Learning Mantras

LEARNING MANTRAS

Handwritten Notes

On

Elimination Reaction

Elimination Reaction

$$-\overset{\overset{\bullet}{|}}{\underset{\underset{\beta^2}{|}}{C}}-\overset{\overset{x}{|}}{\underset{\underset{\alpha}{|}}{C}}-y \xrightarrow{\Delta} -\overset{|}{\underset{|}{C}}-\overset{\ddot{}}{\underset{|}{C}} + xy.$$

$$-\overset{\overset{x}{|}}{\underset{\underset{\beta}{|}}{C}}-\overset{\overset{y}{|}}{\underset{\underset{\alpha}{|}}{C}}- \xrightarrow{\Delta} -\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}- + xy$$

$$\overset{2}{C}\underset{\underset{3}{C}-y}{\overset{C-x}{<}} \xrightarrow{\Delta} C\underset{\underset{C}{|}}{\overset{C}{<}} + xy.$$
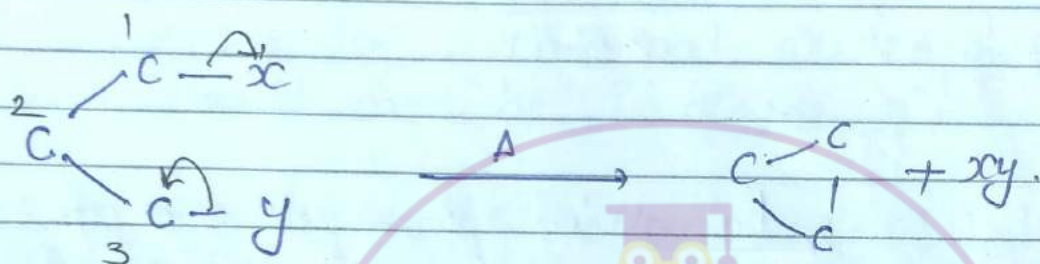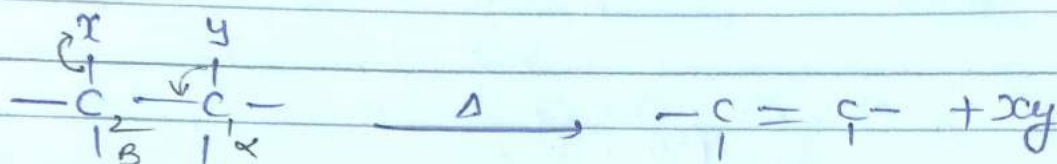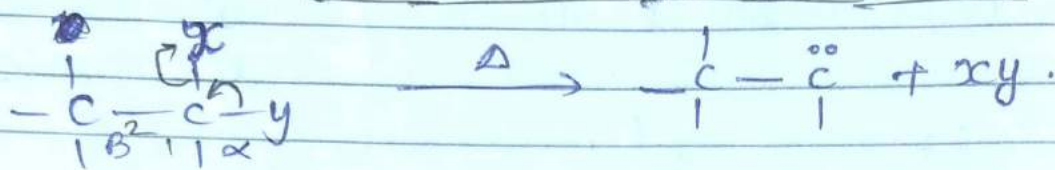
- It is endothermic process occure only on Heating

* **Types of Elimination:**

(1) $1,1 - / \alpha, \alpha - / 1 - / \alpha -$ Elimination → Carben Term

(2) $1,2 - / \alpha, \beta - / 2 - / \beta -$ elimination ⇒ Alkene/Alkyne.

(3) $1,3 -$ elimination Rx^n ⎫

(4) $1,4 - \quad '' \qquad '' \quad ⎬ \begin{array}{l} Cyclic \\ Elimination \end{array}$ ⇒ Cyclic form

(5) $1,5 \quad '' \qquad '' \quad$ ⎪

(6) $1,6 \quad '' \qquad '' \quad$ ⎭

* **β Elimination Rxⁿ :**

That elimination In which one gp depart from α and other group depart from β are known as β elimination Rxⁿ.

ꟼxⁱꟾⁱ

$$-\overset{\underset{|}{H}}{\underset{\beta}{C}} - \overset{|}{\underset{\underset{L}{|}}{\underset{\alpha}{C}}} - \xrightarrow[\substack{-BH \\ -L^{\ominus}}]{B^{\ominus}/\Delta} \quad -\overset{|}{C}=\overset{|}{C}-$$

Ex: 1 Dehydrohalogination of alkyl Halide :

$$-\overset{\underset{H\delta+}{|}}{\underset{|}{\overset{2}{\underset{\beta}{C}}}} - \overset{|}{\underset{\underset{X\delta-}{|}}{\underset{\alpha}{C}}} - \xrightarrow{B^{\ominus}/\Delta} \quad -\overset{|}{C}=\overset{|}{C}- \;+\; BH \;+\; X^{\ominus}$$

$$-\overset{\underset{H}{|}}{\underset{|}{C}} - \overset{\underset{}{|}}{\underset{\underset{L}{|}}{\overset{\delta+}{C}}} - \xrightarrow[Nu^{\ominus}]{A^{\ominus}} \quad -\overset{\underset{}{|}}{\overset{H}{\underset{|}{C}}} - \overset{\underset{}{|}}{\overset{A}{\underset{|}{C}}} - \;+\; L^{\ominus} \quad (NSR)$$
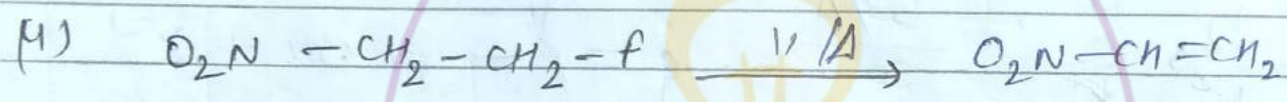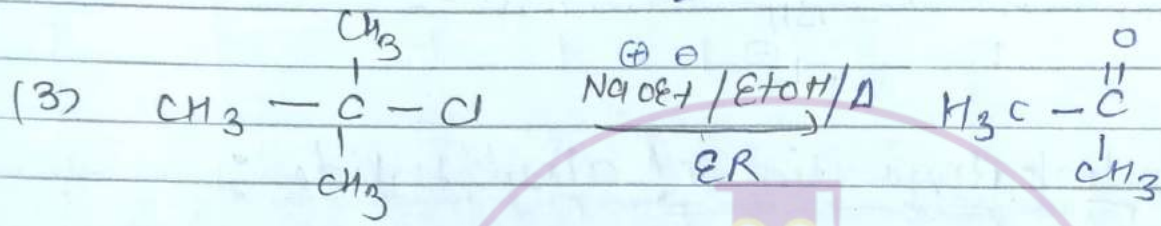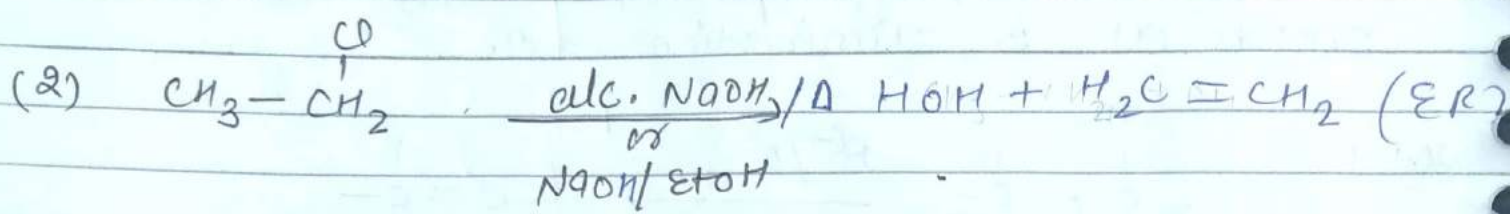
$$-\overset{\underset{H}{\downarrow}}{\underset{|}{C}} \to \overset{|}{\underset{\underset{L}{\downarrow}}{C}} - \xrightarrow[Base]{A^{\ominus}} \quad -\overset{|}{C}=\overset{|}{C}- \;+\; AH \quad (ER)$$

$$A^{\ominus} \begin{cases} \text{aq } A^{\ominus} \Rightarrow Nu^{\ominus} \Rightarrow NSR \\ \text{alc. } A^{\ominus} \Rightarrow B^{\ominus} \Rightarrow ER. \end{cases}$$

$$A^{\ominus} \underset{\text{Nucleophilic} \quad \text{Basic}}{\diagdown\diagup}$$

Que!1 $CH_3 - \overset{Cl}{\underset{|}{CH_2}}$ $\xrightarrow[\underset{NaOH/H_2O}{or}]{aq\ NaOH}$ $CH_3 - \overset{OH}{\underset{|}{CH_2}}$ (NSR)

(2) $CH_3 - \overset{Cl}{\underset{|}{CH_2}}$ $\xrightarrow[\underset{NaOH/EtOH}{or}]{alc.\ NaOH/\Delta}$ $HOH + H_2C = CH_2$ (ER)

(3) $CH_3 - \overset{CH_3}{\underset{\underset{CH_3}{|}}{\overset{|}{C}}} - Cl$ $\xrightarrow[ER]{NaOEt^{\oplus\ \ominus}/EtOH/\Delta}$ $H_3C - \overset{O}{\underset{\underset{CH_3}{|}}{\overset{||}{C}}}$

(4) $O_2N - CH_2 - CH_2 - f$ $\xrightarrow{'' /\Delta}$ $O_2N - CH = CH_2$

(5) $\xrightarrow[\underset{aq\ NaOH}{or}]{NaOH/HOH}$

(6) $\xrightarrow[\underset{alc\ NaOH}{or}]{NaOH/EtOH/\Delta}$

(7) $CH_3 - \overset{OTs}{\underset{|}{CH}} - CH_3$ $\xrightarrow{'' /\Delta}$ $CH_3 - CH = CH_2 + EtOH$

(8) $CH_3 - \overset{OTs}{\underset{|}{CH}} - CH_3$ $\xrightarrow{aq\ NaOH}$ $CH_3 - \overset{OH}{\underset{|}{CH}} - CH_3$

(9) $H_3C - \overset{CH_3}{\underset{\underset{CH_3}{|}}{\overset{|}{C}}} - Cl$ $\xrightarrow[\epsilon_1]{EtOH/\Delta}$ $CH_3 - \overset{CH_2}{\underset{\underset{CH_3}{|}}{\overset{||}{C}}}$

* **Mech^n of β elimination :**

It occur by following three Mech^n.
Depending upon

(1) E_1-Mech^n :
(2) E_2-Mech^n
(3) E_1CB - Mech^m

$$-\overset{|}{\underset{|}{C}}-\overset{\overset{H}{|}}{\underset{\underset{L}{|}}{C}}- \quad \xrightarrow{\quad B \quad}$$
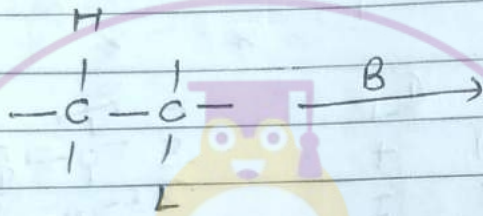
E_1 - Mech^n

* Unimolecular elimination mech^n

$$-\overset{\overset{H}{|}}{\underset{\underset{L}{|}}{C}}-\overset{|}{\underset{|}{C}}- \xrightarrow[-L^{\ominus}]{slow} \left[-\overset{H}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}{}^{\oplus}-\right] \xrightarrow[-BH]{B^{\ominus}} $$

R-L Carbocation

$$\longrightarrow -\overset{|}{C}=\overset{|}{C}- \quad (major)$$

E_1 Product

$$\overset{H^{\oplus}}{\underset{}{} } -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \quad \text{(B)}$$

$$\left[-\overset{\overset{H}{|}}{\underset{\underset{L}{|}}{C}}-\overset{|}{\underset{|}{C}}-\right]$$

SN¹ Product (Minor)

* Rate of Rx^n $R \propto \left[-\overset{H}{\underset{L}{C}}-\overset{|}{\underset{|}{C}}-\right]$
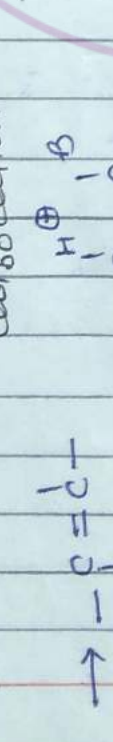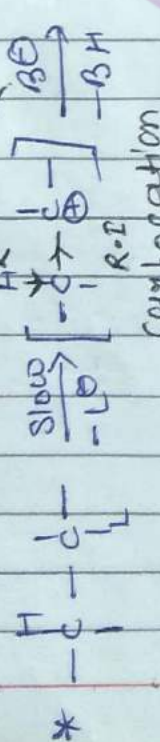
* m = 1, O = 1

* Favoured by weak base

Eg: EtOH, NH₃

E_2 - mech^n

* B⁻

$$-\overset{\overset{H}{|}}{\underset{\underset{L}{|}}{C}}-\overset{|}{\underset{|}{C}}- $$

$$\left[\overset{H^{\delta+}}{\underset{L^{\delta-}}{}}\overset{\delta+}{C}\cdots\overset{\delta-}{C}\right] \xrightarrow{slow} $$

T.S.
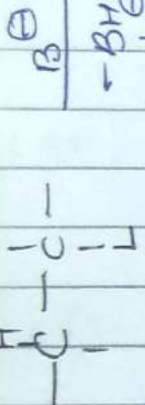
$$\longrightarrow -\overset{|}{C}=\overset{|}{C}- + BH + L^{\ominus}$$
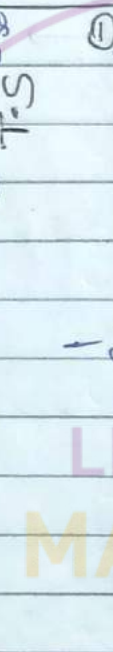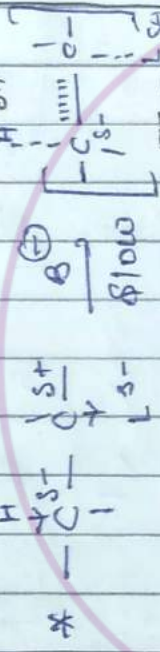
SN² Product Minor

* Rate of Rx^n $R \propto \left[-\overset{H}{\underset{L}{C}}-\overset{|}{\underset{|}{C}}-\right]\left[B^{\ominus}\right]$

* m = 2, O = 2

* Favoured by strong / moderate base

Eg: alc. KOH, alc. KOR, alc. NaOH
alc. NaOR, Na NH₂, K NH₂, KOH, NaOH

E_{1cb} - Mech^n

• Unimolecular elimination by formation of Conjugate base

$$-\overset{\overset{H}{|}}{\underset{\underset{L}{|}}{C}}-\overset{|}{\underset{|}{C}}- \xrightarrow[-BH]{B^{\ominus}\ fast} \left[-\overset{\ominus}{\underset{\underset{L}{|}}{C}}-\overset{|}{\underset{|}{C}}-\right] \xrightarrow{slow} $$

C.B (R.I) or Carbanion.

$$\longrightarrow -\overset{|}{C}=\overset{|}{C}-$$
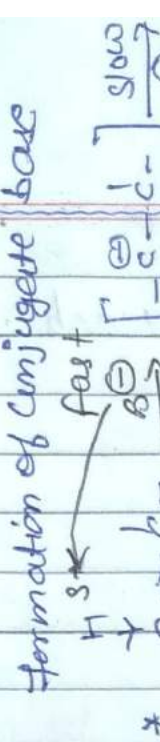
* Rate of Rx^n $R \propto \left[-\overset{\ominus}{C}-\overset{|}{\underset{|}{C}}-\right]$

* Favoured by strong Base

Eg: — alc. KOH —

E₁

* Favoured By Polar Protic Solvent PPS (Et-OH), NH₃ etc)

* Favoured by good Living group

Que : H₃C—$\overset{\underset{CH_3}{|}}{\underset{\overset{|}{CH_3}}{C}}$—Cl   H₃C—CH—Cl   H₃C—CH₂—Cl

R.O.+ : a > b > c
3° > 2° > 1°
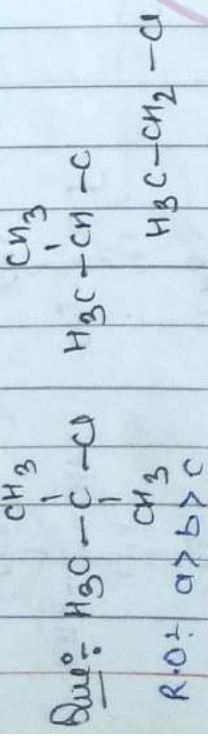
* These comp. are more Reactive towards E₁ Rⁿ bcₒ which Carbocation is more steble.

Reactivity towards E₁ Rⁿ ∝ Stability ∝ $\overset{\oplus}{C}$ ∝ +m/+H/+I effect

E₂

* Favoured by Polar aprotic solvant PAS(→DMF, DMSO, Acetone, ether)

* Favoured by ₁₁₁₁ᵤ ᵢₒₙ moderate Living group

* Reactivity towards → Cmp.

$\dfrac{E_2 R^n}{}$: ∝ Stability ∝ Alkene
∝ Reactivity towards E₂ R^n
∝ CB — H

Acidic nature of Cmp.

E₁cB

* Favoured by PAS.

* Favoured by poor Living gp

* P.LH (—F, —O—$\overset{O}{\underset{||}{C}}$—R)

* Condition for E₁CB° :

① Living group should be Poor Living gp/very poor Living gp.
=—F, —O—$\overset{O}{\underset{||}{C}}$—CH₃(—OAc)

②—m/—H/—I gp at cβ(conjikous)
(H₂O) cβ should be highly Acidic

Q. H₃C—$\overset{\underset{CH_3}{|}}{\underset{\overset{|}{CH_3}}{C}}$—Cl   H₃C—CH—Cl
most Reactive!   most reactive CH₃

$\overset{CH_3}{\underset{CH_3}{H_2C=C}}$ $\overset{CH_3}{\underset{CH_3}{C—CH_3}}$
most stable

$\overset{CH_3}{H_2C=C—CH_2—Cl}$
Least Reactive

$\overset{CH_3}{H_2C=CH}$
Reactive

$H_2C=CH_2$
least Stable

Rxn

B > A > C

1 > 3 > 2

E₁ R^n ∝ 3° Stable.

Test syllabus E.P. St. R

Nu⊖ SR. Carbocation

Titomerism, Relationship. SN¹ and Sn².

E_2 Rn²:-

Anti-periplanar Conf.

Favourable condition for

Reactivity ∝ L.N of L.Grp.
of comb.

Gr.:

$B^{\ominus}, H^{+}$

$LNO: I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$

R.O ⇒ 4 > 3 > 2 > 1
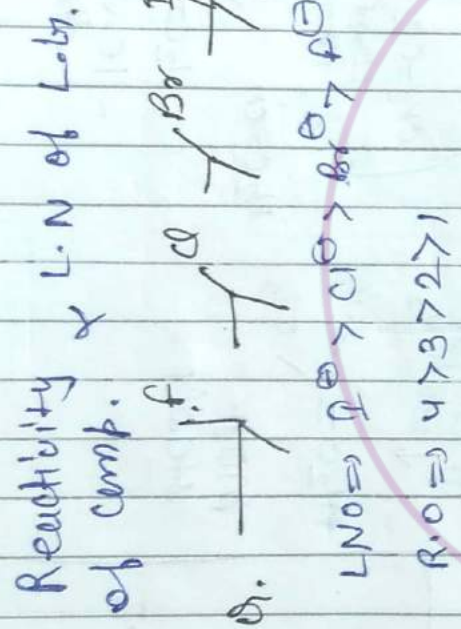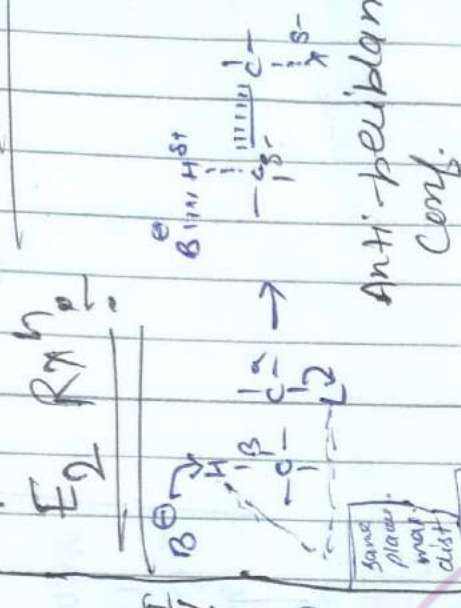
* Hydrogen C, β Carbon and living grp of $C\beta$ should be anti to each other. and living gb of $C\beta$ should be anti to each other: that Conf. should be anti to each other. necessary to E_2

In same plane that Conf. In same plant this conf. necessary to anti-periplanar Conf. Conf. reaction is known as anti-periplanar conf.

It occur mainly in 3° alkyl halide

* when alkyl part is similar then that comb. will more Reactive which have Good leaving group.

* when alkyl gp is similar then

Reactivity of L.N of comp. L.Grp.

Q.

$CH_3-\overset{\underset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-F$ $H_3C-\overset{\underset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-Cl$

$CH_3-\overset{\underset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-Br$ $CH_3-\overset{\underset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-I$

$LNO: I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$

R.O = 4 > 3 > 2 > 1

Weak Neutral Base → Cation Stable → E_1
m strong Base → E_1CB, E_2
ↆ acidic
β-H acidic
—m₋ℓ

Weak ethanol
amonia base.

(orethro → cis like)

E_2 Rₓⁿ.

(1) H me

Cl / Et
$\xrightarrow[\Delta]{\oplus \ominus \text{ Na O Et / EtOH}}$

me / Et — fixed no Rotahi

(2) me / Cl / Et
$\xrightarrow[\Delta]{\text{P}}$
me

(3) Cl / Et
$\xrightarrow[\Delta]{\text{NaOEt / EtOH}}$
me / Cl / Et — **NO Rxⁿ.**

Rotation.

