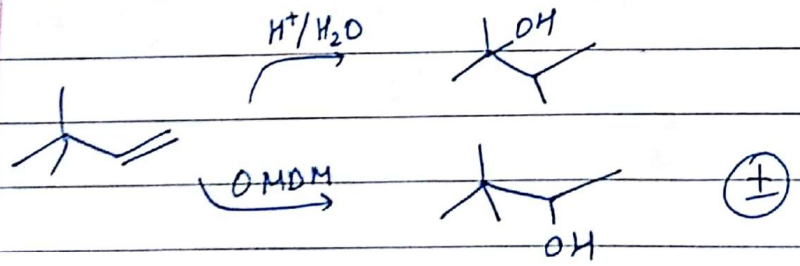
- It is MK addⁿ of H_2O on alkene.
- Rearrangement will not take place.



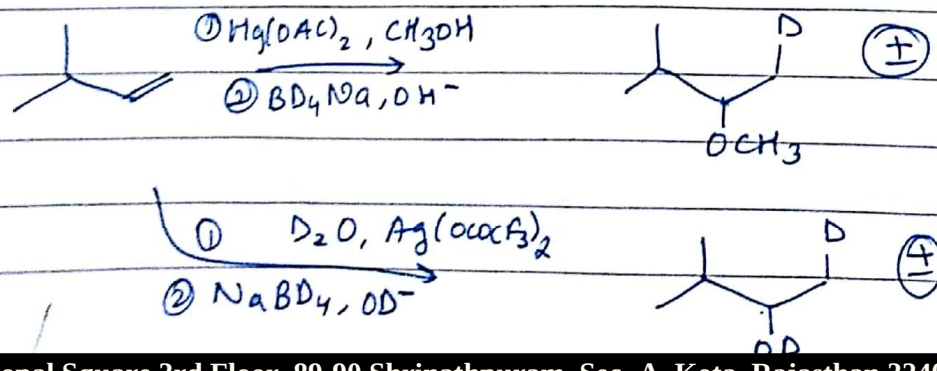


- oxymercuration is anti addition but stereochemistry is lost when de-mercuration takes place.

Q.
1)



2)



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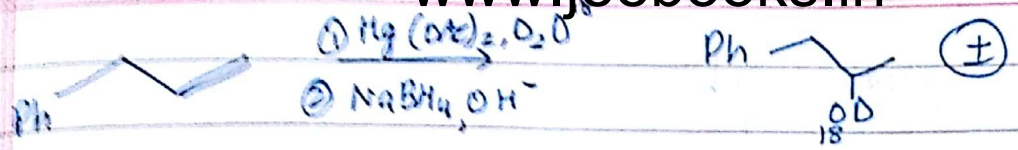
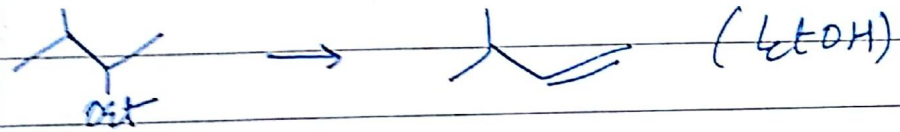
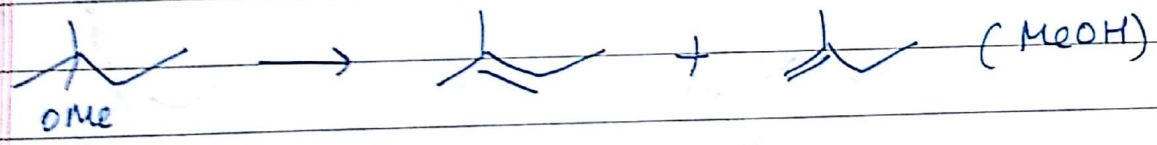
2) 

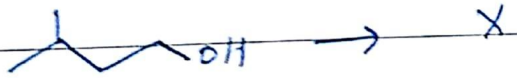
Q. Identify suitable ~~reagents~~ reactants to produce compounds in good yield (if any):

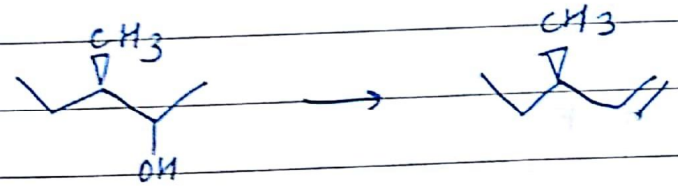
1)

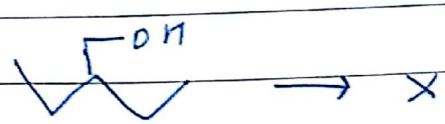
2)

3) alkoxy. 

4) 

5) 

6) 

7) 

- If alcohol is taken instead of water then it is alkoxy mercuration de-mercuration.

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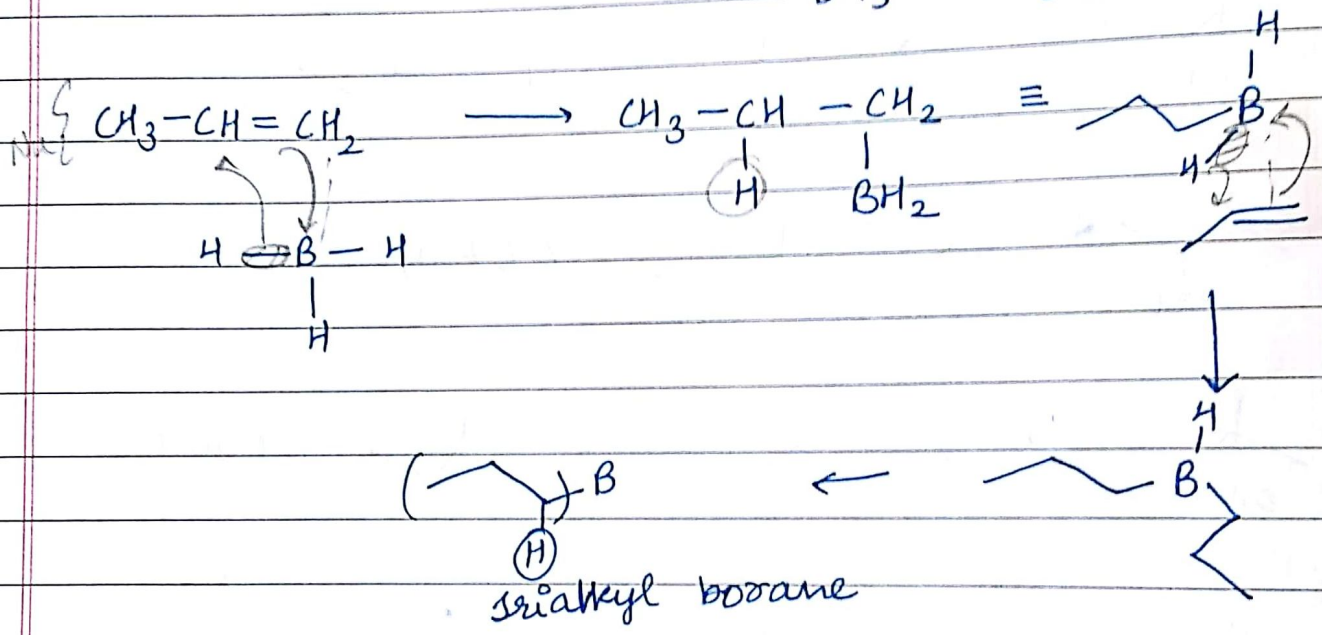
Q.

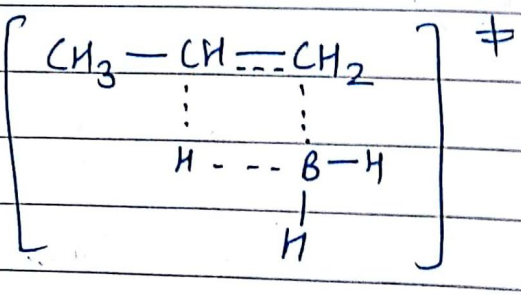
* Hydroboration - Oxidation :
(H.B.O)

$$CH_3-CH=CH_2 \xrightarrow[\text{② } H_2O_2/OH^-]{\text{① } BH_3,\ THF} CH_3-\underset{\underset{BH_3}{|}}{\overset{H}{CH}}-\underset{\underset{H_2O_2}{|}}{\overset{OH}{CH_2}}$$

(R) MECH



- Add^n of BH_3 is syn add^n.
- It follows MK add^n rule.



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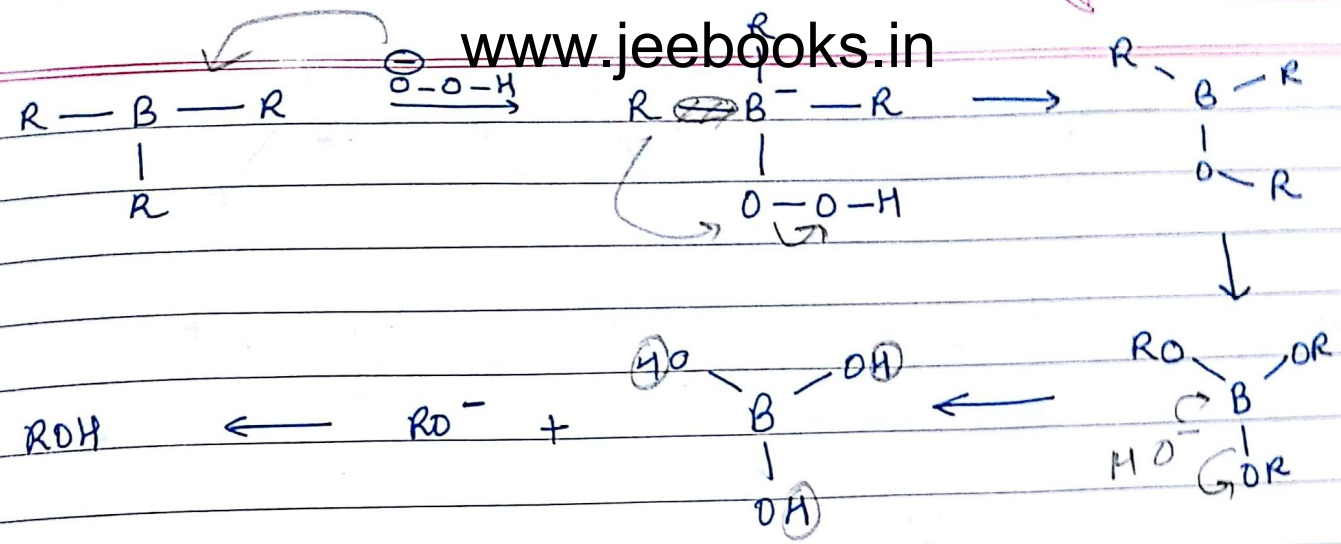
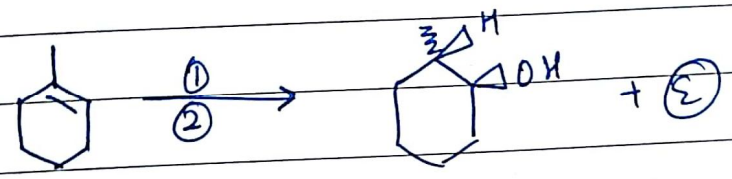
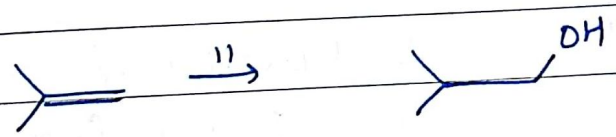
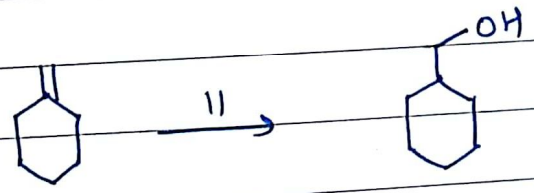


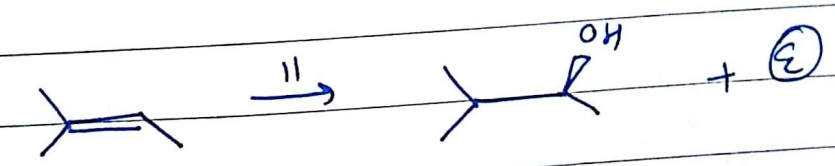
- Overall syn addⁿ takes place & H_2O is added as per A.M.K rule
- Rearrangement is not possible.

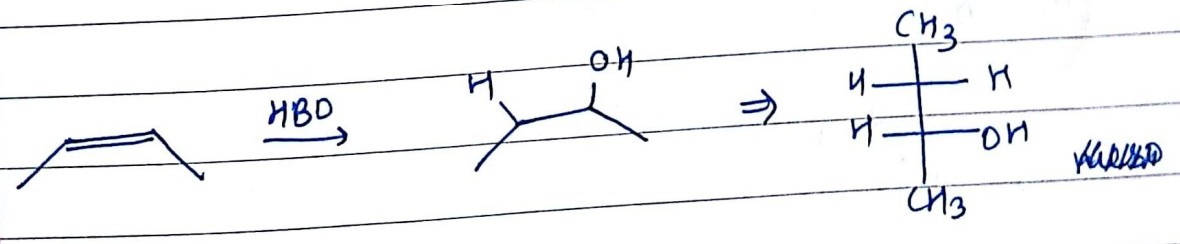
Q.

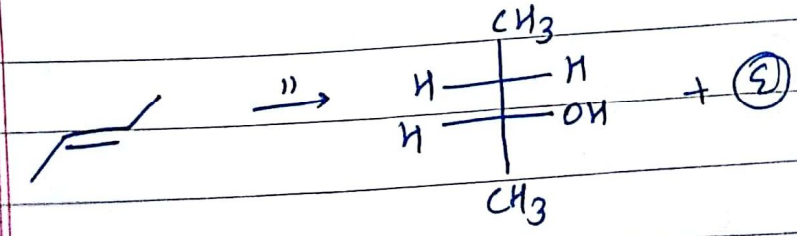
1) 

2) 

3) 

4) 

5) 

6) 

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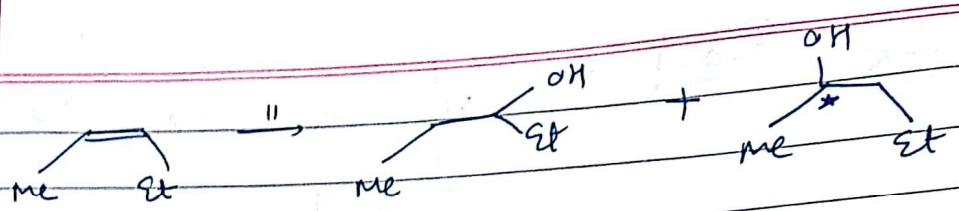
7)



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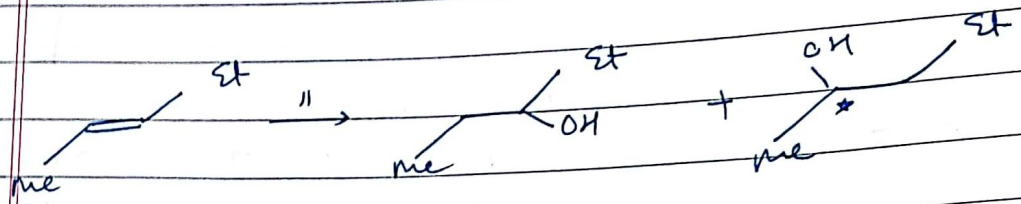

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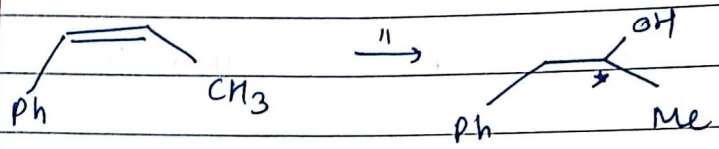

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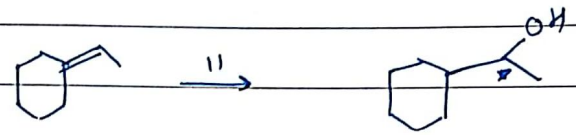
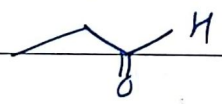
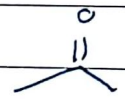


Relⁿ b/w A & B

11] $CH_3-C\equiv C-H \xrightarrow{HBO}$

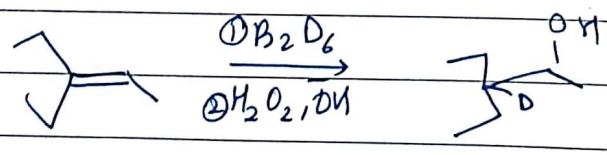


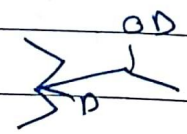
$\xrightarrow{\text{Kucherov}}$



} functional isomerism

12]





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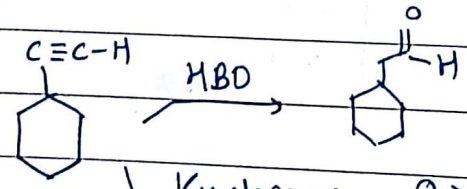

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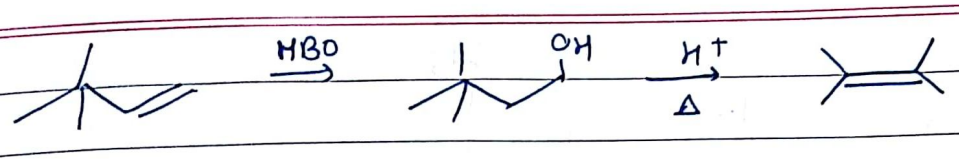
14)



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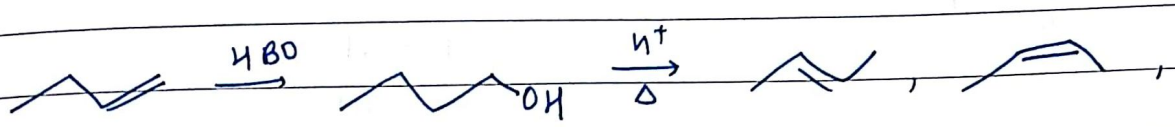
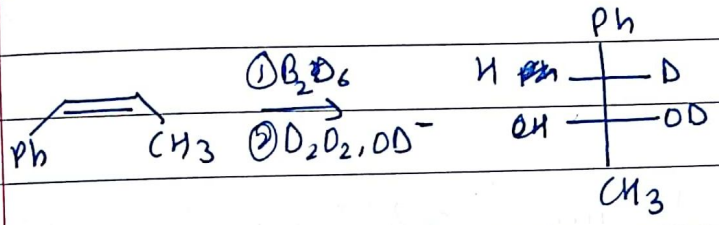


②

$\xrightarrow[CCl_4]{Br_2}$ ① + ② + ②

16]



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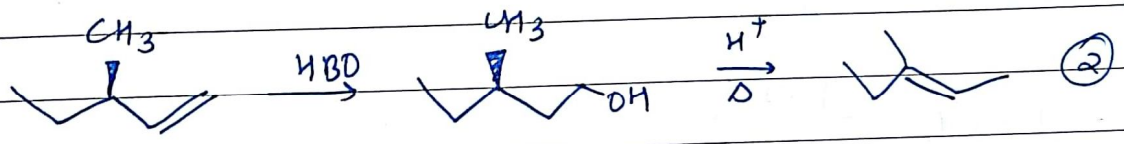
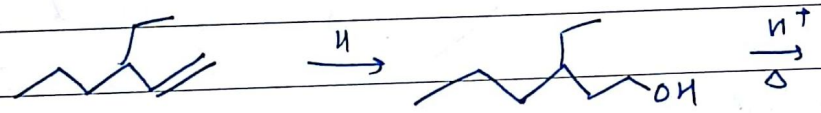


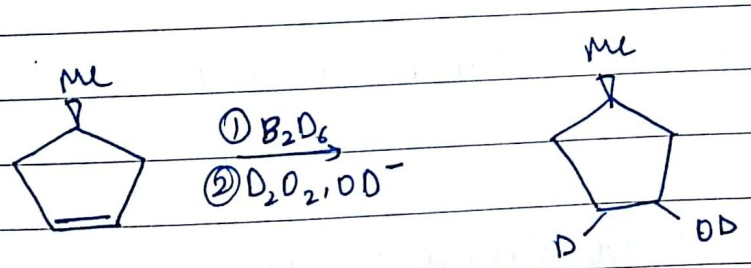
②

18]



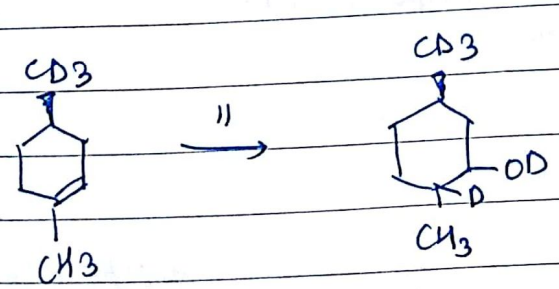
19] $CH_3-CH=CH-D \xrightarrow{HBO} CH_3-CH_2-\underset{OH}{CHD}$

20]



Enantiomer (4)

21]



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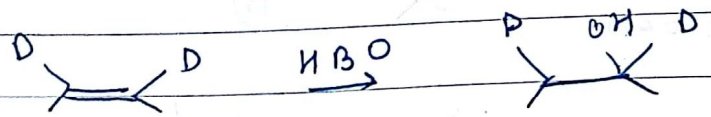

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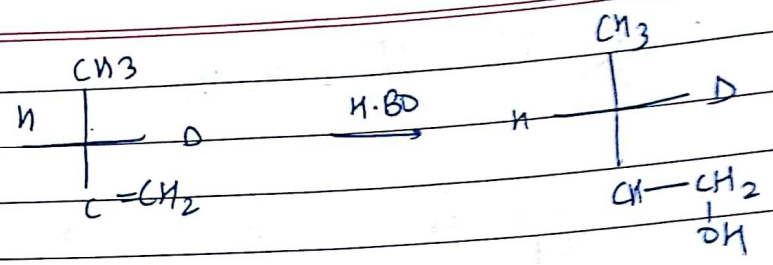
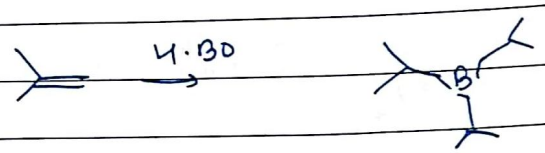
23]



which 24] trialkyl borane is formed.

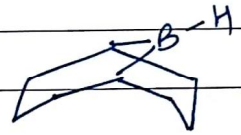


- In case of bulkier boranes selectivity is more as per anti M-K addⁿ.

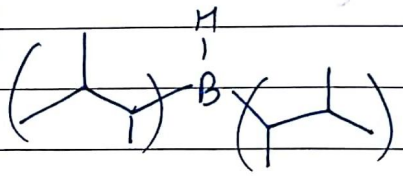
• $CH_3-CH=CH_2$ $\xrightarrow[\text{② } H_2O_2, NaOH]{\text{① 9-BBN}}$

{yield is Excellent}

$\xrightarrow[\text{② } H_2O_2, NaOH]{\text{① } (Sia)_2BH}$



⇒ 9-Bora Bicyclo nonane

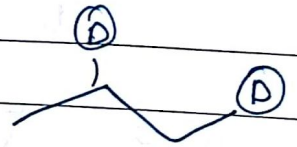


⇒ Disianyl borane

<u>Variations:</u>

of H.BD

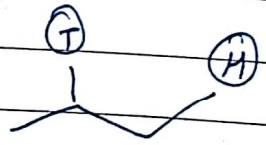
• $CH_3-CH=CH_2$ $\xrightarrow[(CH_3COOD)]{BD_3, THF}$



Acid

T.B.R

$\xrightarrow[CH_3COOH]{BT_3, THF}$



Acid

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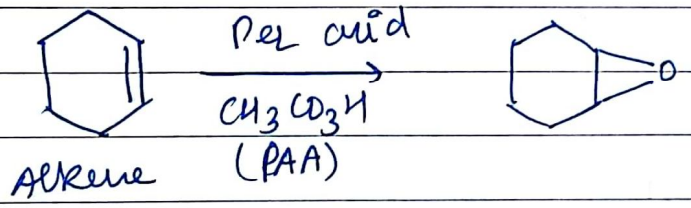
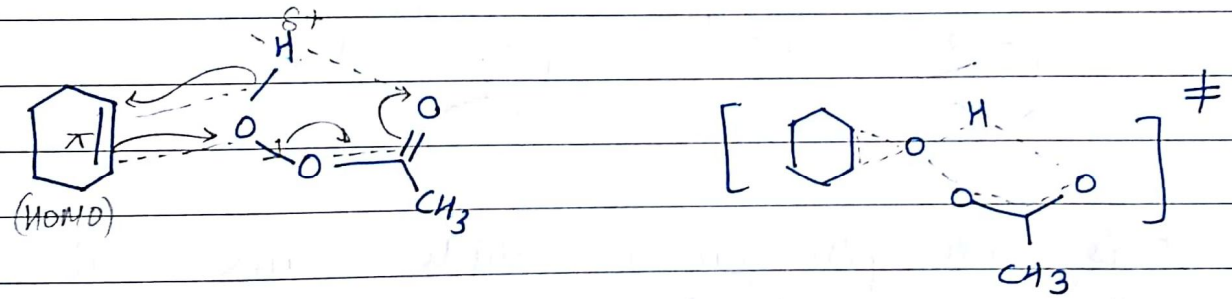
- $CH_3-CH=CH_2 \xrightarrow[\text{② } AgNO_3]{\text{① } BH_3,\ THF} CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

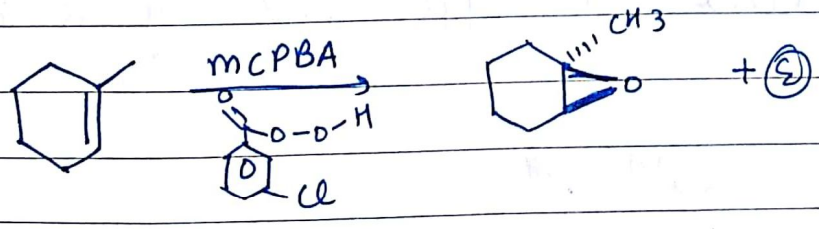
- $CH_3-C\equiv CH \xrightarrow{''} CH_3-CH=CH-CH=CH-CH_3$

Formation of epoxy compound from Alkene is epoxidation.
It takes place in presence of per acid.