(4) Rotation
me — Ph — Cl
me — H
Ph

(5) Ph
me — Cl
H — me
Ph

Ph / Ph / me / me . Cis

Thereo Isomer

Ph / Ph / me H / me Cl
$\xrightarrow{60'}$
H Ph / Ph / me / me / Cl S⁻   (S⁺)
$\xrightarrow{NaOEt}$
Ph / Ph / me / me

(4) Ph
me / H
me / Ph / Cl
$\xrightarrow{-60'}$
H / me / Ph

(4)

Trans.
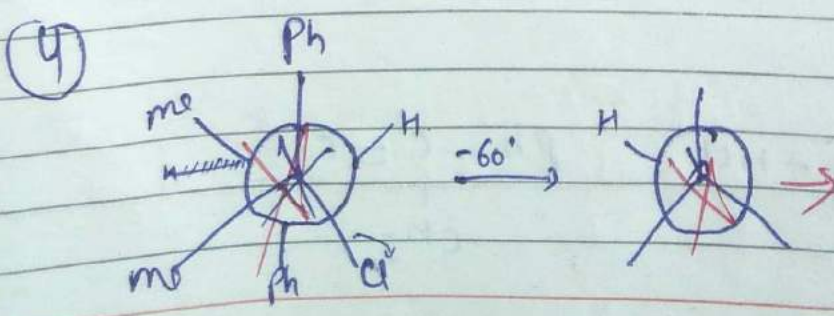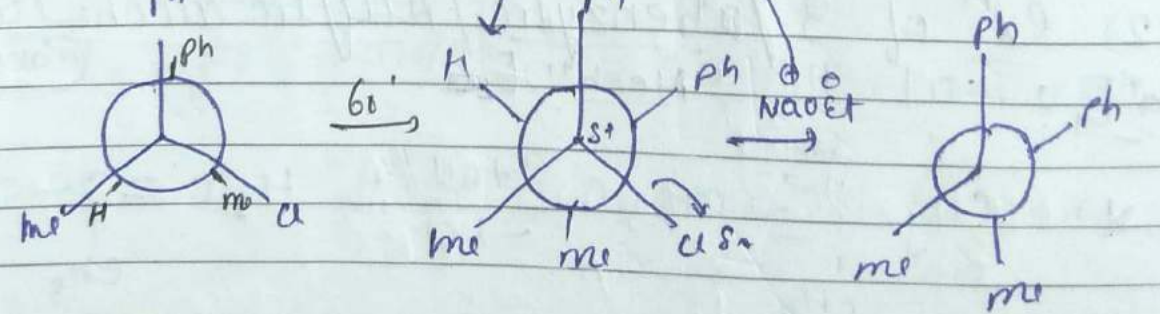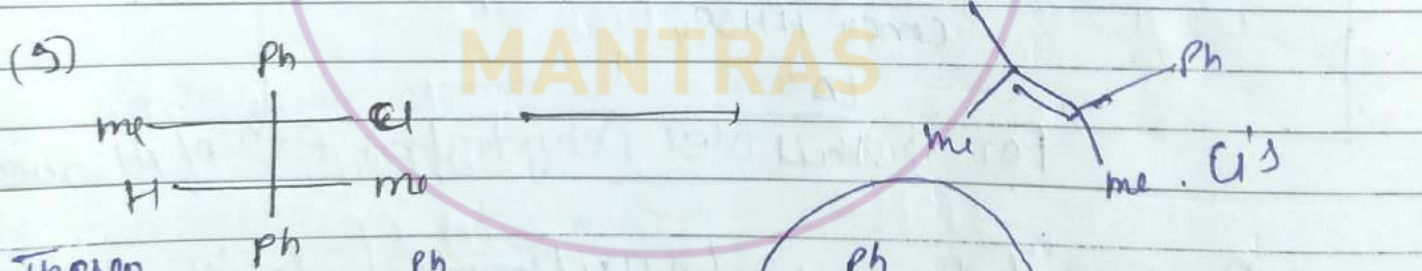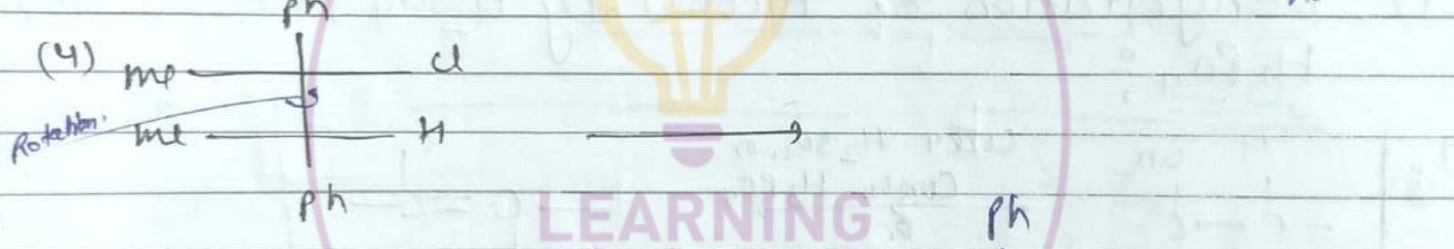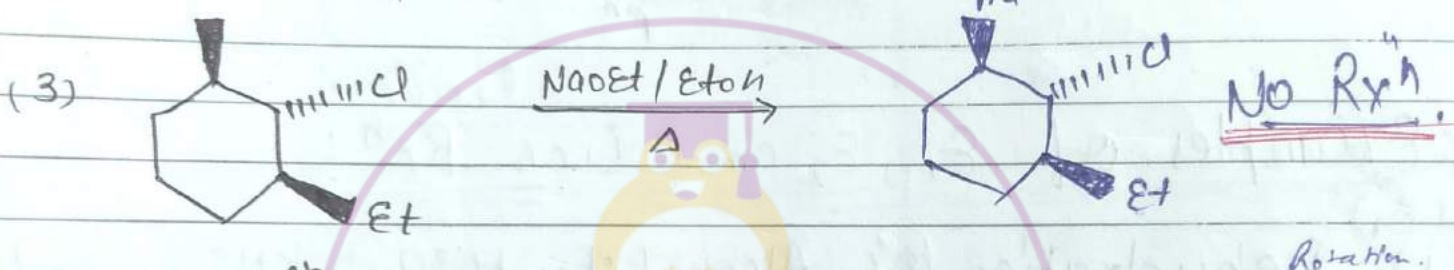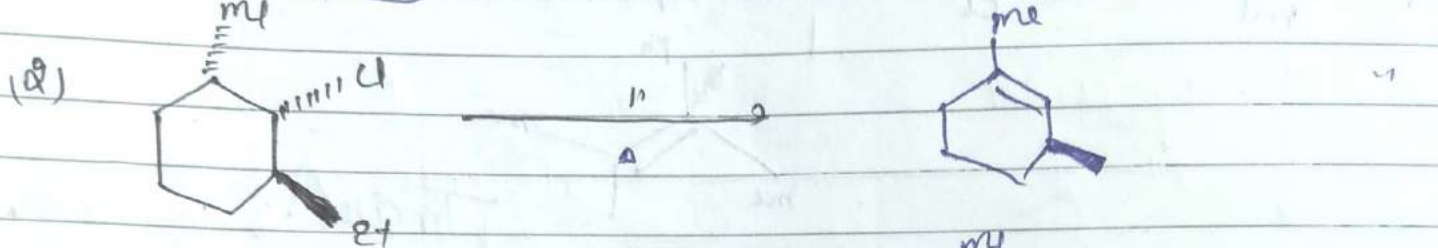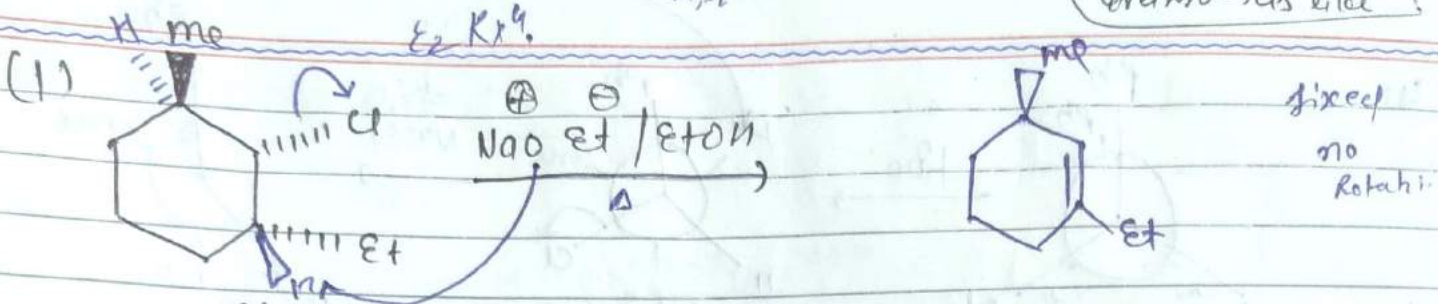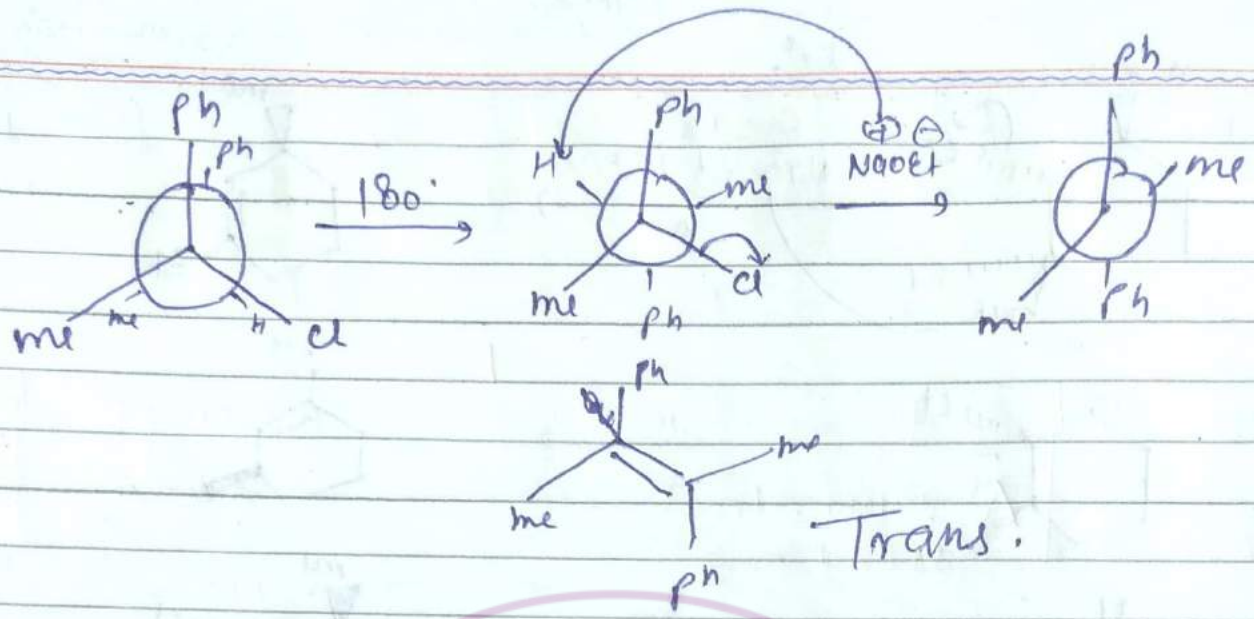
* **Examples of E_1, E_2 and E_1CB Rxn:**

(E_1)

(1) **Dehydration of Alcohol by H_2SO_4, $KHSO_4$ and H_3PO_4:**

(I)

$$-\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle OH}{|}}{C}- \xrightarrow[\substack{or \\ Conc^n \ HHSO_4 \\ \Delta}]{\substack{Conc^n \ H_2SO_4 \ or \\ Conc^n \ H_3PO_4}} \quad -\overset{|}{C}=\overset{|}{C}-$$

for Detail see Dehydration Rxn of Alcohol
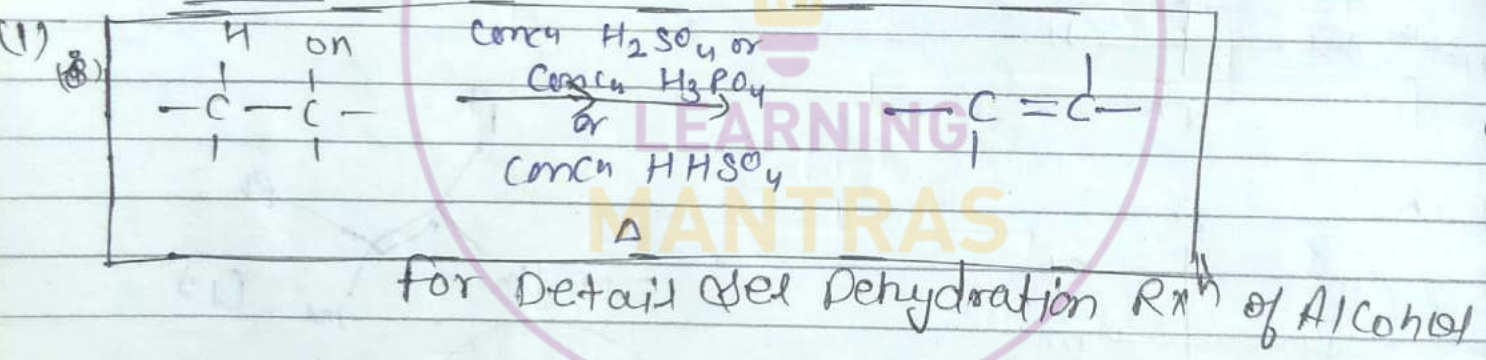
(2) **Rx^n of $3°$/Benzylic/Allylic alcohol with EtOH** make alkene

Mech E_1 : at $H^{\oplus}$: Mech : E_1CB

(1) $CH_3-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3 \xrightarrow[-HCl]{EtOH/\Delta} H_2C=\overset{\overset{}{}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$

(ii) $Ph-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3 \xrightarrow[-HCl]{} Ph-\overset{}{\underset{\underset{\displaystyle CH_3}{|}}{C}}=CH_2$

※ Examples of E₁CB :

(1)
$$CH_3-\underset{NO_2}{\underset{|}{C}}-\underset{Cl}{\underset{|}{C}}-H \xrightarrow[\Delta]{NaOEt/EtOH} CH_3-\underset{NO_2}{\underset{|}{C}}=\overset{H}{\underset{}{C}}-H$$

(2)

$$\xrightarrow{NaOEt/Eton/\Delta}$$

(3) $Ph-CH_2-CH_2$
$$\xrightarrow{NaOEt/EtOH/\Delta}$$

(4)
$$\underset{h}{\overset{f}{>}}C=C\underset{f}{\overset{f}{<}} \xrightarrow{NaOEt/Eton} \underset{f}{\overset{A}{>}}C\equiv C.$$
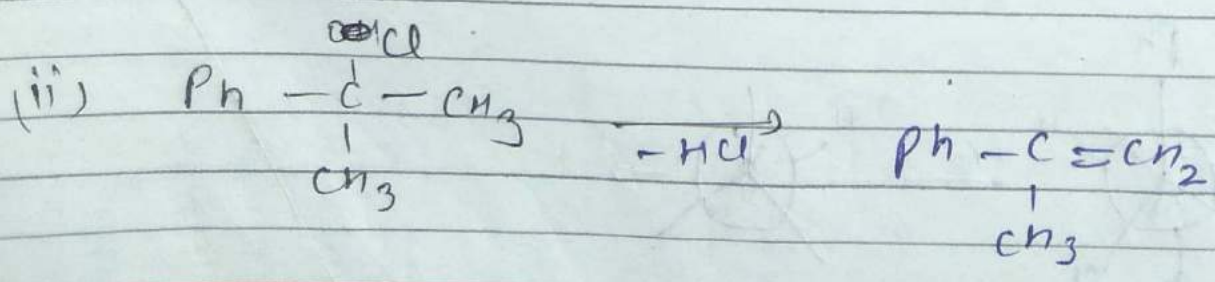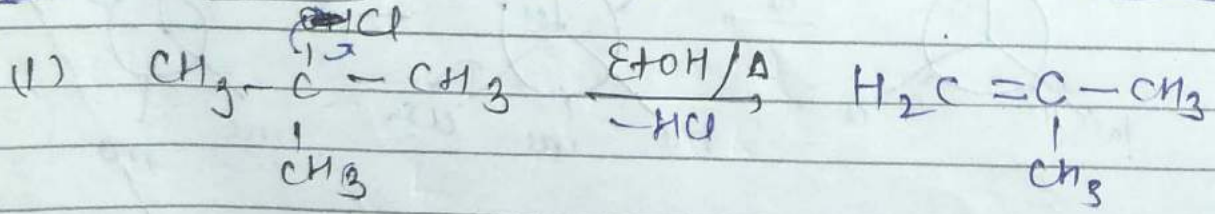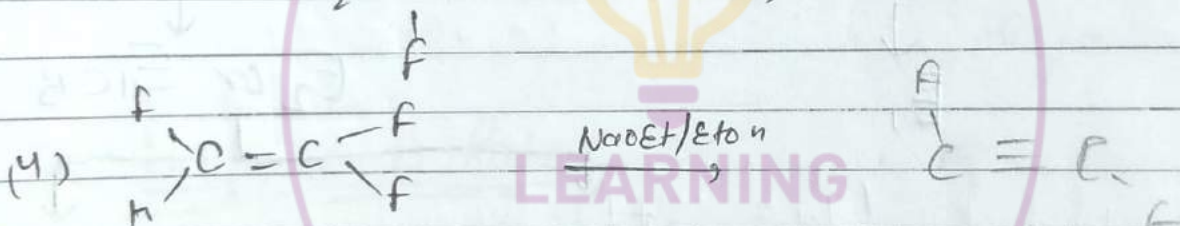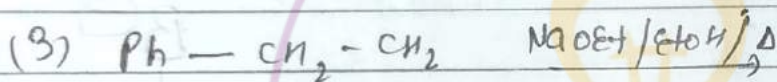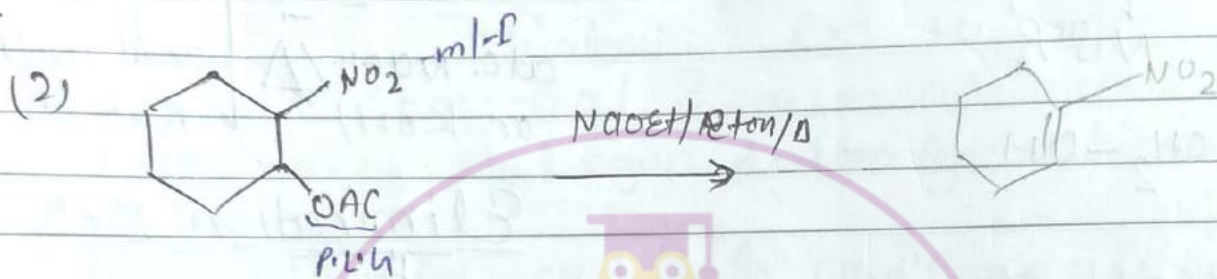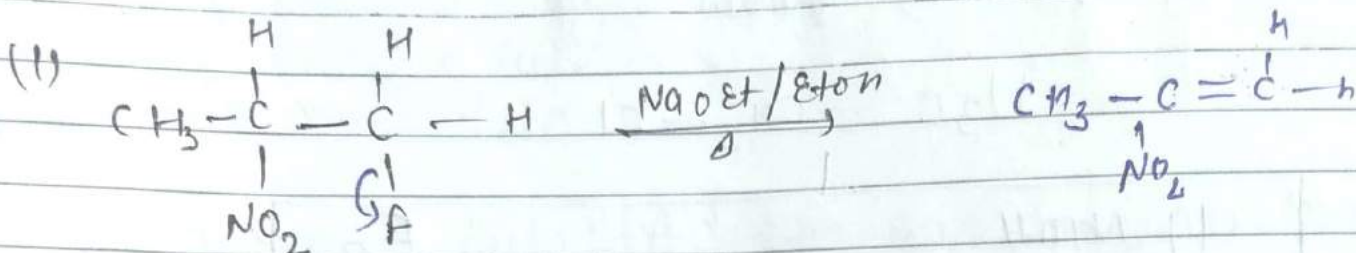
Rest other Elimination is E₂

⧫ Examples of E₂ - Rxn :

(1) $H_3C-CH_2-Cl \xrightarrow[r_1]{KOH/\Delta} H_2C=CH_2 + HOH + KCl$

(2) $D_3C-CH_2-Cl \xrightarrow[r_2]{KOH/\Delta} D_2C=CH_2 + HOH + KCl$
$r_1 \, \& \, r_2 \text{—order}$
Slow Rn

(3)
 $\xrightarrow{NaOEt}$ + EtOH + NaCl.
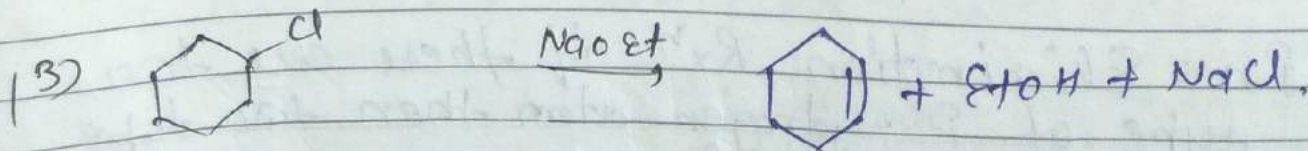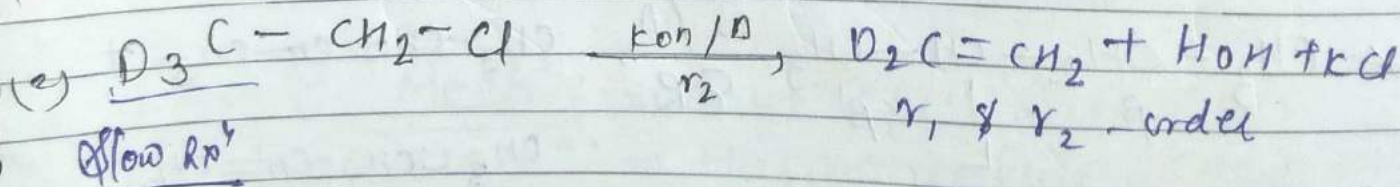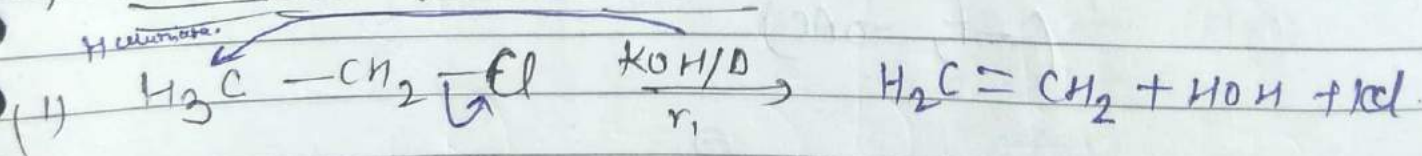
* Orientation in Elimination Rx^n :

$$H_3C - CH_2 - Cl$$

aq NaOH
NSR

$$H_3C - CH_2 - OH$$

E_2
alc. NaOH/Δ | or NaOH/Δ
or KOH/ | $\downarrow$ ROH/Δ

Elimination Rx^n

B:
$\downarrow$
E_1

B$^\ominus$
$\downarrow$
E_2 or E_{1CB}

E_{1CB}

E_2

L·m
→ PLm
(−f, −OAc)

−m/−H/−I
at CP

Rest
other

* $CH_3 - CH_2 - \underset{\underset{L}{|}}{CH} - CH_3 \xrightarrow[ER]{B^\ominus/\Delta} CH_3 - CH = CH - CH_3 +$
$\quad\quad\quad\, \beta \quad\quad \beta'$

$$CH_3 - CH_2 - CH = CH_2$$
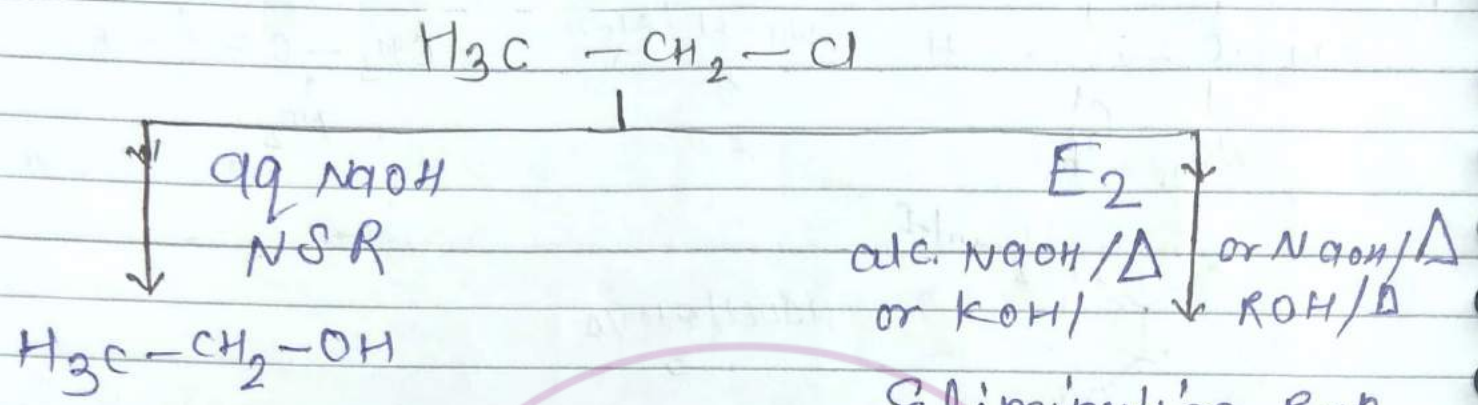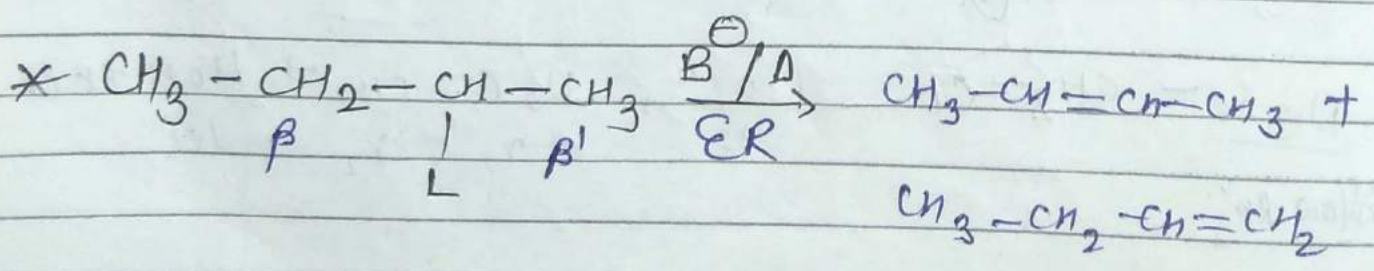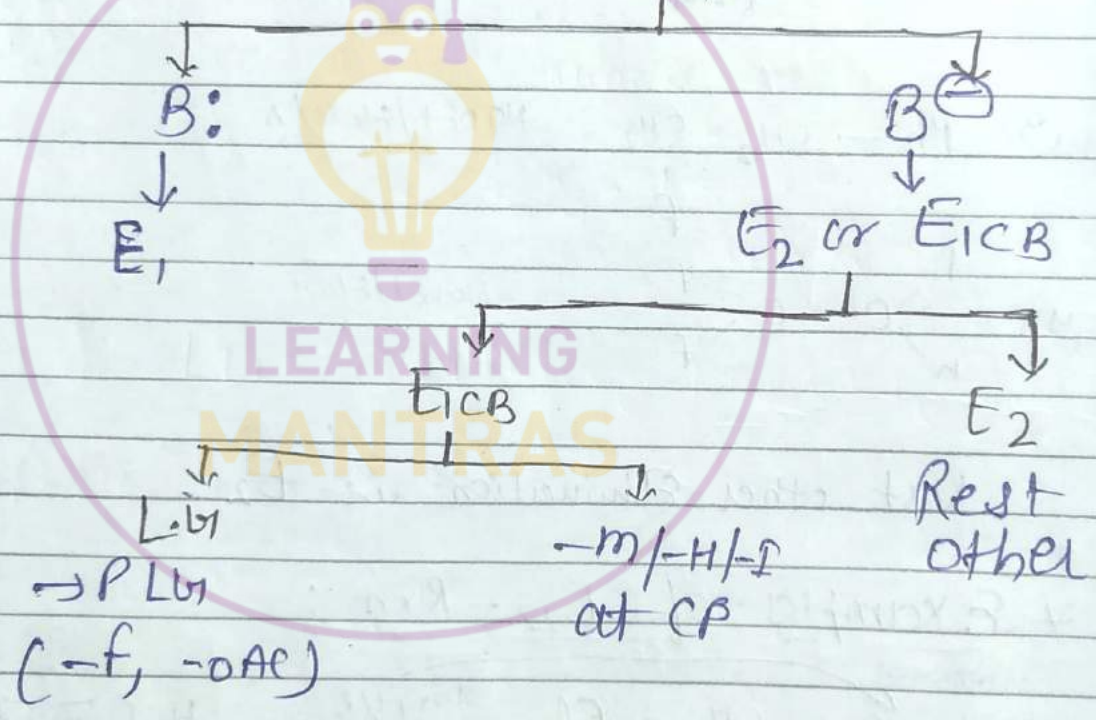
In Elimination Rx^n if there are two type of β Hydrogen atom then two type of alkene are form

and which alkene are major and minor, it is decided by Two Rule.