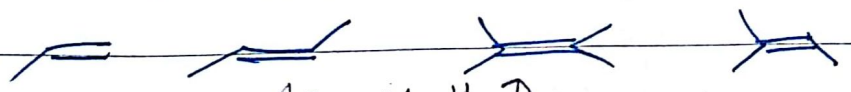
* EPOXIDATION (Prilezhaev rxn) :→





- 

Q. Compare rate of Epoxidation

1) 

c > d > b > a

As α-H ↑
$Nu^{\ominus}$ ↑ & rxn α $Nu^{\ominus}$ of alkene

same for Br_2 addⁿ

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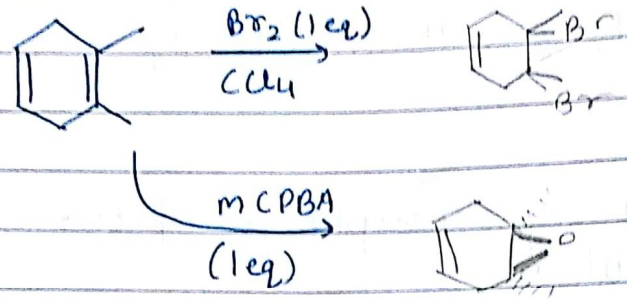
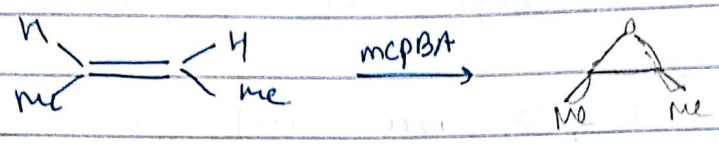
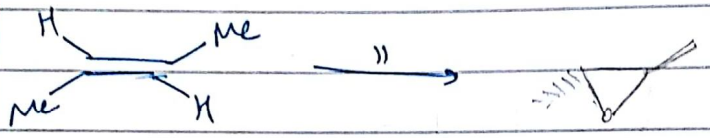
* 2)

Charge concentrated on just on on c in (b)

3) 

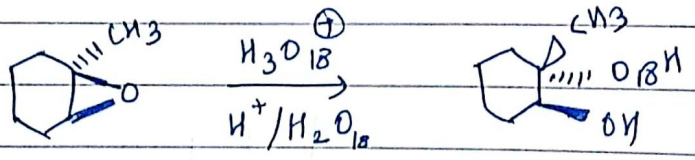
4) 

meso (1)

5) 

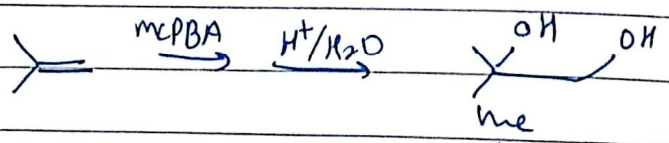
(2)

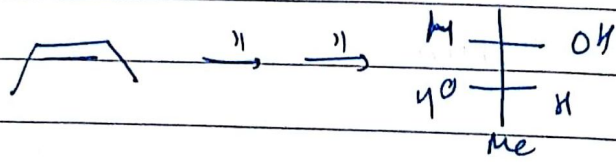
* Anti Hydroxylation



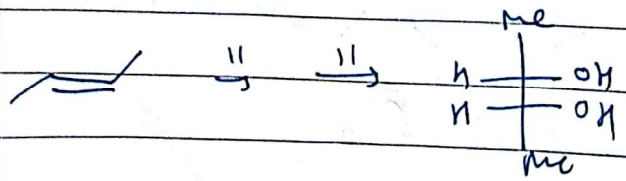
It is anti hydroxylation which means that two OH grps are added on opp. sides of π-bond.

Q.

1) 

2) 

+ (2)

3) 

meso

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* BAEYER'S TEST

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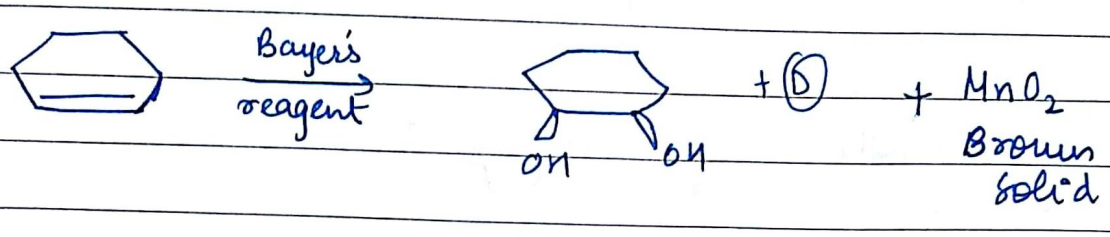
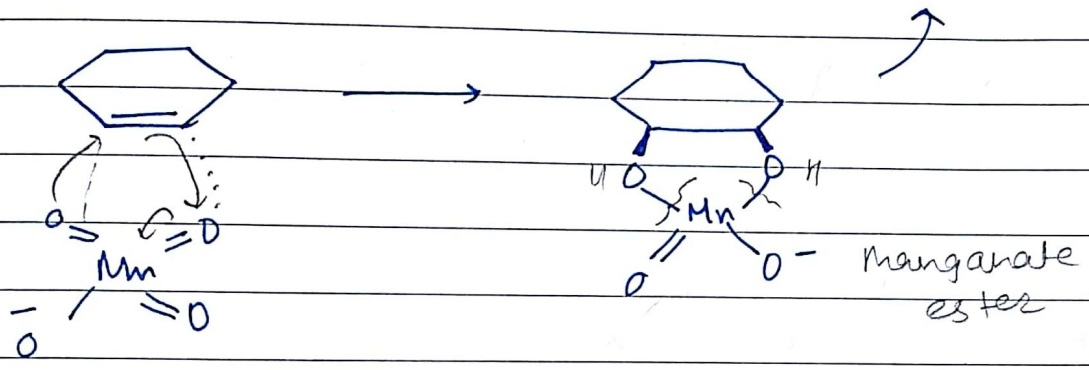
- This test conforms the presence of alkene / alkyne in the given sample.





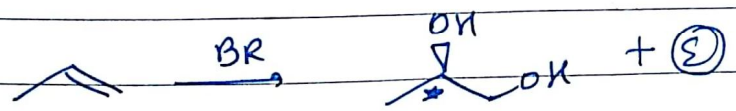
- Observation,
  Dark pink → colourless

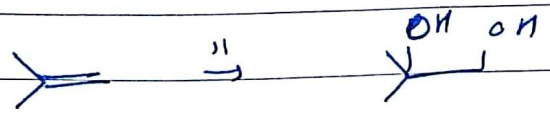
- B.R = cold dil. alkaline $KMnO_4$

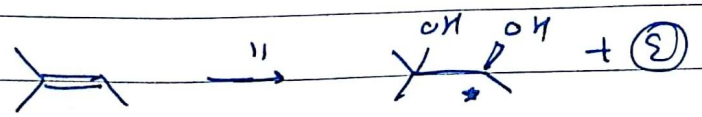
- Syn hydroxylation

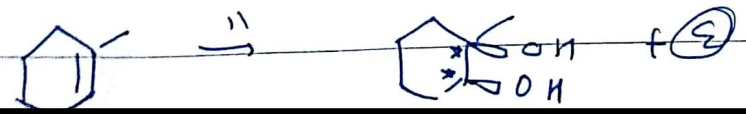
- OsO_4 / $NaHSO_3$ (costly, toxic)

Q.

1) 

2) 

3) 

4) 

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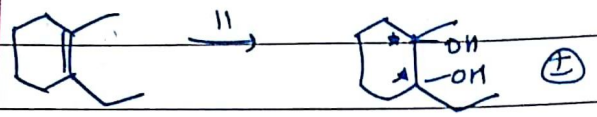
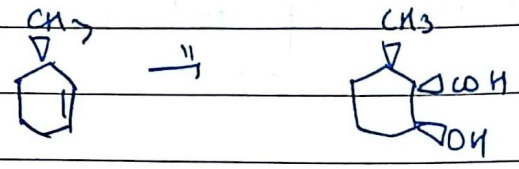
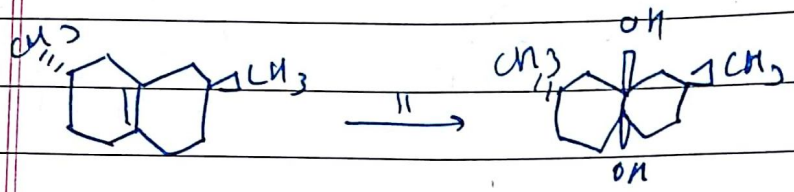
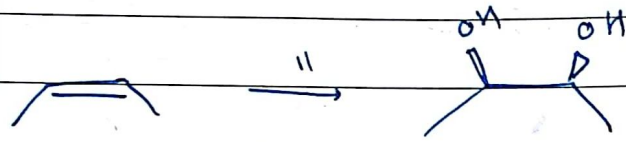
5) 

(I)

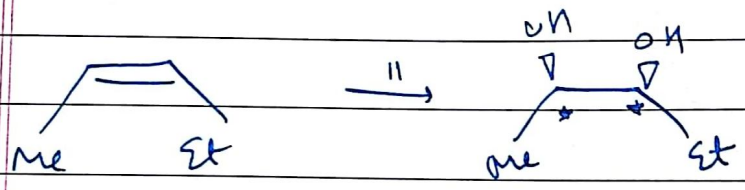
6) 

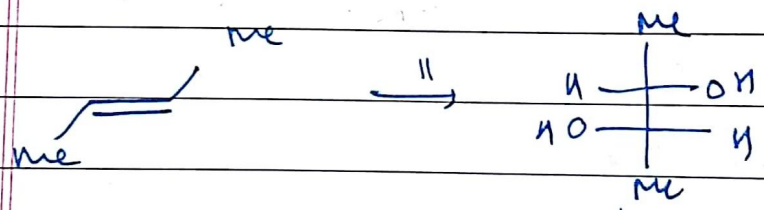
+ (D)

7) 

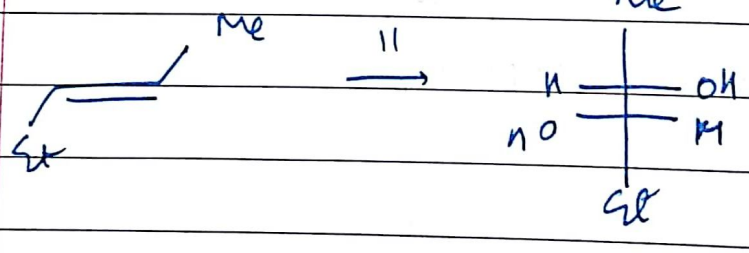
8) 

Meso

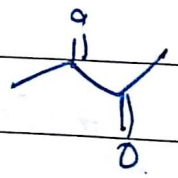
9) 

10) 

+ (E)

11) 

+ (E)

12) $CH_3-C\equiv C-CH_3$ $\xrightarrow{H^+}$ 

13) $C_5H_{10} \xrightarrow{Br_2, CCl_4}$ (8) (12)

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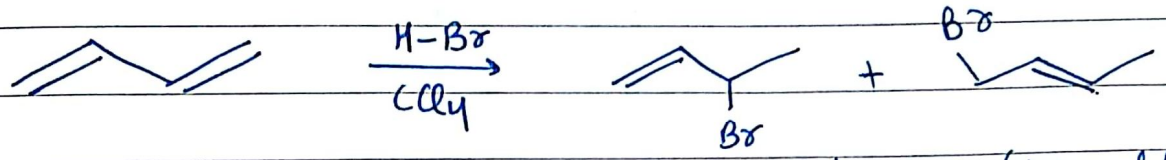
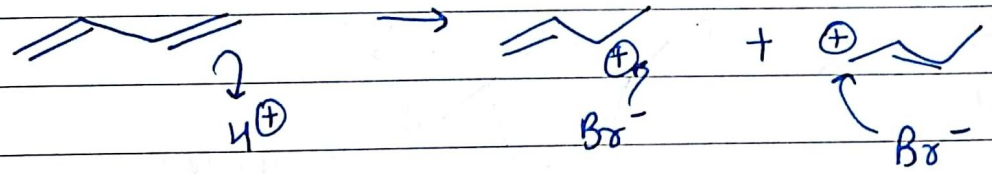
* ADDITION REACTIONS ON CONJUGATED DIENES :

K.C.P → Kinetically controlled product
T.C.P → Thermodynamically controlled product

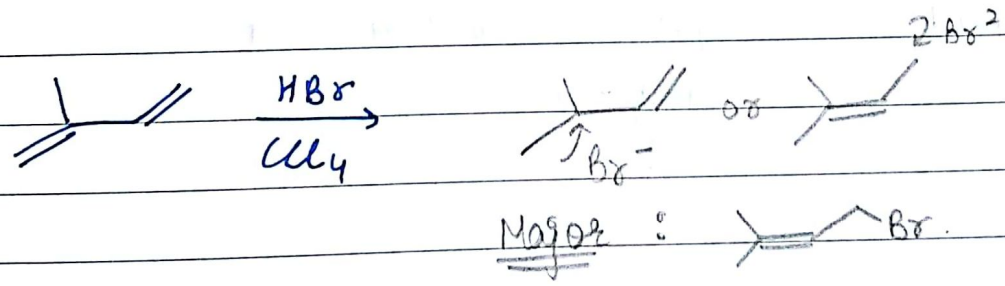


(1,2-addⁿ) KCP (easy) (1,4-addⁿ) TCP (Stable)

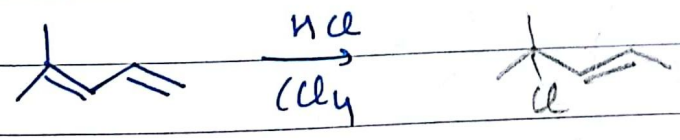


- KCP is formed by easier path. It is major at low temp.
- TCP is thermo. no stable product. It is major at high temp.

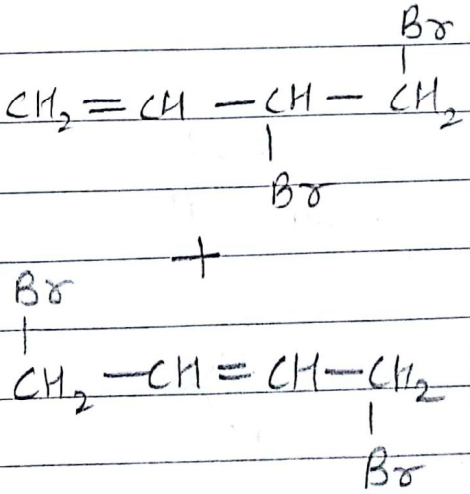
1]



2]



3] $CH_2=CH-CH=CH_2 \xrightarrow[CCl_4]{Br_2}$



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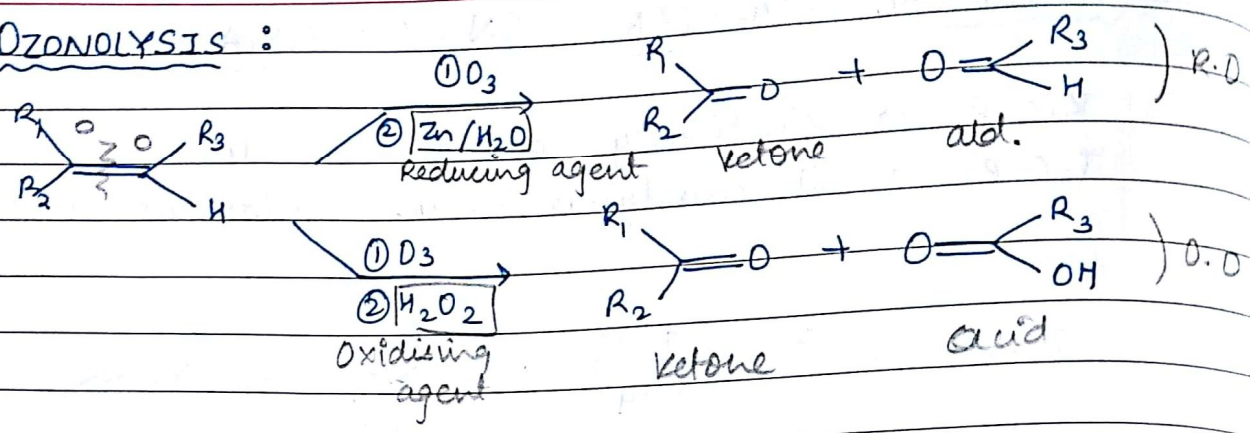
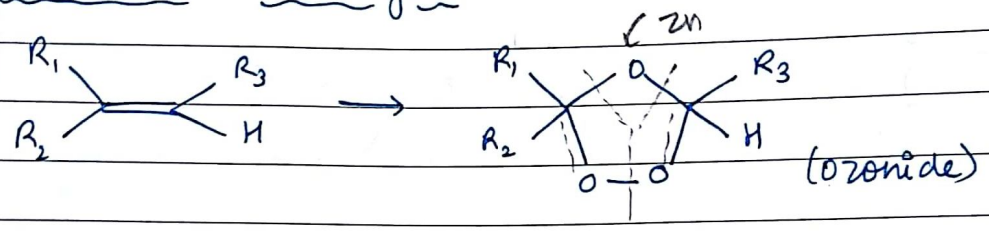
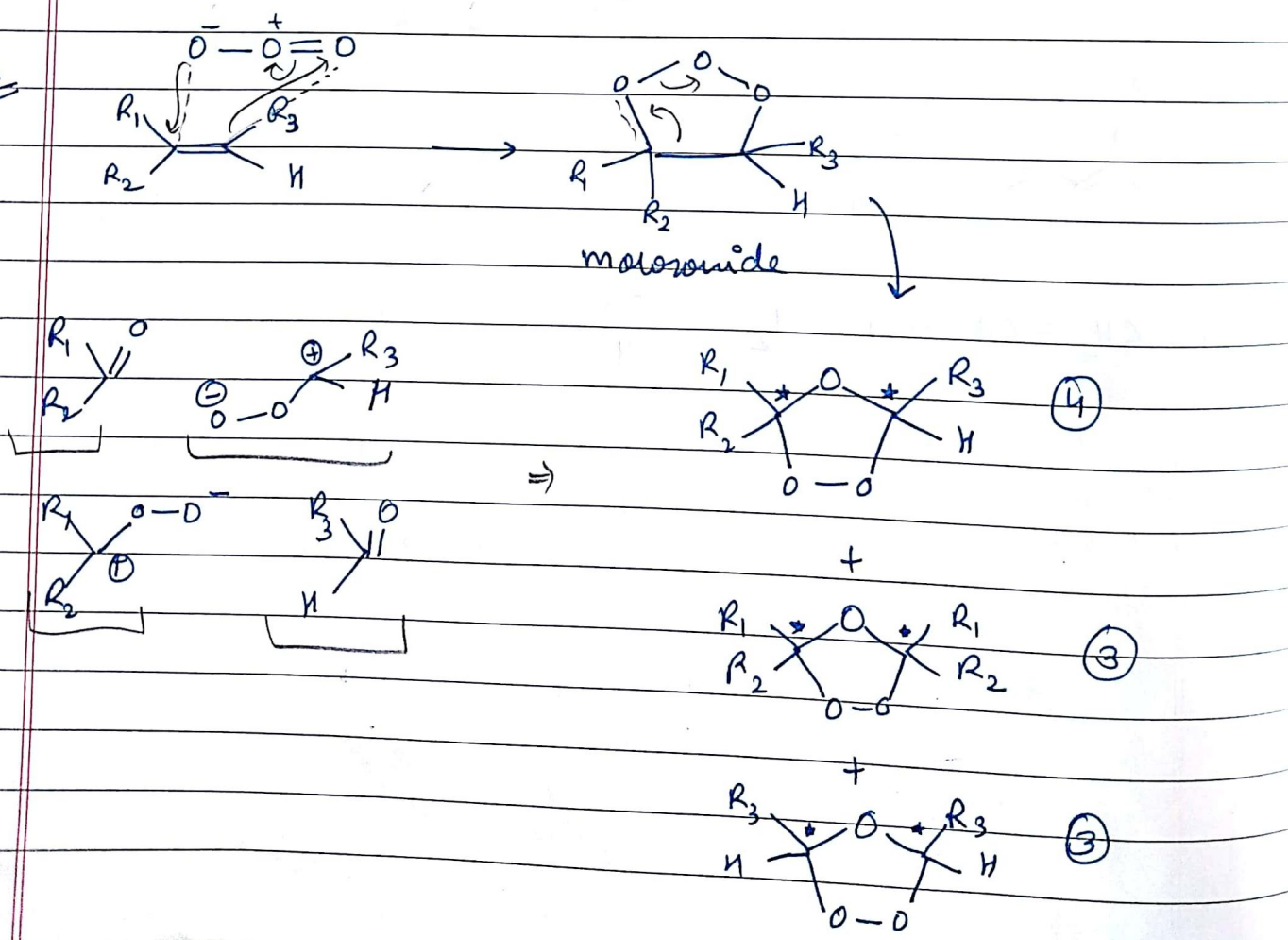
* Ozonolysis :



- **Reductive Ozonolysis :**



Reducing agents : Zn/H_2O, Zn/CH_3COOH, $(CH_3)_2-S$ (DMSO), $(Ph)_3-P$, $(Ph)_3-PO$



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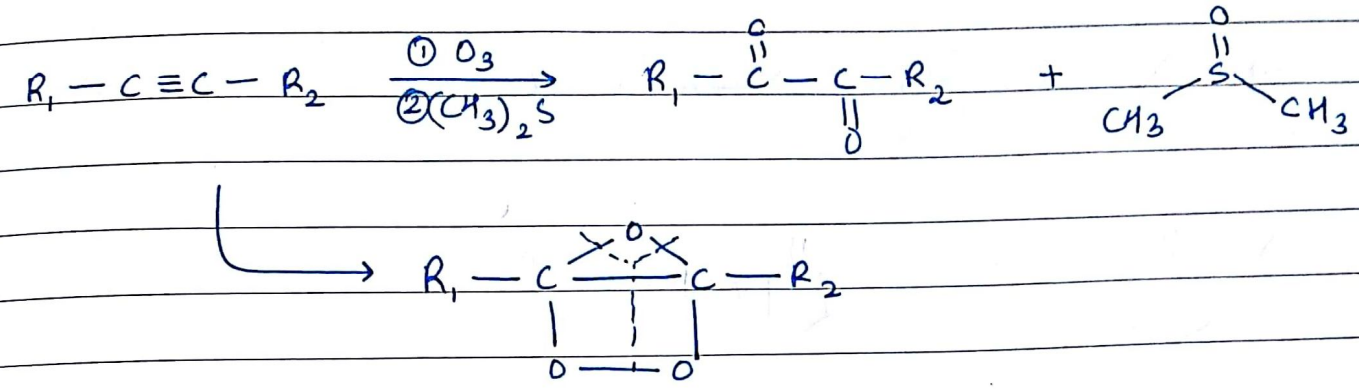
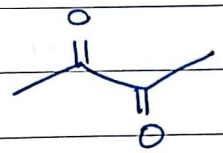
- Alkyne on reductive ozonolysis produces vicinal diketo compound.



Q. $CH_3-C\equiv C-C_2H_5 \xrightarrow{\text{''}}$



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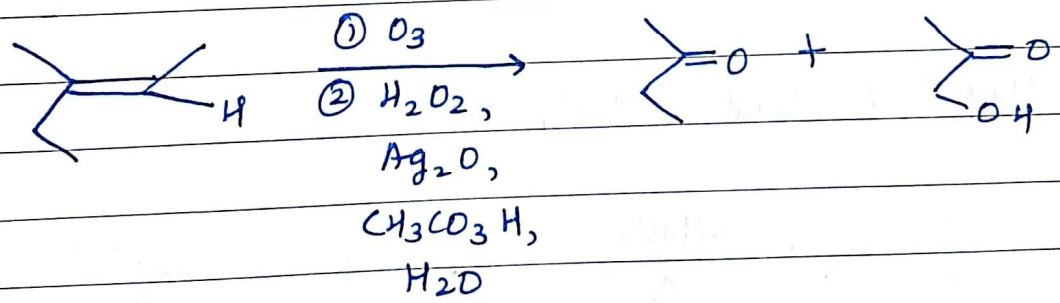
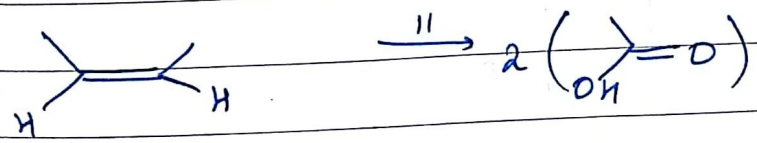
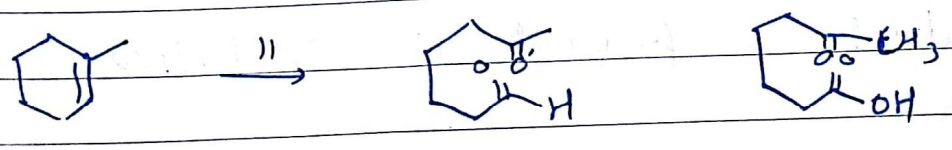
- <u>Oxidative ozonolysis</u> :→

When addⁿ of ozone takes place in presence of oxidising agent then it is oxidative ozonolysis. In presence of OA, ketone will not get oxidised further. Aldehyde is oxydised to acid.



Q.

1) 

2) 

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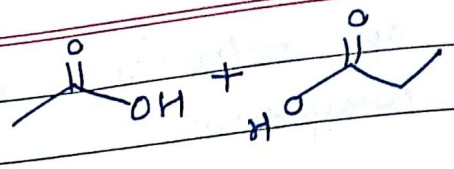
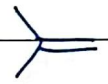
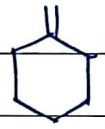
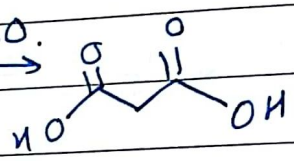
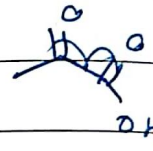
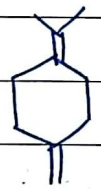
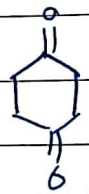
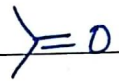
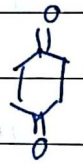
3) $CH_3-C\equiv C-CH_2CH_3 \xrightarrow[H_2O]{O_3}$ 

4)  $\xrightarrow[H_2O_2]{O_3}$ $+ CO_2 \uparrow$

5)  $\xrightarrow{''}$ $+ CO_2 \uparrow$

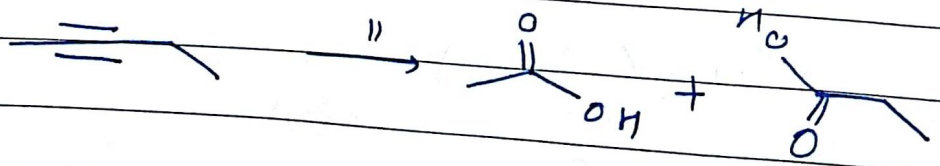
6) $H_2C=CH-CH_2-C\equiv C-CH_3 \xrightarrow{O.O.}$  $+$  $+ CO_2 \uparrow$

7)  $\xrightarrow{\text{Oxidative}}$  $+ CO_2 +$ 

$\xrightarrow{\text{Reductive}}$  $+ HCHO +$

8) $CH_3-C\equiv CH \xrightarrow{O.O} CH_3COOH + CO_2 (\uparrow)$

* <u>Uses of hot $KMnO_4$</u> :→



same product is formed as oxidative Ozonolysis.

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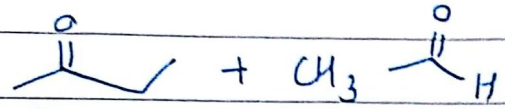
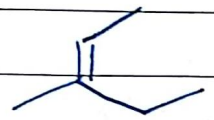
* Retro Ozonolysis :→

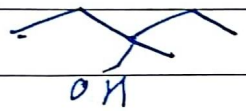
Q. C_6H_{12} A $\xrightarrow[Zn/H_2O]{O_3}$ 

$H_3O^{\oplus}$ ↙ ?

↓ H_2/Pd (1 eq.)

→ A =  (C+T)

↓ H_3O^+

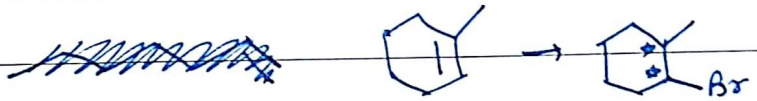


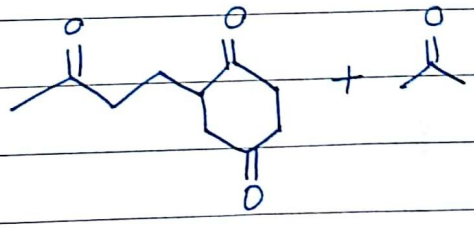
Q. C_7H_{12} A $\xrightarrow[H_2O_2]{O_3}$ $CH_3-C(=O)-(CH_2)_4-COOH$

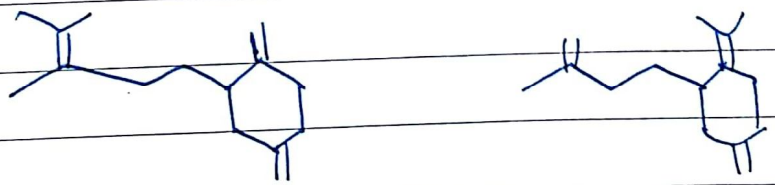
HBr ↙ Poor

How many OA pro are obt.?

$\boxed{4}$

→ A = 

Q. A $C_{13}H_{20}$ $\xrightarrow[Zn, H_2O]{O_3}$ 

→ A = 

- Parent ring size ≥ 8 will not violate Bredt's rule.

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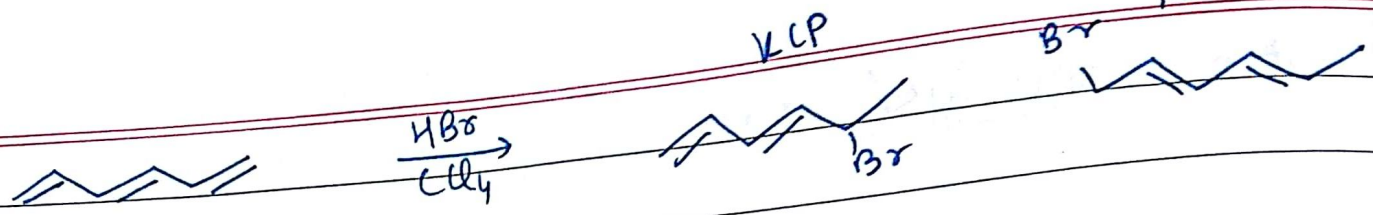
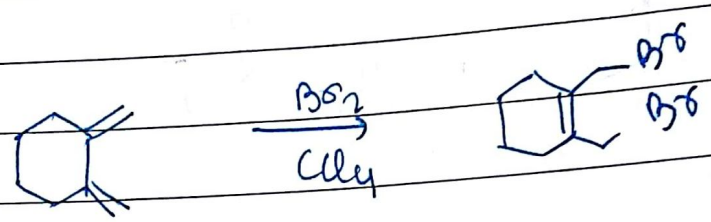
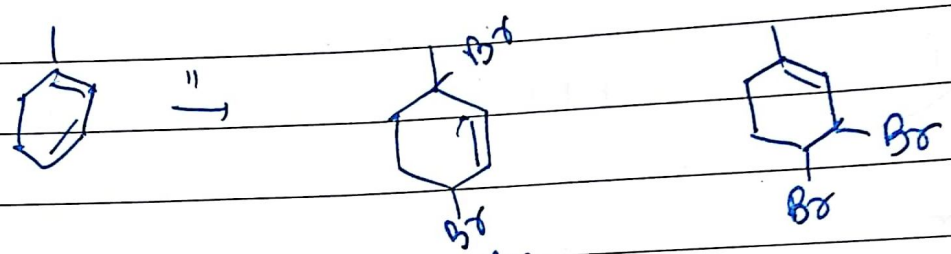
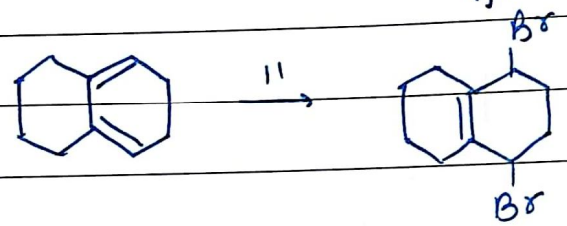
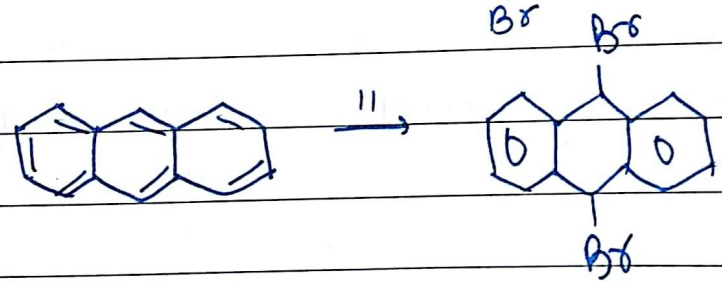
Q. 

Q. 

Q. 

Q. 

Q. 

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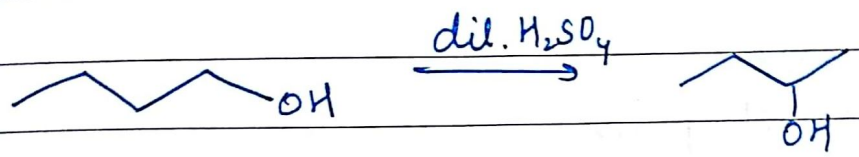
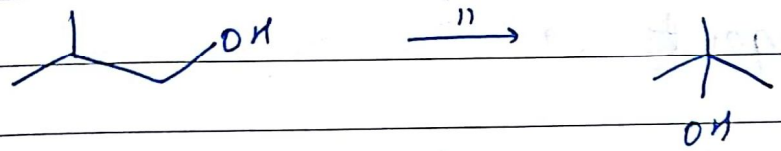
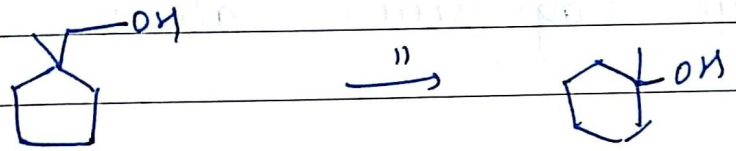
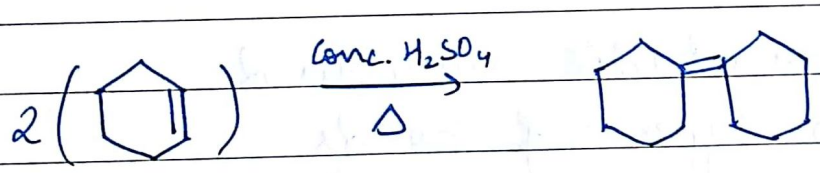
* Isomerisation of Alcohol :→

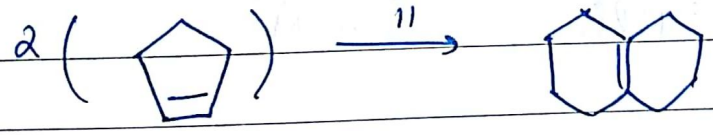
- 

- 

- 

* Dimerisation of Alkene :→

- 

- 

Trick

Bromination

↑

H S B A

(Syn) (Anti)

Hydrogenan

Hydroxylation (B.R)

Hydroboration

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Carbanion & its Reactions

$>C^{\ominus}$ (highly reactive (EN))

→ Base
→ Nucleophile

* Grignard Reagent :→

It is alkyl / aryl magnesium halide.

$R - MgX$

Eg : $CH_3 - MgBr$, $Et - MgCl$, $Bu - MgBr$
$Ph - MgBr$, etc.

- It is an organometallic compound.
- It contains two types of bonds
  - i) Ionic $M^+ X^-$
  - ii) organometallic $\overset{\delta-}{R} \leftarrow \overset{\delta+}{M}$

$R - MgX$

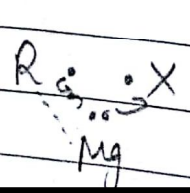
$\overset{\delta-}{R} \leftarrow \overset{\delta+}{Mg}$ — organo metallic

$Mg^+ X^-$ — Ionic

- Polar
- Covalent (easier to break)
- R^- → Base, → Nucleophile

• Preparation of G.R. :

$$R - X \xrightarrow[\text{dry ether}]{Mg} R - MgX$$



NR
MECH

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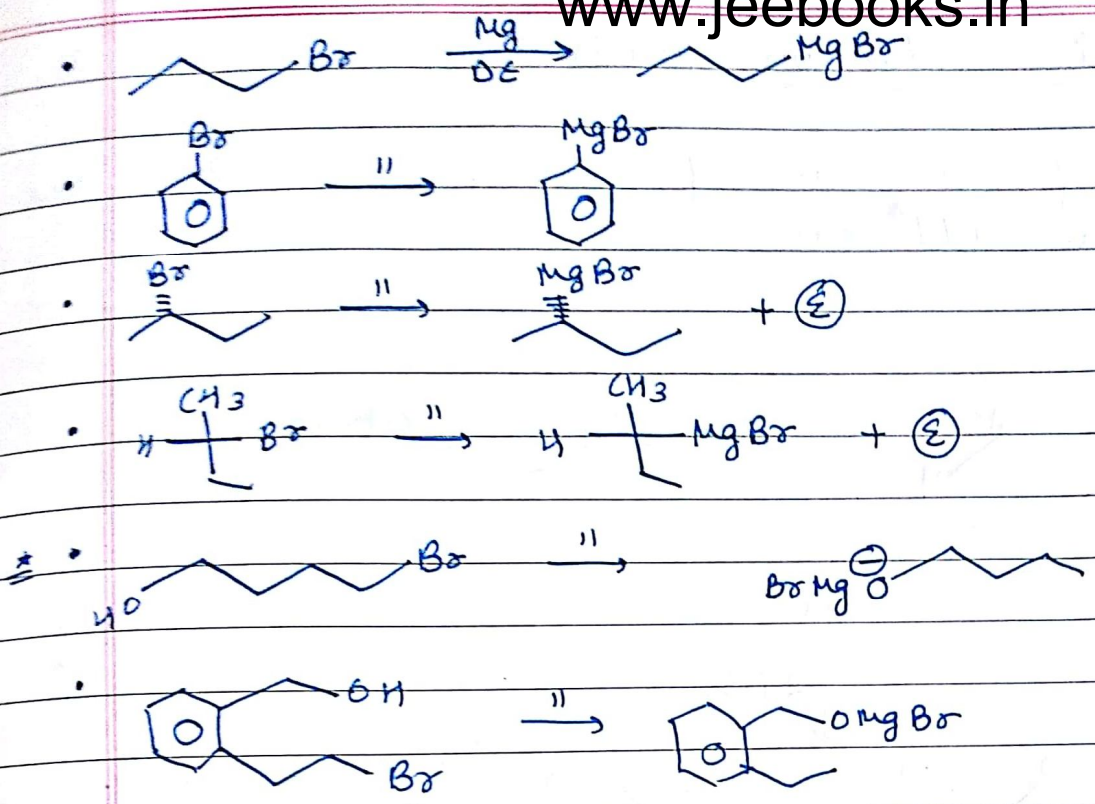


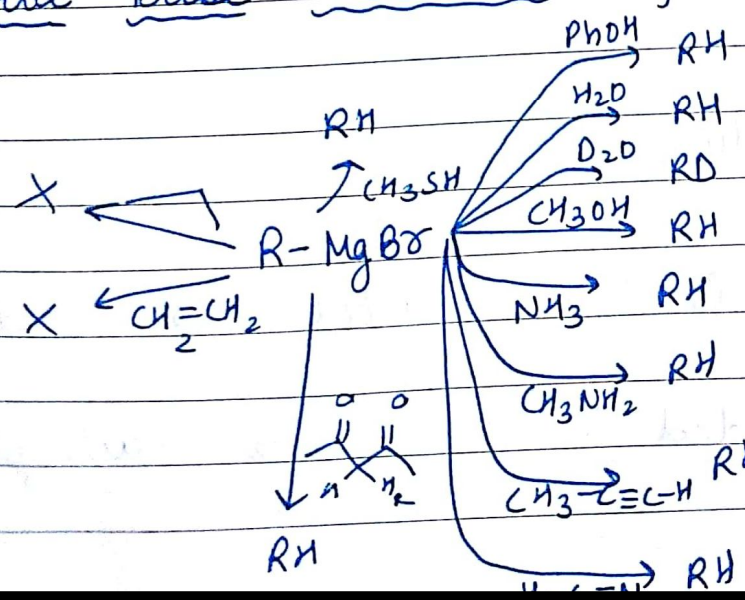
- G.R. will not be formed in case some acidic hydrogen is present.

Why dry ether is used ?

→ $R-\overset{\delta+}{Mg}X$ (solvated by two ether molecules, $\delta-$ on O)

It solvates G.R. & controls its reactivity.

- <u>Acid - Base reactions</u> (of GR) :



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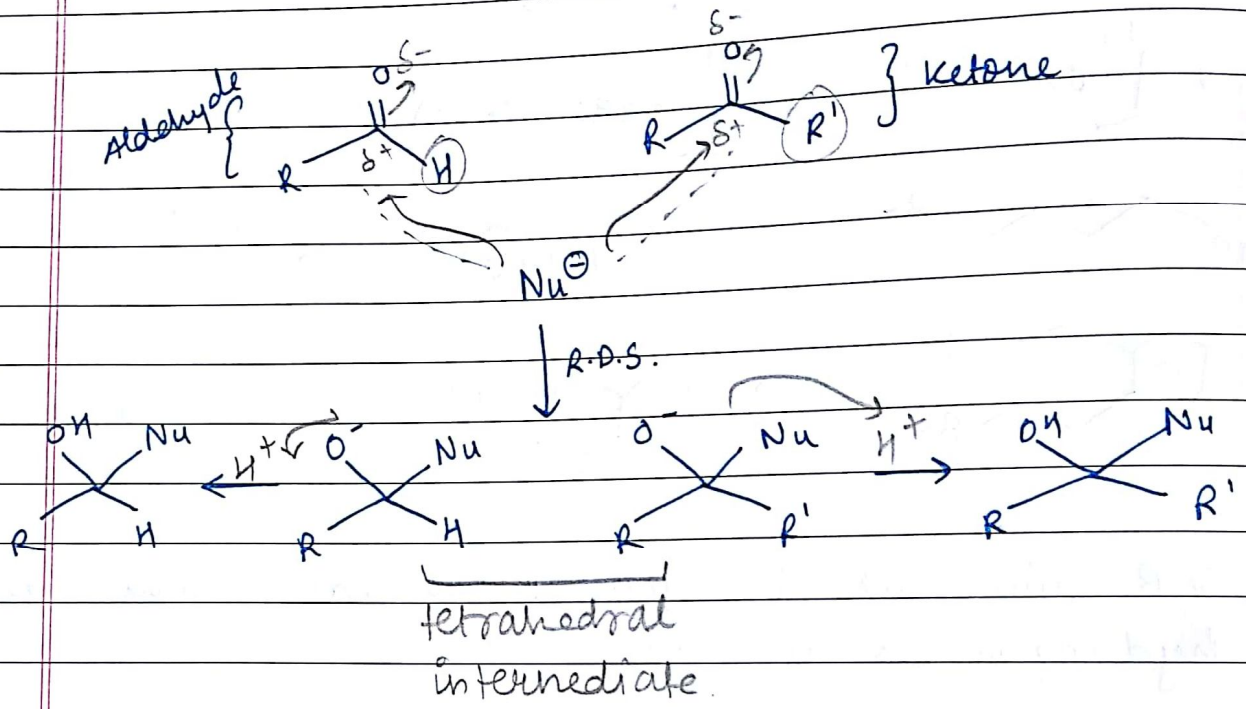
- **Nucleophilic Addition Reactions :**

- Majority of the rxns of aldehyde & ketone are nucleophilic addⁿ rxn.

(1)



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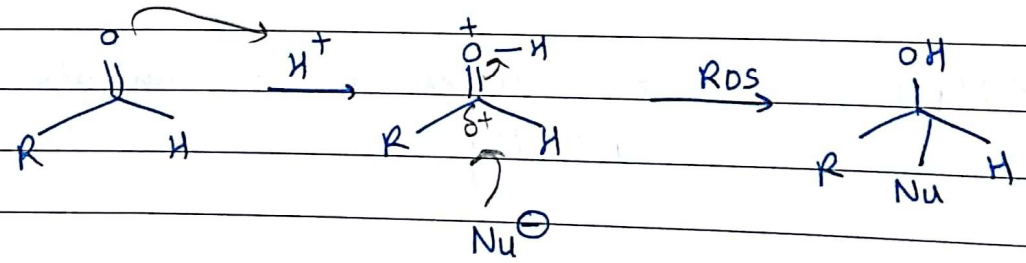

Rate $\propto \delta^+$
$\propto \frac{1}{\text{Steric crowding}}$

Generally Ketone is less reactive than aldehyde.

Nucleophile is added in R.D.S hence nucleophilic addⁿ.

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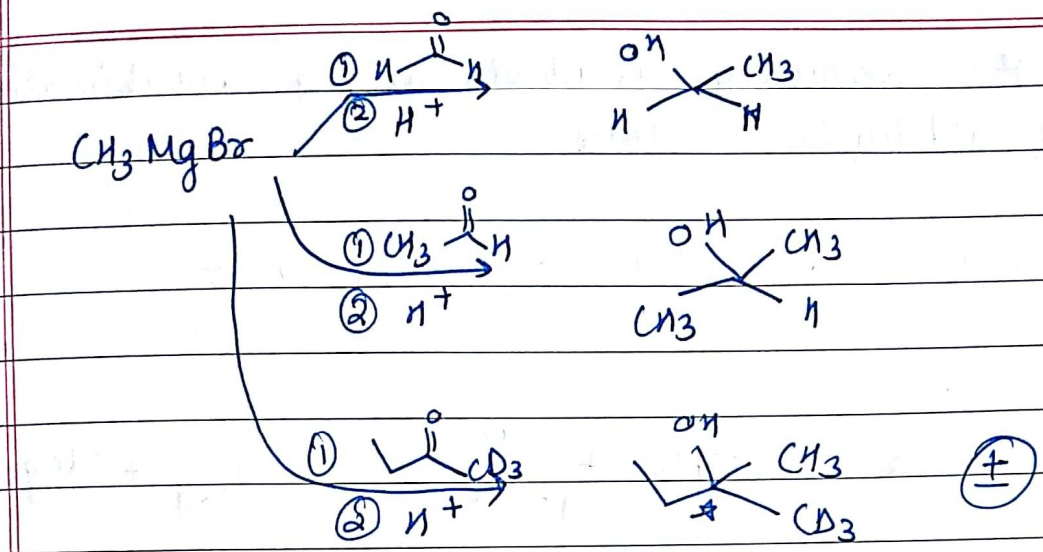
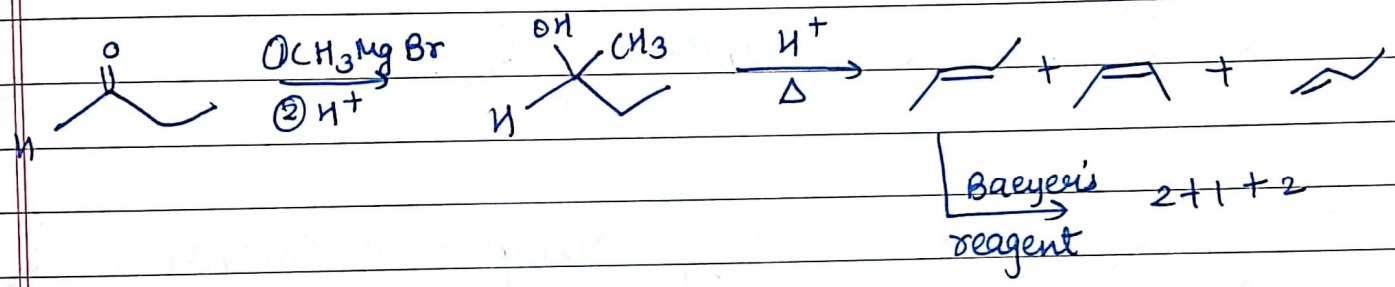
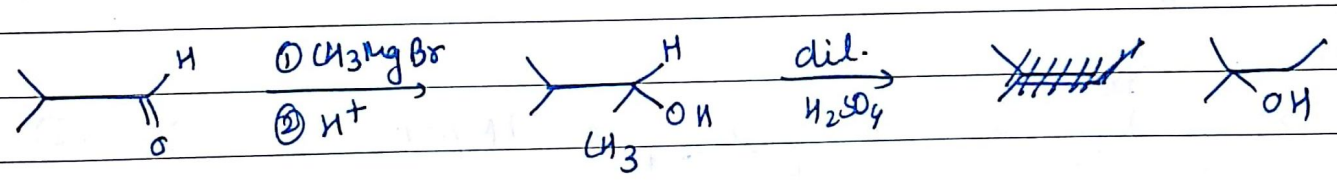
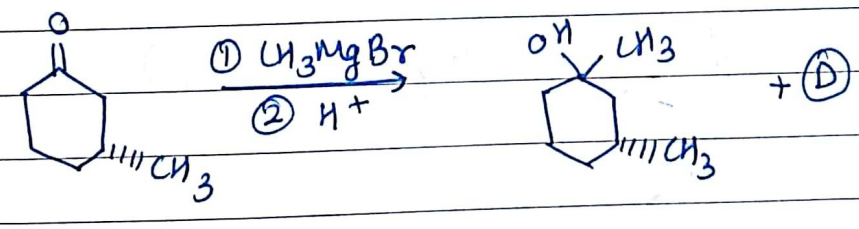
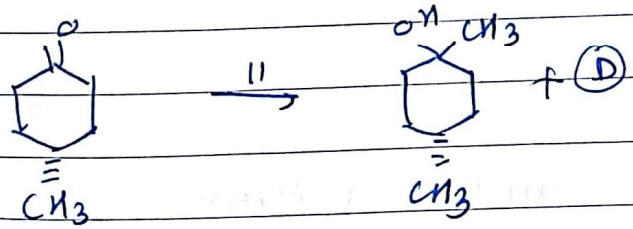
Q.

1. 

2. 

3. 

4. 

5. 

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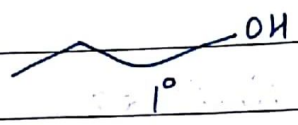
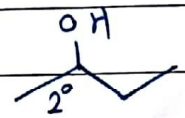
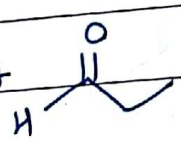
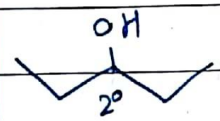
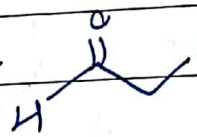
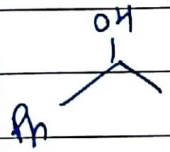
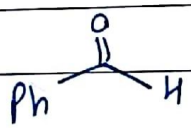
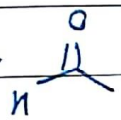
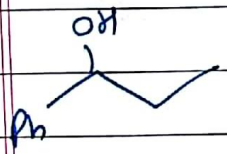
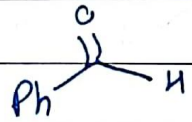
Q. Prepare the following alcohols using combination of G.R. & aldehyde / Ketone.

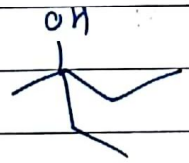
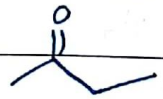
1)  → $HCHO + CH_3CH_2MgBr$ (1)

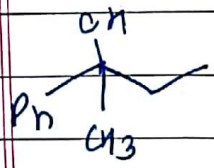
2)  → $MeMgBr$ +  ; + $EtMgBr$ (2)

3)  → $EtMgBr$ +  (1)

4)  →  + $MeMgBr$; $PhMgBr$ +  (2)

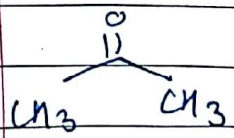
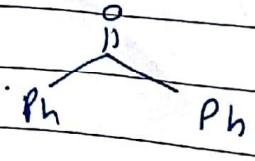
5)  →  + $EtMgBr$ (2)

6)  →  + $EtMgBr$ (2)

7)  → (3)

Q. Compare rate of rxn with CH_3MgBr

1) CH_3CHO ; $HCHO$; CH_3COCH_3 b>a>c

2)  ;  a>b

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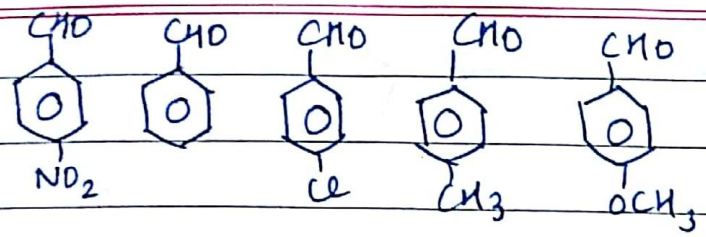
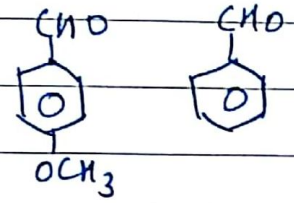
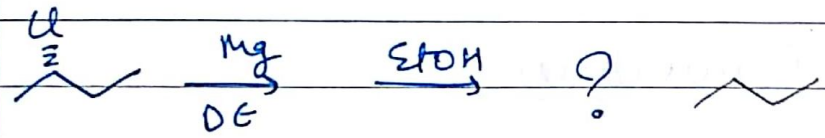
3) 

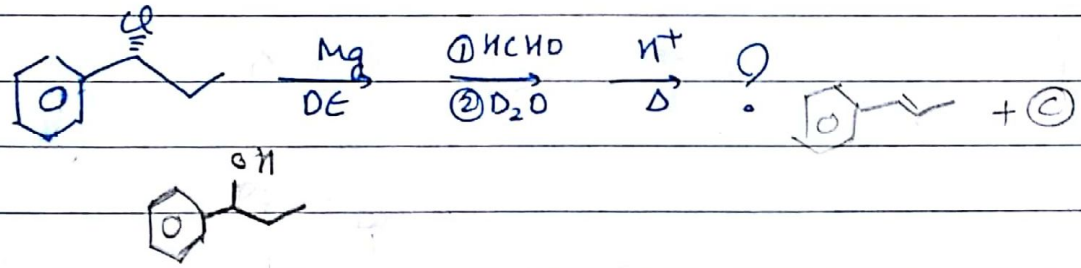
a > c > b > d > e

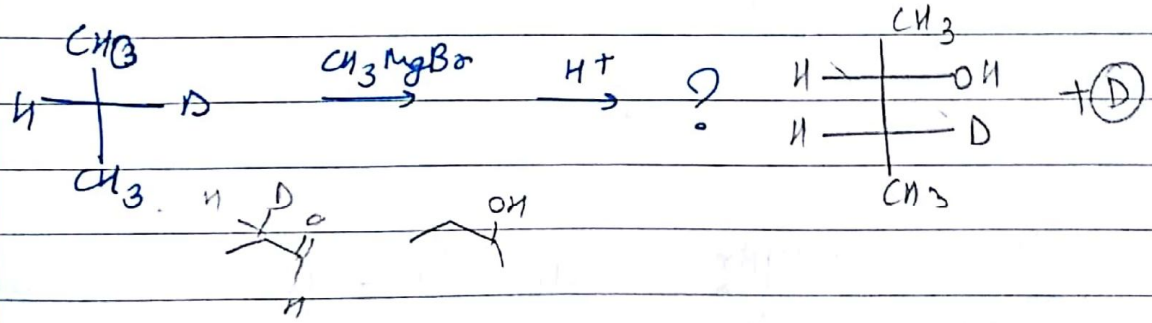
4) CH_3-CHO HCHO 

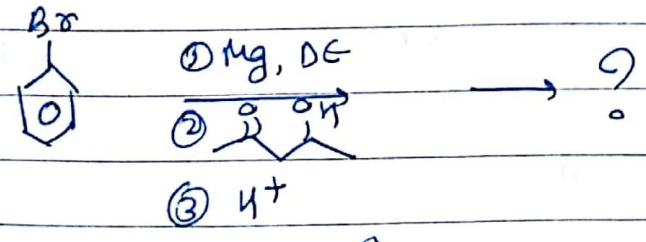
b > a > d > c

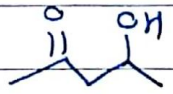
Q.