(1) Saytzeff's Rule

(2) Hafmann Rule

(1) **Saytzeff's Rule:** Acc. to this rule during the elimination R^n Hydrogen eliminate from that β carbon atom which have Less no. of Hydrogen atom (poor becomes poorer).

$$CH_3 - CH_2 - CH - CH_3 \xrightarrow{\ominus/\Delta} CH_3 - CH_2 - CH = CH_2 +$$

minor

$$CH_3 - CH = CH - CH_3$$

Major
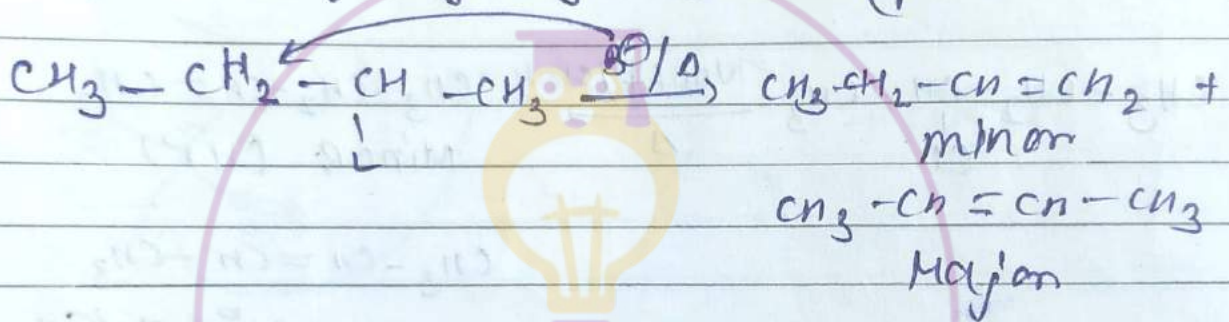
✳ **Hafmann Rule:-**

Acc. to this Rule H eliminate from that β carbon atom which have more no. of H atom.

$$CH_3 - CH_2 - CH - CH_3 \xrightarrow{\ominus/\Delta} CH_3 - CH_2 - CH = CH_2 +$$

Major (HP)

$$CH_3 - CH = CH - CH_3$$

minor
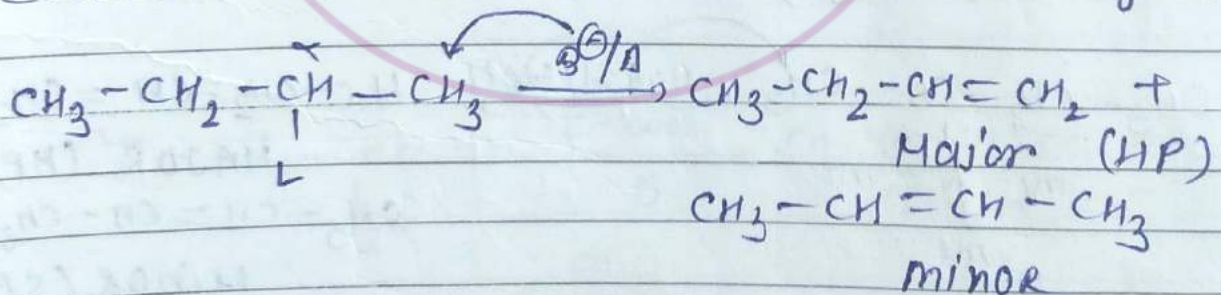
✳ for E_1 Mech^n : ⇒ Saytzeff's Rule (SR)
✳ for $E_1 CB$ Mech^n : ⇒ Hafmann Rule. (HR).
✳ for E_2 Mech^n : Both (~~&~~ → SR + HR).
                                    ↓   ↳ In '4' Cases
                              In most
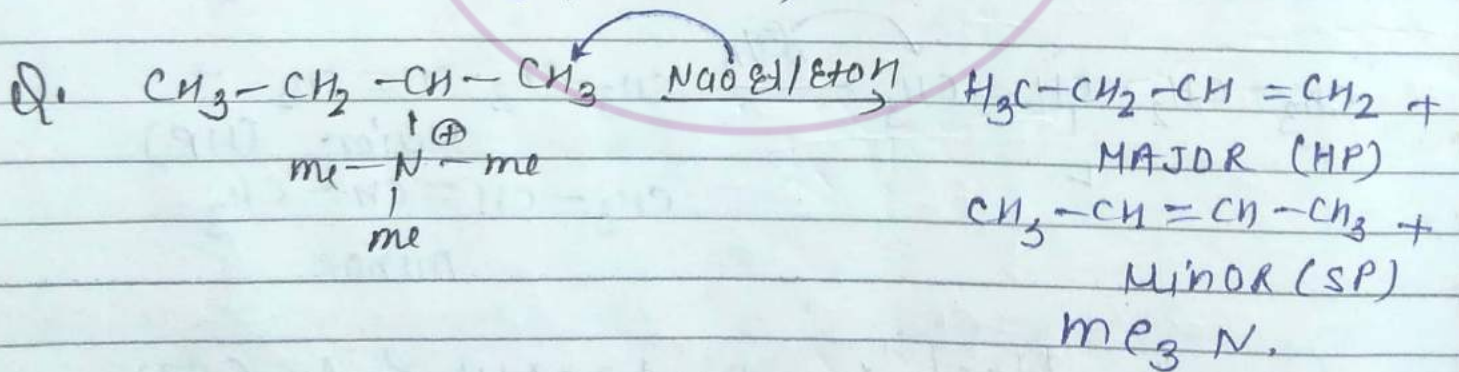   of the case

Case: Haf

(1) when L.G. is VPLG (very Poor Living gt).
$$[-F, -O-\overset{O}{C}-CH_3 (-Ac)]$$

EX) $CH_3 - CH_2 - \underset{F}{CH} - CH_3 \xrightarrow{NaOEt/EtOH} CH_3 - CH_2 - CH = CH_2 +$
Major (HP)

$$CH_3 - CH = CH - CH_3$$

Ex. $CH_3 - CH_2 - \underset{Cl}{CH} - CH_3 \xrightarrow[\Delta]{NaOEt/EtOH} CH_3 - CH_2 - CH = CH_2 +$
Minor (HP)

$$CH_3 - CH = CH - CH_3$$
Minor (SP)

Case: 2   when L.G = VLLG (very Large Living gt).
$$(-\overset{\oplus}{NR_3}, -\overset{\oplus}{SR_2})$$

Q. $CH_3 - CH_2 - \underset{\underset{me}{\overset{|}{\underset{me-N-me}{\oplus}}}}{CH} - CH_3 \xrightarrow{NaOEt/EtOH} H_3C - CH_2 - CH = CH_2 +$
MAJOR (HP)

$$CH_3 - CH = CH - CH_3 +$$
Minor (SP)
$me_3 N.$

Q. $CH_3 - CH_2 - \underset{\underset{CH_3}{\overset{|}{\underset{S}{\overset{\oplus}{\diagup}}\diagdown}CH_3}}{CH} - CH_3 \xrightarrow{NaOEt/EtOH}$ "   +   "

$+ me_2 S$

Ex:

$$CH_3-CH_2-\underset{\underset{Et}{\overset{\oplus}{\underset{|}{N}}-me}}{\overset{\overset{CH_3}{|}}{\underset{|}{CH}}}-CH_2-CH_3 \xrightarrow{NaOEt/EtOH/\Delta}$$

$H_3C-CH_2-CH=CH_2$ + (major)

$CH_3-CH=CH-CH_3$ ✗ minor

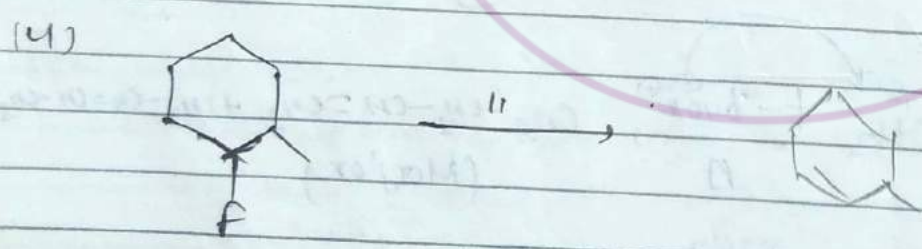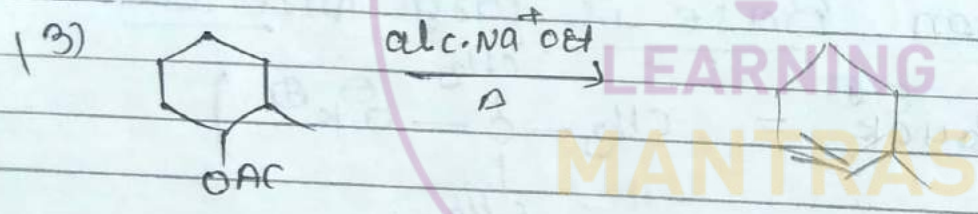$$\longrightarrow CH_3-\underset{\underset{CH_3-\overset{|}{N}-CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH}}-CH-CH_3 \quad + H_2C=CH_2$$

(4)

$+ Me_3N$
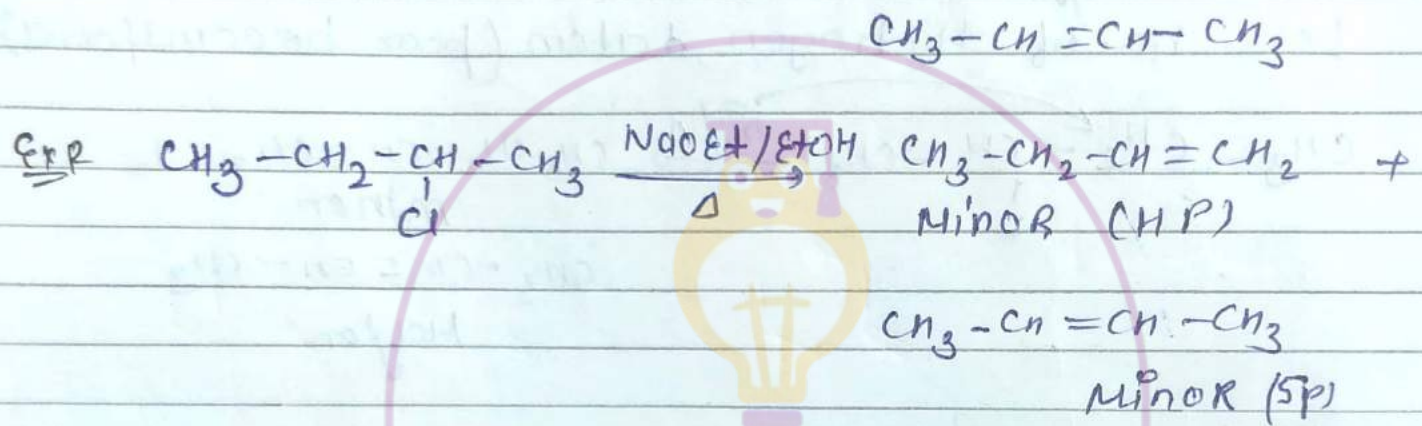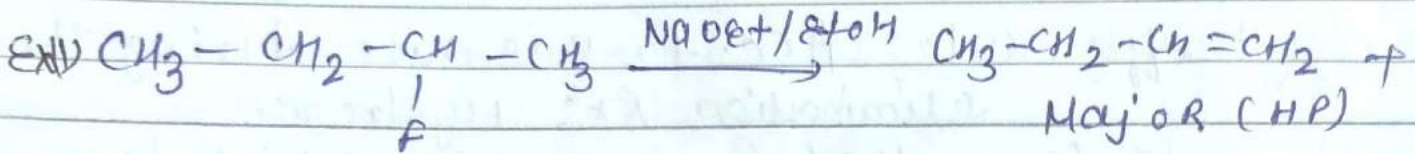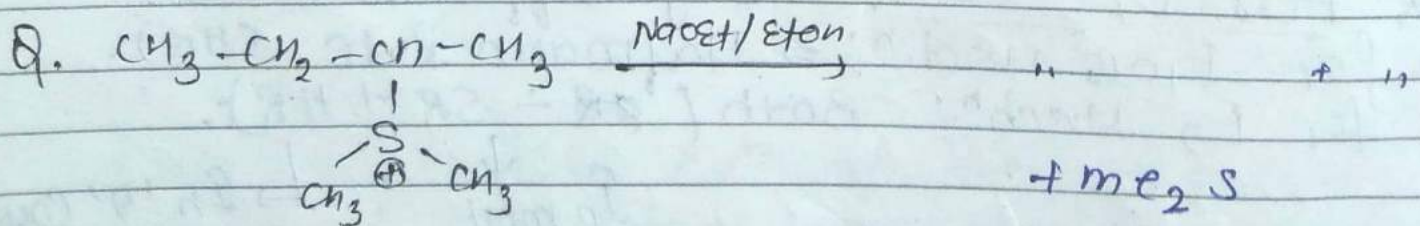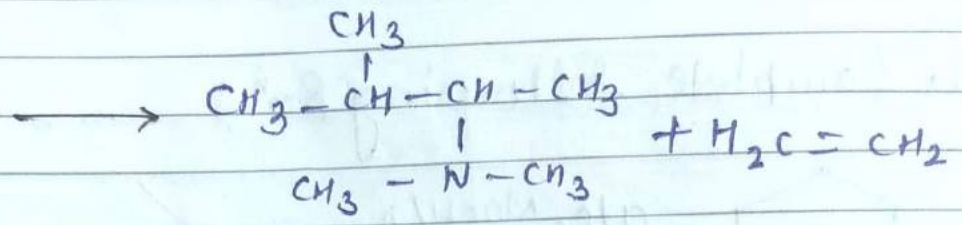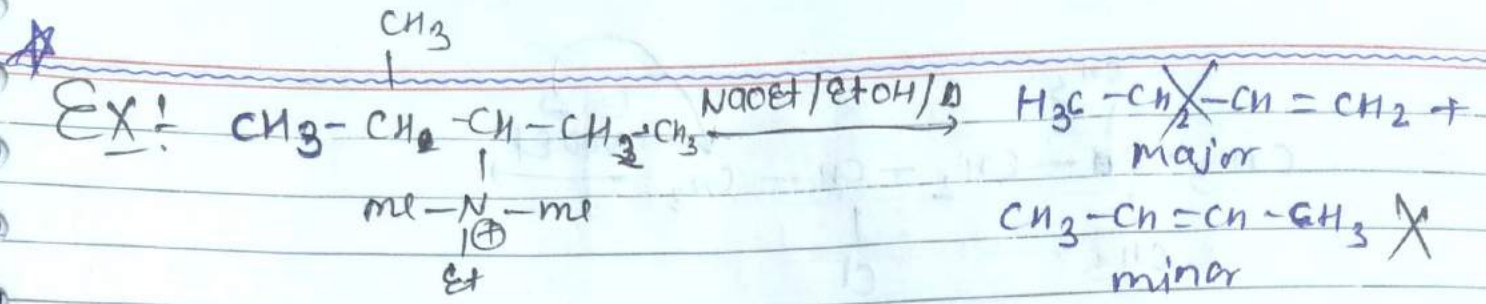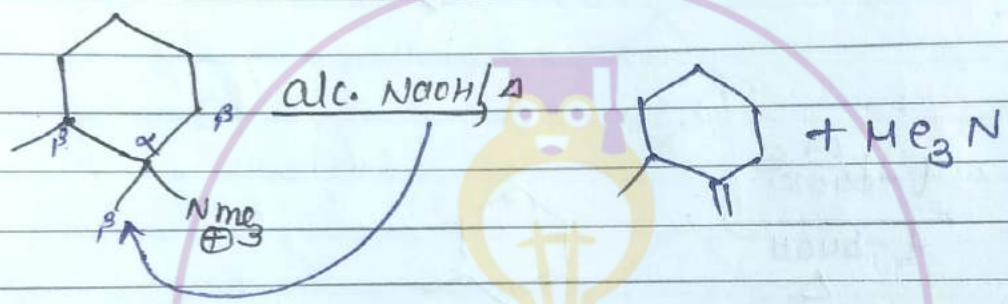
__Case: 3__ when Base is large size Base

Ex: $\left(t-buOK \equiv CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\ominus}{O}K^{\oplus} \right)$

Q.1 $CH_3-\overset{\beta}{CH_2}-\underset{\underset{Cl}{|}}{\overset{\alpha}{CH}}-\overset{\beta'}{CH_3} \xrightarrow[\Delta]{t-buOK^{\oplus}}$ $CH_3-CH_2-CH=CH_2 + CH_3-CH=CH-CH_3$ (Major)

$CH_3-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_3 \xrightarrow{NaOEt}$ " $+ CH_3-CH=CH-CH_3$ (MAJOR.)
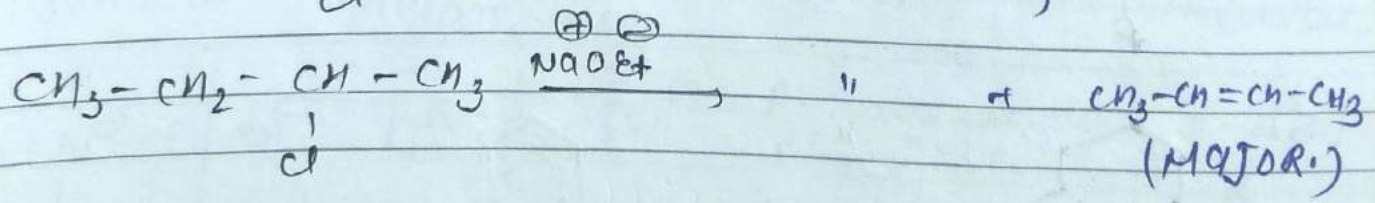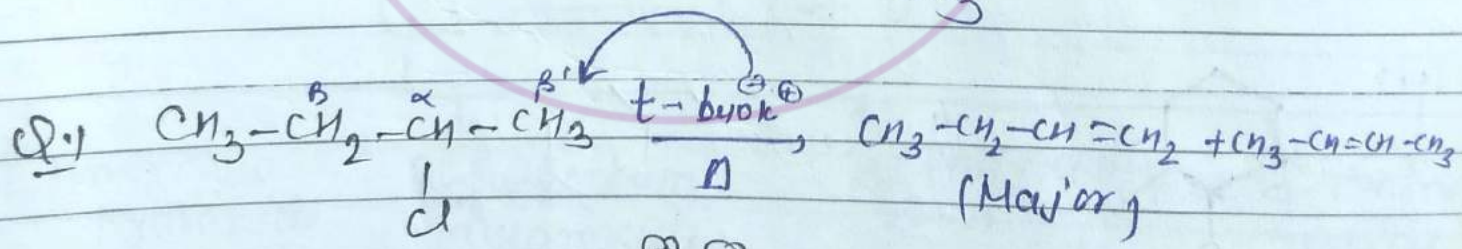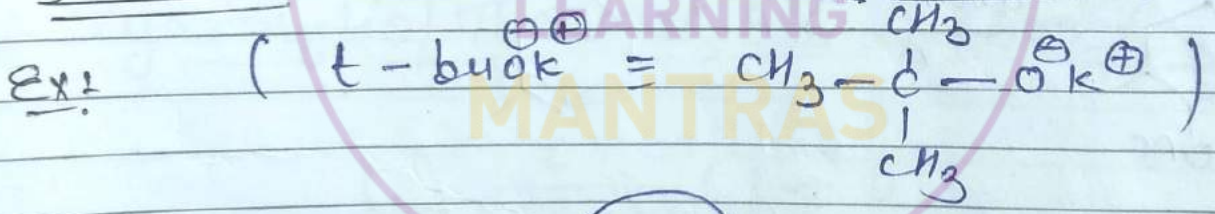
__Case: 4__ When their is Crowding around H Responsible for sed. Product then also elimination occur by Halfmann Rule

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH}}-CH_2-\underset{\underset{d}{|}}{CH}-CH_3 \xrightarrow{\overset{\oplus}{Na}\overset{\ominus}{OEt}}$$
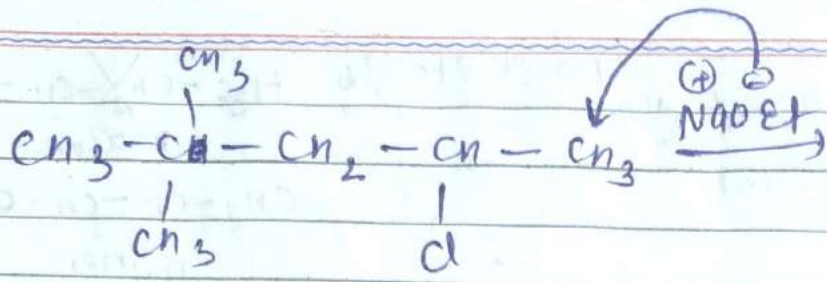
Q. Complete following Rxⁿ :

(1)

$$\xrightarrow{alc.\ NaOH/\Delta}$$

(2)

$$\xrightarrow[\underset{\Delta}{t-buOH}]{t-b\overset{\ominus}{uO}\overset{\oplus}{K}}$$

(3)

OAC

$$\xrightarrow[\Delta]{alc.\ Na^+\ OEt}$$

(4)

F

$$\xrightarrow{\ \ ll\ \ },$$

(5)

$$\overset{\oplus}{N}me_3$$

$$\xrightarrow{\ \ ll\ \ },$$

(6)

$$\overset{\oplus}{S}Me_2$$

$$\xrightarrow{\ \ ll\ \ }$$

 $+ \ SMe_2$

(7)

 $\xrightarrow{\;\Delta\;}$ $\rightarrow$ $+ H_2C=CH_2$

me $- N^{\oplus} -$ me
et

(8)

 $\xrightarrow{\;\Delta\;}$

$S^{\oplus}$

(9)

 $\xrightarrow{\;\Delta\;}$

F

(10)