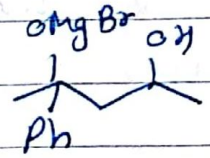
1) 

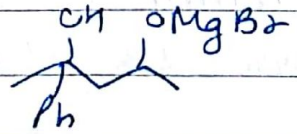
2) 

3) 

4) 

A) ; B) 

C) 

D) 

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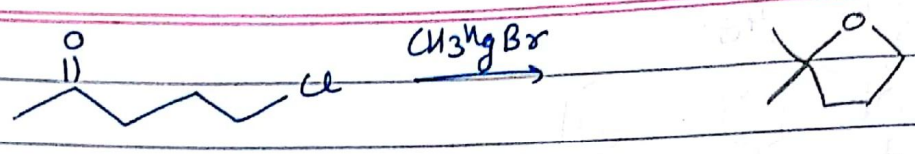
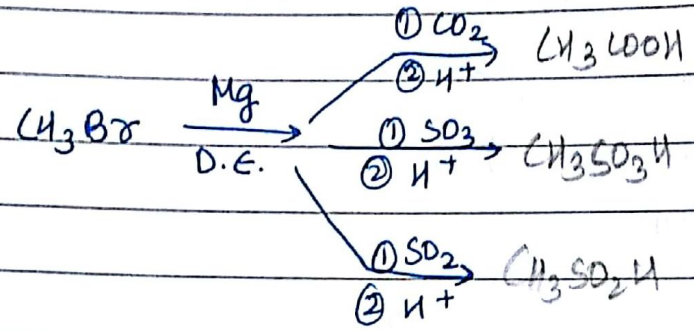
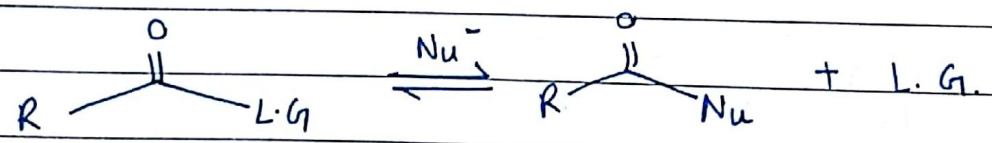
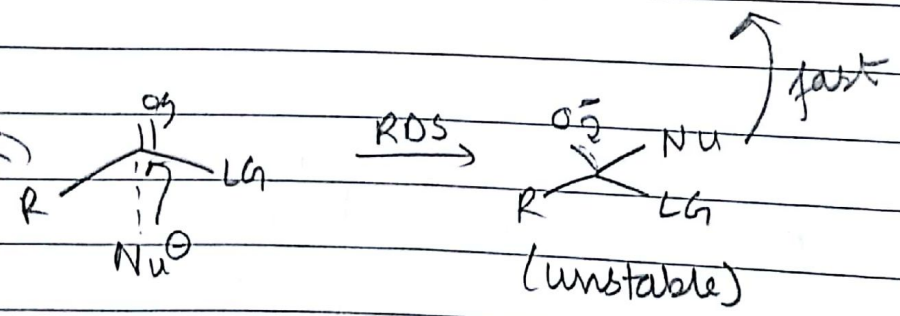
*. 

• 

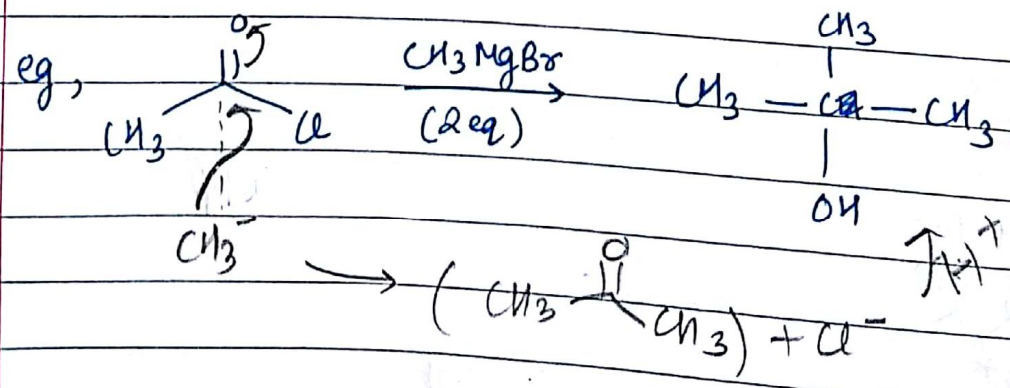
* Rxns of Acid Derivatives :→
(S_NAE)



(2) Mech (interaction)



eg,



* It involves
- nucleophilic subs.
- nucleophilic addⁿ.

— For feasability of the rxn -ve charge should move from less stable to more stable position

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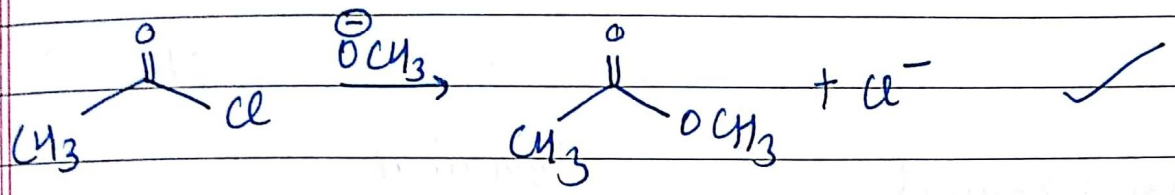
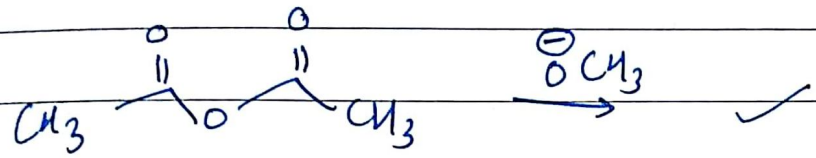
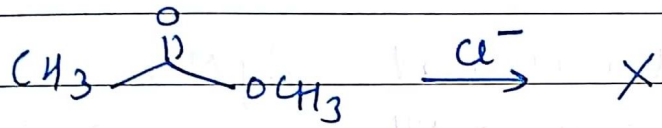
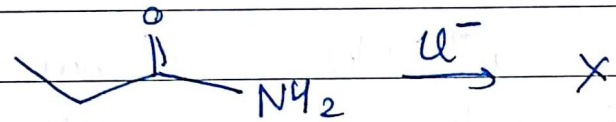
Q. Check feasibility :

1) 

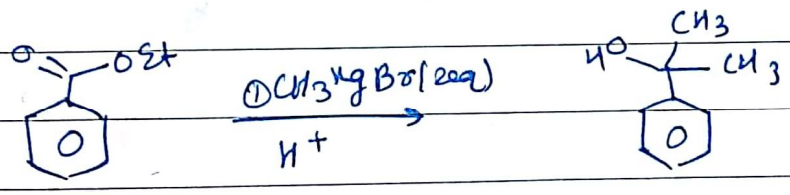
2) 

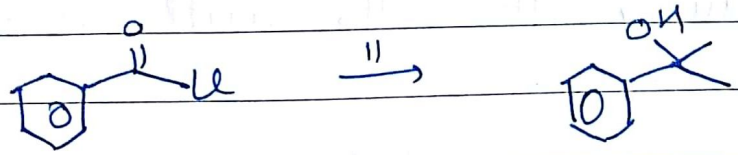
3) 

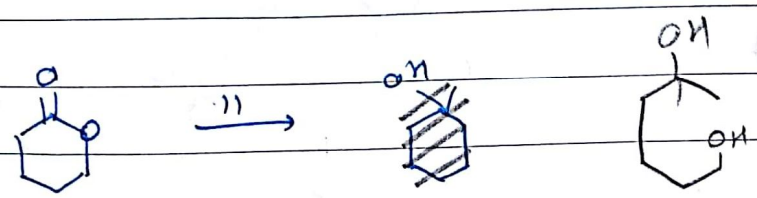
4)

5) 

Q.

1) 

2) 

* 3) 

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- **Test for terminal alkyne :**

$\underbrace{R-C\equiv C-R'}_{\text{Non-terminal}}$ $\qquad$ $\underbrace{R-C\equiv C-H}_{\text{Terminal}}$ (acidic H)

1] **Tollen's Test**

Tollen's reagent - ammoniacal $AgNO_3$

$(AgNO_3 + NH_3\,(aq.)) \longrightarrow Ag(NH_3)_2^{\oplus}$

Basic

$R-C\equiv C-H \xrightarrow{T.R} R-C\equiv C^{\ominus}\,Ag^{\oplus}\ (\downarrow)$

(∵ Basic med.)

white ppt

(Silver acetylide)

{ Slow as base is weak)

★ $R-C\equiv C^{\ominus}$

↳ Acetylide

Q. How compounds having MF C_6H_{10} will form acetylide ?

→ $C\equiv C-C-C-C-C$ ①

① $C-C-C-C\equiv C$ ②

③

$C-C-C-C$
|
C ①
|
C

$C-C-C$
|
C
|
C
|
C

5

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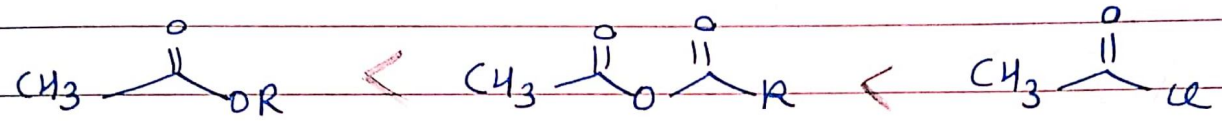
2] Ammoniacal Cu_2Cl_2 sol^n

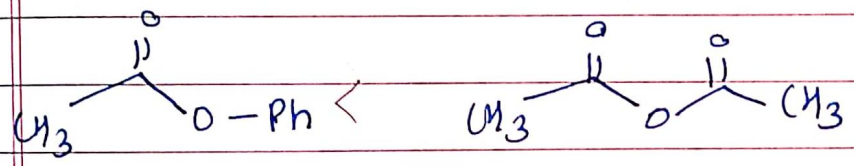
$$R-C\equiv C-H \longrightarrow R-C\equiv C^{\ominus}\,Cu^{\oplus}\ (\downarrow)$$

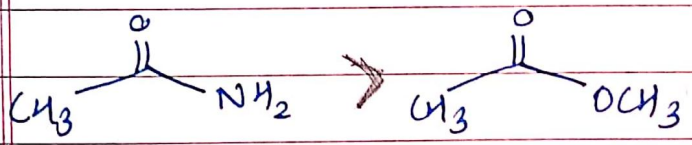
Reddish-Brown ppt

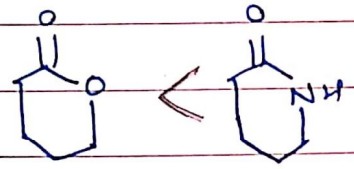
— x —

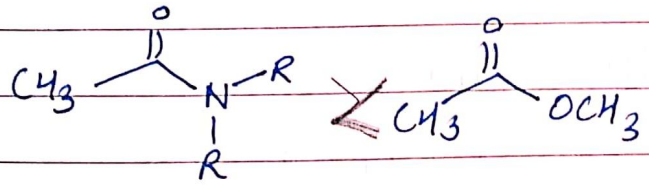
Q. Compare rate of rxn with CH_3MgBr

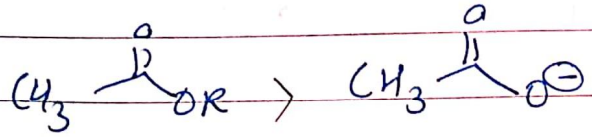
1] 

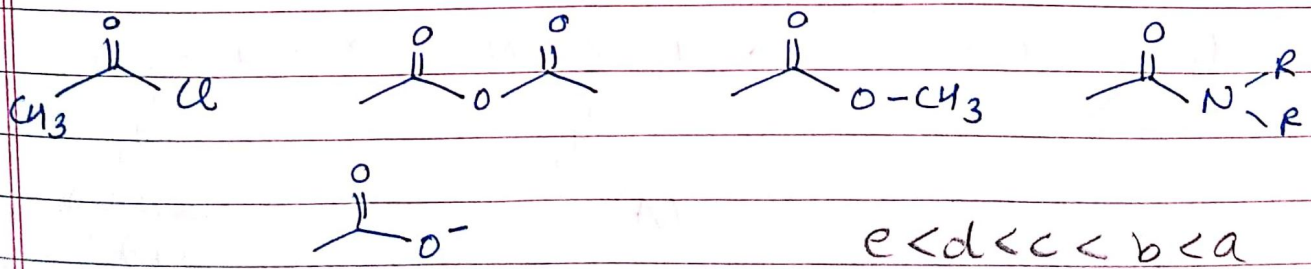
2] 

* 3]  (Acidic nature of amide)

4] 

5] 

6] 

7] 

$e < d < c < b < a$

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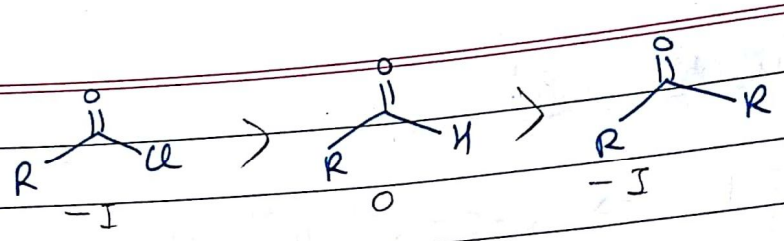
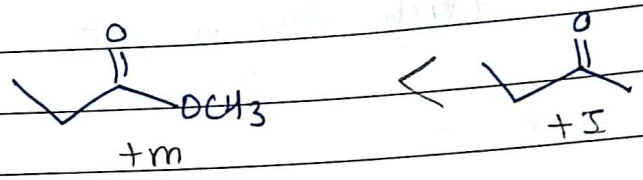
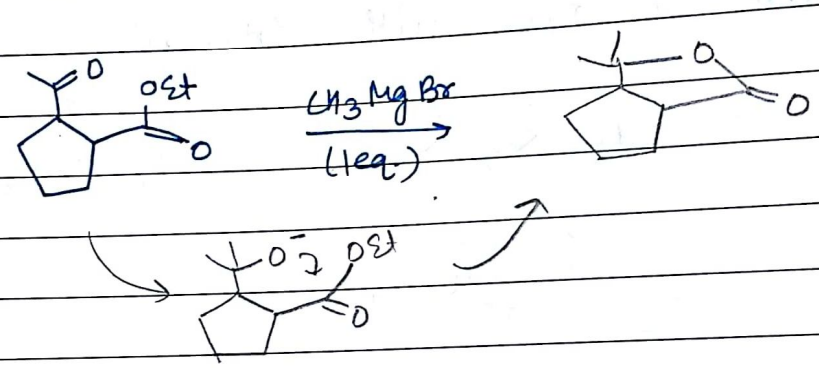
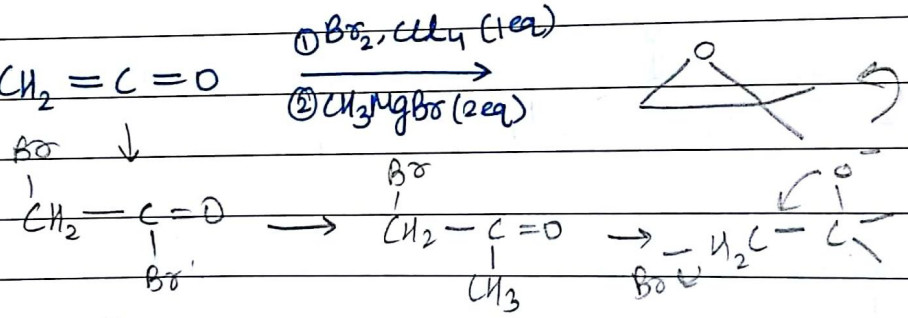
★ 

★ 

★ Q. 

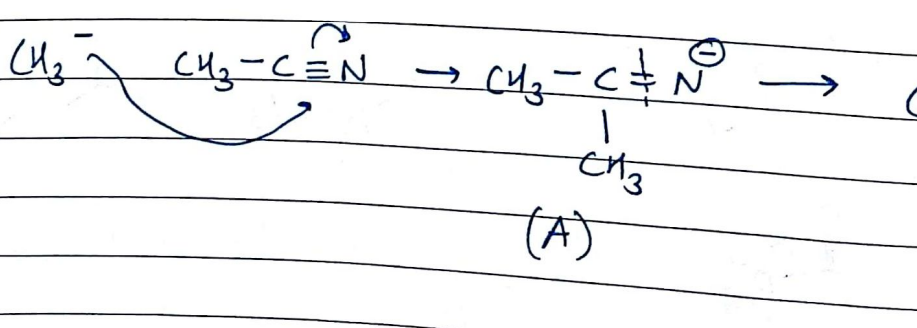
→ $Nu^{\ominus}$ addⁿ
→ $Nu^{\ominus}$ subⁿ

★ Q. 

Grignard reagent with Cyanide :

$$CH_3MgBr + CH_3-C\equiv N \longrightarrow A \xrightarrow{H_3O^{\oplus}} B$$

Mech



Q.
1) $Ph-C\equiv N \xrightarrow{GR} Ph-\overset{O}{\overset{\|}{C}}-CH_3$

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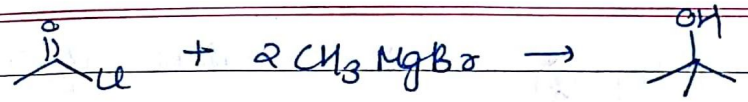
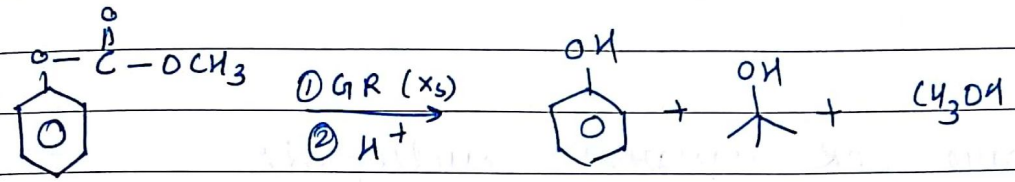
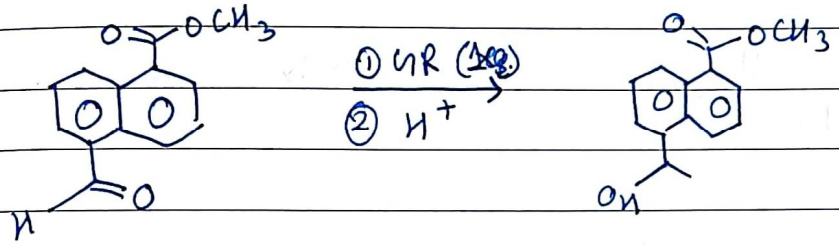
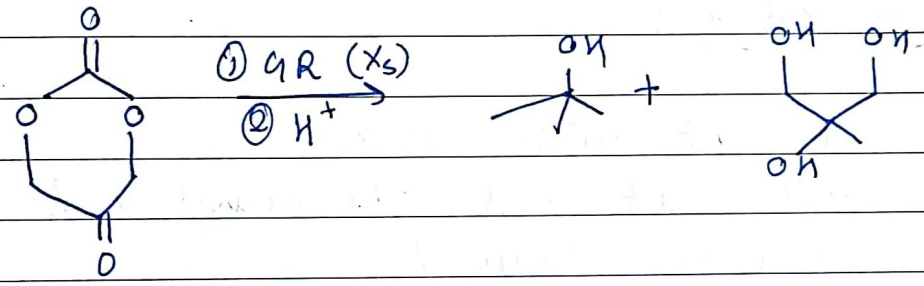
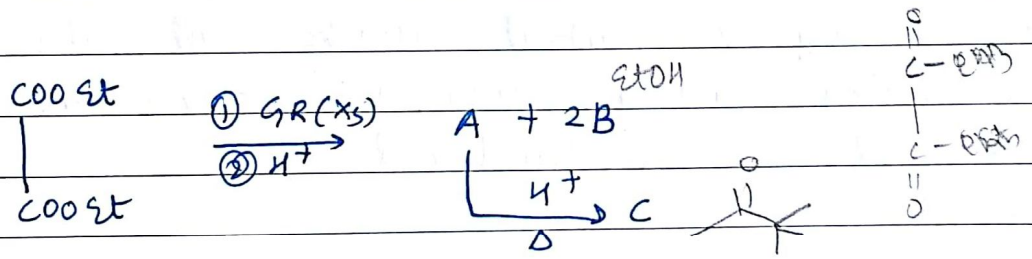
2) 

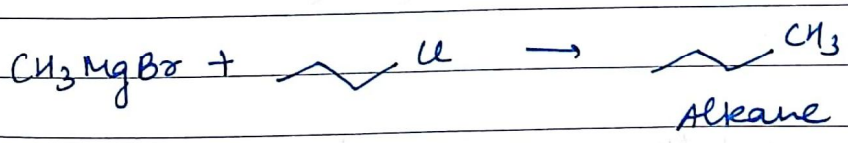
3) 

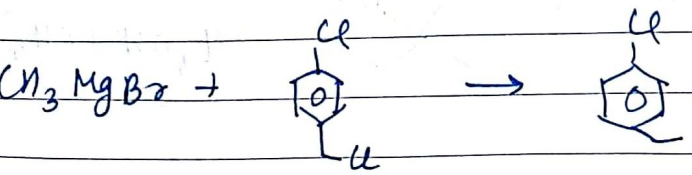
4) 

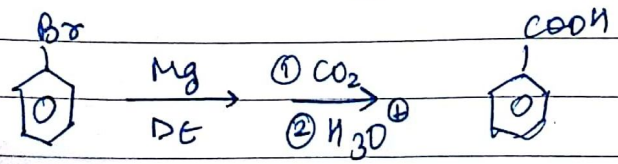
5) 

6) 

7) $2CH_3MgBr + HgCl_2 \longrightarrow (CH_3)_2Hg$.

8) 

9) 

10) 

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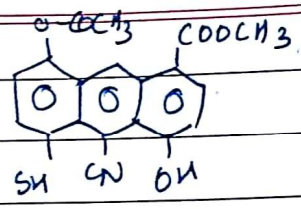
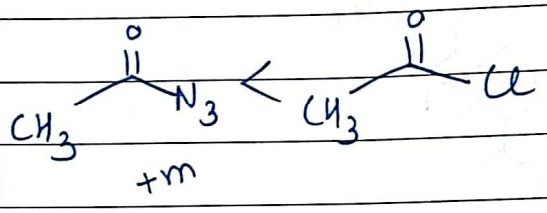
11) 

$\xrightarrow{x(GR)}$ (X) (Max. value of x)

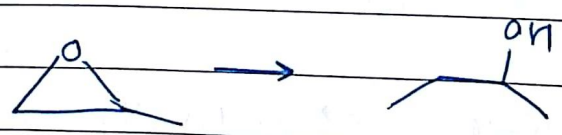
Q. Compare ROR towards nucleophile

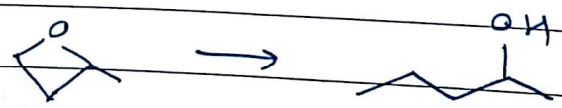
1) 

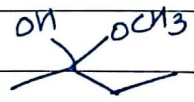
* G.R. with Ether :

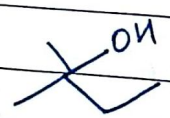
- GR will not react with ether
- GR will will react with 3/4 membered cyclic ether. (coz they are strained).
- When the ring is neutral attack will take place on the carbon having more "δ^+", in general that position will be less hindered.

eg,

- CH_3MgBr + 

- CH_3MgBr + 

Q. 

$\xrightarrow[\text{② } H^+]{\text{① } CH_3MgBr \text{ (2eq)}}$ 

$+ CH_3OH + CH_4$

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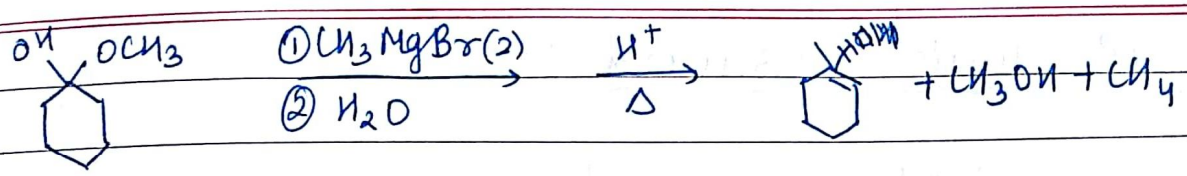
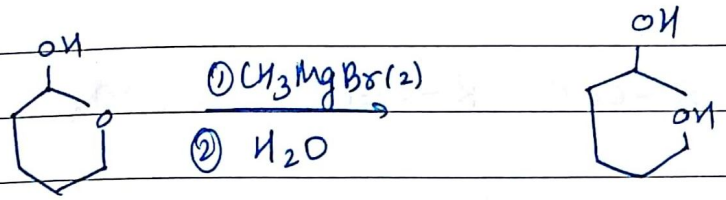
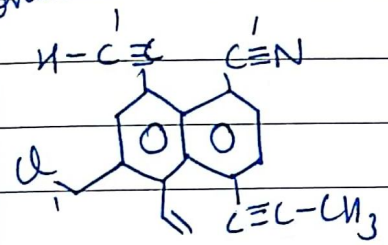
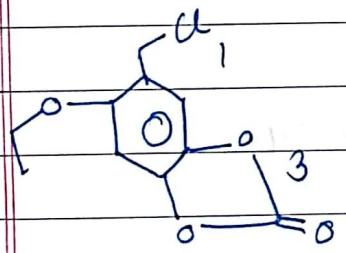
Q. 

Q. 

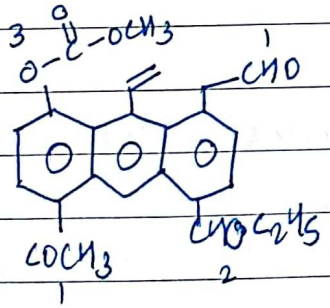
units of HR consumed?

Q. 

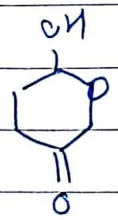
1) ③



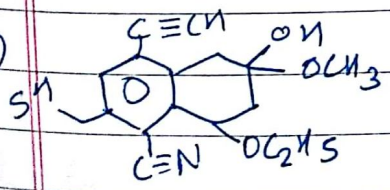
2) ④



3) ⑦



4) ③



5) ⑥

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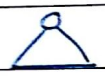
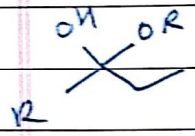
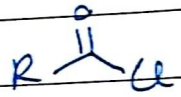
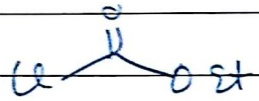
* GR units consumed :

→ Acid - Base = 1

→  , R-CHO, R-COR, R-C≡N, CO_2, SO_3 = 1

→  , R-C(=O)-OR',  = 2

→  = 3

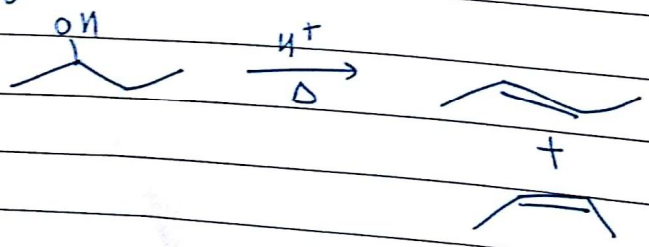
→ , , , = 0

* Few terms in organic chemistry :

1] Stereoselective Rxns :

- In these rxns diff. stereoisomers are formed but one of them predominates becoz the rxn pathway had a choice (kinetic or thermod.)

eg,



(major)

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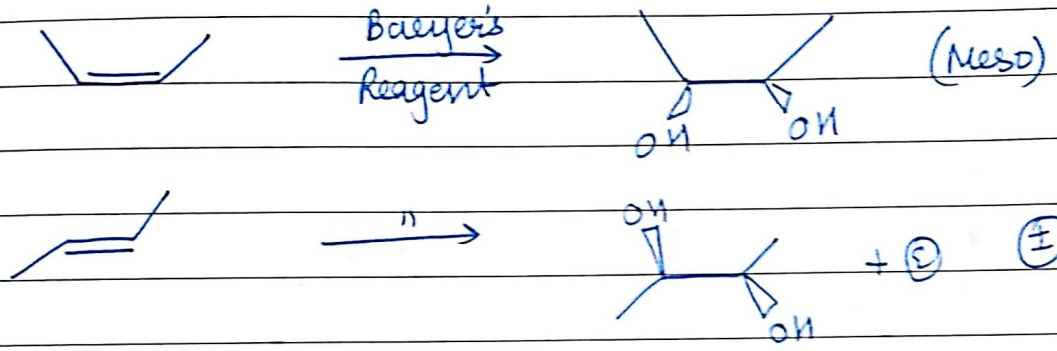
2] Stereospecific Rxns :

- When diff. stereoisomers of the reactants gives diff. stereoisomeric products then the rxn is stereospecific.

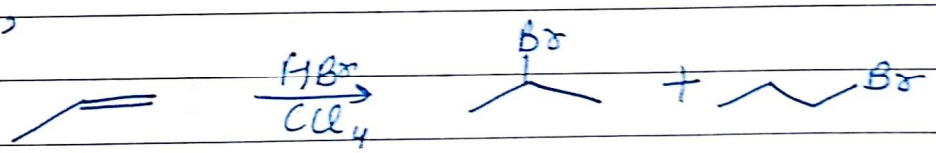
Eg,



3] Regioselective Rxns :

- In these rxns diff. structural isomers are formed but one of them predominates.

Eg,



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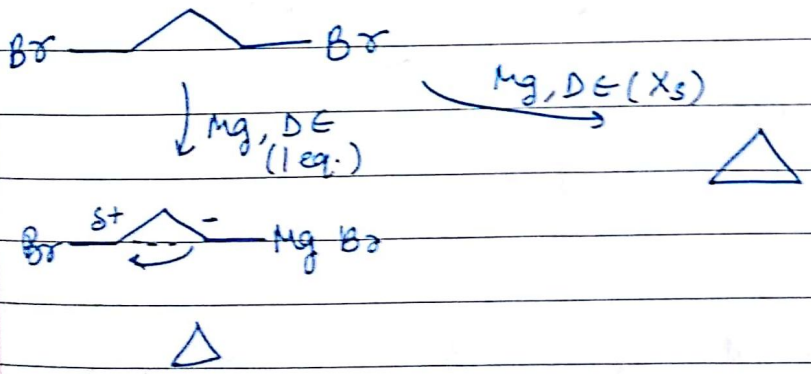

- All stereospecific rxns are stereoselective but not the converse.

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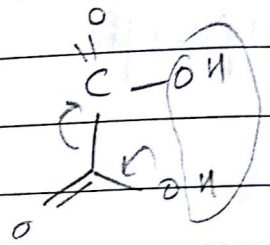
* Heating of dicarbonylic acid :→

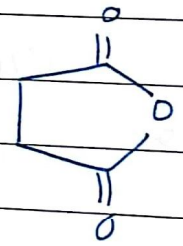
- $\begin{array}{l} COOH \\ | \\ COOH \end{array} \xrightarrow{\Delta} CO_2 + CO + H_2O$

oxalic acid.

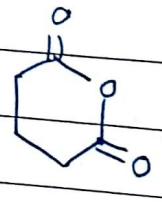


- $CH_2(COOH)_2 \xrightarrow{\Delta} CH_3COOH + CO_2$

Malonic acid

- $CH_2(COOH)CH_2COOH \xrightarrow{\Delta}$  $+ H_2O$

Succinic acid

- $(CH_2)_3(COOH)_2 \xrightarrow{\Delta}$  $+ H_2O$

Glutaric acid

- $(CH_2)_4(COOH)_2 \xrightarrow{\Delta}$ $+ CO_2 + H_2O$

Adipic acid

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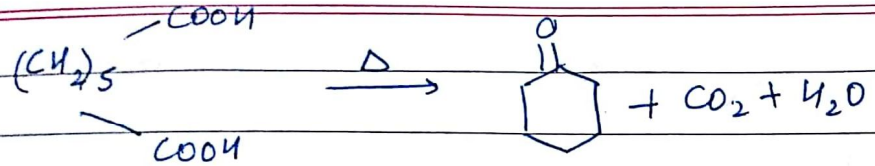
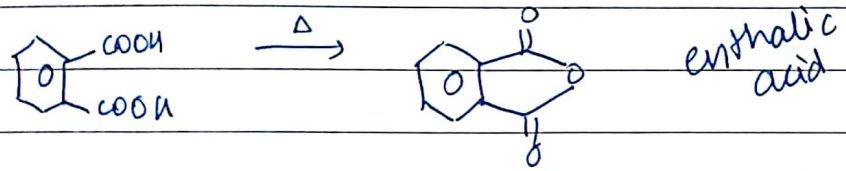
- 

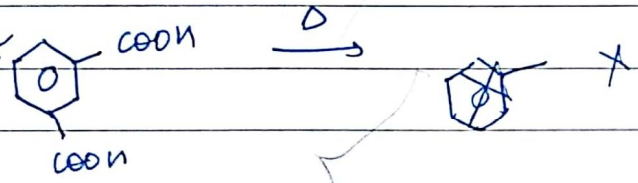
Pimelic acid

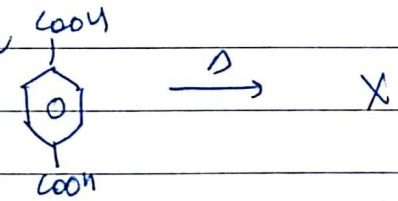
<u>Blank's rule</u> : When aditic & pimelic acid are heated ketone with one lesser carbon is formed.

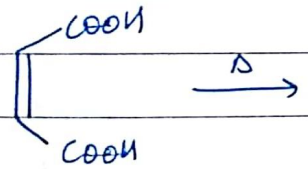
Q.

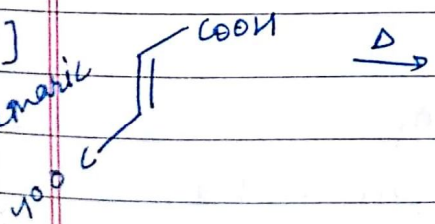
1] 

enthalic acid

2] Isophthalic 

3] Terephthalic 

4] Maleic 

5] Fumaric 

- <u>β-γ unsaturated acid</u> :

- $CH_2 = CH - CH_2 - COOH \xrightarrow{\Delta} CH_3 - CH = CH_2 + CO_2 \ (\uparrow)$

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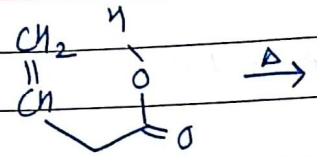
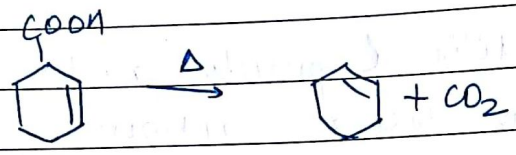
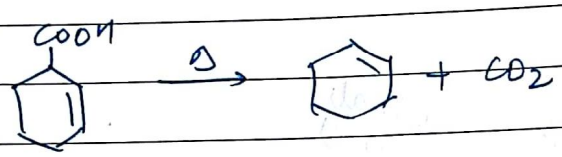
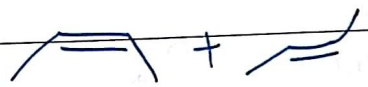
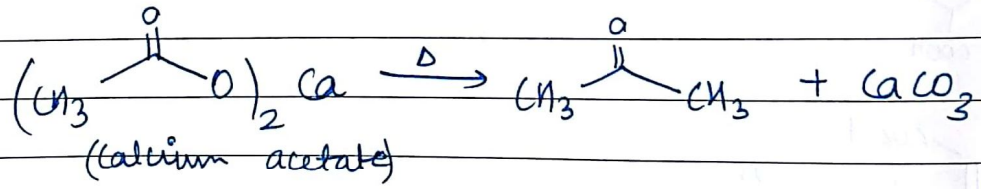
- 

- 

- 

- $CH_2 = CH - \underset{\underset{CH_3}{|}}{CH} - COOH \xrightarrow{\Delta}$ 

- **Heating of Calcium salts :**



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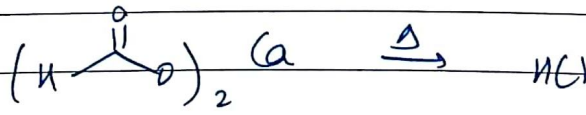
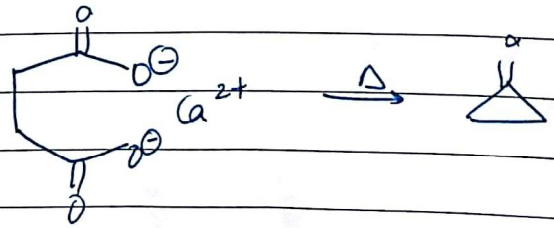
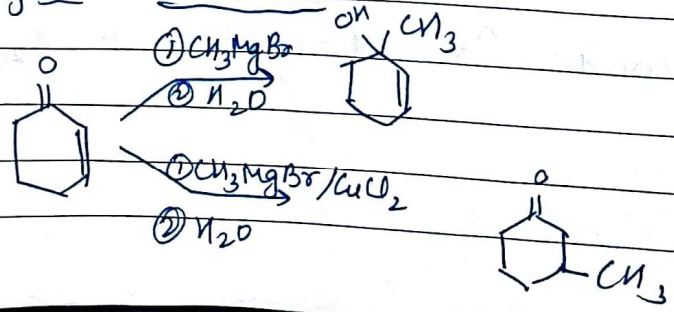
1) 

2) 

- **Conjugate Addition :→**



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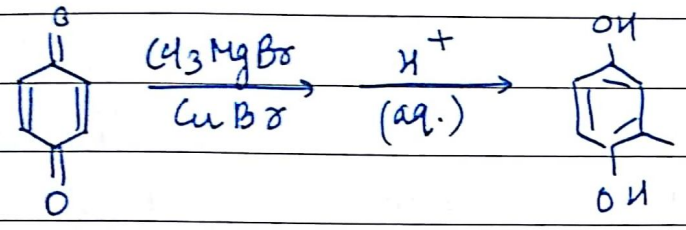
- Transmetallation : $CH_3-\overset{1.9}{Cu}$

- Hard nucleophile / Soft

OH^-, H_2O $\qquad$ S^-H, H_2S

$RMgX$ $\quad$ RLi $\qquad$ $R-Cu$

Q. 

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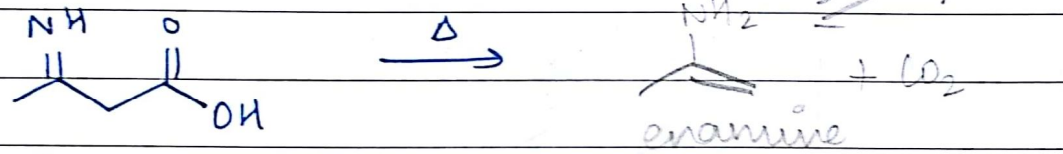
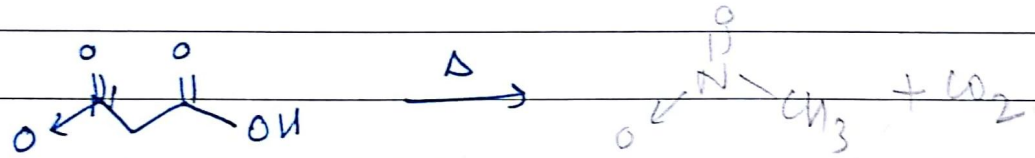
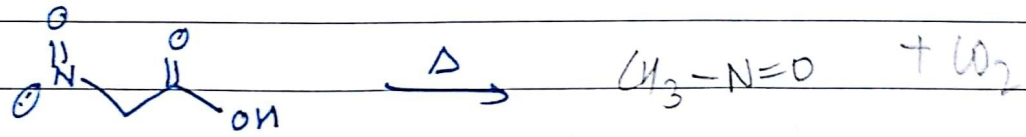
1. 

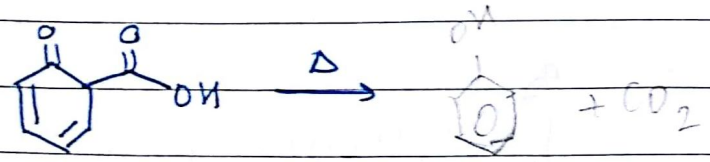
β-Imino acid

2. 

α-Nitro acid

3. 

α-Nitroso acid

4. 

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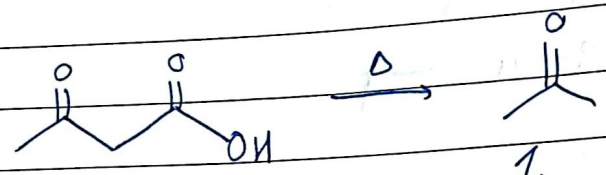
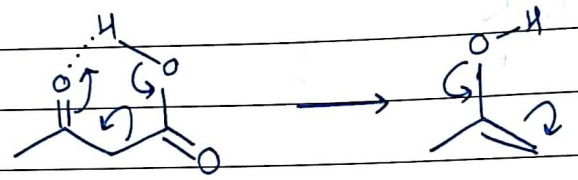
* HEATING EFFECTS

- β-keto acids on heating releases CO_2 gas.

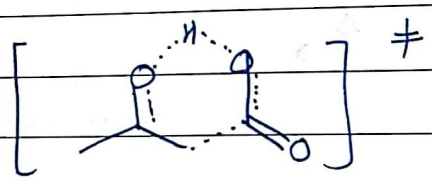


(R) MECH.



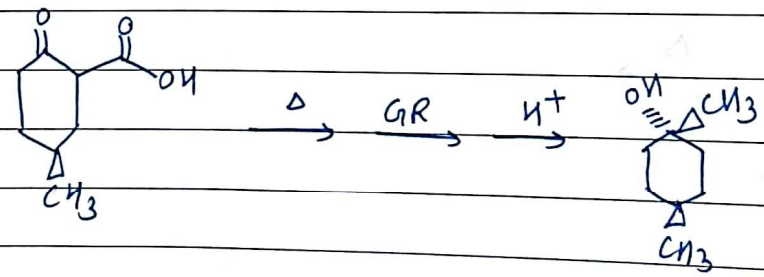
- Rxn is fav. due to formn of 6MCTS so energy req. is less.

6MCTS ⇒



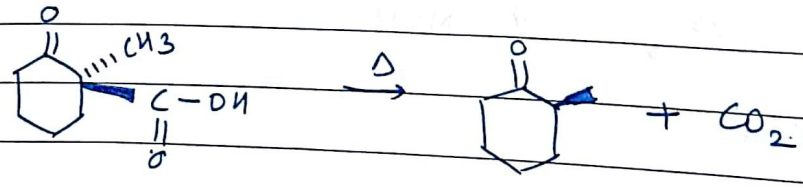
Q.

1.



+ Trans.

2.



(±)

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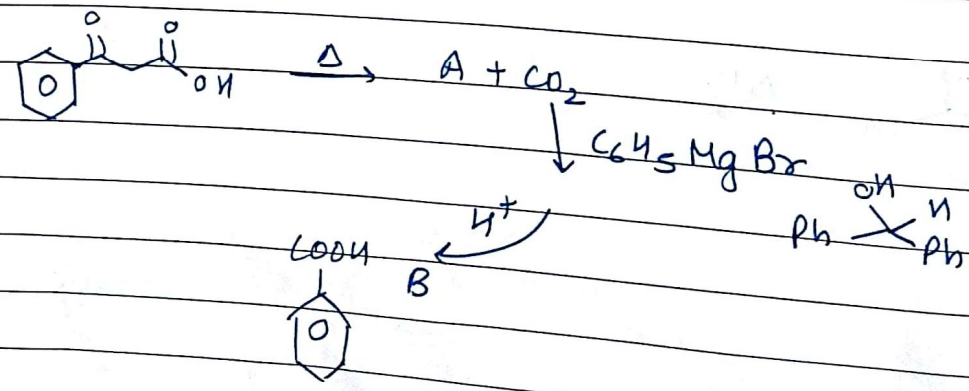

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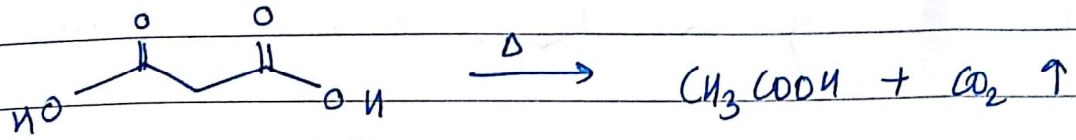
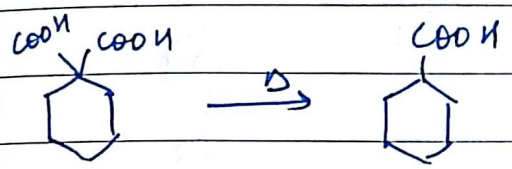
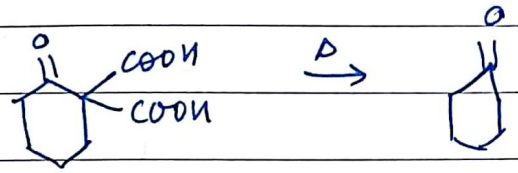
- **Heating of Gem di-carbonylic acids :**



(Malonic acid)

\# 

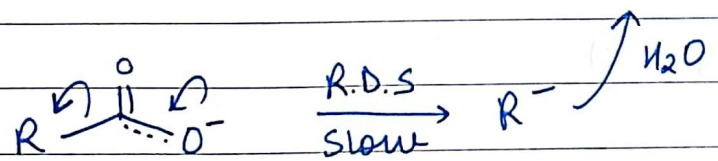
\# 

- **Soda-lime process :**

Soda lime mixture = NaOH + CaO

$$R-COONa \xrightarrow[\Delta]{NaOH + CaO} R-H + Na_2CO_3$$

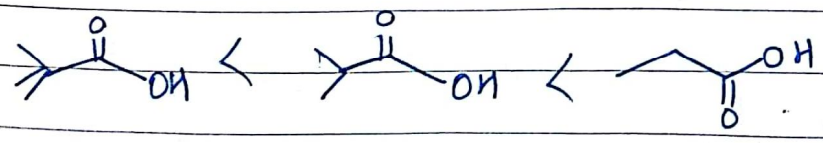
MECH.



Note :

- Rate $\propto$ Stability of R^-
- Decarbonylation
- NaOH + CaO (Easier to handle)

Q. Compare rate of decarboxylation

1] 

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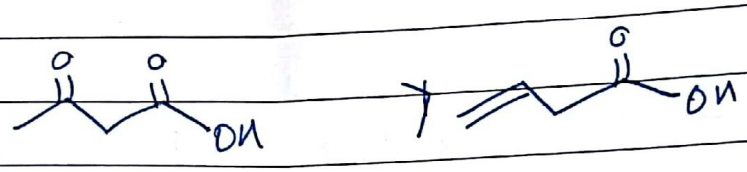
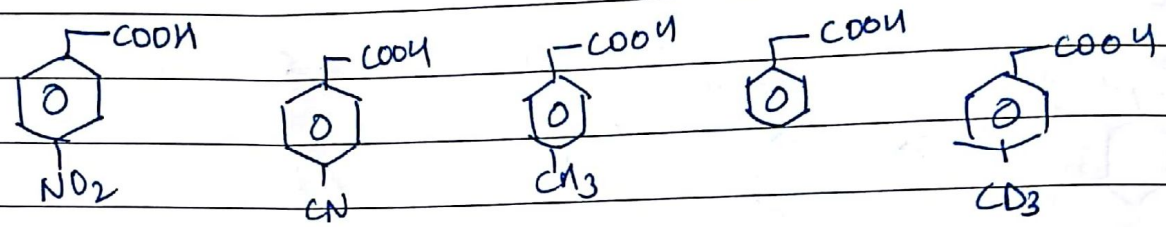
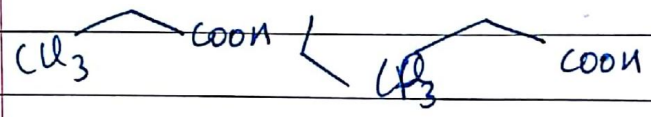
2) $H-C\equiv C-CH_2COOH > CH_2=CH-CH_2-COOH$ b)a

3] 

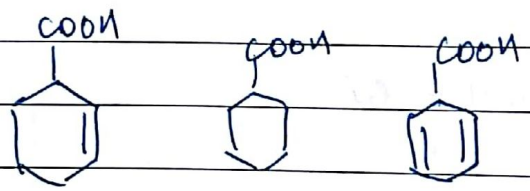
4] 

c < e < d < b < a

5] $CCl_3COOH > CF_3COOH$ b)a

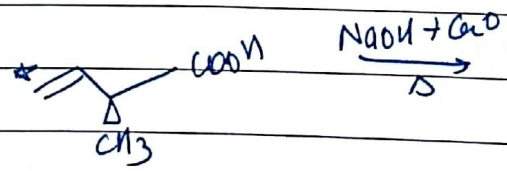
6] 

b)a

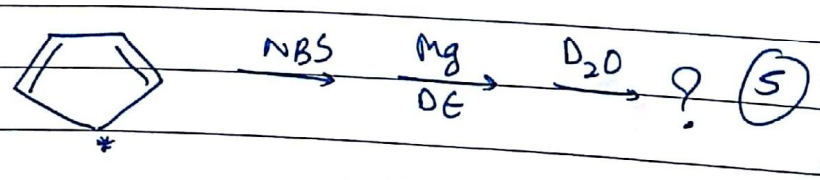
7] 

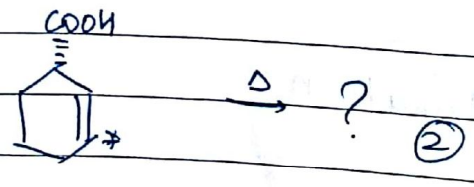
c > a > b

Q.

1) 

$C^* = 4$

2) 

3) 

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- Use of R_2Cd :

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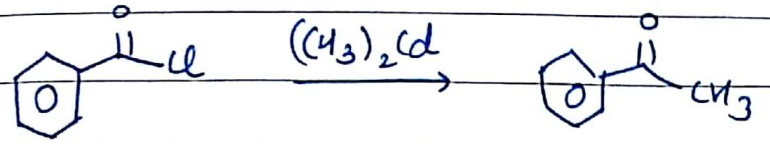
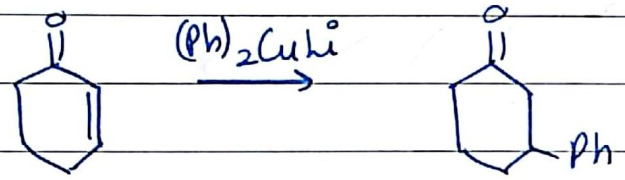


This reagent will not react with ketone. So rxn is stopped at this stage.

- Gilman's reagent :→

$(R)_2 \overset{\ominus}{Cu}\overset{\oplus}{Li}$ (Dialkyl / Aryl lithium cuprate)

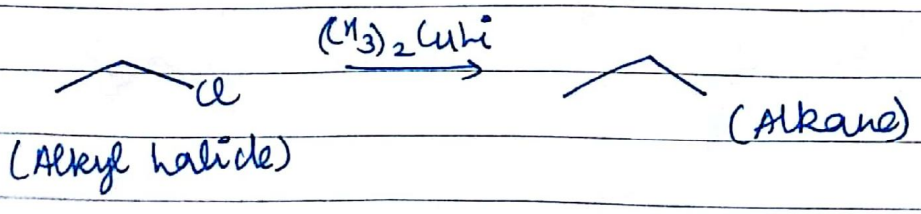


(1,2) → R–Li, R–MgX

(1,4) → R–MgX/CuX , R_2CuLi

- Corey-house reaction :

In This reaction Gilman's reagent reacts with alkyl halide to give alkane in good yield.
Excellent yield is obtained which is not possible in case of R-Li & R-MgX.
In case of R-Li & R-MgX, additional products such as elimination, reduction, ~~metal~~ halide exchange products can be formed.



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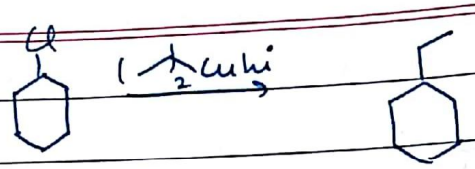
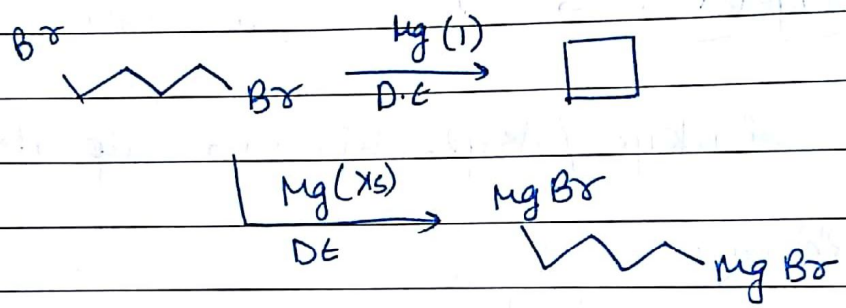
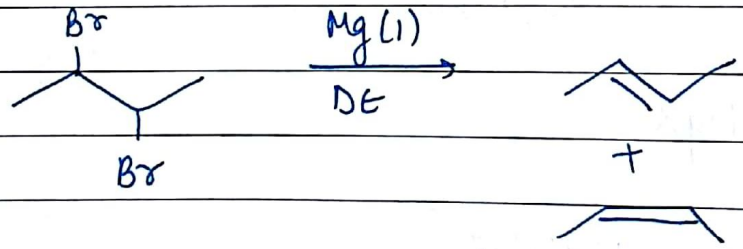
Q. 

- $Br-(CH_2)_n-Br$

  if $n \geq 4$ ⇒ Di grignard reagent will be formed.

  eg,



- 

※ $CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\Delta]{MnO} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

(same as Ca salts)

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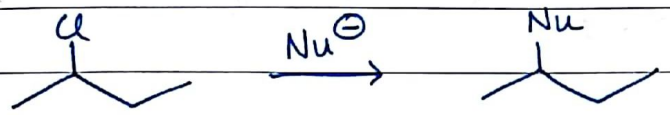
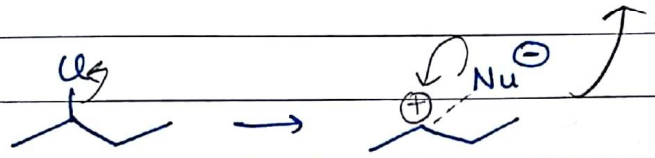
Halogen Derivatives

* Nucleophilic Substitution reactions on saturated carbon :→



Two mechanisms are possible.