 $\xrightarrow{\;\Delta\;}$

Cl
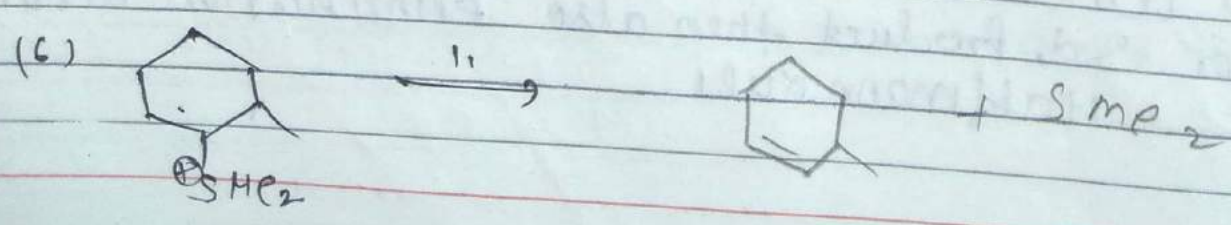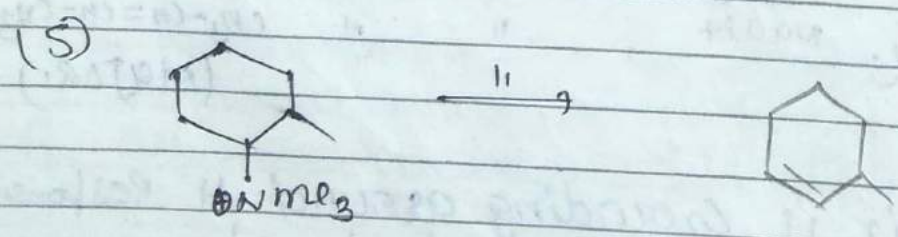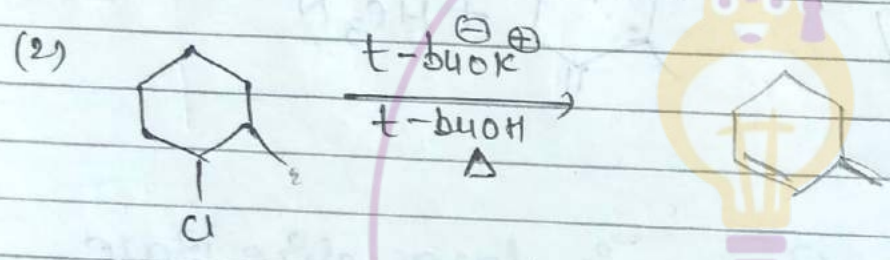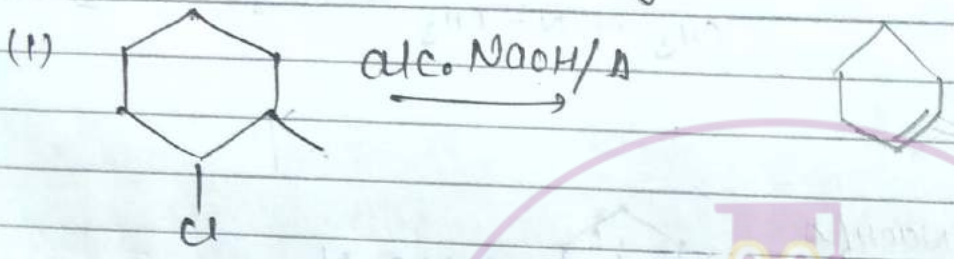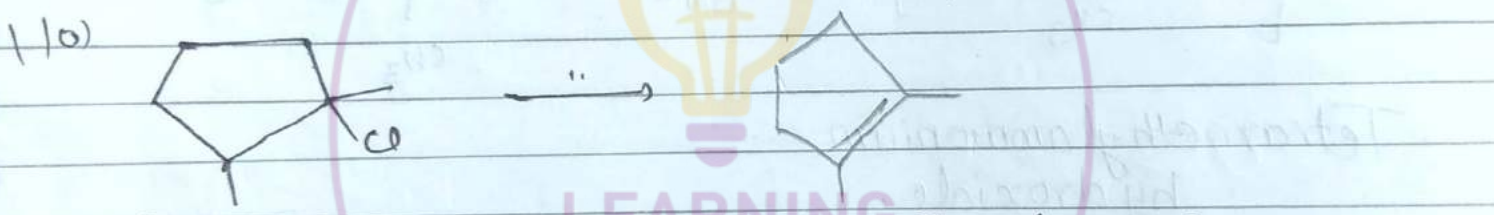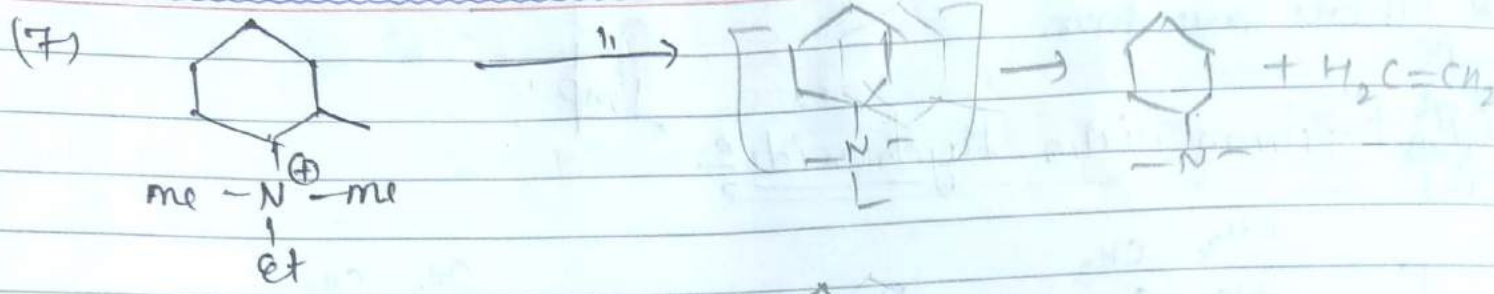
* Pyrrolytic / Thermal Elimination Reaction:

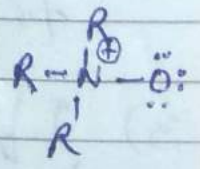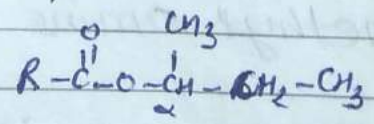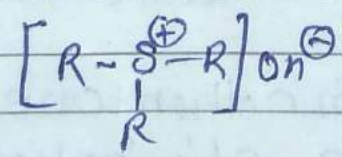$$ \bigcirc \xrightarrow{\;\Delta\;} \mathsf{a} + \mathsf{D} $$
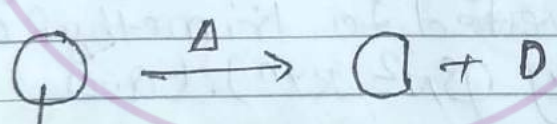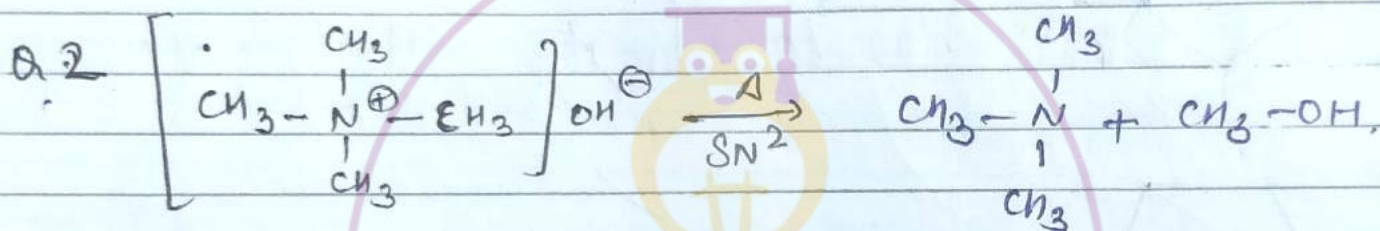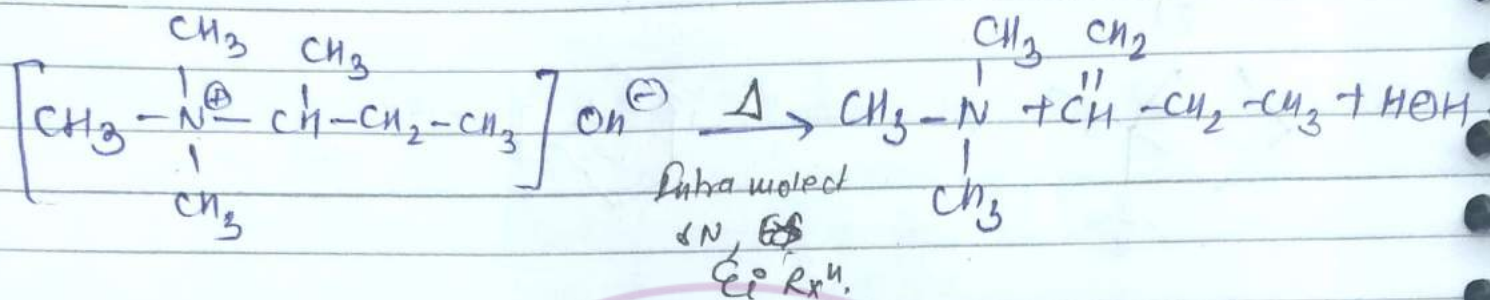
4° Ammonium Hydroxide	3° Sulfonium Hydroxide	ester having β-H	3° Amine oxide

$\begin{bmatrix} R \\ R-N^{\oplus}-R \\ R \end{bmatrix} OH^{\ominus}$ $\qquad$ $\begin{bmatrix} R-S^{\oplus}-R \\ R \end{bmatrix} OH^{\ominus}$ $\qquad$ $R-\overset{O}{\overset{\|}{C}}-O-\overset{CH_3}{\underset{2}{CH}}-CH_2-CH_3$ $\qquad$ $R-\overset{R}{\underset{R}{N^{\oplus}}}-\overset{..}{\underset{..}{O}}:$
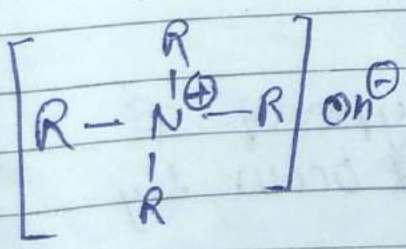
* There are four

Imp.

4° - Ammonium hydroxide :-

$$\left[CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^{\oplus}}} - \overset{CH_3}{\underset{}{CH}} - CH_2 - CH_3 \right] OH^{\ominus} \xrightarrow{\Delta} CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}} + \overset{CH_2}{\overset{||}{CH}} - CH_2 - CH_3 + HOH$$

Intramoleced
δN, $E_i^{\ominus} Rx^n$.

Q.2 $\left[CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^{\oplus}}} - CH_3 \right] OH^{\ominus} \xrightarrow[SN^2]{\Delta} CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}} + CH_3 - OH.$

Tetramethylammonium
hydroxide.

(1) when all alkyl gp are methyl gp. then on
heating Converted to trimethyl amine and
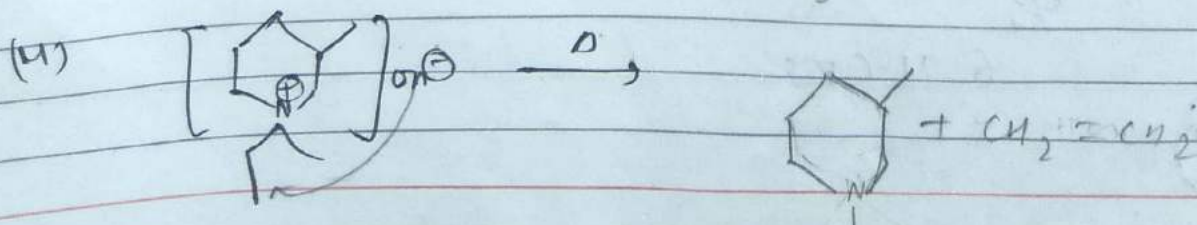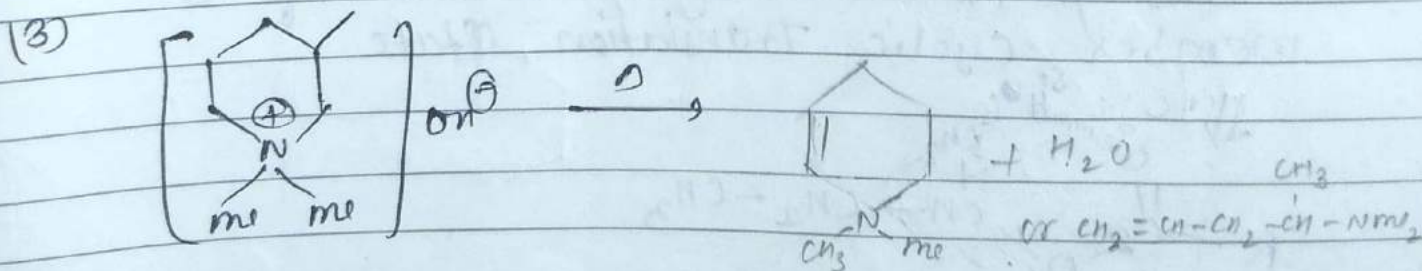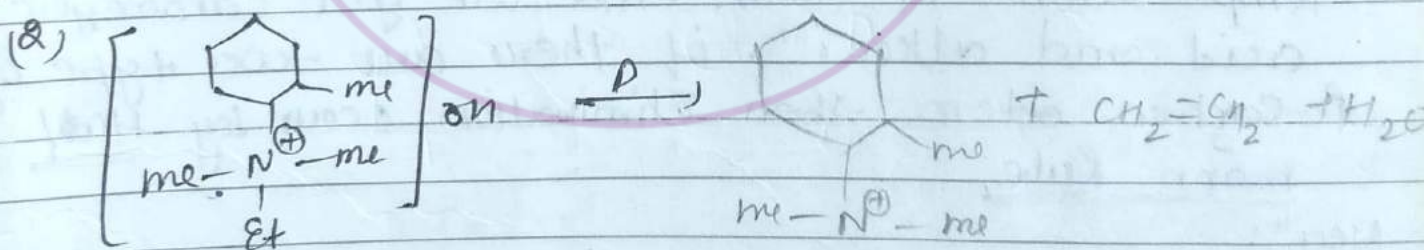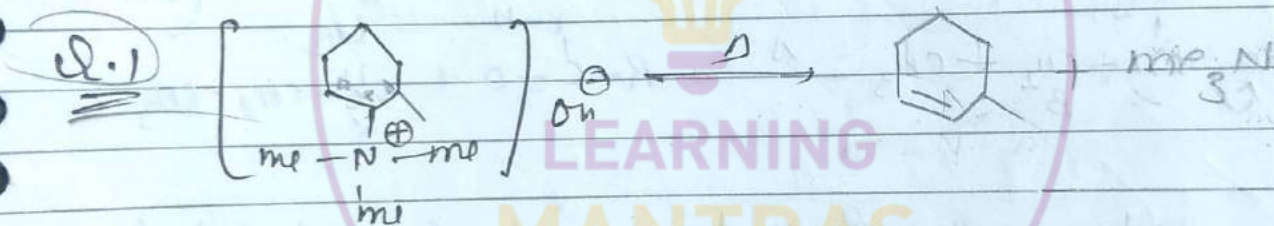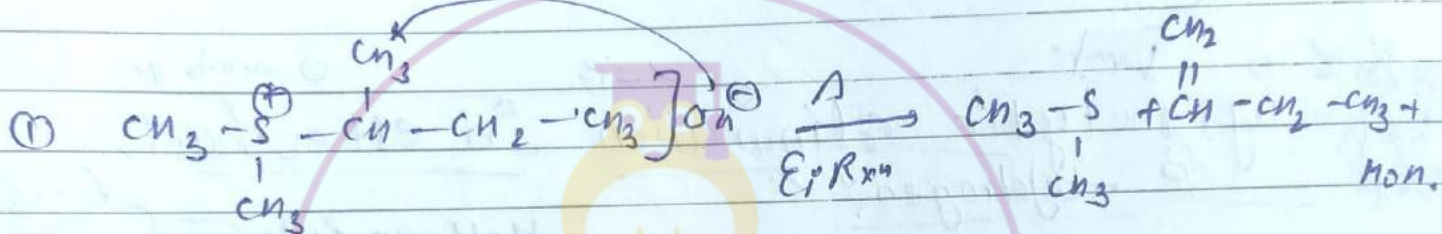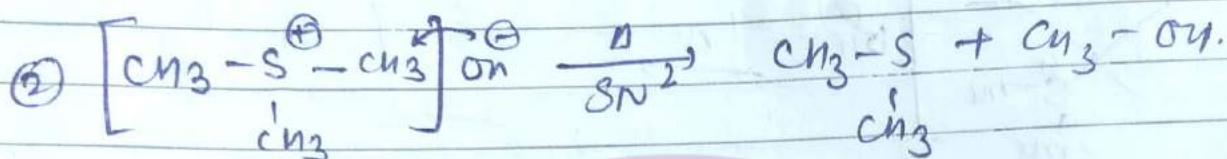methanol. (by $SN^2 Rx^n$). (Q.2)

2) when any alkyl gp larger the alkyl gp than
intramolecular Rx^n occur and we get
trimethyl amine + Alkene.
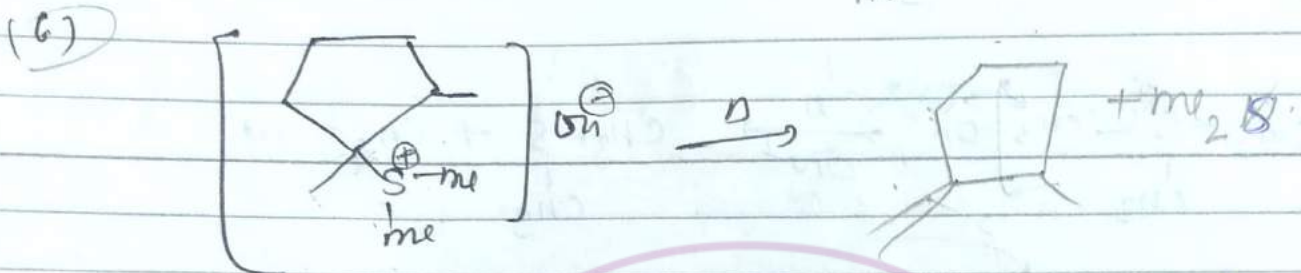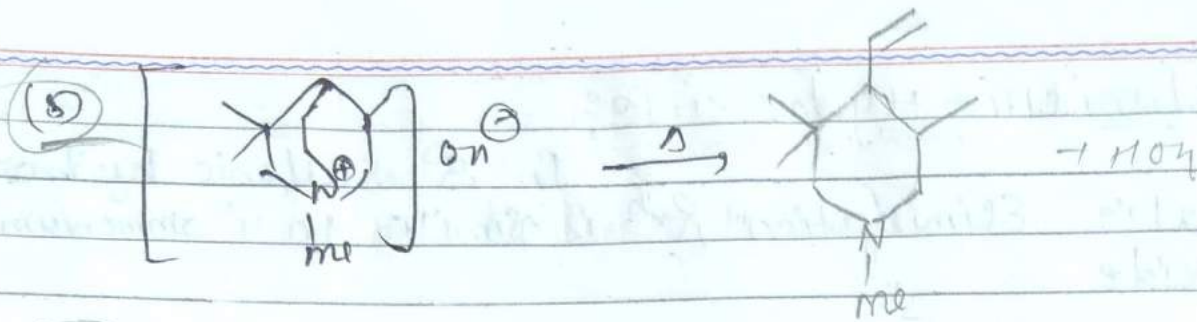
3) If there are more than one type of β
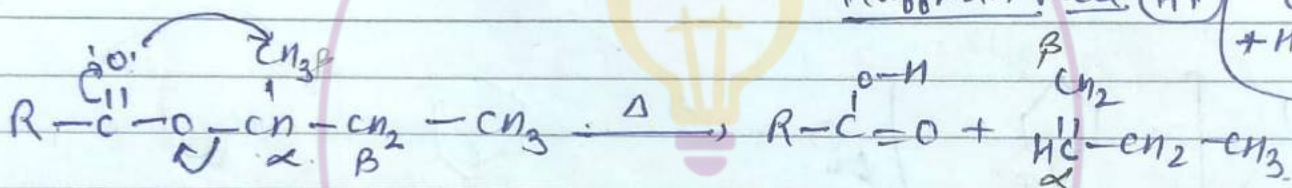hydrogen atom the elimination occur by
hafmann.

*3° Sulfonium Hydroxide:-

An S° Sulfonic hydroxide

Pyrolatic Elimination Rxⁿ is similar to 4° ammonium hydroxide

(2) $\left[CH_3 - \overset{\oplus}{S} - CH_3 \right] \overset{\ominus}{OH} \xrightarrow[SN^2]{\Delta} CH_3 - S + CH_3 - OH$
$\quad\quad\quad\quad \underset{CH_3}{|}$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \underset{CH_3}{|}$

(1) $CH_3 - \overset{\oplus}{\underset{CH_3}{S}} - CH - CH_2 - CH_3 \Big] \overset{\ominus}{OH} \xrightarrow[Ei\,Rxⁿ]{\Delta} CH_3 - \overset{\underset{CH_3}{|}}{S} + \overset{CH_2}{\overset{||}{CH}} - CH_2 - CH_3 + $ Hofm.

Q.1

$\left[\text{(ring)} - \overset{\oplus}{\underset{me}{N}} \begin{smallmatrix} me \\ me \end{smallmatrix} \right] \overset{\ominus}{OH} \xrightarrow{\Delta} \text{(ring)} + me_3 N$

(2)
$\left[\text{(ring)} - \overset{\oplus}{\underset{Et}{N}} \begin{smallmatrix} me \\ me \end{smallmatrix} \right] OH \xrightarrow{\Delta} \text{(ring)} - \overset{\oplus}{\underset{me}{N}} \begin{smallmatrix} me \\ \end{smallmatrix} + CH_2 = CH_2 + H_2O$

(3)
$\left[\text{(ring with N)} \overset{\oplus}{\underset{me\ me}{N}} \right] \overset{\ominus}{OH} \xrightarrow{\Delta} \text{(ring)} + H_2O$
or $CH_2 = CH - CH_2 - \overset{CH_3}{\overset{|}{CH}} - NMe_2$
$\overset{N}{\underset{CH_3\ me}{}}$

(4)
$\left[\text{(ring with N)} \overset{\oplus}{N} \right] \overset{\ominus}{OH} \xrightarrow{\Delta} \text{(ring)} + CH_2 = CH_2$

(5)

$\qquad$ $+ HO_4$

(6)

$+ me_2 \emptyset$

✦✦✦ Pyrolytic elimination in ester having β-Hydrogen:

Haffman Rule (H1)

$$R-\overset{\overset{:O:}{\|}}{C}-O-\underset{\alpha}{CH}-\underset{\beta}{CH_2}-CH_3 \xrightarrow{\Delta} R-\overset{O-H}{\overset{|}{C}}=O + \overset{\beta}{\overset{CH_2}{\underset{\alpha}{HC}}}=CH_2-CH_3$$

When ester with β Hydrogen is heated at high temp. then Ei occur. and we get carboxylic acid and alkene. if there are two type of β carbon atom then Elimination occur by Haffmann Rule.