MECH 1]

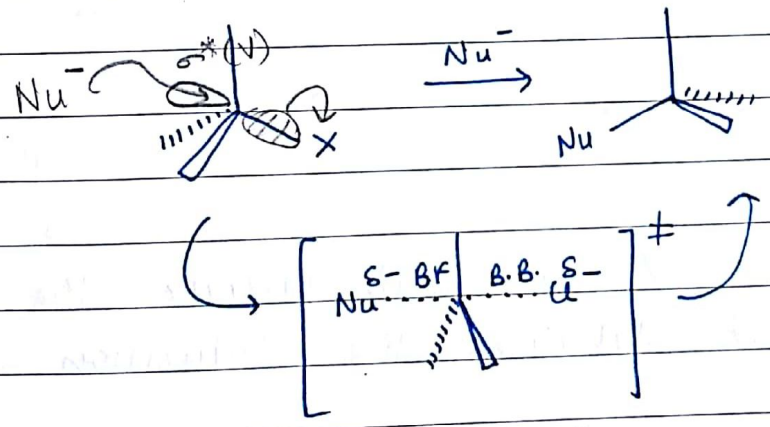


(2 step)

2]

(single step)

- S_N2 Reaction (Substitution Nucleophilic Bimolecular) :→



sp^2 / T.B.P

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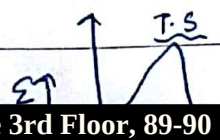
- It is one step rxn.
- $R = K[\text{Alk. hal.}]^1[Nu^-]^1$; so if conc. of R−X as well as nucleophile is doubled then rate becomes four times.
- Order = molecularity = 2 so it is known as S_N2



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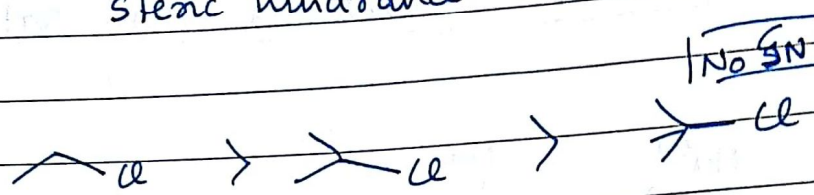
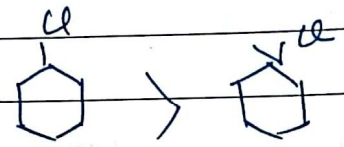
- $R \propto \frac{1}{\text{steric hindrance}}$

- 

- 

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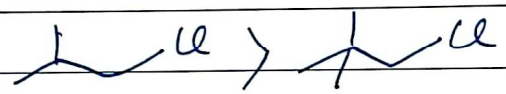
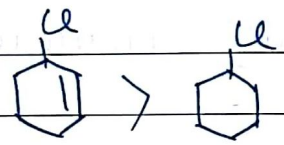
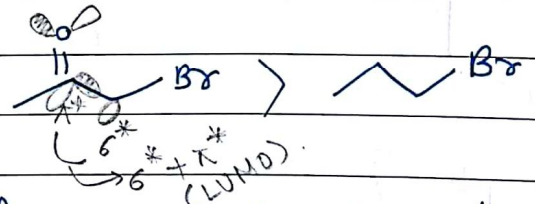
-  → (Notorious towards S_N2)

- 

α - keto bromo

JEE * - 

(exceptionally ↑ rate due constructive overlap b/w π & σ*)

- Presence of C=C / C=O will favour the rate of S_N2. Coz it stabalizes the transition state by conjugation.

- Polar aprotic solvent is preferred. Coz Nu^- is stronger in this case.

$SN^{\ominus}$ in DMF ✓
$SN^{\ominus}$ in H_2O

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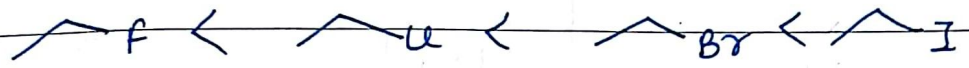
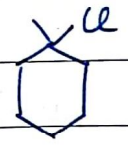
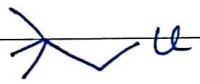
- R α Better leaving group.



- Compound — Why S_N2 rxn is not favourable

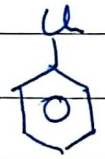
1.  steric crowding (3°)

2. steric crowding (3°)

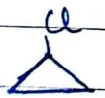
3.  steric crowding

4. double bond chr

5. double bond chr

6. 
   - repn b/w $Nu^{\ominus}$ & e^- cloud of benzene
   - partial double bond chr

7. Bredt's rule in T.S.

8.  Angle strain in T.S.

9. Bad leaving gp.

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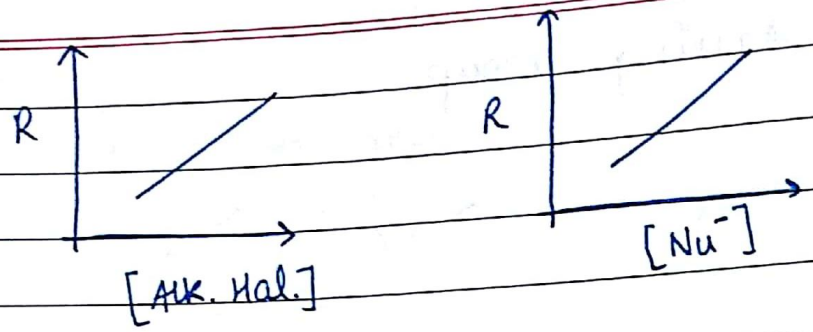
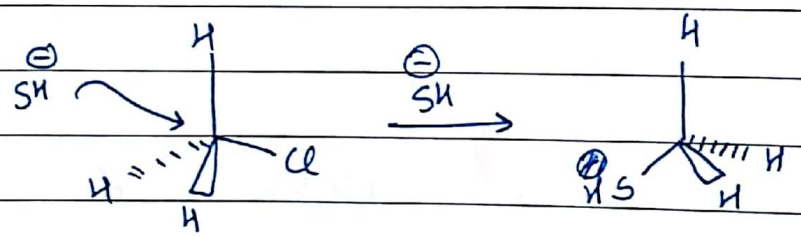


$R = k\,[\text{Alk. Hal.}][Nu^-]$

- Strong Nu^- favours S_N2.
  generally a -vely charged Nu^- is considered strong
  I^-, $\overset{\ominus}{S}H$, $CH_3\overset{\ominus}{S}$, $Ph\overset{\ominus}{S}$, $N_3^{\ominus}$, $\overset{\ominus}{O}H$, $R\overset{\ominus}{S}$, $AcO^{\ominus}$, $HC\equiv C^{\ominus}$, $\overset{\ominus}{C}N$

- <u>Inversion</u> :→



Q. Which of the following will undergo complete stereochemical inversion ?

a) CH_3-Cl
b) $(CH_3)_2CHCl$
c) $(CH_3)_3CCl$
d) CH_3CH_2Cl

- Inversion will take place even if chiral centre is not present.

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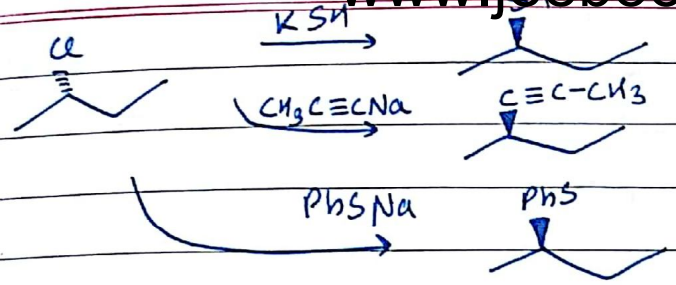
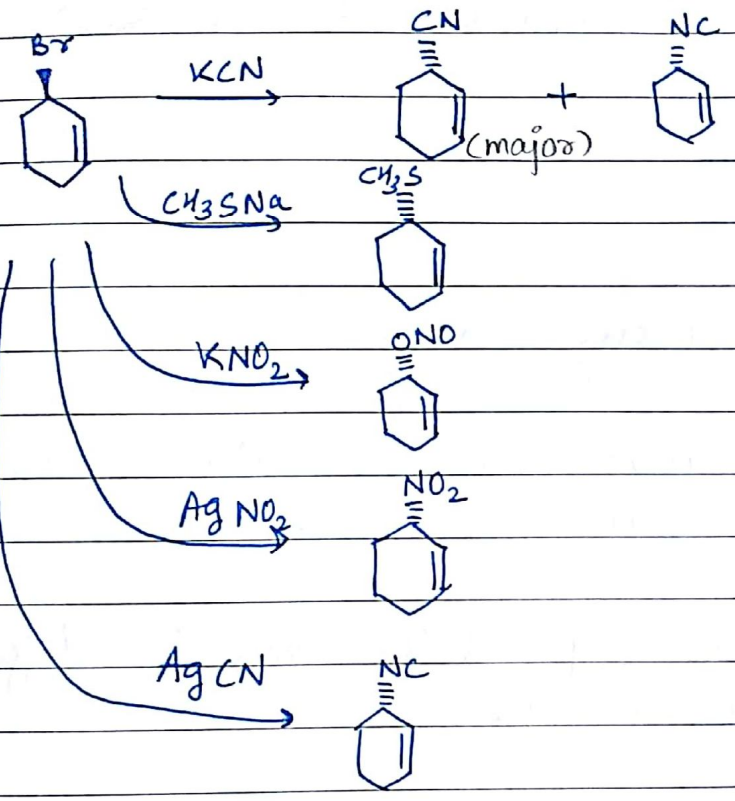
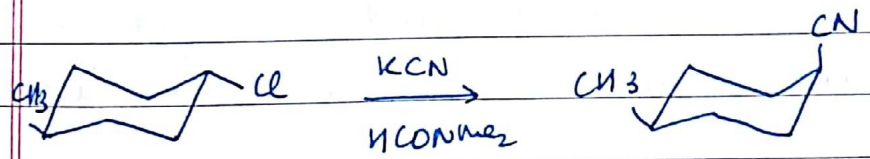
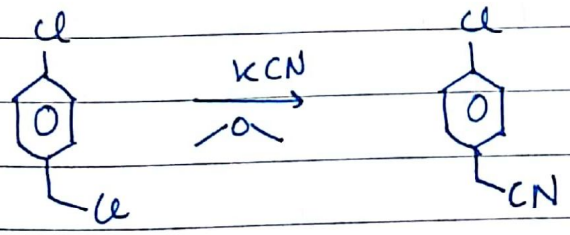
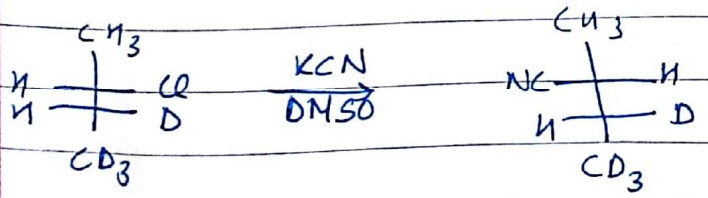
Q. 

Q. 

Q. 

Q. 

Q.

Q. 

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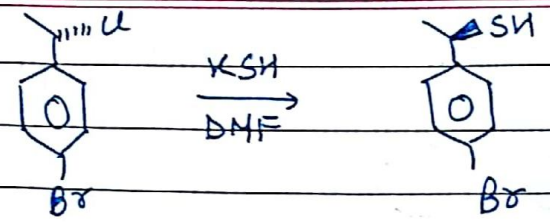
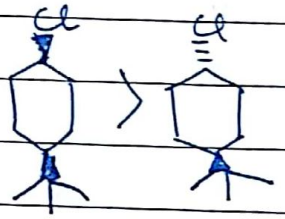
Q.



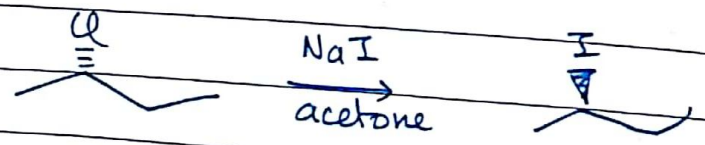
Q.



(compare rate of S_N2)

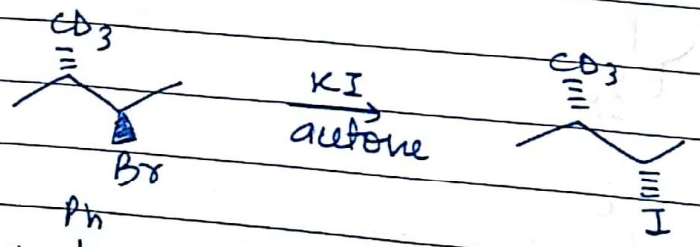
* FINKELSTEIN Rxn :→

- It is halide exchange rxn in which one halogen is replaced by Iodine.
- The basic principle of this rxn is difference in solubility in acetone.
- In the given rxn, NaCl will be ppt out and equilibrium will shift in → direcⁿ.



Q.

1)



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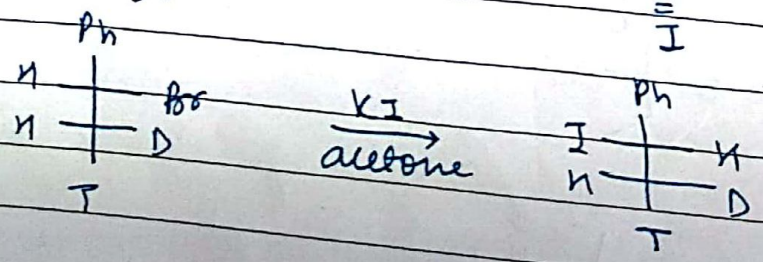

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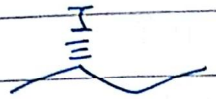
3) What is the direc^n of final optical rotation ?

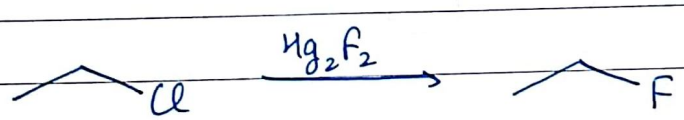
(+)  $\xrightarrow[\text{Acetone}]{NaI}$ (I)

Racemisation will take place due to formation of equimolar mixture of enantiomers.

* SWARTS Rxn :

- It is halide exchange rxn in which halogen is replaced by flourine.

- Transition metal flourides are used. (AgF, Hg_2F_2, CoF_2, SbF_3)



* WILLIAMSON ETHER SYNTHESIS :→

- In this rxn alkoxide reacts with alkyl halide to produce ether.

- For best yield,
  - less hindered alkyl halide
  - less hindered alkoxide ion
  - good leaving group.

$$\underset{\text{Alkoxide ion}}{RO^-Na^+} + \underset{\text{alk. halide}}{R'\overset{\delta+}{-}\overset{\delta-}{X}} \longrightarrow \underset{\text{ether}}{R-O-R'} + NaX$$

$$CH_3O^-Na^+ + CH_3-Cl \longrightarrow CH_3-O-CH_3$$

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- **Preparation of alkoxide :**

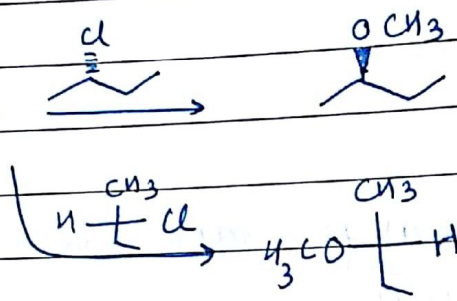
$$R-OH \xrightarrow{Na/K} R-O^-Na^+ + \tfrac{1}{2}H_2\uparrow$$

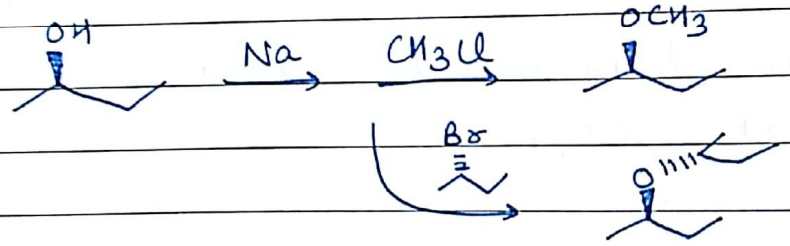
$$R-OH \xrightarrow{NaNH_2} R-O^-Na^+ + NH_3\uparrow$$

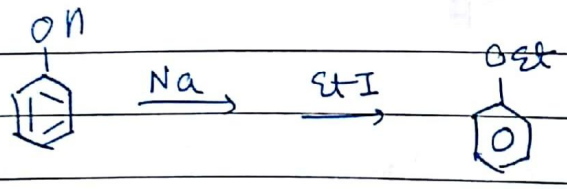
$$R-OH \xrightarrow{NaH} R-O^-Na^+ + \tfrac{1}{2}H_2\uparrow$$

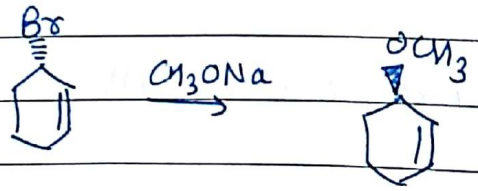
$$R-OH \xrightarrow{R-Li} R-OLi + RH$$

Q.

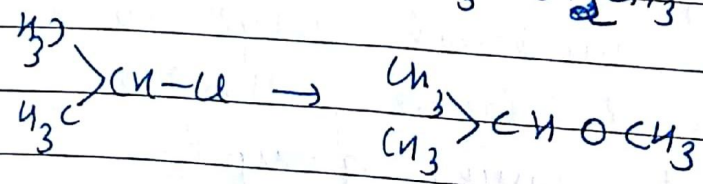
1] $CH_3OH \xrightarrow{Na}$ 

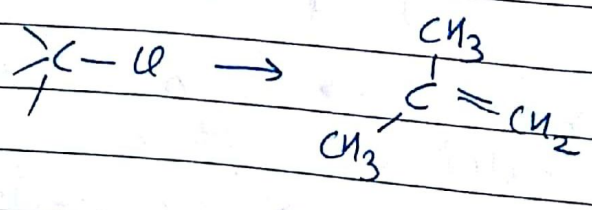
2] 

3] 

4] 

5] $CH_3ONa + CH_3CH_2Cl \longrightarrow CH_3OCH_2CH_3$





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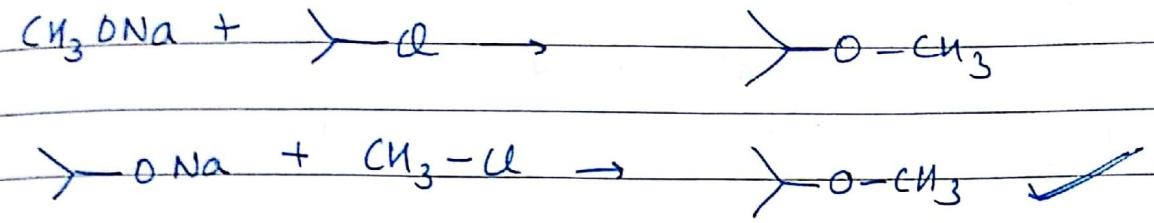
6] Which is more suitable?



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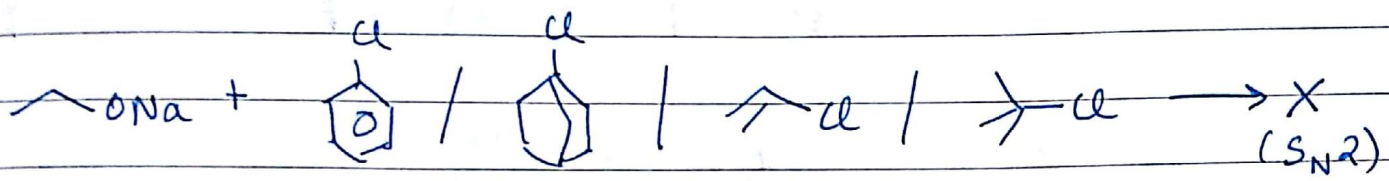
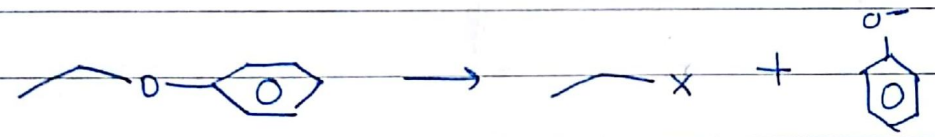


8] Identify the suitable combination to prepare the ether.

a)

b)



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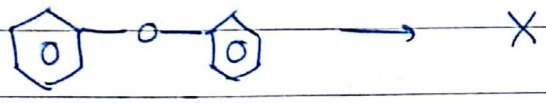
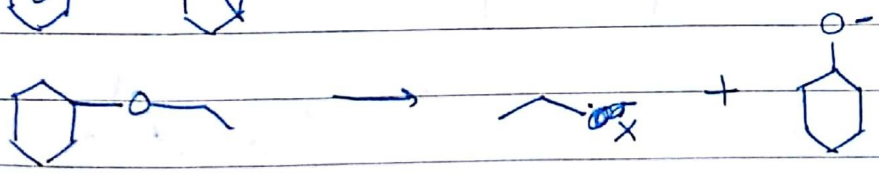


d)

e)



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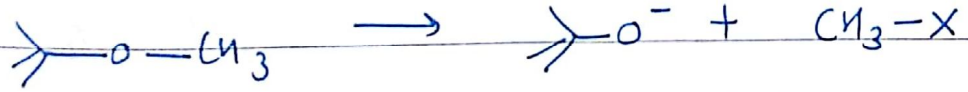
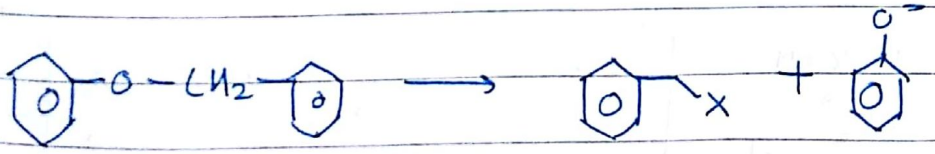


g)



h)

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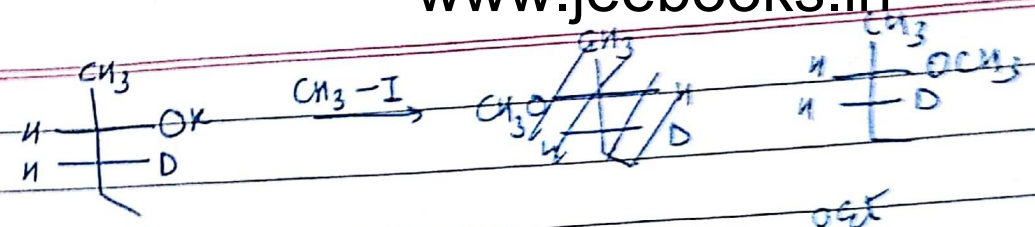
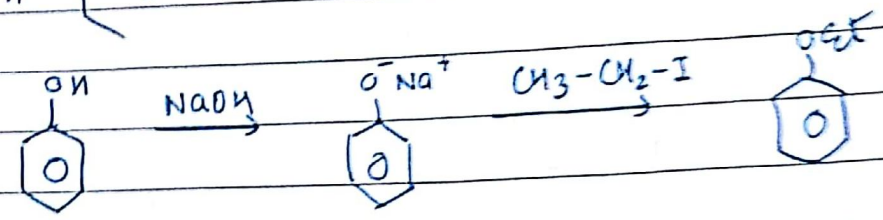
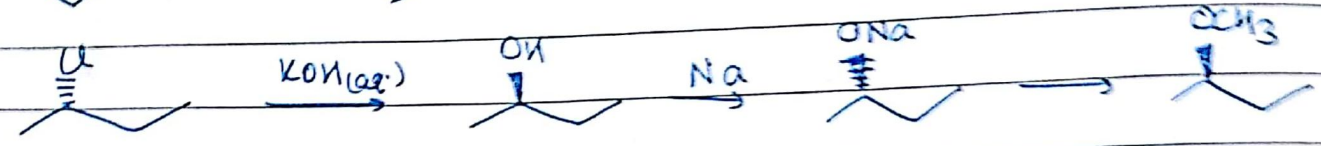
Q. 1)



2)



3)



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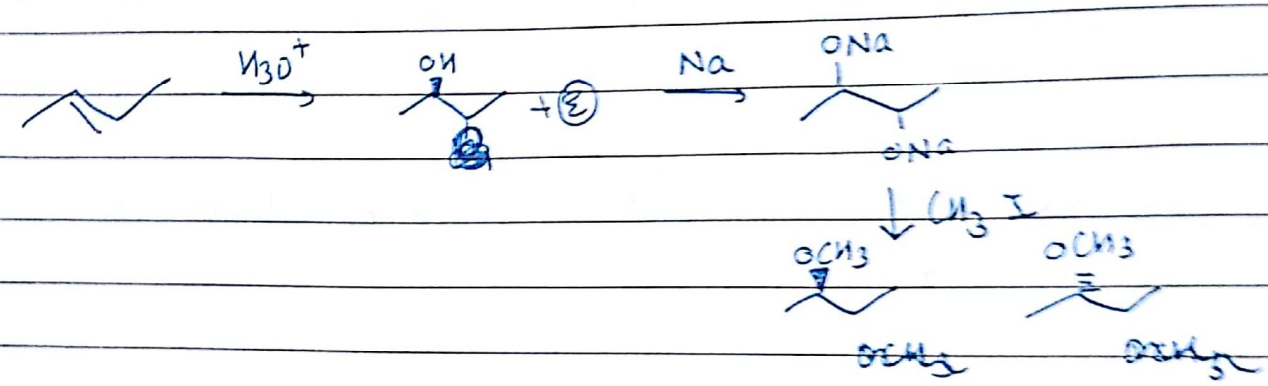

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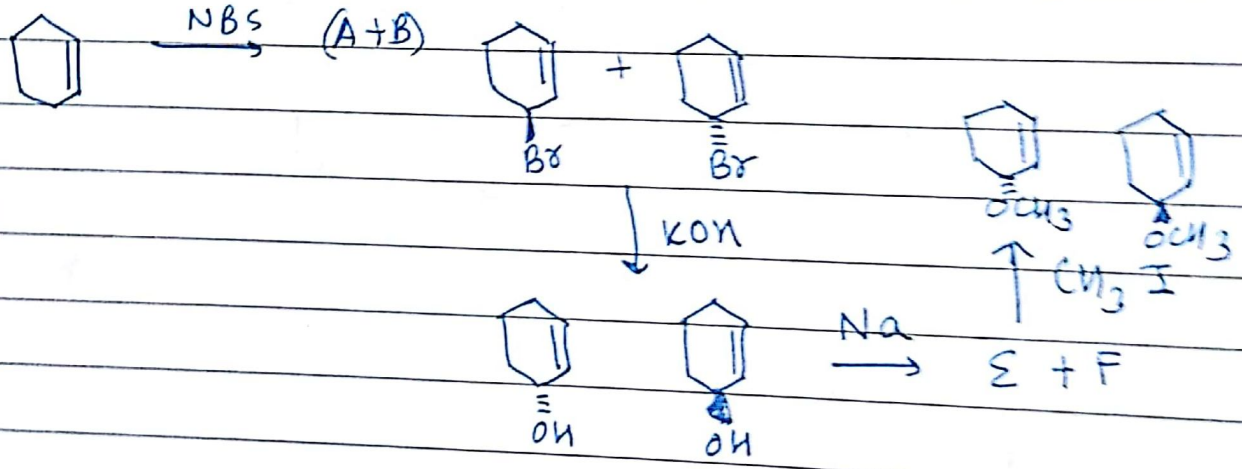