Mech^n:

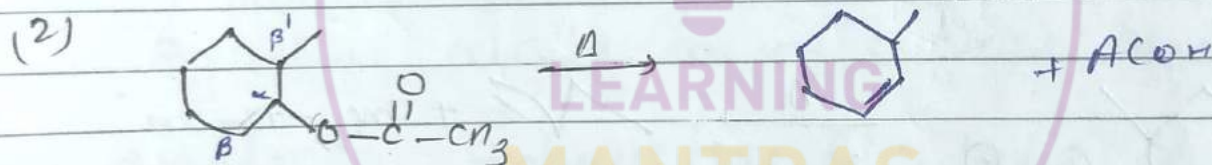This for Rx^n occur by formation of 6 member cyclic Translation State
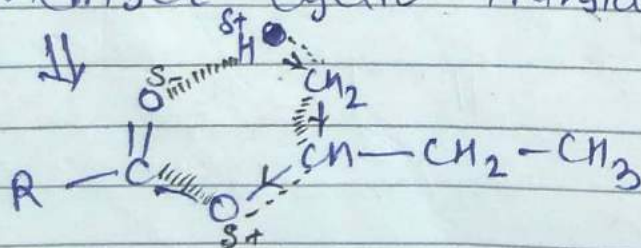
6 M-CTS

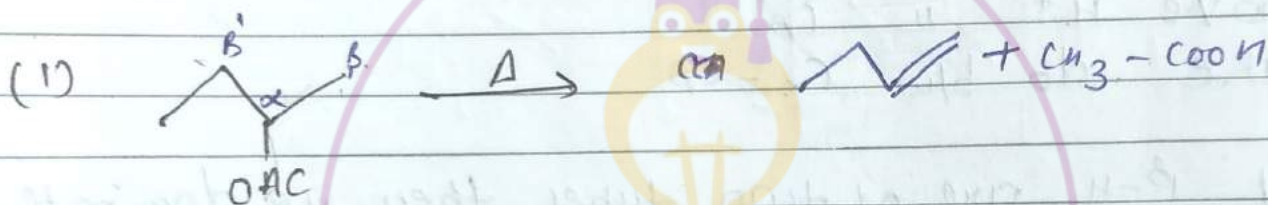(Syn elimination)

TTMP (Trick to make product) (formation)

- Remove R−COO⁻ from Cα.
  Remove H⁺ " Cβ.
  make db b/w Cα − Cβ

- If β-H are of two type then H R dominate.

Que:

(1) $\xrightarrow{\Delta}$ $+ CH_3 - COOH$

OAC

(2) $\xrightarrow{\Delta}$ $+ ACOH$

$O-\overset{O}{\overset{||}{C}}-CH_3$

(3) $\xrightarrow{\Delta}$ $+ ACOH$

$O-\overset{O}{\overset{||}{C}}-CH_3$

(4) $CH_3 - COOH \xrightarrow[-H_2O]{AgOH} \boxed{A} \xrightarrow[-AgCl]{} \boxed{B} \xrightarrow{\Delta} \boxed{C} + D$

$CH_3 - COO^⊖ Ag^⊕$
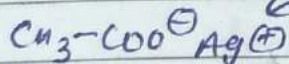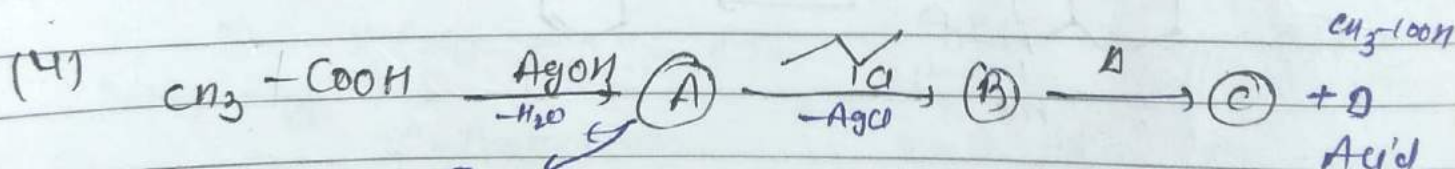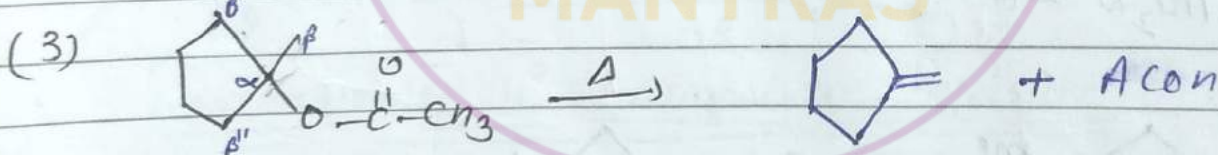
silver salt of Acid
(silver acetate)

$\overset{\displaystyle \curlyvee}{O-C-CH_3}$
$\overset{||}{O}$

$CH_3 - COOH$

Acid

(5) $\overset{O}{\overset{||}{Cl-C}}-CH_2-CH_2-CH_2-CH_2-Cl$

$\downarrow CH_3-COOAg (xs)$

$\boxed{A}$ $\overset{\alpha}{CH_3-COO}-\overset{\beta}{CH_2}-CH_2-\overset{\beta}{CH_2}-\overset{\curlyvee}{CH_2}-O-\overset{O}{\overset{||}{C}}-CH_3$

$\downarrow \Delta$

$\boxed{B} + \boxed{C}$ $H_2C=CH-CH=CH_2$ $2 CH_3 - COOH$.
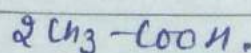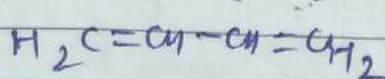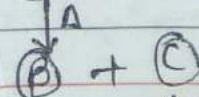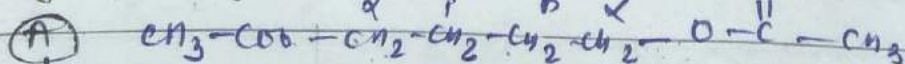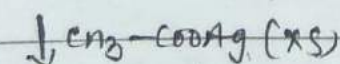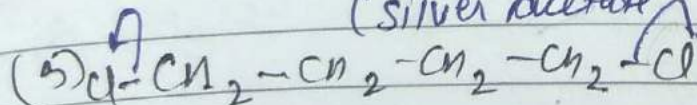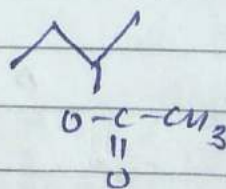
Acid.

Q. * Pyrrolytic elimination in 3° - Amine oxide :

OR

(Cope - elimination)

$$CH_3 - \overset{\beta}{C}H_2 - \overset{\alpha}{C}H - \overset{\oplus}{N} \overset{\ominus}{-} O \xrightarrow{\Delta} CH_3 - CH_2 - \overset{CH_2 \, me}{\overset{||}{CH}} + \overset{N - OH}{\underset{me}{N}}$$

with β CH₃, CH₃ groups — 5 member cyclic T.S

- TTHP
  Remove $N^{\oplus}$ from C_α
  Remove H^+ " C_β
  make db b/w $C_\alpha - C_\beta$
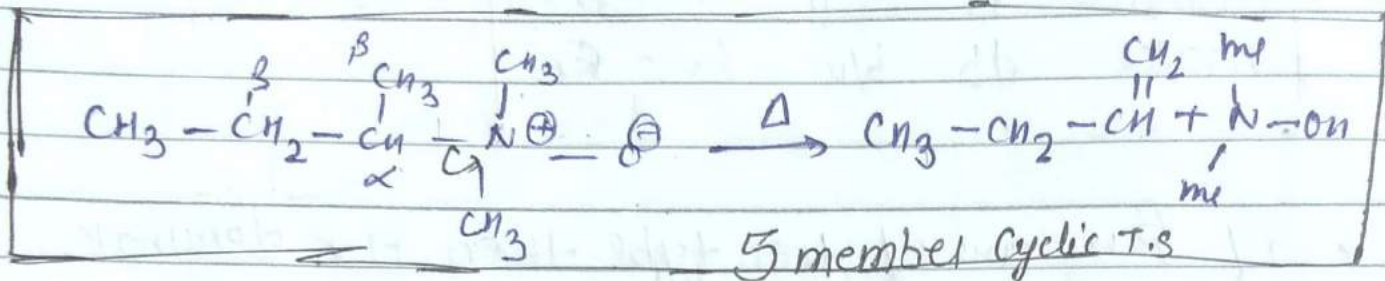
- ff $\beta - H$ are of two types then HR dominate.

Qu: $\xrightarrow{\Delta}$ + $me_2 - N - OH$

(ii) $\xrightarrow{\Delta}$ + " + "

(iii) $\xrightarrow{\Delta}$ + $Me_2 N - OH$.

Not
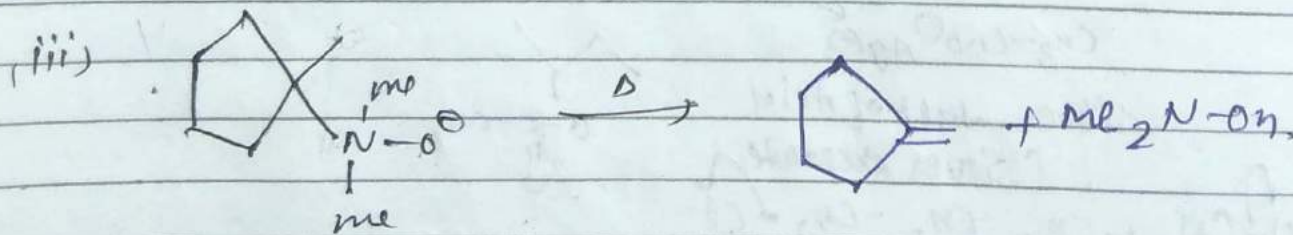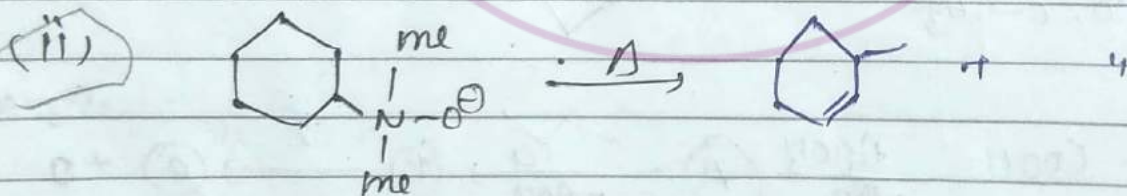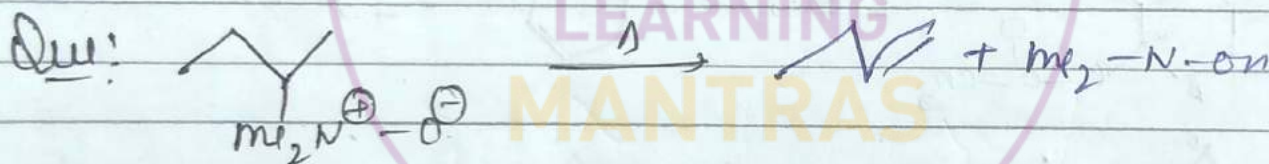
Note! 3° Ammine oxide can be prepared by R_x^u of 30° Ammine with H_2O_2 or Ag_2O or CH_3/Ag

$$R_3 \overset{\bullet\bullet}{N}\colon \xrightarrow[\overset{\bullet\bullet}{O}\colon + H_2O]{H_2O_2} R_3 \overset{\oplus}{N} - \overset{\ominus}{N}$$
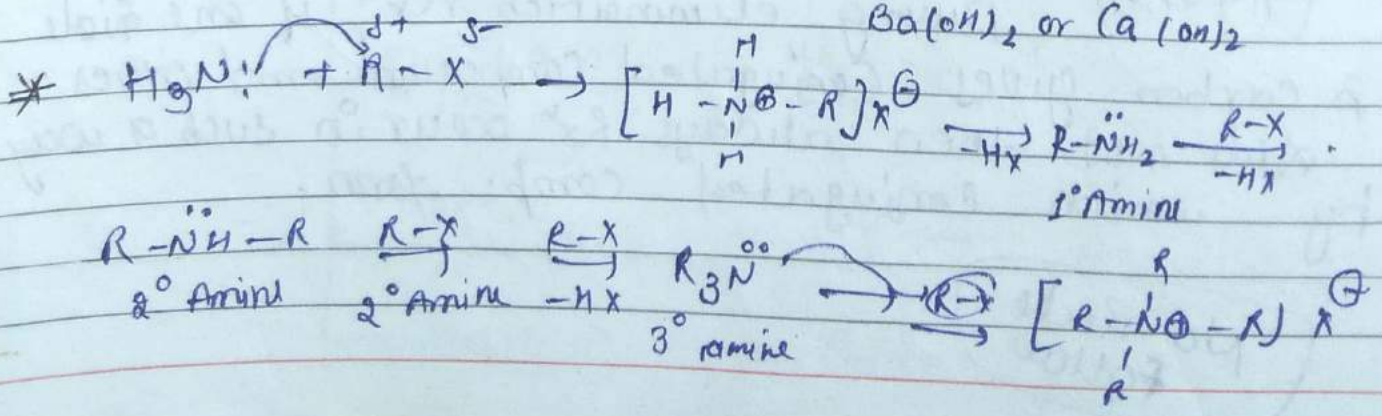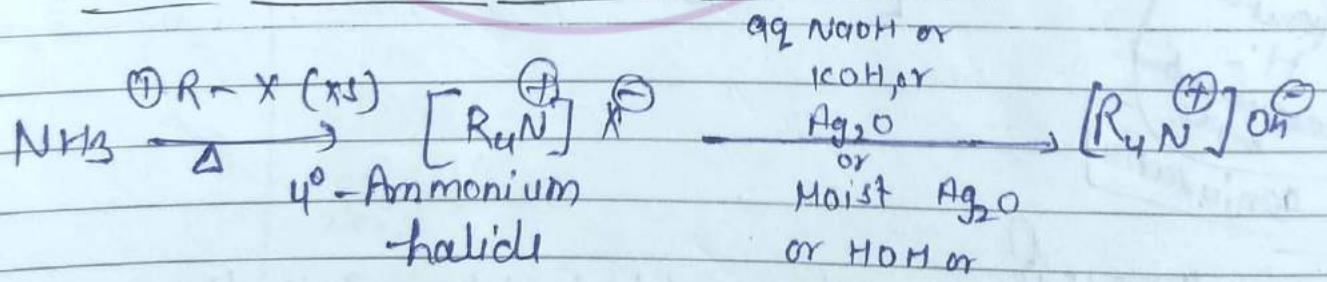
Q.
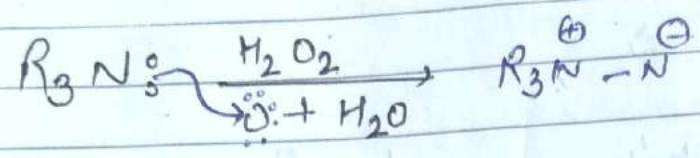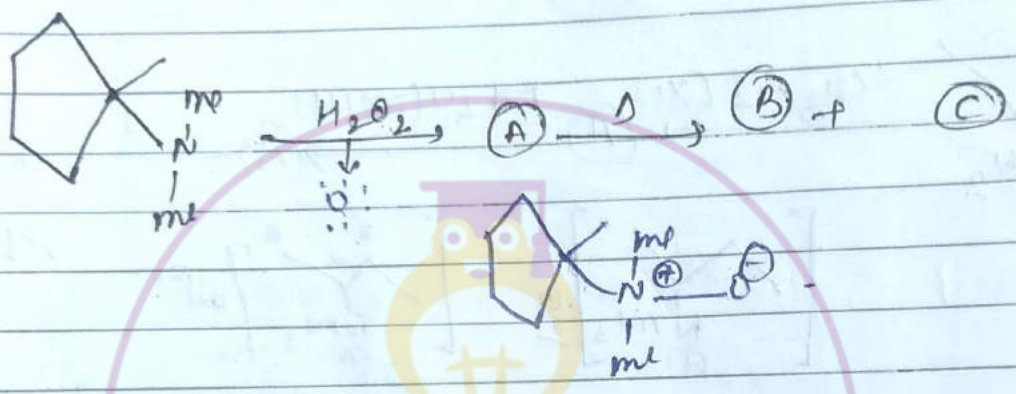
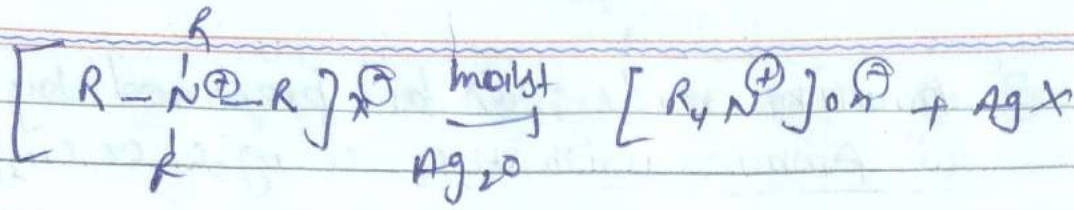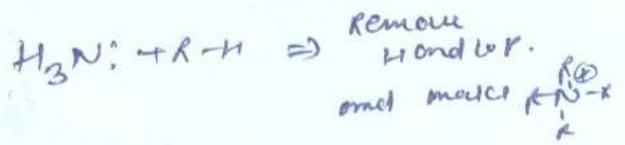* 4° Amino Amonium Hydroxide can be Prepared by Exastive alkilation of amines or Amonium.

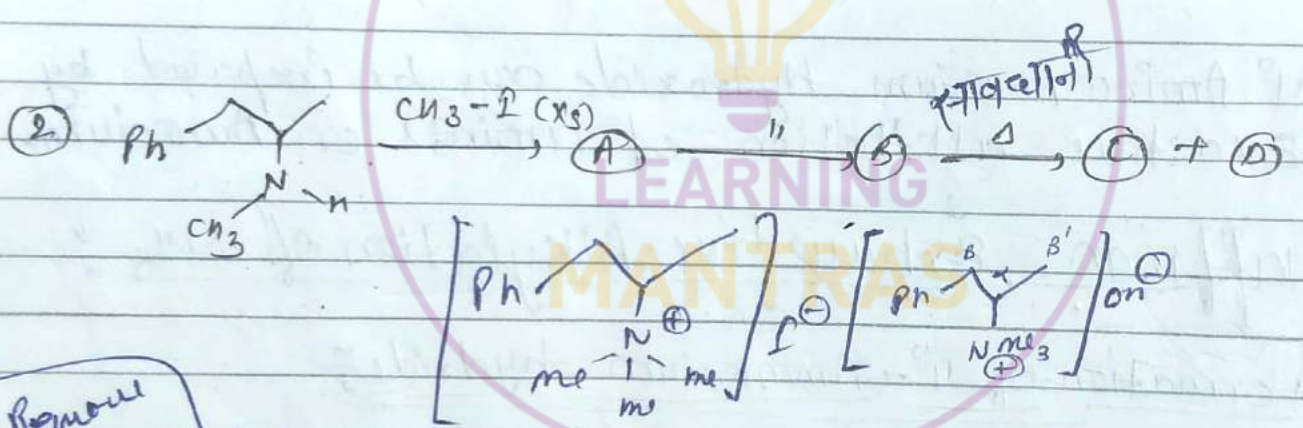* <u>Haffman</u> <u>Exhaustive Alkylation of NH_3</u> :
OR.
<u>Formation of 4° - Ammonium hydride</u> :

$$NH_3 \xrightarrow[\Delta]{\textcircled{1} R-X \,(xs)} \overset{4°\text{-Ammonium}}{\underset{halide}{[R_4\overset{\oplus}{N}]\overset{\ominus}{X}}} \xrightarrow[\underset{\text{Ba(OH)}_2 \text{ or } Ca(OH)_2}{\text{or HOH or}}]{\underset{\text{Moist } Ag_2O}{\overset{\text{aq NaOH or}}{\overset{\text{KOH, or}}{Ag_2O}}}} [R_4\overset{\oplus}{N}]\overset{\ominus}{OH}$$

* $H_3\overset{\bullet\bullet}{N}\colon + \overset{\delta+}{R} - \overset{\delta-}{X} \longrightarrow [H - \overset{H}{\underset{H}{\overset{\oplus}{N}}} - R]\overset{\ominus}{X} \xrightarrow{-HX} R-\overset{\bullet\bullet}{N}H_2 \xrightarrow[-HX]{R-X}$
1° Amine

$R-\overset{\bullet\bullet}{N}H-R \xrightarrow{R-X} \underset{2° \text{ Amine}}{} \xrightarrow[-HX]{R-X} R_3\overset{\bullet\bullet}{N} \xrightarrow{R-X} [R-\overset{R}{\underset{R}{\overset{\bullet\bullet}{N}}} - N]\overset{\oplus}{R}$
2° Amine   2° Amine   3° amine

$$H_3N: + R-H \Rightarrow \text{Remove H and L.r. and make } R-\overset{R}{\underset{R}{N}}-x$$

$$\left[R-\overset{R}{\underset{R}{N^{\oplus}}}-R\right]x^{\ominus} \xrightarrow[Ag_2O]{\text{moist}} \left[R_4 N^{\oplus}\right]OH^{\ominus} + AgX$$

* Key point ⇒

By this method 1°, 2°, 3° Amine Can also prepared.

Q.

$$\xrightarrow{CH_3-I \,(xs)} \text{(A)} \xrightarrow{Ag_2O \,(moist)} \text{(B)} \xrightarrow{\Delta} \text{(C)} + D$$

$$\left[\overset{}{\underset{\overset{N}{+}me_3}{}}\right]I^{\ominus} \quad \left[\overset{\delta'}{\underset{\overset{N}{+}me_3}{\overset{\alpha}{\wedge}}}\overset{\beta}{}\right]OH^{\ominus}$$

$$\nwarrow + Me_3N$$

(2) Ph

$$\xrightarrow{CH_3-I \,(xs)} \text{(A)} \xrightarrow{} \text{(B)} \xrightarrow{\Delta} \text{(C)} + \text{(D)}.$$

सावधानी

$$\left[Ph\overset{}{\underset{me-\overset{N^{\oplus}}{\underset{me}{|}}-me}{\wedge}}\right]I^{\ominus} \quad \left[Ph\overset{\beta}{\underset{\overset{N}{+}me_3}{\wedge}}\overset{\beta'}{}\right]OH^{\ominus}$$
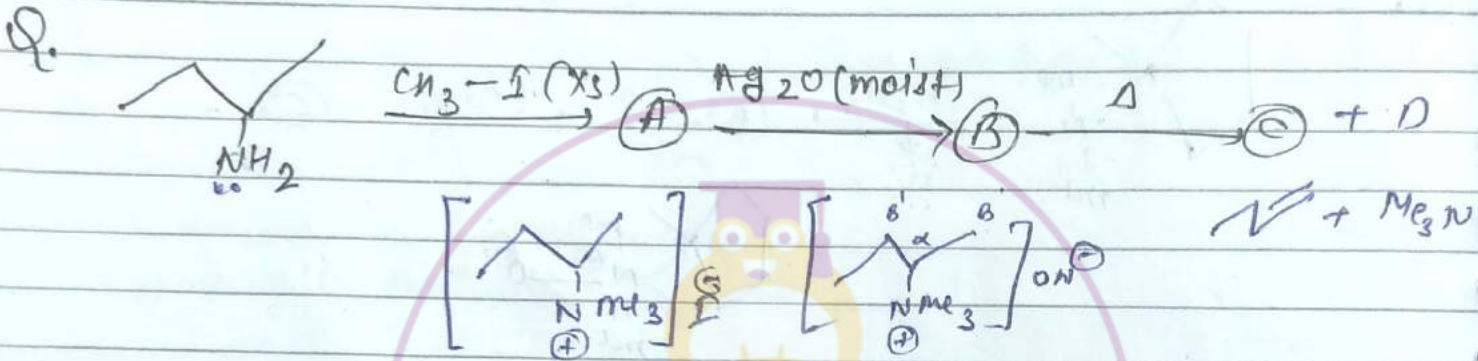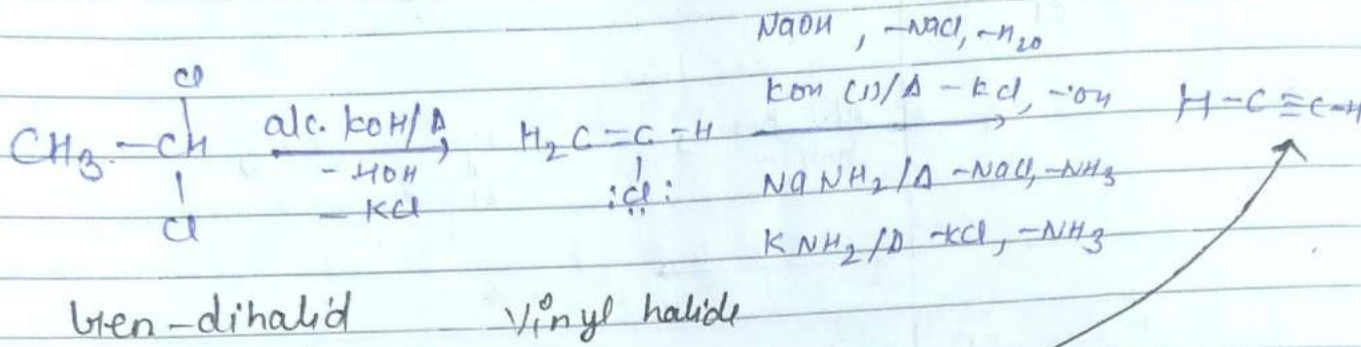
Remove H.
Resonance bnd make
conjugation

सावधानी During elimination Rx⁴ if one side β carbon gives Conjugated Compound and other did not then always Rxⁿ occur in such a way by which conjugated comp. form.