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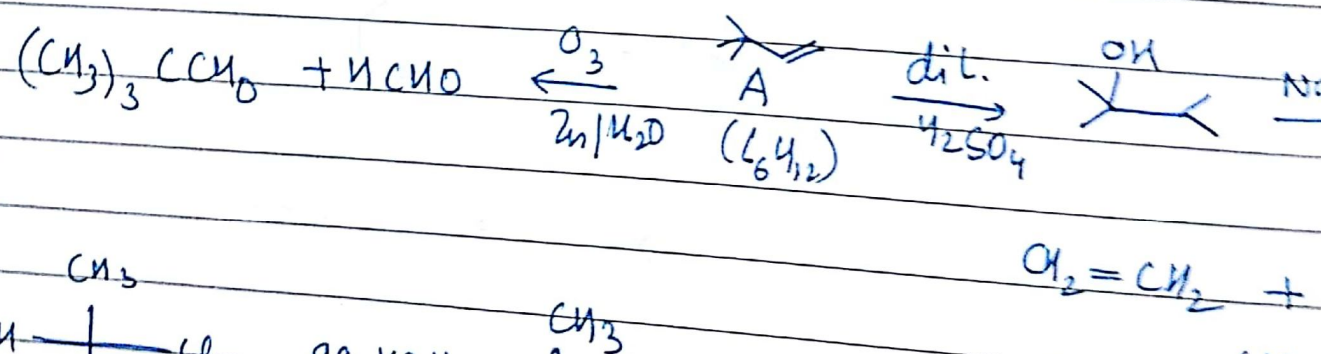

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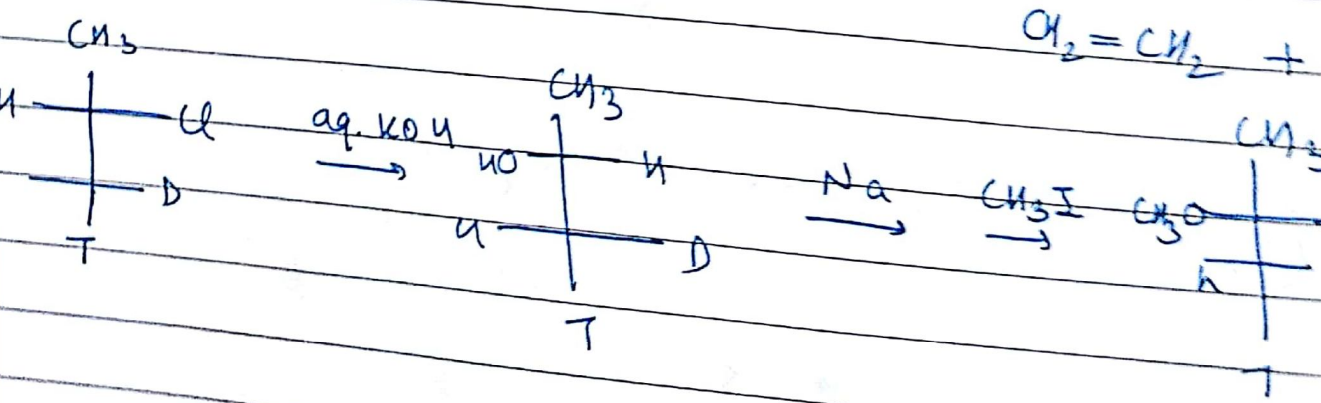

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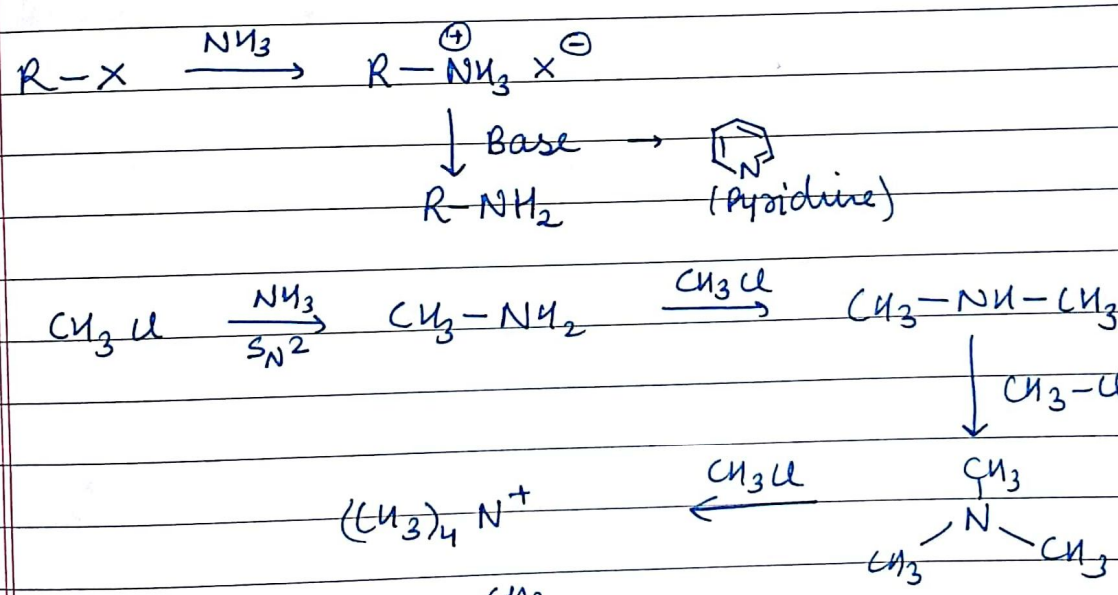
* Ammonolysis :→

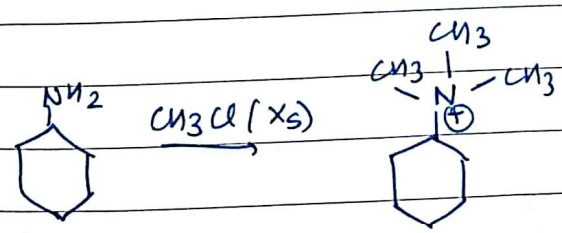
- In this ran, NH_3 reacts with alk. halide to give alk. ammine which on reaction with excess alk. halide produces quaternery ammonium salt.

- Mild base is added to get the neutral ammine.

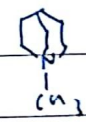
- Follows S_N2 mechanism coz it is a strong nucleophile.



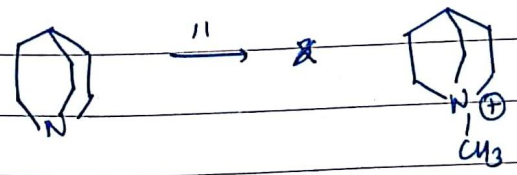
Q. 1)



H.E.M
(Hoffmann exhaustive methylation)

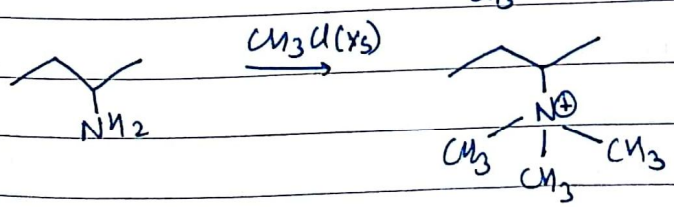


* 2)



- Replace l.p. & H with methyl.

3)



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- NOTE :

- Walden Inversion is also known as inversion

- Beilstein test :

It is a test for alkyl halides.
R-F, R-Cl, R-Br, R-I

Obs : greenish blue flame is observed when is heated with Cu.

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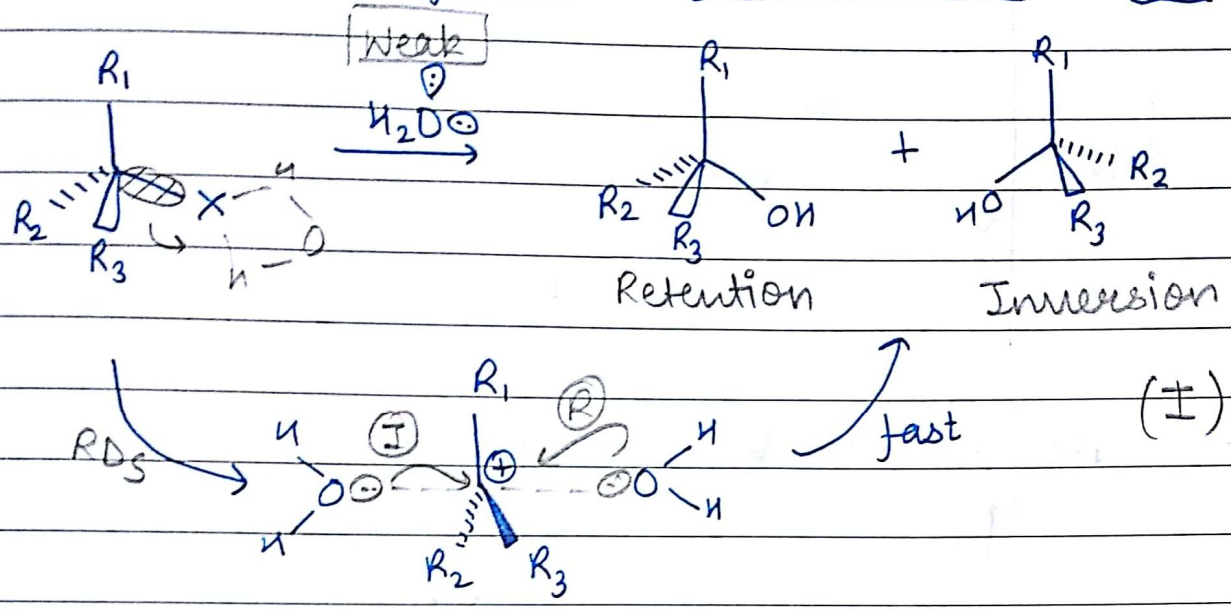
Substitution Nucleophilic Unimolecular (S_N1) :→



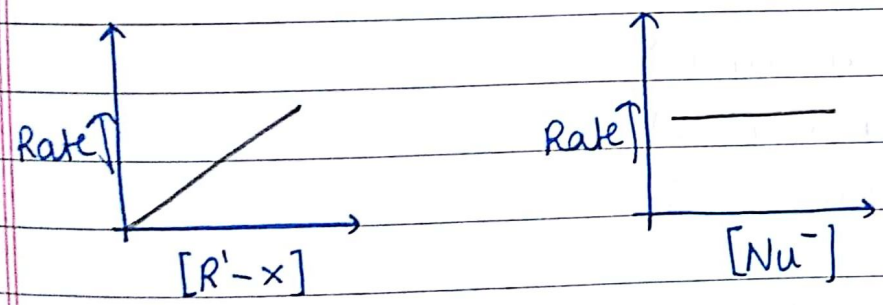
Formation of carbocation is RDS. So,

Rate ∝ stability of carbocation

3° > 2° > 1°

only one specie is involved in R.D.S

Rate = $k[\text{Alk. Hal.}]^1$ (Hence it is known as S_N1)



→ Rate is independent of conc of Nu^-

* Both mech. S_N1 as well as S_N2 will compete simultaneously on the basis of combined rate law.

$$R = \underbrace{k_1[R'x][Nu^-]}_{S_N2} + \underbrace{k_2[R'-x]}_{S_N1}$$

i.e, for favouring S_N1 conc. of Nu^- should be less.

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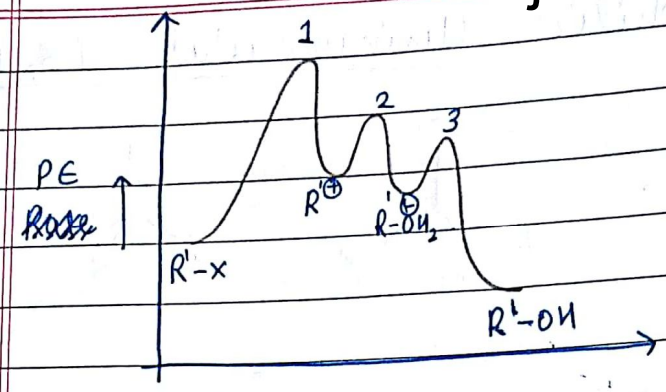
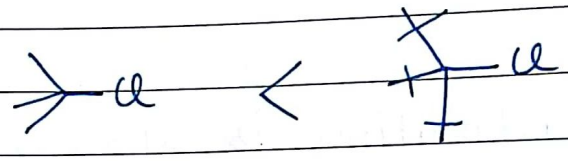


- Rate ∝ Steric acceleration.

  eg,



{Rate}

- Weak nucleophile is commonly used. Most of the rxns are solvolysis (S_N1) in which solvent acts as a nucleophile.

  eg,

  H_2O (hydrolysis)
  CH_3OH (methanolysis)
  C_2H_5OH (Ethanolysis)
  $HCOOH$ (formylysis)

Polar protic solvent ~~if~~ is favourable for S_N1 coz it solvates quite effectively cation as well as anion.
Energy released in this process is used to break carbon halogen bond.

- Better l.g. favours S_N1 rxn.

$$F < Cl < Br < I$$

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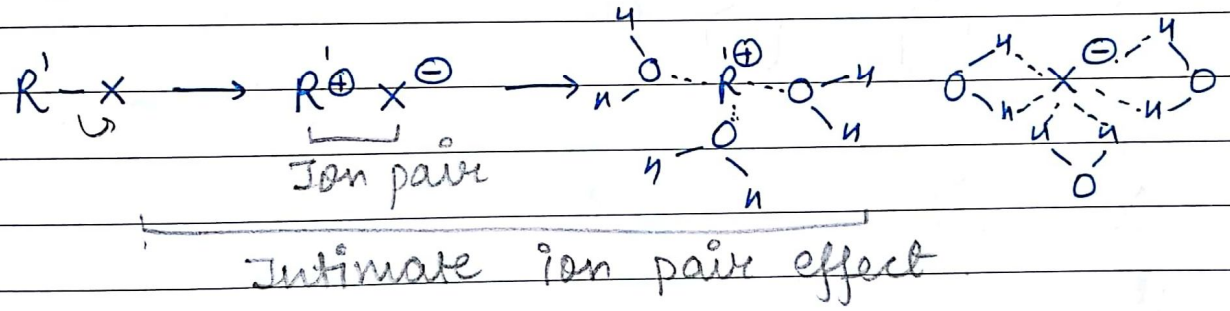
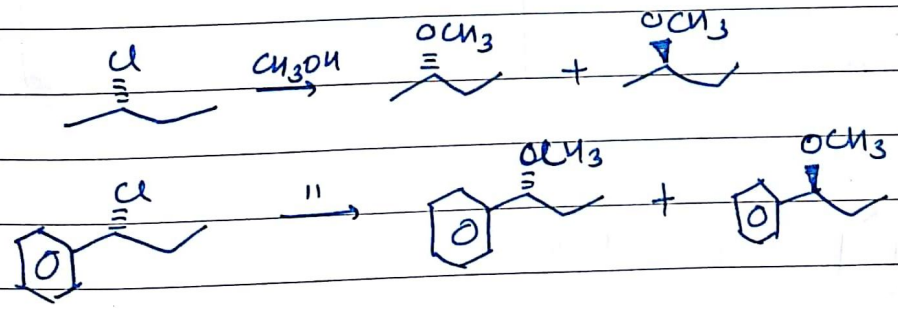
- Two type of products will be obtained if chiral centre is present.
  - a) Retention product : Formed by same side attack in which ~~spectat~~ spacial arrangement of groups remains same.
  - b) Inversion product : Formed by opp. side attack.

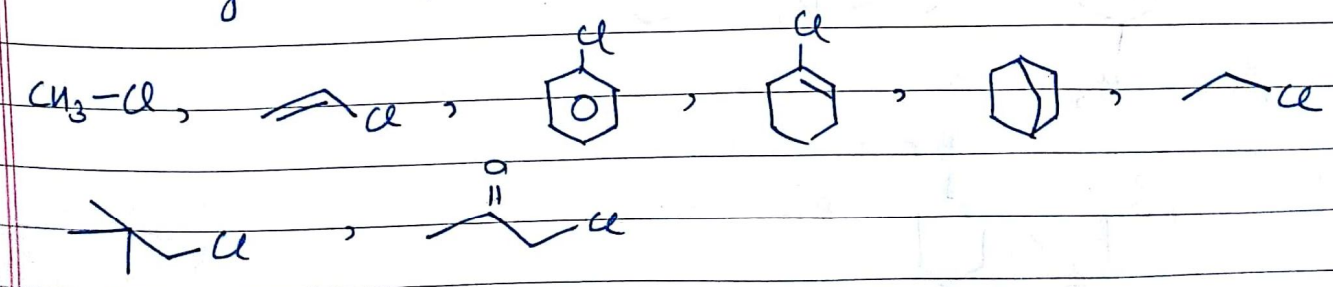
Racemic mixture is formed. But it is not 100%. Inversion product dominates over retention coz l.g. blocks the path from front.



- Racemisation ∝ stability of cation.



- Following compounds will not undergo S_N1,



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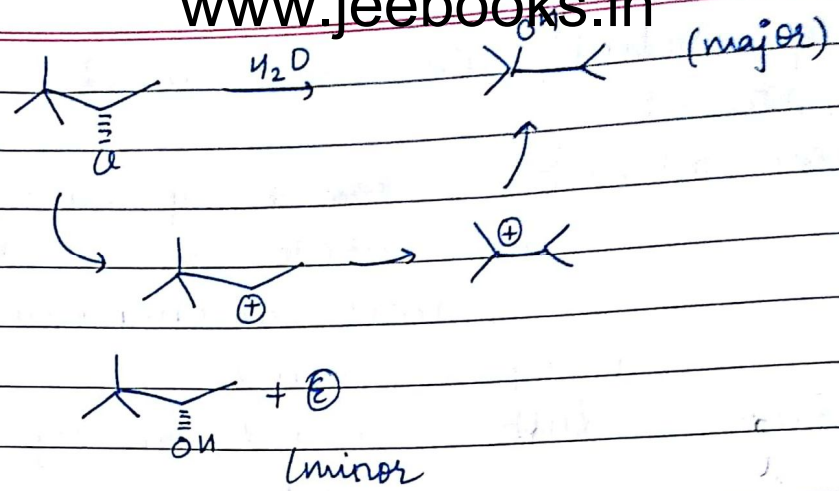
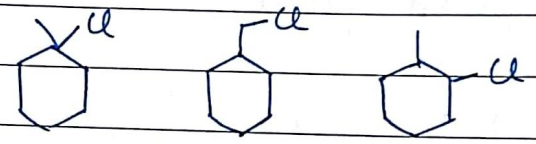
Q. 1)



∴ Rearrangement is possible.

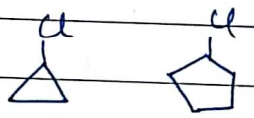
Q. Compare rate of S_N1

1)



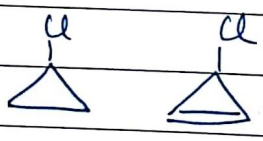
a > c > b

2)



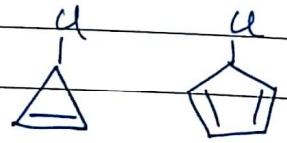
b > a

3)



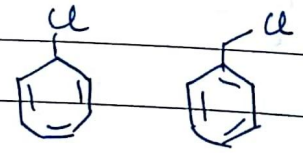
b > a

4)



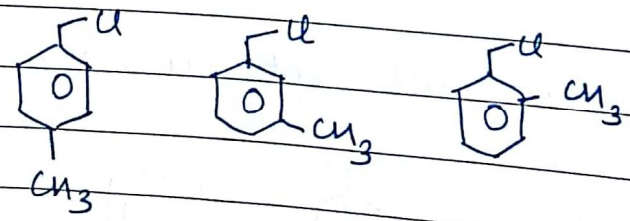
a > b

5)



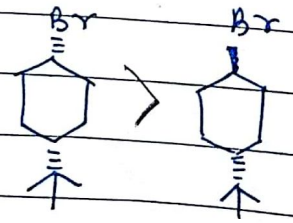
a > b

6)



c > a > b

7)



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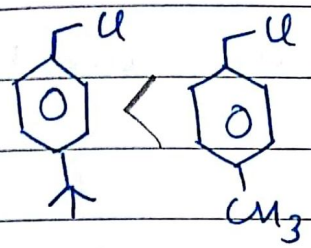
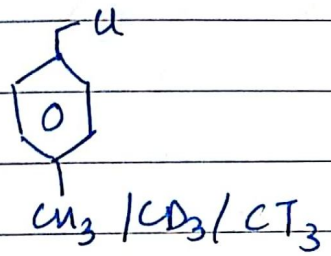
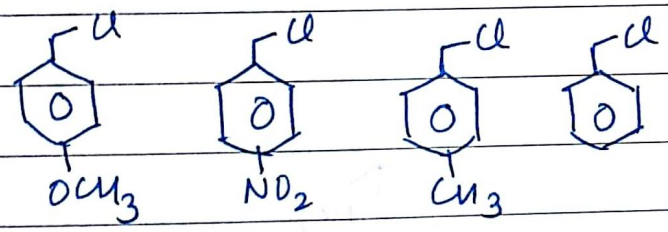
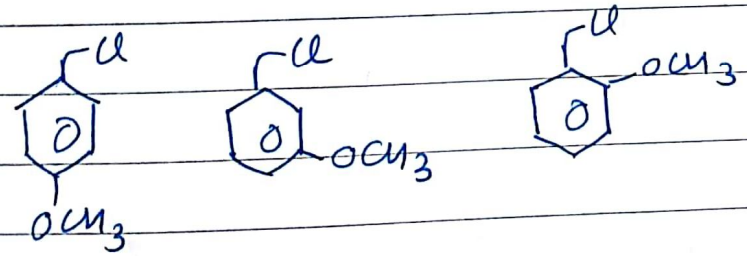
8) $[R-X] = 1M$ b > a
$[R-X] = 2M$

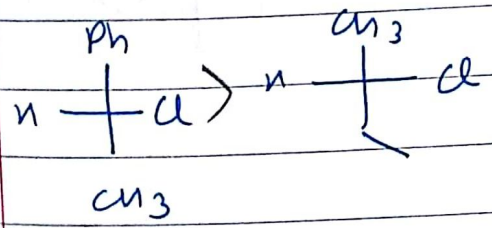
9) $[Nu^-] = 1M$ a = b
$[Nu^-] = 2M$

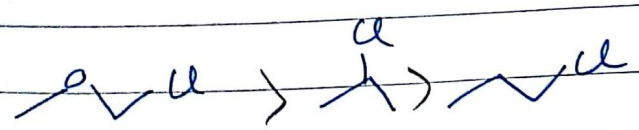
10)  a > b

11)  $CH_3 > CD_3 > CT_3$

12)  a > c > d > b

13)  a > c > b

14) 

15) 

16) b > a

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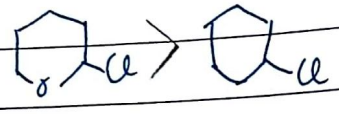
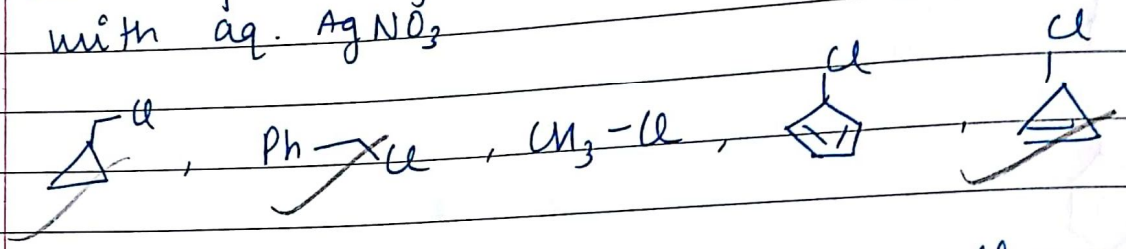
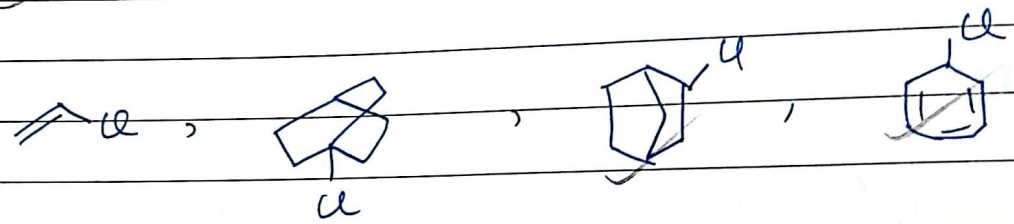
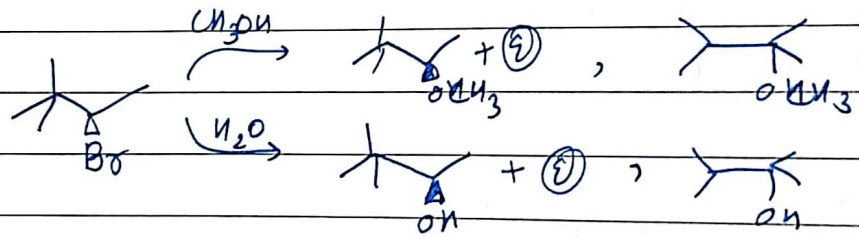
17)

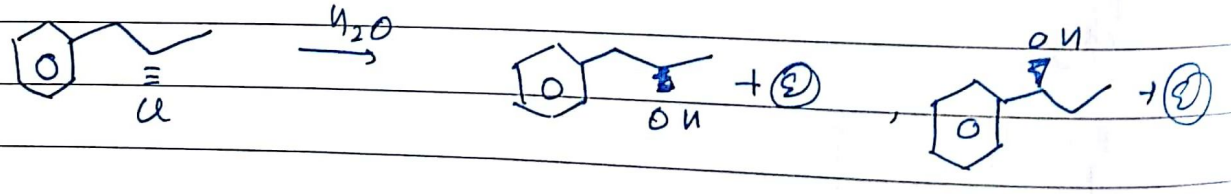
18) 

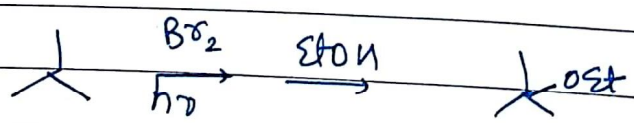
Q. Which of the following will give which ppt with aq. $AgNO_3$

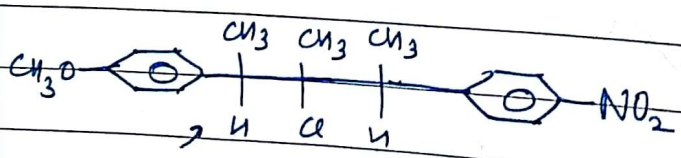
1) 

2) 

Q. 1) 

2) 

3) 

4) 

↓ hydrolysis in aq. acetone

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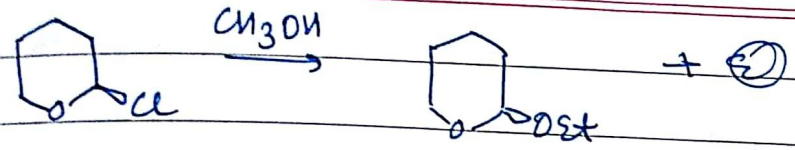
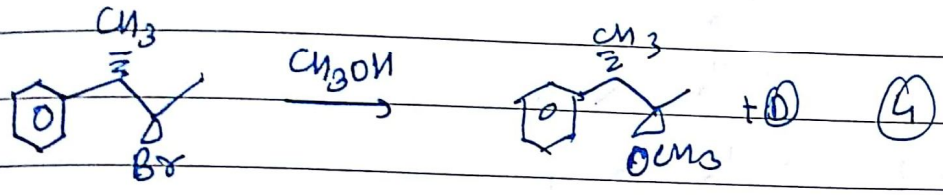
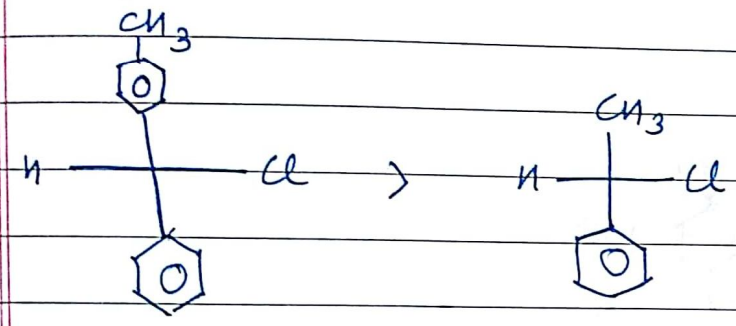
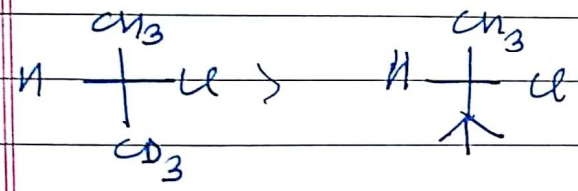
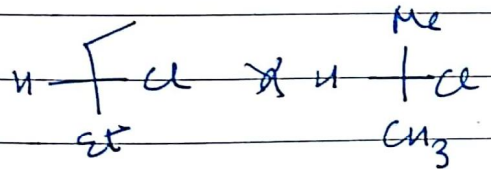
5) 