No Rule
follow

✳ Double elimination Rxⁿ:-

$$CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{CH}} \xrightarrow[-HOH]{\text{alc. KOH/}\Delta} \underset{\underset{:\ddot{C}l:}{|}}{H_2C=C-H} \begin{array}{l} \xrightarrow{NaOH, -NaCl, -H_2O} \\ \xrightarrow{KOH\,(s)/\Delta\,-KCl,\,-OH} \\ \xrightarrow{NaNH_2/\Delta\,-NaCl,\,-NH_3} \\ \xrightarrow{KNH_2/\Delta\,-KCl,\,-NH_3} \end{array} H-C\equiv C-H$$
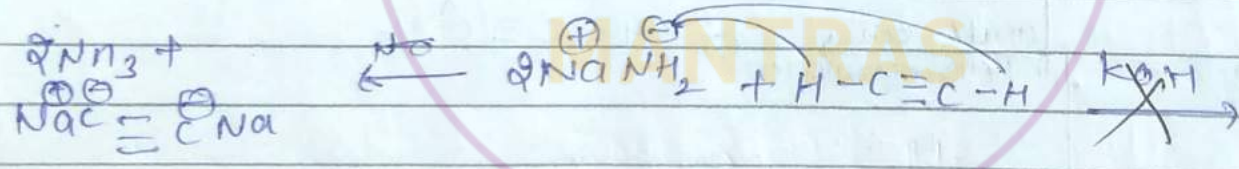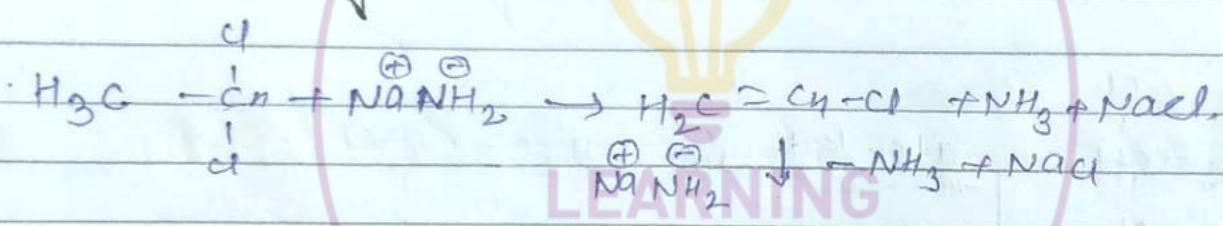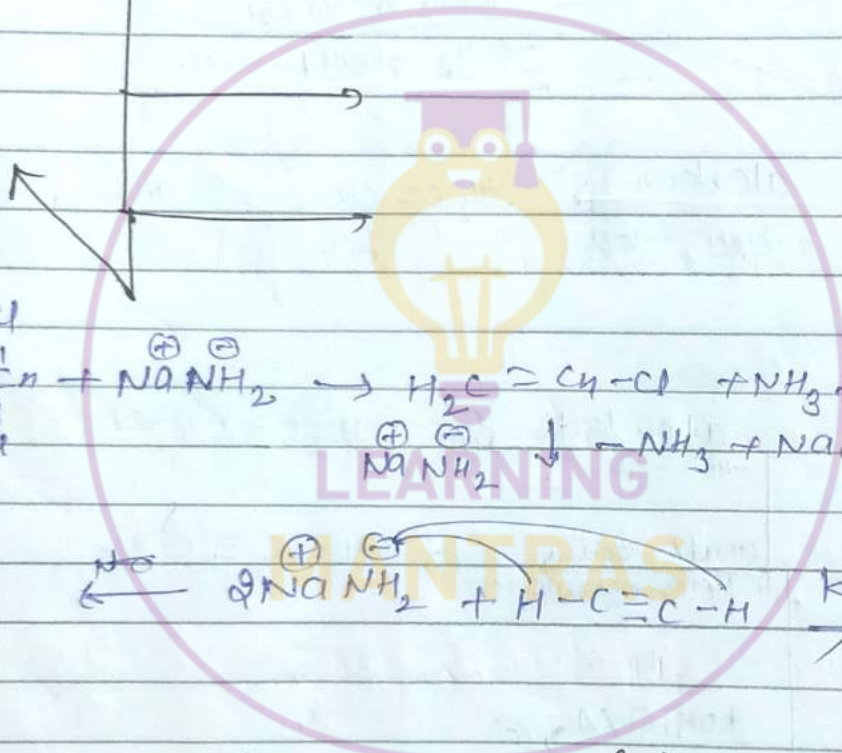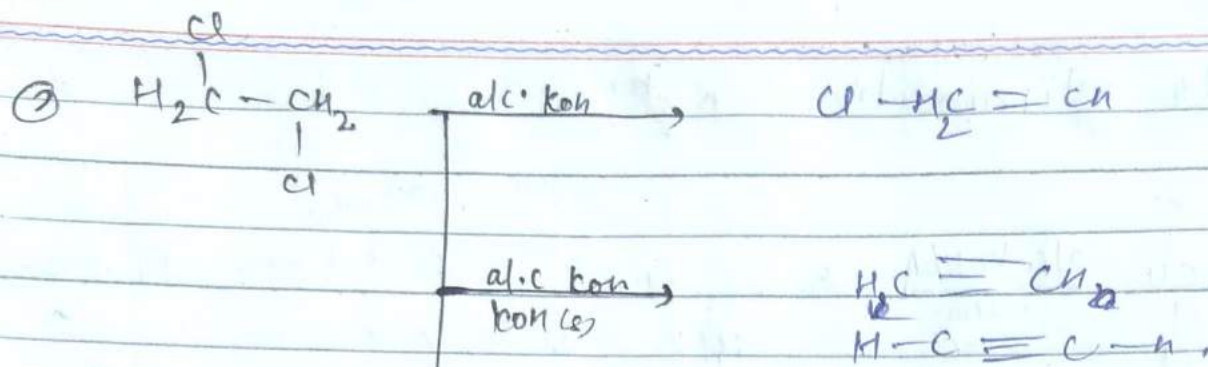
gem-dihalid   Vinyl halide

$$\xrightarrow[-NH_3\ -KCl\,/\,-NaCl.]{KNH_2\ or\ Na\,NH_2,}$$

(a) $$H_2\underset{\underset{Cl}{|}}{C}-\underset{\underset{Cl}{|}}{CH_2} \xrightarrow[-HOH,\ -KCl]{\text{alc. KOH}} \underset{\underset{Cl}{|}}{H_2C=CH} \quad \xrightarrow{\ "\ } \quad H-C\equiv C-H$$

(1) $$CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{CH}} \begin{array}{l} \xrightarrow[-HOH\ -KCl]{\text{alc. KOH}} \text{(A)} \quad H_2C=CH-Cl \\ \\ \xrightarrow[(ii)\ KOH(s)\ or\ NaNH_2(1eq)]{(i)\ alc.\ KOH} \text{(B)} \quad H-C\equiv C-H. \end{array}$$

(2) $$H_2\underset{\underset{Cl}{|}}{C}-CH_2 \begin{array}{l} \xrightarrow[2eq]{KOH(s)/\Delta} \text{(C)} \quad " \\ \\ \xrightarrow[2eq]{NaNH_2(s)/\Delta} \text{(D)} \quad " \\ \\ \xrightarrow[(XS)]{KOH(s)/\Delta} \text{(E)} \quad H-C\equiv C-H \\ \\ ✰\quad \xrightarrow[(XS)]{NaNH_2/\Delta} \text{(F)} \quad H-C\cancel{\equiv}C-H \quad Na\overset{\oplus}{C}\equiv\overset{\ominus}{C}Na+ \\ \hspace{8cm} 2NH_3 \\ \\ \xrightarrow[]{NaNH_2(1eq)/\Delta} \text{(G)} \quad H_2C=CH-Cl. \end{array}$$

③
$$H_2\overset{Cl}{\underset{Cl}{C}}-CH_2 \xrightarrow{\text{alc. KOH}} Cl-\overset{}{\underset{2}{H}}C=CH$$

$$\xrightarrow[\text{KOH }(c)]{\text{alc. KOH}} \quad \begin{array}{l} H_2C\equiv CH_2 \\ H-C\equiv C-H \end{array}$$

$$H_3C-\overset{Cl}{\underset{Cl}{C}}-H + Na\overset{\oplus}{N}\overset{\ominus}{H_2} \longrightarrow H_2C=CH-Cl + NH_3 + NaCl.$$

$$\downarrow Na\overset{\oplus}{N}\overset{\ominus}{H_2} \quad -NH_3 + NaCl$$

$$\begin{array}{l} 2NH_3 + \\ Na\overset{\oplus}{C}\equiv\overset{\ominus}{C}Na \end{array} \xleftarrow{\quad} 2Na\overset{\oplus}{N}\overset{\ominus}{H_2} + H-C\equiv C-H \xrightarrow{\cancel{KOH}}$$

(1)
$$CH_3-\overset{O}{\overset{||}{C}}-H \xrightarrow{PCl_5} Ⓐ \xrightarrow{KOH (xs)} Ⓑ$$

$$CH_3-\overset{Cl}{\underset{Cl}{C}}-H \qquad\qquad H-C\equiv C-H$$

(2)
$$H_2C=CH_2 \xrightarrow{Cl_2} Ⓐ \xrightarrow[Na\bar{N}H_2\,(2eq)]{KOH\,(2eq)}$$

$$Cl-CH_2-CH_2-Cl \qquad\qquad HC\equiv CH$$

Q.3 Convert

(a) $CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow{(A)} H-C\equiv C-H$

b) $H_2C=CH_2 \xrightarrow{(B)} H-C\equiv CH$

(4)

$CH_3-\overset{Cl}{\underset{Cl}{\overset{|}{\underset{|}{C}}}}-H \xrightarrow[xs]{NaNH_2} \textcircled{A} \xrightarrow[xs]{\overset{\oplus}{CH_3}-\overset{\ominus}{I}} \textcircled{B} \quad CH_3-C\equiv C-CH_3 + 2NaI$

$Na\overset{\oplus}{\underset{}{}}\overset{\ominus}{C}\equiv \overset{\ominus}{C}\overset{\oplus}{Na}$

(5) Convert

$H-C\equiv C-H \xrightarrow{NaNH_2} CH_3-C\equiv C + CH_3$

* **Dehydration Rxⁿ.**

$-\overset{H}{\underset{|}{\overset{|}{C}}}-\overset{OH}{\underset{|}{\overset{|}{C}}}- \xrightarrow[\Delta \ -H_2O]{\substack{Concu\ H_2SO_4\ or\ H_3PO_4\ or\ KHSO_4\ (E1)\\ Al_2O_3\ or\ P_2O_5\ or\ SOCl_2\ (E2)\\ ThO_2\ (E_{1cB})}} -\overset{|}{C}=\overset{|}{C}-q$

Q.

(circle structure with OH) $\xrightarrow{}$

- concu H_2SO_4/Δ
- concu H_3PO_4/Δ
- concu $KHSO_4/\Delta$
- AlO_3/Δ
- P_2O_5/Δ
- ThO_2/Δ

Rearrangemen Not occur

✳ Dehalogenation Rxⁿ:

$$-\underset{\underset{X}{|}}{\overset{\overset{X}{|}}{C}}-\underset{|}{\overset{|}{C}}- \xrightarrow[\substack{NaI/Acetone \text{ or} \\ Zn/ether \text{ or} \\ mg/ether \text{ or} \\ 2Ag \text{ ether}}]{} -\overset{|}{C}=\overset{|}{C}-\ + \ \substack{NaX+IX \\ or \\ ZnX_2 \text{ or} \\ MgX_2 \text{ or} \\ 2AgX}$$

Mechⁿ:

$$I^{\ominus} \quad -\underset{\underset{X}{|}}{\overset{\overset{X}{|}}{C}}-\underset{2}{\overset{}{C}}- \longleftrightarrow -\overset{|}{C}=\overset{|}{C}- + NaI + IX$$

(11) with Zn/mg/2Ag $(Zn \longrightarrow Zn^{++} + 2e^{\ominus})$

$$2e^{\ominus} + -\underset{\underset{X}{|}}{\overset{\overset{X}{|}}{C}}-\overset{|}{C}- \longrightarrow \ \overset{}{>}C=C\overset{}{<} \ + 2X^{\ominus}$$

Q.1

$$\underset{\underset{\underset{Cl}{|}}{Cl}}{H_2C}-CH_2 \xrightarrow{Zn \text{ or } mg \text{ or } NaI} H_2C=CH_2 + NaCl + Cl$$

(2)

$+ 2nCl + Zn$

(3)

(4)

$1,1 \rightarrow$ __Dimer.__

(5)

Cl—⋀⋁⋀—Cl $\longrightarrow$ (pentagon)

(6)

$+ PCl + NaCl.$

(7)

(8) $Cl-CH=CH-Cl \xrightarrow{Zn/ether/\Delta}$ en $CH\equiv CH + \overset{\ominus}{Zn}.$

(9) $CH_3-CH \underset{Cl}{\overset{Cl}{\diagdown}} \xrightarrow{Ag/\Delta}$ $CH_3-\overset{..}{C}H$ $\quad CH_3-CH$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad CH_3-\overset{..}{C}H \rightarrow \overset{\parallel}{CH_3-CH}$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow$

(10) $CH_3-C \underset{Cl}{\overset{Cl}{\underset{\diagdown}{\diagdown Cl}}} \xrightarrow{Ag/\Delta}$ $CH_3-CH=CH-CH_3$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad CH_3-C\equiv C-CH_3.$

$\qquad \llcorner\!\rightarrow$

$\qquad\qquad CH_3-\overset{.}{\underset{.}{C}} \quad \overset{.}{\underset{.}{C}}-CH_3$
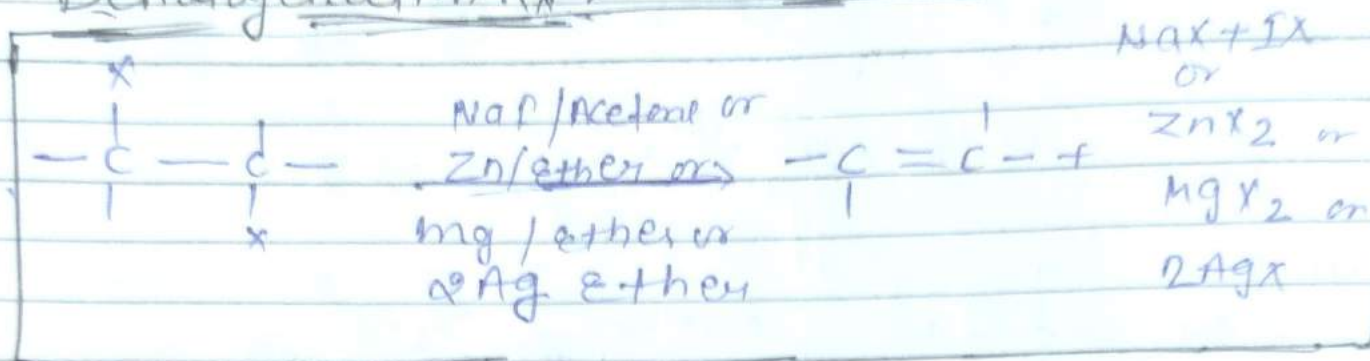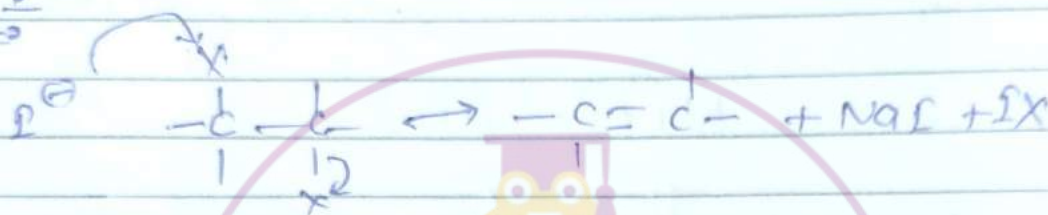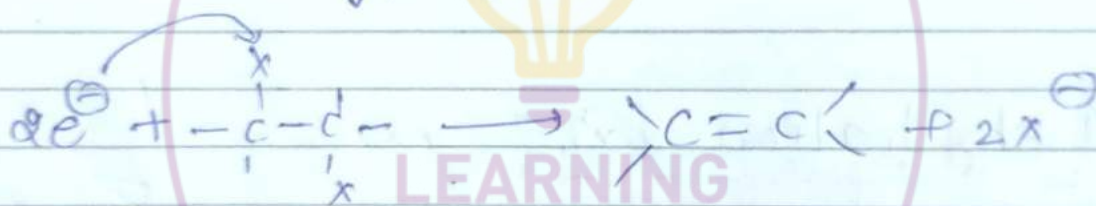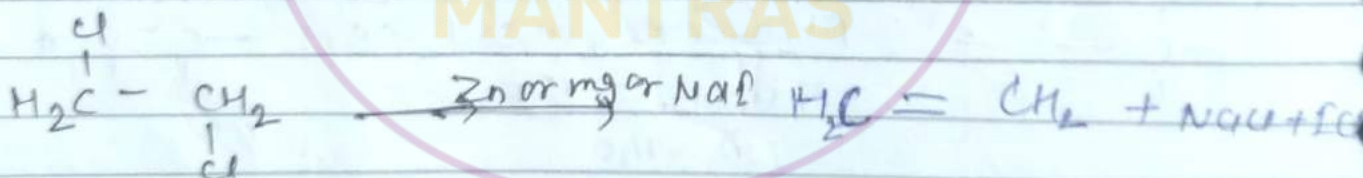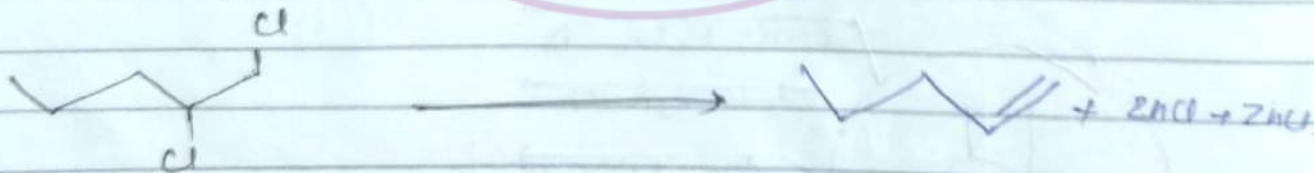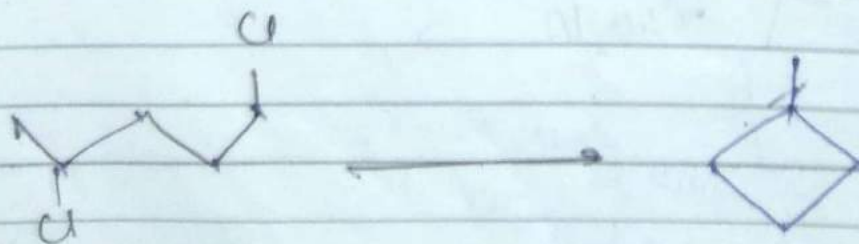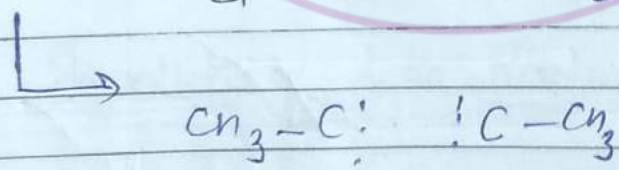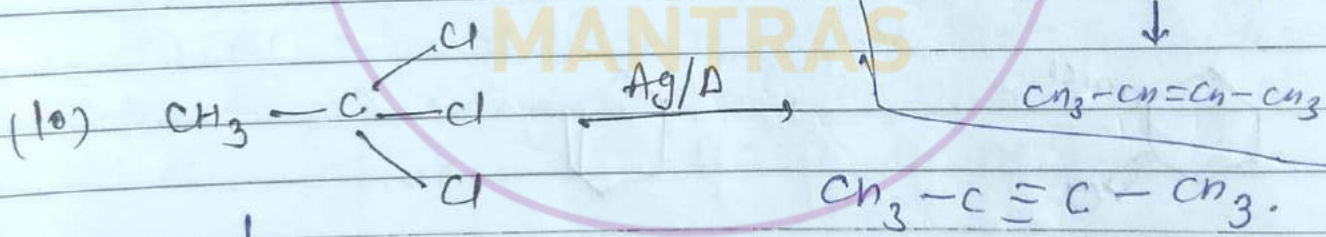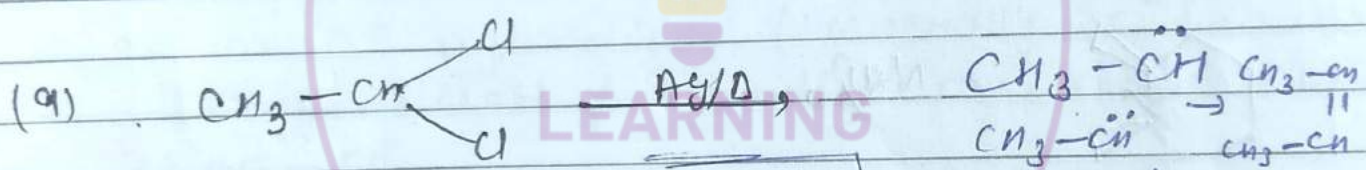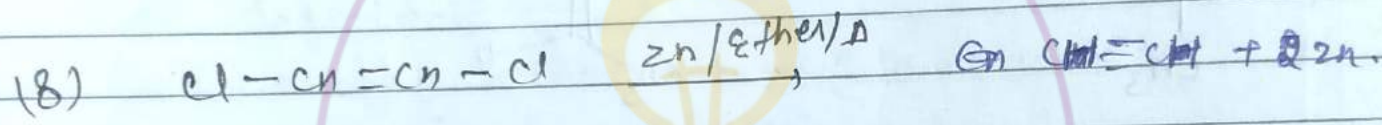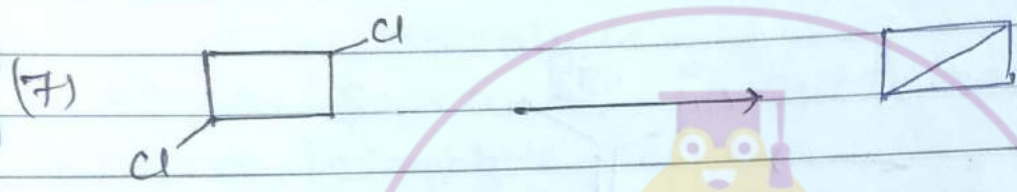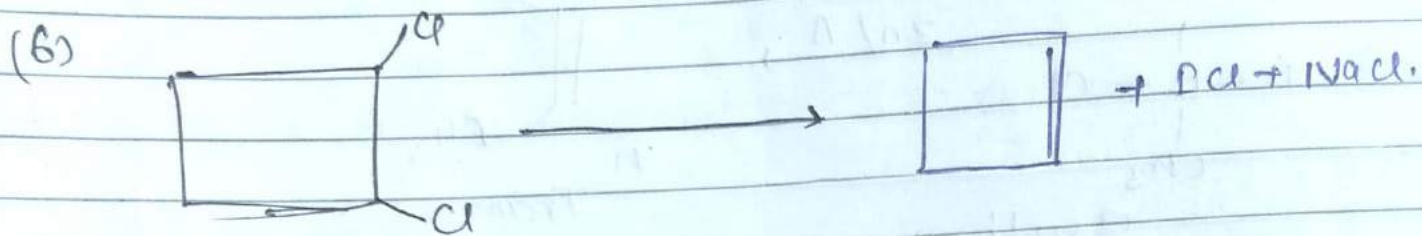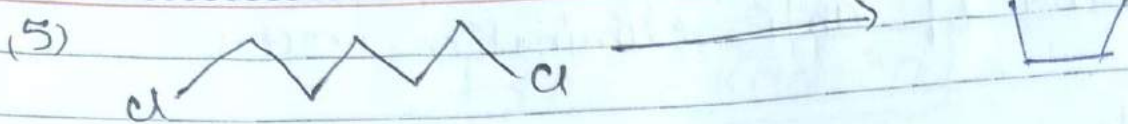
* $1,1-DH \rightarrow$ Dimer (Alkene)
* $1,11-TH \rightarrow$ " (Alkyne)
$1,2- \rightarrow$ Alkene/Alkene
$\left.\begin{array}{l}1,3- \\ 14- \\ 15- \\ 16-\end{array}\right\}$ DH $\rightarrow$ cyclic compound.
$\left.\begin{array}{l}17 \\ 18\end{array}\right\} \rightarrow$ Polymer

* It is a kind of anti elimination process

Q.

$H-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{\overset{|}{C}}-Cl}$ $\xrightarrow{Zn/\Delta}$

Erythro

Trans

CH₃ — Cl
Cl — H
CH₃

$\xrightarrow{}$

$\xrightarrow{Naf}$

$\xrightarrow{}$

* Free - Radical *

$\overset{\bullet}{C}H_3$ $\underset{SP^2}{SP^2}$ $\underset{SP^2}{CH_3 - \overset{\bullet}{C}H_2}$ $\underset{SP^2}{H_2C = \overset{\bullet}{C}H}$ $\overset{\bullet}{Na}$ $\overset{\bullet}{K}$, etc
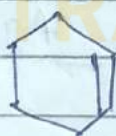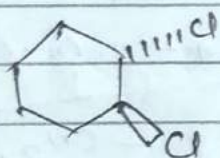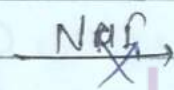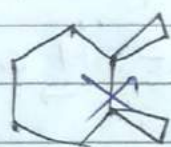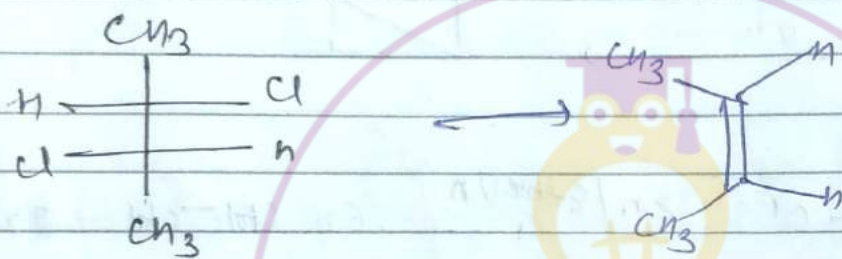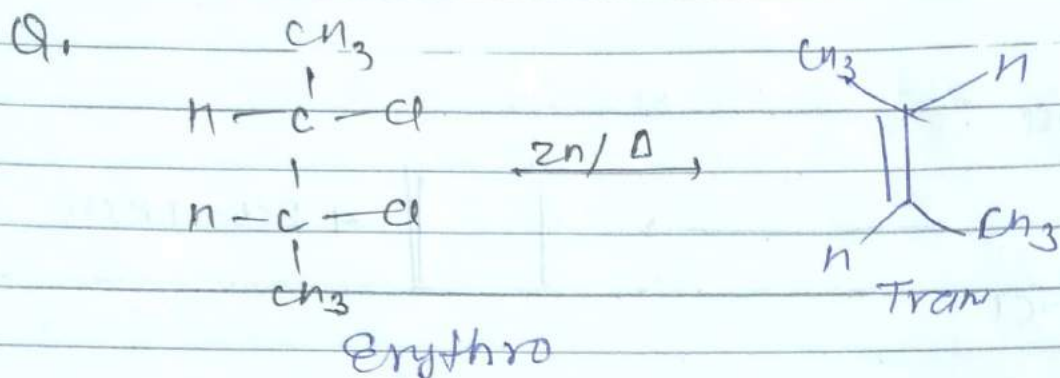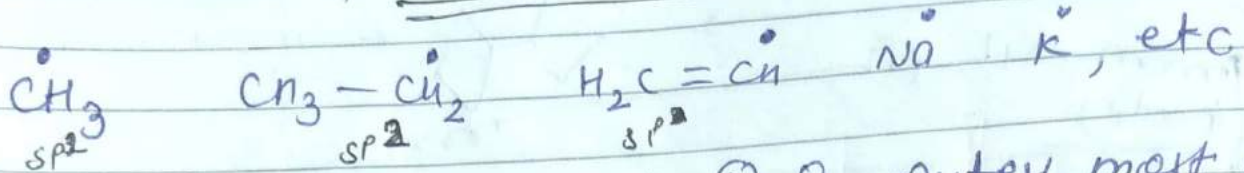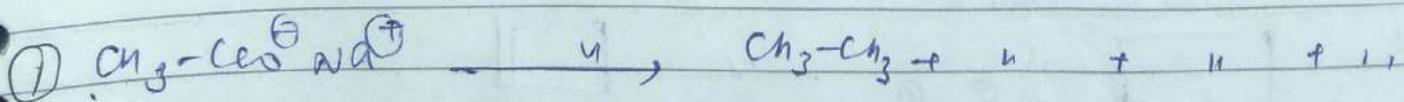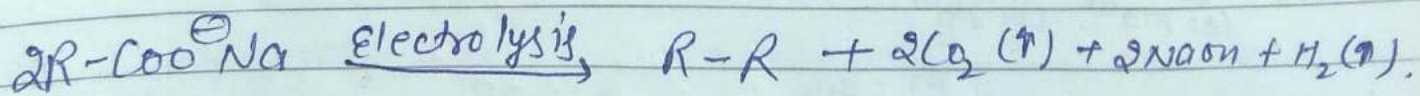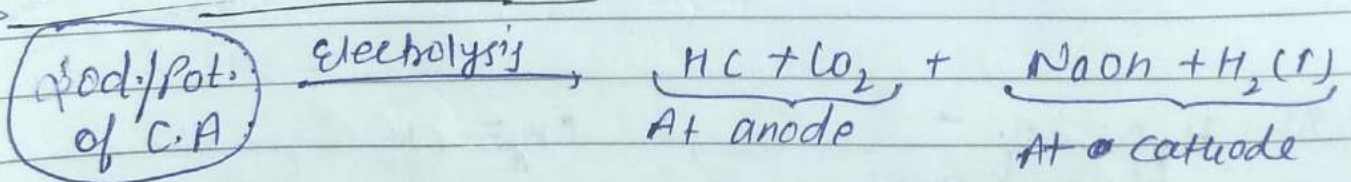
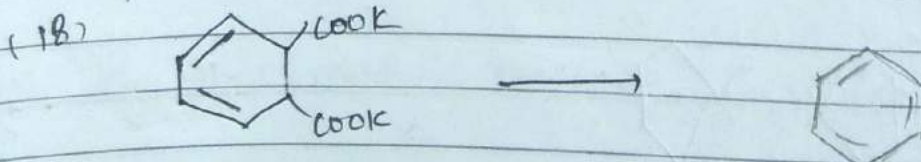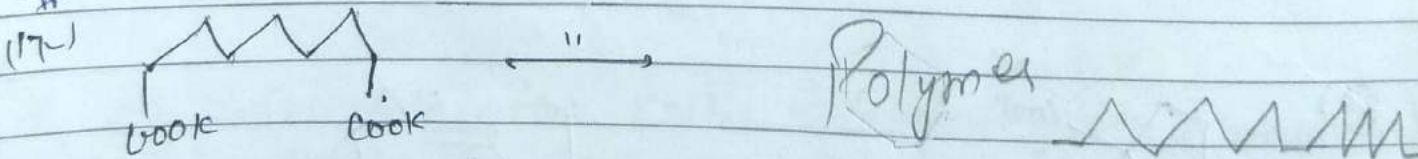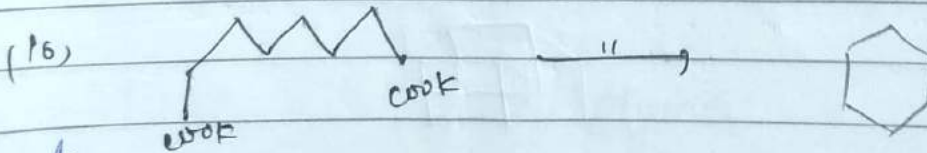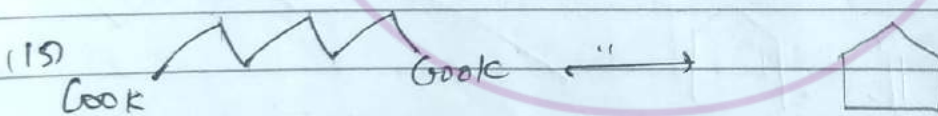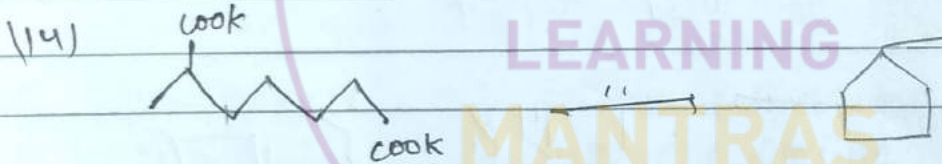* Species with unpaired $e^\ominus$ in outer most shell.
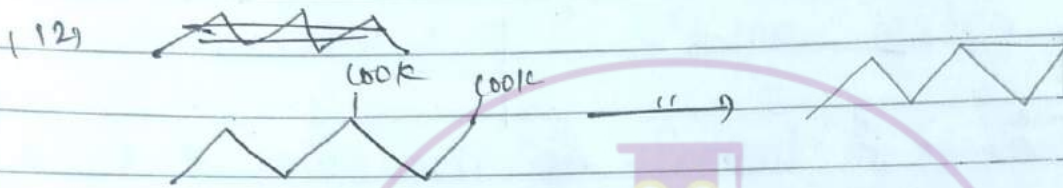
⇒ They are -
* form by Homolysis
* have Seven $e^\ominus$ in outer most shell
* have incomplete octet
* $e^\ominus$ deficient.
* Behaves as electrophile (but not lewis acid).
* Paramagnetic in nature
* SP^2 or SP Hybridised (Generally SP^2 because SP^2 hybridised free radical are more stable then SP
* T.P. (Trigonal Planar (when SP^2 hybridised)).
* have one unhybridised P- orbital with one unpair $e^\ominus$ lie ⊥ to sigma bond.

* Rxⁿs involving free Radicals :-

(1) Kolbe's Electrolysis :-

$$\underset{of\ C.A}{\boxed{Sod./Pot.}} \xrightarrow{Electrolysis} \underset{At\ anode}{HC + CO_2} + \underset{At\ cathode}{NaOH + H_2 (r)}$$

$$2R-COO^\ominus Na \xrightarrow{Electrolysis} R-R + 2CO_2 (\uparrow) + 2NaOH + H_2 (\uparrow).$$

$$① CH_3 - C\overset{\ominus}{O}O^\ominus Na^\oplus \xrightarrow{\quad \quad} CH_3 - CH_3 + " + " + "$$

(1) $Ph - COO^{\ominus} Na^{\oplus} \xrightarrow{\quad ''\quad} Ph - Ph$ on $\overline{(CH_2)_n}^{\ominus}$

$2\ CH_3 - CH_2 - COO^{\ominus} Na^{\oplus} \xrightarrow{\quad''\quad} CH_3 - CH_2 - CH_2 - CH_3 + '' + '' + ',$

(3) $\diamondsuit - COO^{\ominus} Na^{\oplus} \xrightarrow{\quad''\quad} \diamondsuit - \diamondsuit + '' + '' + '|$
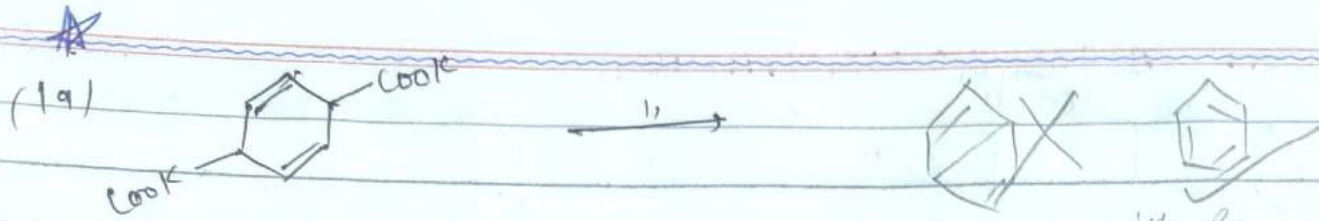
$\dashv\vdash (-)$
+ (Anode)   Cathode $\ominus$

$2\ RCOO Na^{\oplus}$
$\Updownarrow$

$2\overset{\ominus}{O} - \overset{O}{\overset{\|}{C}} - R \longleftarrow 2R - COO^{\ominus} + 2Na^{\oplus} \xrightarrow{\quad''\quad} 2Na^{\oplus}$

$\downarrow\ 2H_2O$

$2\ e^{\ominus} + 2\overset{O}{\overset{\cdot\|}{O} - \overset{\cdot}{C}} \{ R \qquad\qquad 2\ NaOH + 2H^{\oplus}$

$2\ CO_2(\uparrow) + 2R^{\cdot}$ $\downarrow$
                            $2H^{\cdot}$

$R^{\cdot} + R^{\cdot} \longrightarrow R - R$ $\downarrow$
                            $H_2(\uparrow)$

(5) $\searrow\nearrow - COO Na^{\oplus} \xrightarrow{\quad''\quad} \searrow\nearrow - \searrow\nearrow +$

(6) $\searrow\nearrow - COO Na^{\oplus} \xrightarrow{\quad''\quad} \searrow\!\!\!\times\!\!\!\nearrow + \searrow\nearrow - COO \nwarrow$

     $\underset{COO Na^{\oplus}}{} \underset{COO Na^{\oplus}}{}$

(7) $H_2\overset{|}{C} - \overset{|}{C}H_2 \xrightarrow{\quad''\quad} H_2C = CH_2$ $CH_3 - \overset{|}{C}^{\cdot} \quad \overset{O}{\overset{\|}{O - C}} - COO \overset{CH_3}{\underset{CH_3}{\overset{|}{C}}}$

(8) $H_2C = CH \xrightarrow{\quad''\quad} CH \equiv CH$
    $\underset{COO Na^{\oplus}}{} \underset{COO Na^{\oplus}}{}$

(9) $\square \underset{COO Na^{\oplus}}{\overset{COO Na^{\oplus}}{}} \xrightarrow{\quad''\quad} \square|$

(10)

COONa$^\ominus$

NaOO

(11)

COOK

COOK

(12)

COOK

COOK

(13)

COOK   COOK

(14)

COOK

COOK

(15)

COOK

COOK

(16)

COOK

COOK

(17)

COOK   COOK

Polymer

(18)

COOK

COOK

8 member → 3 π Bond.

(19) benzene ring with two COOK groups → cross-out structure + pentagon, **with Resonance.**

(20) chain with COOK groups → crossed-out box + zigzag structures, Res-

(21) square structure with COOK groups → bowtie structure

(22) four-membered ring with two COOK → crossed boxes, **Anti Aromatic**, box + box

(23) six-membered ring with COOK groups → resonance structures

(24) cube structure with COOK, COOK → cube structure

(25) five-membered ring with COOK, COOK → fused ring structures

* Key points:- When aquas Sodium and Pot. Salt of acid is electrolysed then we get alkane (Hydrocarbon) and CO_2 gas anode and NaOH + H_2(gas) at Cathode

* As time increases Ph of solution increases

* When Alkyl gp is $3°$ then ester form (Exam. 6)

* When two salt gp Present in same molecules then Rx^n is known as intramolecular Colbe's electrolysis (Ex- 7-24)

* In Intramolecular Colbe's electrolysis we get either alkene, Alkyne or Cyclic Compound.

* 1,1 -Disalt $\longrightarrow$ Dimer (Alkene)
  1,2 -Disalt $\longrightarrow$ Alkene / Alkyne.
  1,3 -
  1,4 - $\bigg\}$ $\longrightarrow$ Cyclic Compound.
  1,5 -
  1,6 -

  1,7 $\bigg\}$ " $\longrightarrow$ Polymer.
  1,n

* By Intermolecular Kolbe's electrolysis symmetrical alkene with even Carbon Can be prepare.

* By this method methane Can not form.

Q: Which of the following alkane can be prepared by Colbe's electrolysis effectively

(i) methane CH_4 ✗

(ii) $C-C$ ✗ ✓   mid cut: Pos (sym fami

(iii) $C-C-C$ · ✗

(iv) $C-C-C-C$ ✓

(v) $C-C-C-C-C$ ✗

(vi) $C-C-C-C-C-C-C$ ✗

(7)
```
        C
        |
   C-C-+C-C-C    ✗
```

(8) ⬡—◇ ✓   (9) ▷◁—◇ ✗

(10) $C-C-C-|-C-C-C$ ✓   Cross EEL

(11)
$CH_3-COO^\ominus K^\oplus$ $CH_3-CH_2-COO^\ominus K^\oplus$ → $CH_3-CH_2-CH_3$
$\downarrow$ $+$
CH_3 CH_3-CH_2 CH_3-CH_3

$CH_3 + CH_2 CH_3$	
$CH_3 + CH_3$	$Et° + Et°$

                            $+$
                            $C-C-C-C$
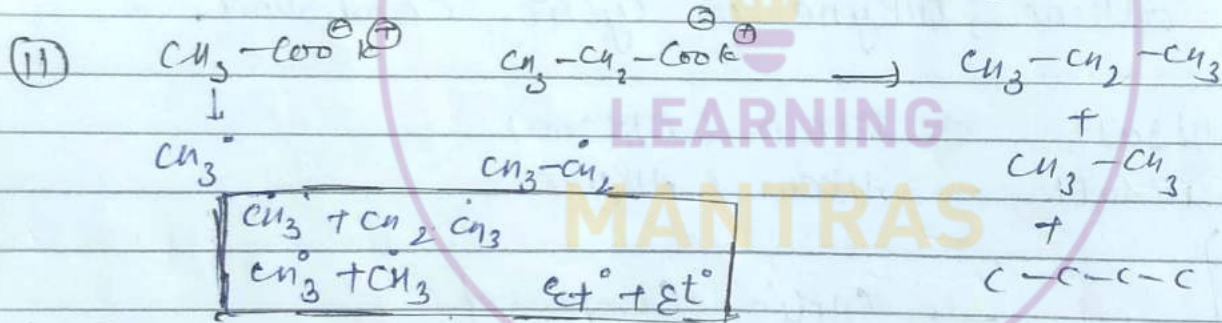
※ Cross KE:
        The KE in which both salt are different is known as Cross KE.

✱✱ (12) $H-COO^\ominus K^\oplus$ → $H_2(\uparrow) + CO_2(\uparrow)$ & $KOH + H_2O$
         $\downarrow_{,\oplus}$ ⎣A⎦   C.
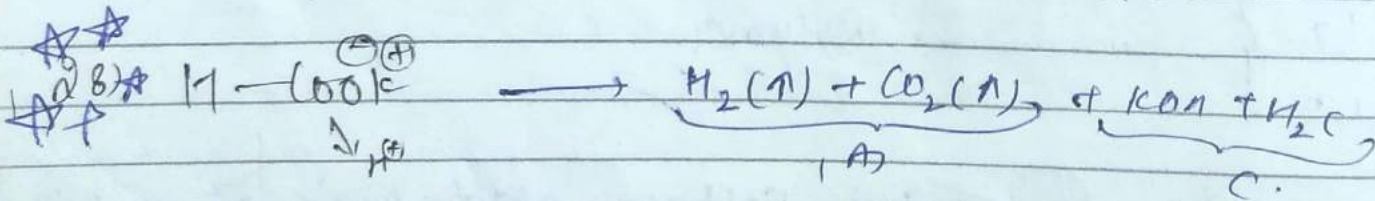
※ Salt of formic Acid (sod. or pot. formate) give H(gas) on both electrode.

(29)

$$\begin{bmatrix} COOH \\ COOH \end{bmatrix} \xrightarrow{\text{NaOH}} \text{(A)} \xrightarrow{\text{Electrolysis}} \text{(B)} \quad CH_2 = CH_2$$

Succinic acid

$$\begin{bmatrix} COO^\ominus Na \\ COO^\ominus Na \end{bmatrix} ;$$

(30)

$$\begin{bmatrix} COOH \\ COOH \end{bmatrix} \xrightarrow{} \text{(A)} \xrightarrow{\text{''}} \text{(B)} \quad H-C \equiv C-H$$

meleic acid

(31)

$$\begin{matrix} COOH \\ \parallel \\ HOOC \end{matrix} \xrightarrow{} \text{(A)} \xrightarrow{\text{''}} \text{(B)} \quad H-C \equiv C-H.$$

fumeric acid

★★★★★

* **Wurtz Rxn :**

$$R-X \xrightarrow[\text{Dry ether}]{Na} R-R + NaX$$

$$2R-X \xrightarrow{2Na} R-R + 2NaX.$$
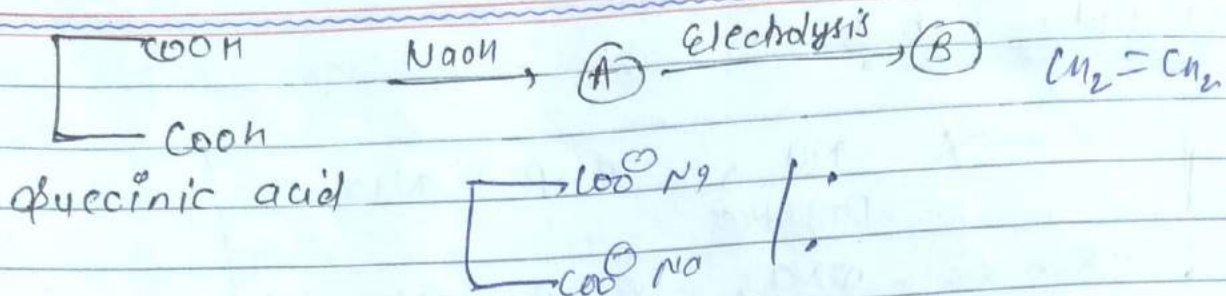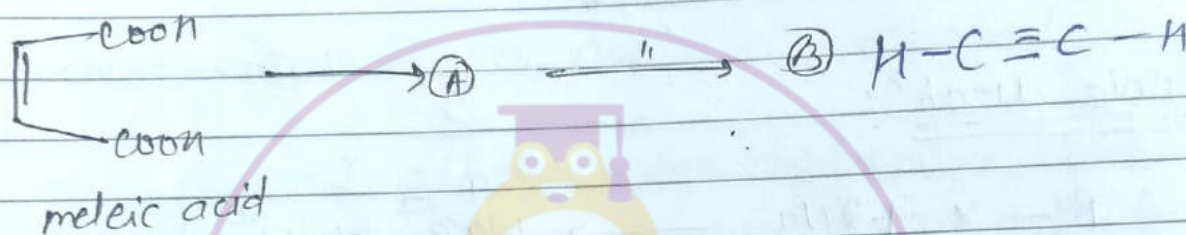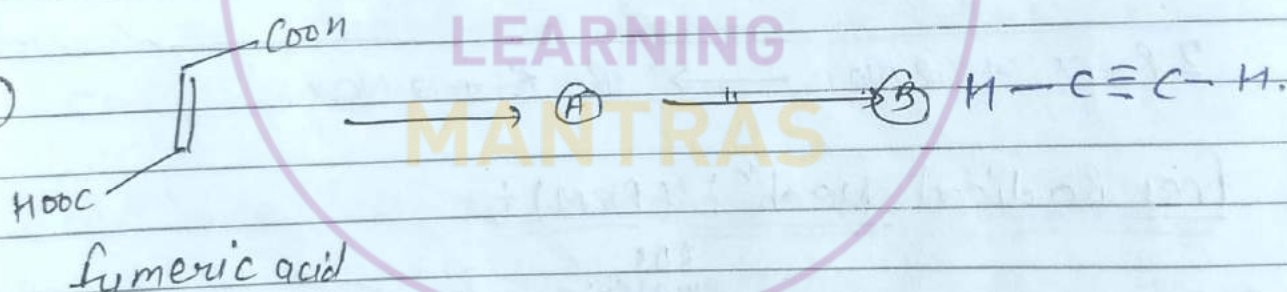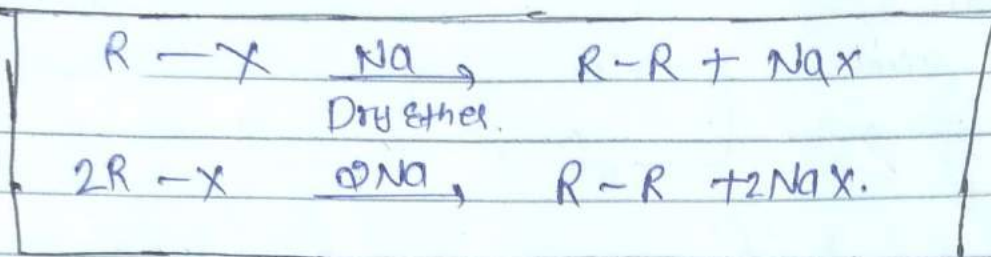
Mech : ① Ionic Mechⁿ

② free Radical Mechⁿ.