6) 

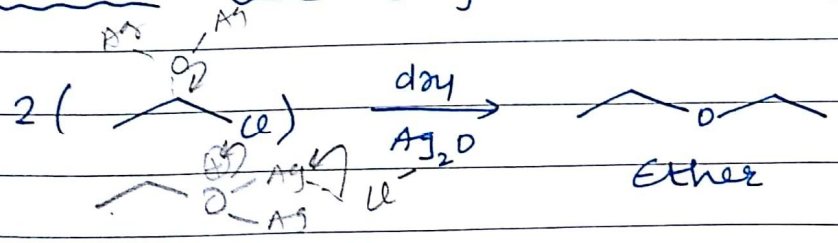
Q. Compare % racemization

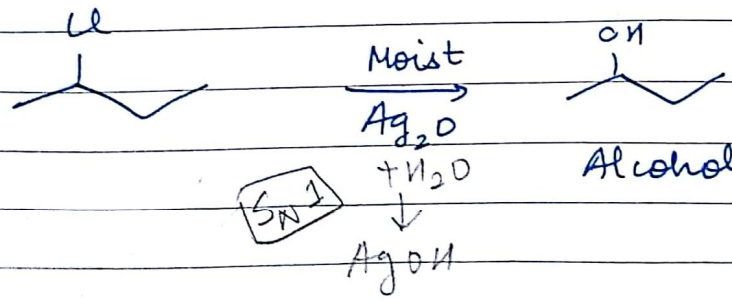
1) 

2) 

3) 

* Reaction with dry & moist Ag_2O





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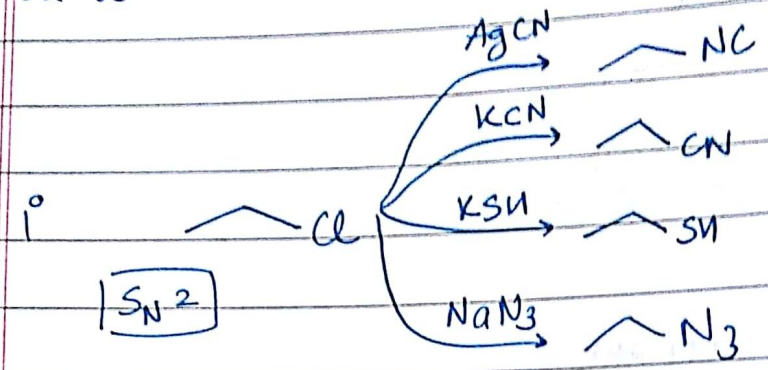
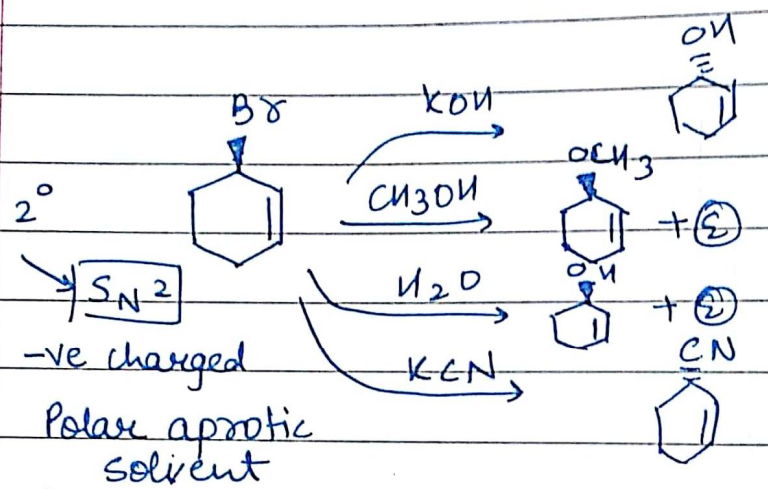
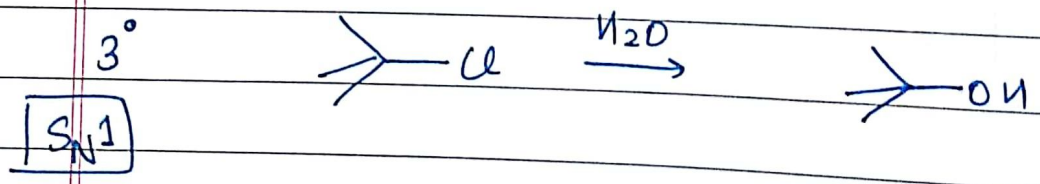
* S_N1 v/s S_N2 :-





neutral
polar protic solvent
solvolysis



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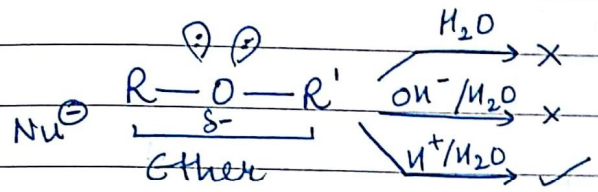
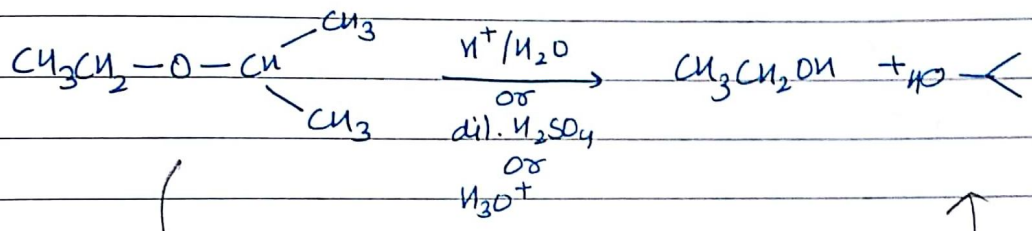
* Hydrolysis of Ether :

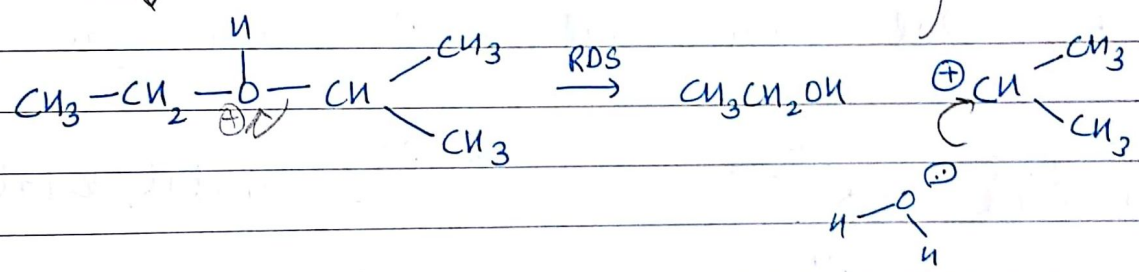
- Ether can undergo only acidic hydrolysis.



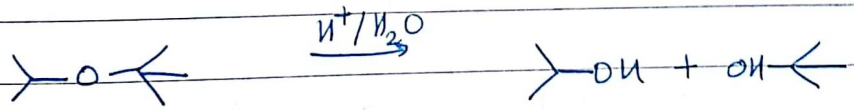
eg,

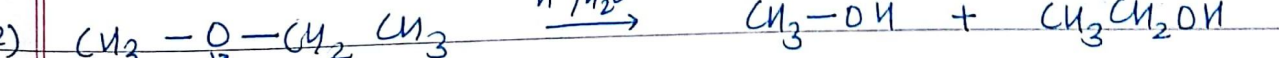


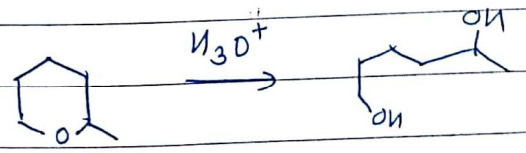
MECH

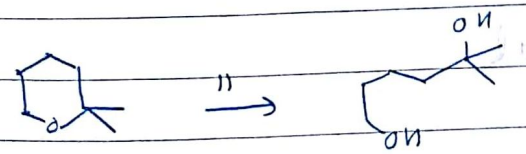


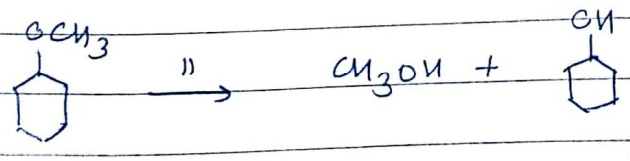
Q.

1) 

SN2 2) 

3) 

4) 

5) 

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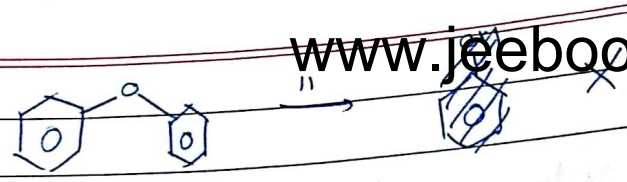
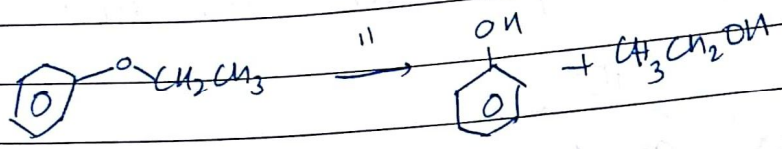
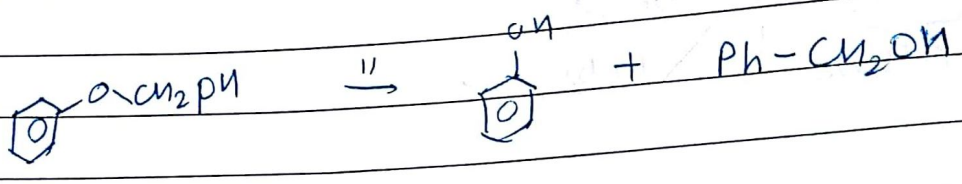
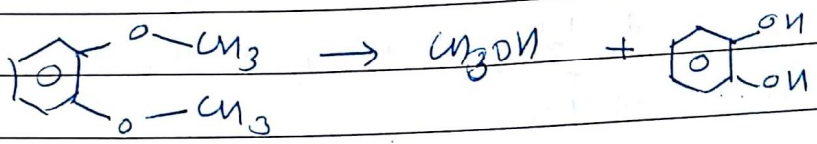
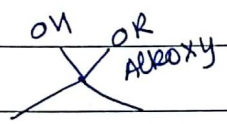
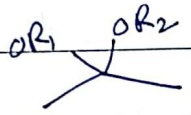
* 6) 

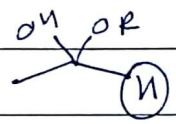
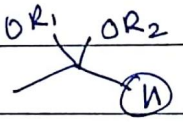
7) 

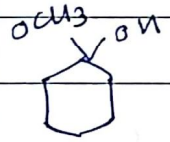
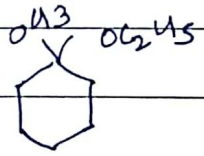
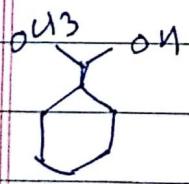
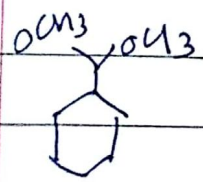
8) 

9) 

* Acetal, Hemi-acetal, Ketal, hemi-Ketal :→

hemi Ketal) Hemi acetal   Acetal / Ketal

hemi acetal   Acetal

-  hemi acetal / hemi Ketal
-  Acetal / Ketal
-  hemi - acetal
-  acetal

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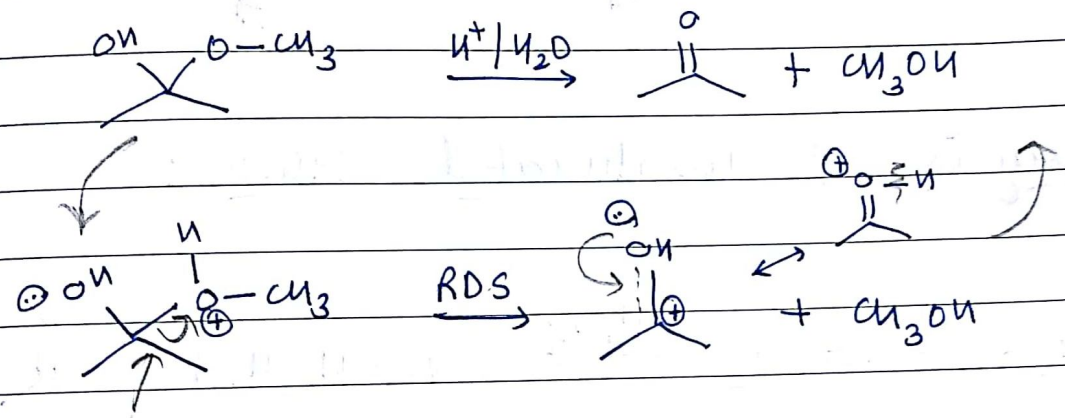
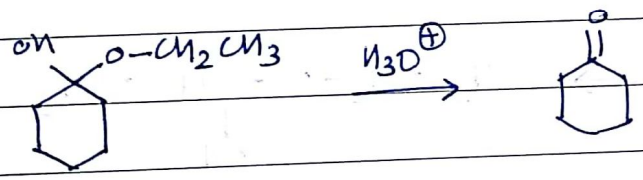
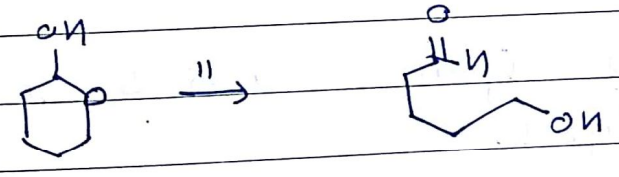
- Ketals are derived from ketones.
  Each ketal is an acetal but not the converse.

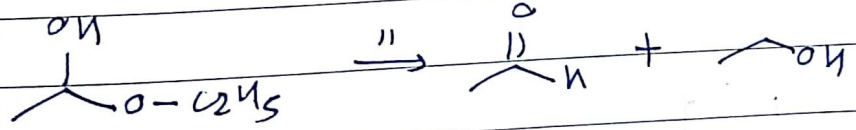
- **Hydrolysis of Hemi acetals :**



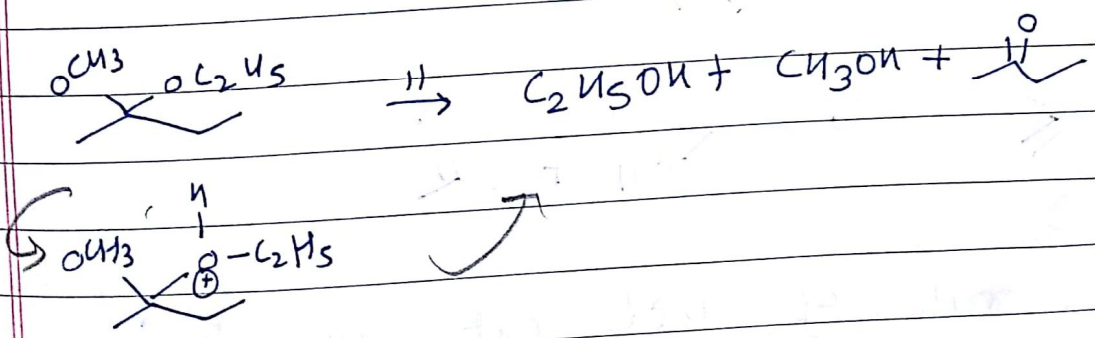
Q.

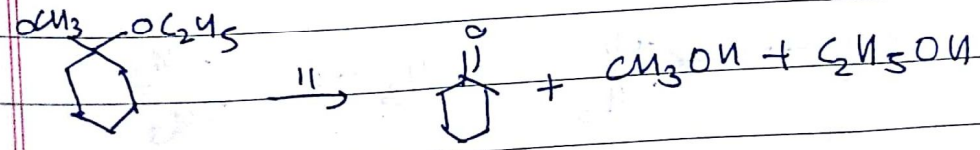
1) 

2) 

3) 

ACETALS

4) 

5) 

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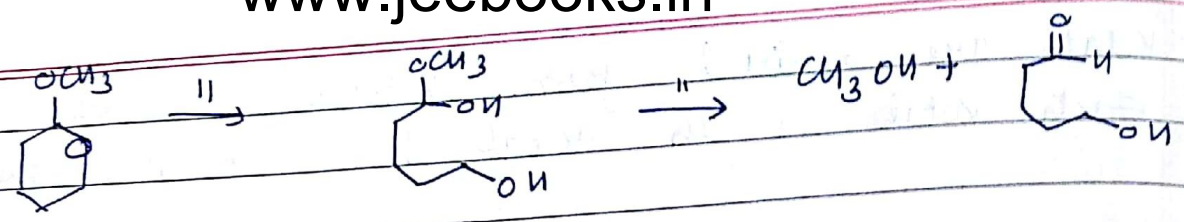
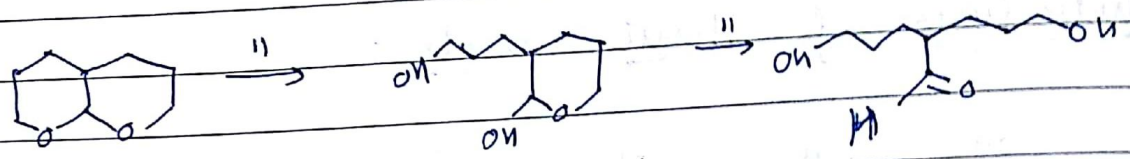
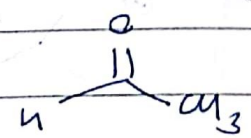
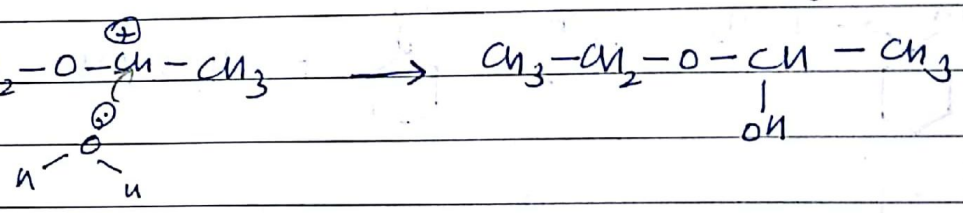
6) 

7) 

- **Hydrolysis of Unsaturated Ether :**

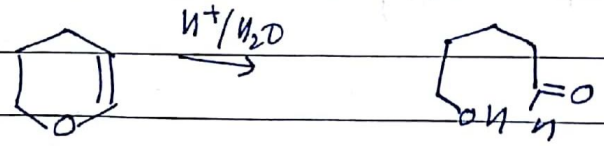
$CH_3-CH_2-O-CH=CH_2 \xrightarrow{H^+/H_2O} CH_3-CH_2OH +$ 

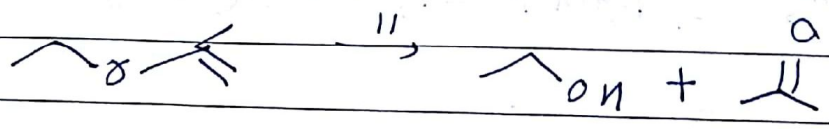
MECH



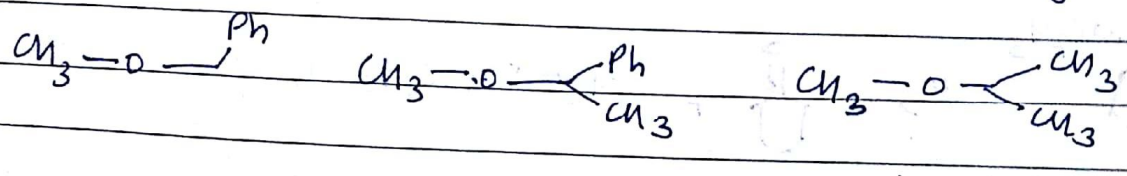
- Unsaturated ethers are highly reactive towards acid - catalysed hydrolysis.

Q.

1) 

2) 

Q. compare rate of acid cat. hydrolysis

1) 

b > a > c

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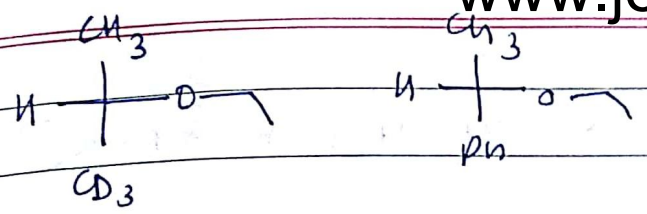
2) 

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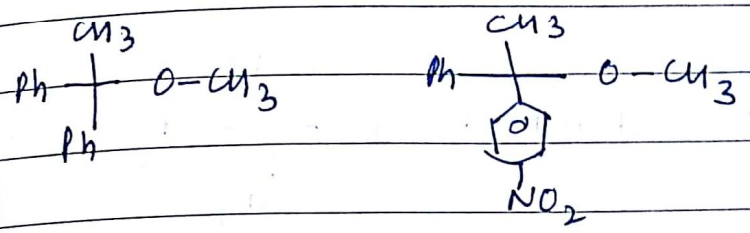
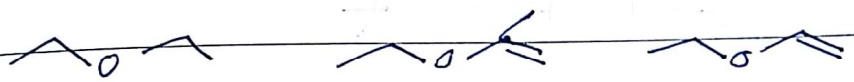
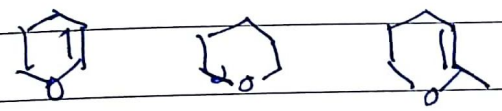
3) 

a > b

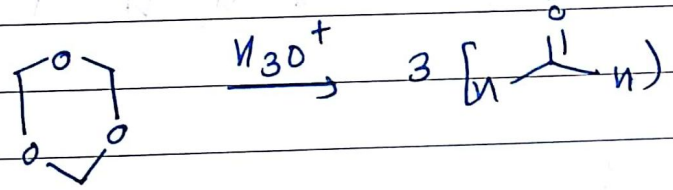
4) 

b > c > a

5) 

c > a > b

6) $Ph-O-Ph-OMe \xrightarrow{H_3O^{\oplus}} Ph-OPh-OH + MeOH$

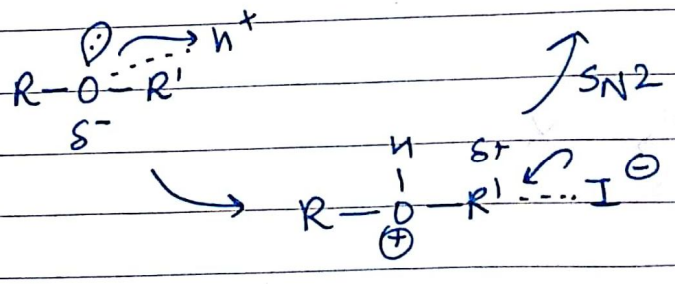
7) 

* **Reaction of Ester with HI:**

- S_N2 mech. is favourable due to presence of -vely charged $Nu^{\ominus}$
- S_N1 will take place in case of highly stable carbocation.

$$R-O-R' \xrightarrow{HI} R-OH + R'-I$$

Mech :



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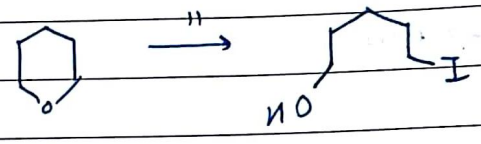
Q.

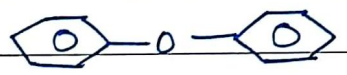
1] $CH_3CH_2-O-CH(CH_3)_2 \xrightarrow{HI} CH_3CH_2I + OH-$

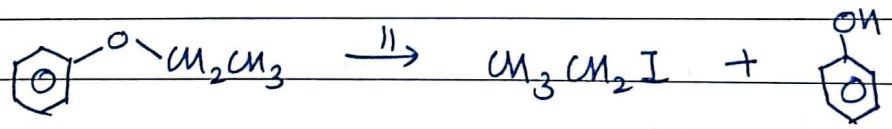
NCERT 2] $CH_3-O-C(CH_3)_3 \xrightarrow{HI} CH_3OH + I-C(CH_3)_3$

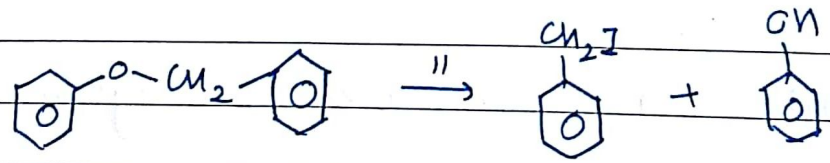
3] $-O- \xrightarrow{HI} -OH + I-$

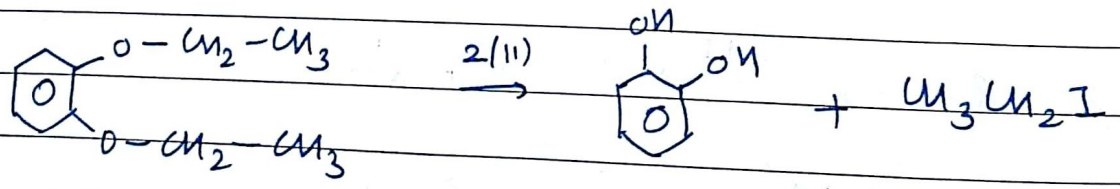
4] 

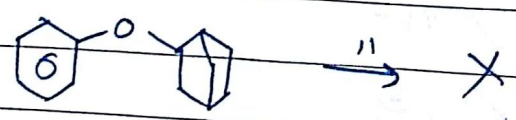
5] $CH_3-O-CH_2CH_2CH_3 \xrightarrow{HI} CH_3I + CH_3CH_2CH_2OH$

6] 

7] 

8] 

9] 

10] 

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* Reaction of alcohol with HX:

$$R-OH \xrightarrow{HCl} RCl + H_2O$$

MECH

$$ROH \xrightarrow{H^+} R-\overset{\oplus}{O}(H)(H) \xrightarrow{S_N1} R^{\oplus} \leftarrow Cl^{\ominus}$$

S_N2 Cl^-

In this ran, S_N1 mech. is favourable except primary alcohols.

Q.

1] $>-OH \xrightarrow{HI} >-I + H_2O$

2] $\rightarrow-OH \xrightarrow{HBr} \rightarrow-Br$

3] $\xrightarrow{HI}$ X

4] $\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} \xrightarrow{3HI} \begin{array}{l} CH_2-I \\ | \\ CH_3 \end{array}$