⓵ $Rx - 2Nax$

(1) **Ionic Mechⁿ :**

$$R-X + 2Na \longrightarrow \overset{\oplus}{N}a\overset{\ominus}{R} + \overset{\oplus}{N}a\overset{\ominus}{x}$$

Nucleophile
(Carbanion RI)

$$\overset{\oplus}{N}a\overset{\ominus}{R} + R\overset{\delta+}{-}\overset{\delta-}{X} \longrightarrow R-R + NaX$$

$$2R-X + 2Na \longrightarrow R-R + 2NaX.$$

*② **free Radical Mechⁿ : (FRM) :**

$$2R-X + 2NaX \xrightarrow[\text{slowstep}]{RDS} 2R^{\bullet} + 2NaX$$

$$R^{\bullet} + R^{\bullet} \longrightarrow R-R$$
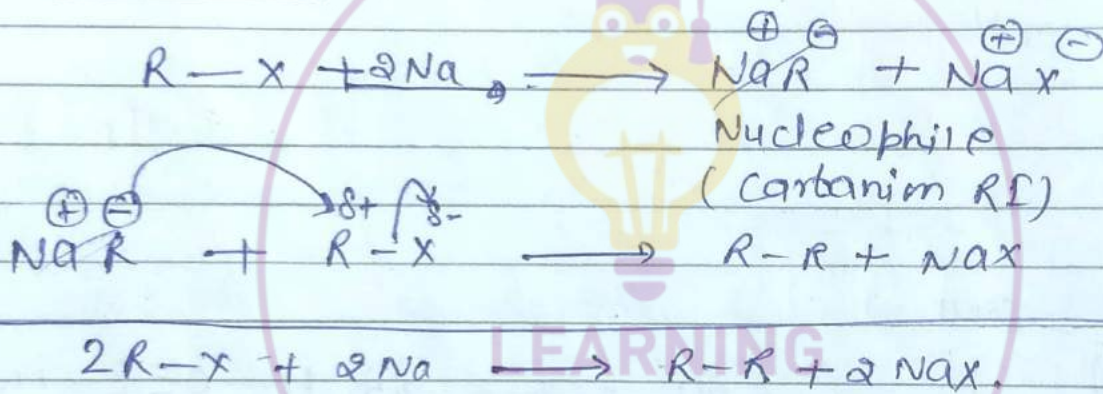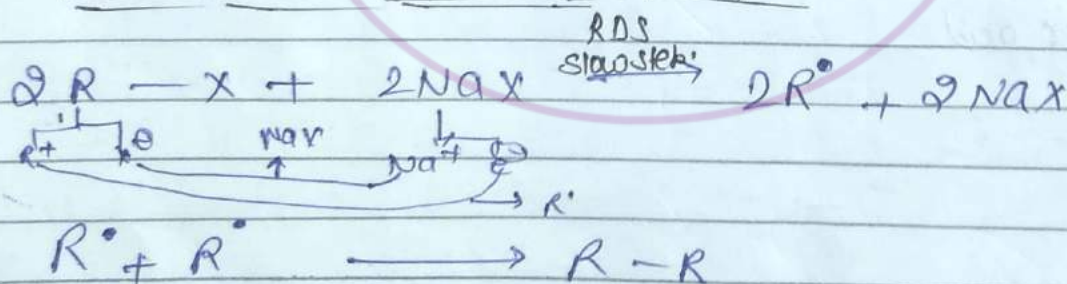
* **Key points :**
    This Rxⁿ occur by ionic and free Radical both Mechⁿ.

* By this Rxⁿ alkyl halide converted into Hydrocarbon
* when two halogen present in same molecules

then R_i^u is known as ImWR (Interamolecular wourtz Rx^u)

* In ImWR Product is either alkene or alkyne or cyclic compounds. By ~~Inter~~ Inter molecular wurtz Rx^n Alkane with even carbon and asymetrical structure can be prepared.
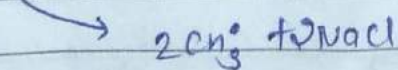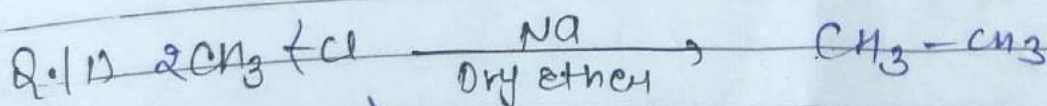
* By this method CH_4 can not prepared

* By this method alkane with odd no. of Carbon atom like Propane, Pentane, Hectane can not prepared effectively.

* When two different alkyl halide React then more then One Product form. The Rx^h is known as CWR (cross wurtz Rx^h).

* CWR are less Important for us.

* If alkyl halide is $3°$ alkyl halide then in the place of combination Rx^n disprobotation Rx^h occur and we get alkane + alkene.
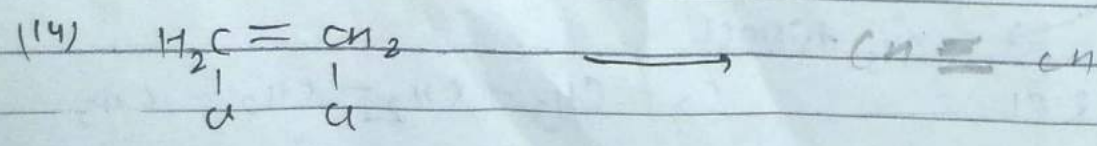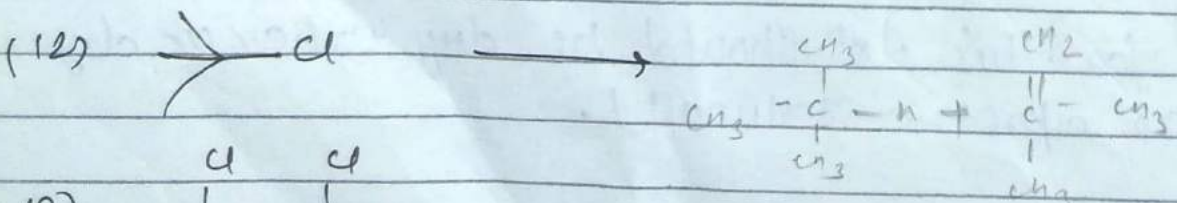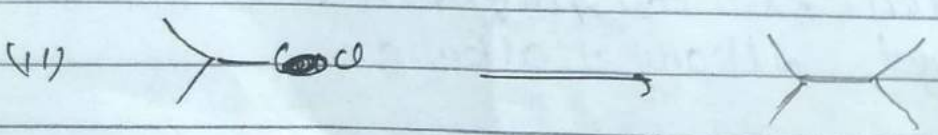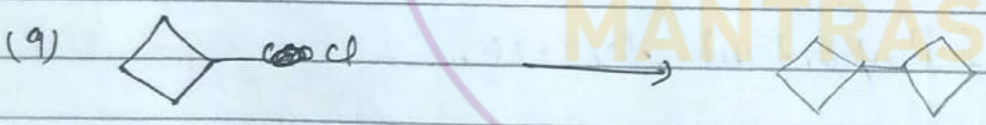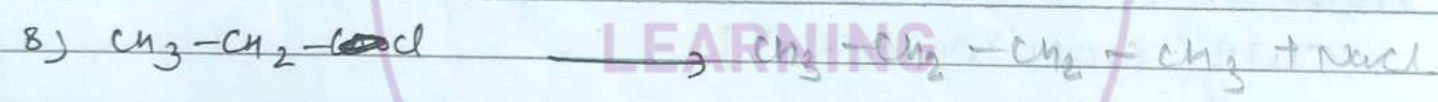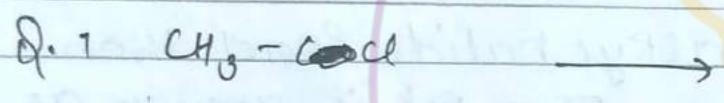
* Solvent for this Rx^h should be dry ether or dry PAS (polar aprotic soluant).
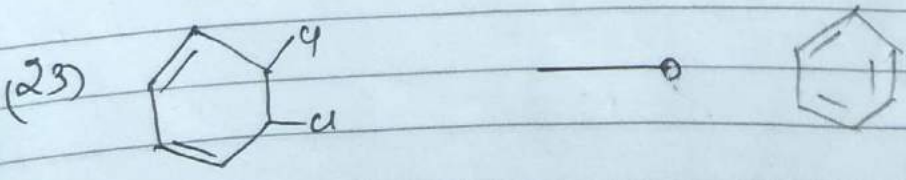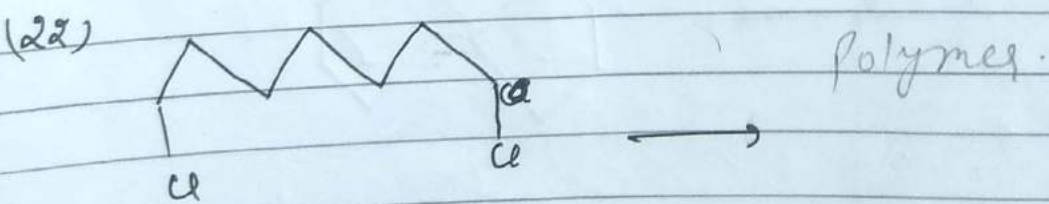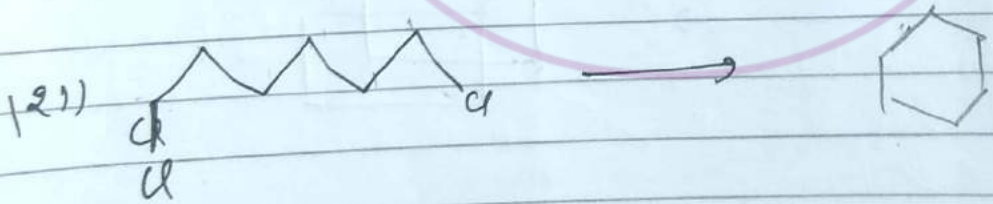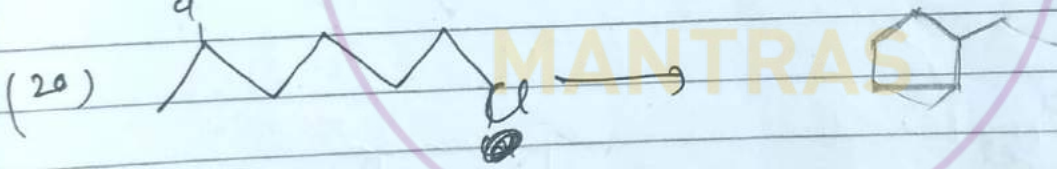
Q.1) 1) $2CH_3 \dot{+} Cl \xrightarrow[\text{Dry ether}]{Na} CH_3 - CH_3$

$\longrightarrow 2CH_3^\circ \dot{+} NaCl$

(2) $CH_3 - CH_2 \dot{+} Cl \longrightarrow CH_3 - CH_2 - CH_2 - CH_3$

(3) [square]—Cl $\longrightarrow$ [square]—[square]

(4) $\searrow$—Cl $\longrightarrow$ (product)

(5) $\searrow$—Cl $\longrightarrow$ (product) $\quad$ $H_3C-\overset{CH_3}{\underset{CH_3}{C}}-H \;+\; \overset{CH_2}{\underset{CH_3}{C}}-CH_3$

$\longrightarrow$ $H_3C-\overset{CH_3}{\underset{CH_3}{C}}\cdot \quad H\overset{CH_2}{\underset{CH_3}{\underset{|}{C}}} \cdot\overset{|}{C}-CH_3$

(8) $\overset{CH_2-CH_2}{\underset{\;Cl\quad\;\;Cl}{|\quad\quad|}}$ $\longrightarrow$ $CH_2=CH_2$

* 8° alkyl $Q \cdot 7, 8 - - - - - 26.$

Q. 7 CH_3-COCl $\longrightarrow$

8) CH_3-CH_2-COCl $\longrightarrow$ $CH_3-CH_2-CH_2-CH_3 + NaCl$

(9) [square]—COCl $\longrightarrow$ [square]—[square]

(10) $Ph-COCl$ $\longrightarrow$ $Ph - Ph$

(11) $\searrow$—COCl $\longrightarrow$ $\searrow\!\!\diagup$

(12) $\searrow$—Cl $\longrightarrow$ $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-H + \overset{CH_2}{\underset{CH_3}{C}}-CH_3$

(13) $\overset{Cl\quad\;Cl}{\underset{}{H_2C-CH_2}}$ $\longrightarrow$ $CH_2=CH_2.$

(14) $\overset{H_2C=CH_2}{\underset{Cl\quad\;\;Cl}{|\quad\quad|}}$ $\longrightarrow$ $CH\equiv CH$

15)

16)

17)

18)

19)

20)

21)

22) Polymer.

23)

(24) ⟶

(25) ⟶

(26) ⟶

(27) ⟶

(28) ⟶

(29) ⟶

(30) ⟶

✳ **Note!**

Q.27 $CH_3 - F$ $\xrightarrow{Na/Dry\ ether}$ $CH_3 - CH_3 - NaF$

     $CH_3 - Cl$ $\longrightarrow$ "   " $+ \ NaCl$

     $CH_3 - Br$ $\longrightarrow$ " $+ \ NaBr$

     $CH_3 - I$ $\longrightarrow$ " $+ \ NaI$
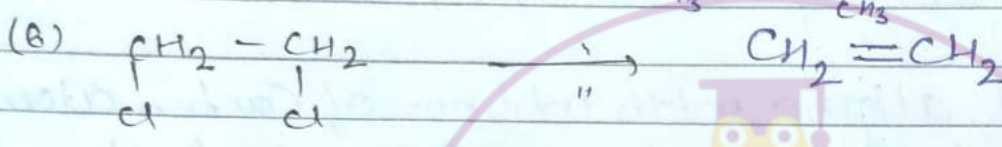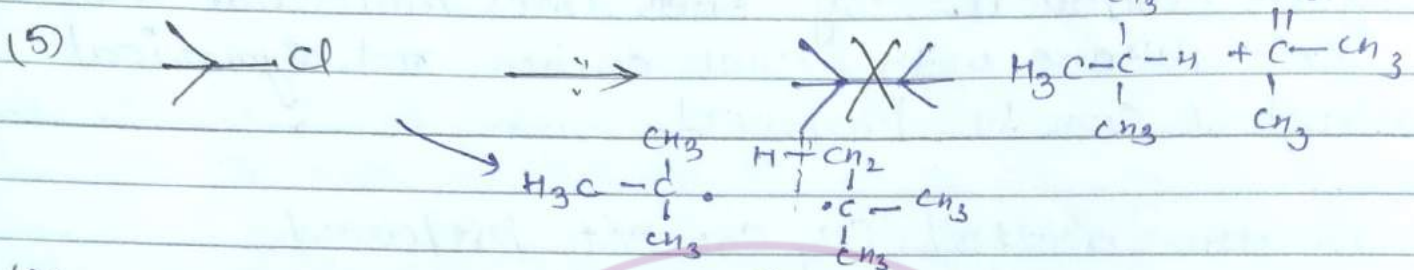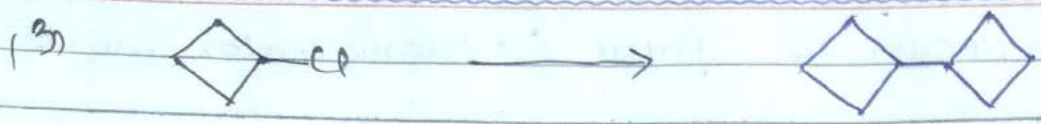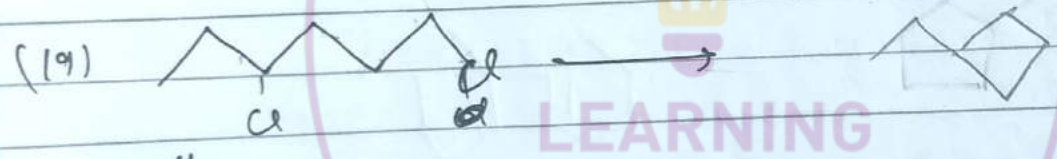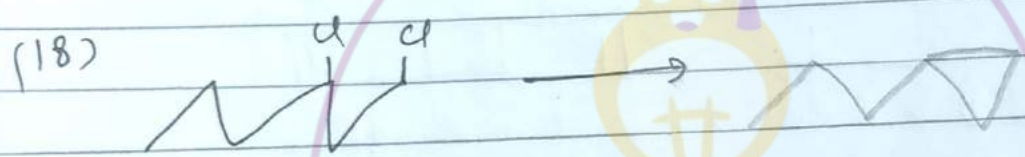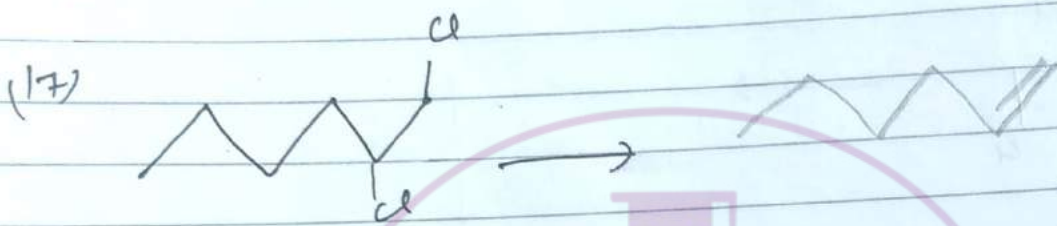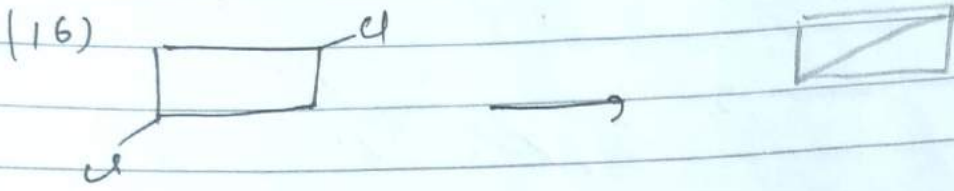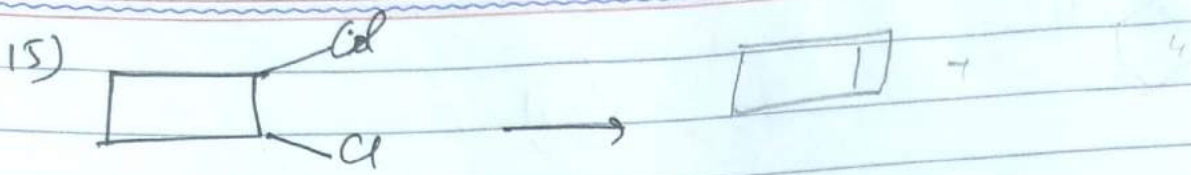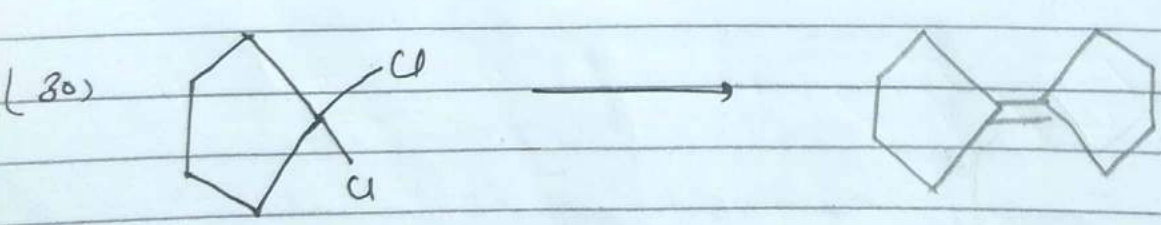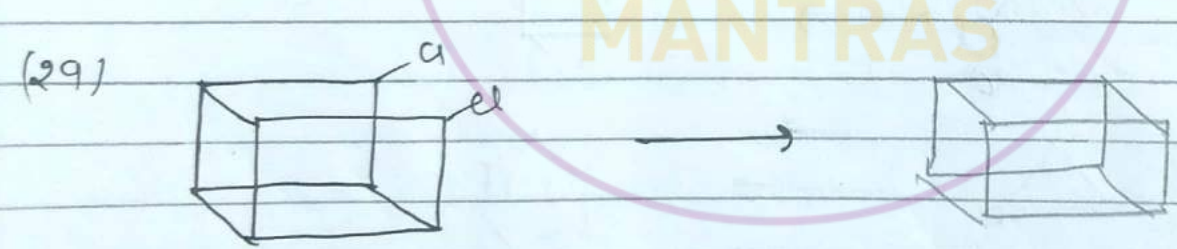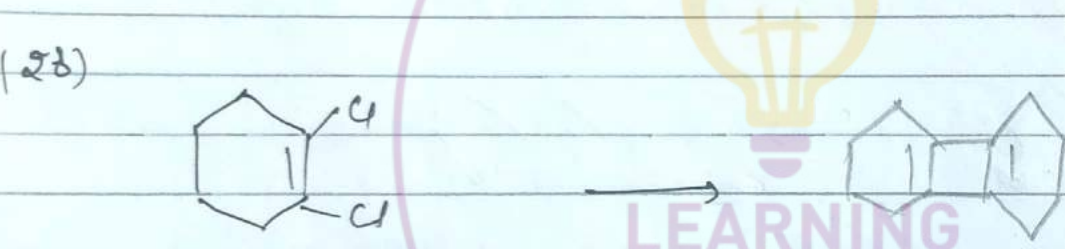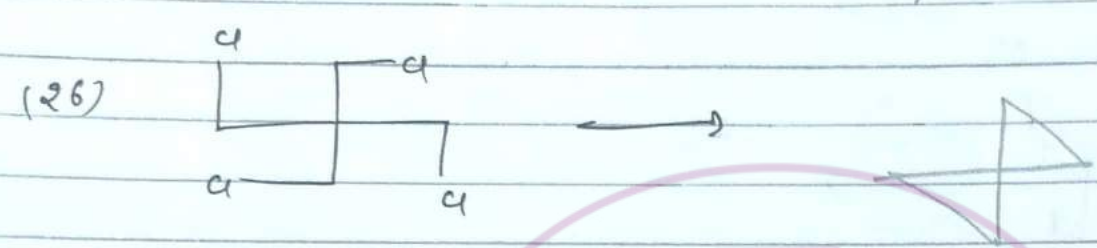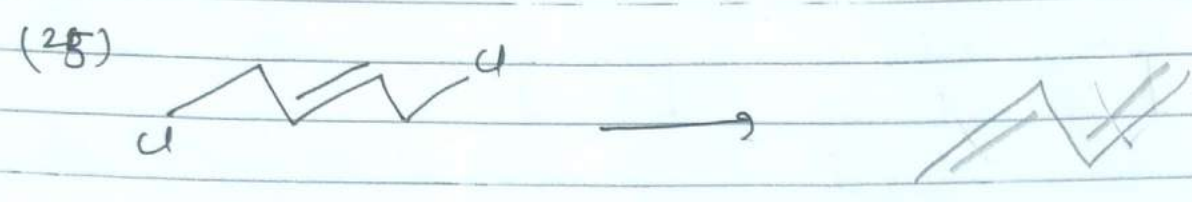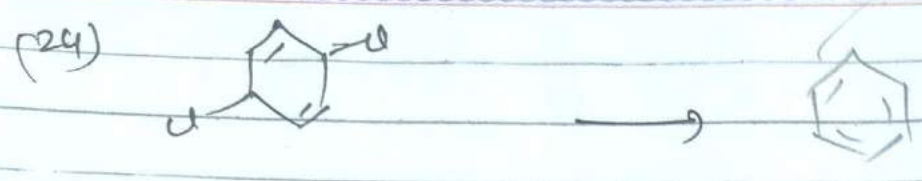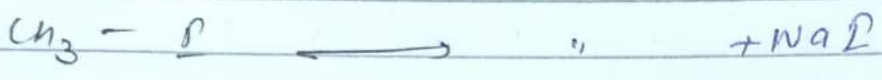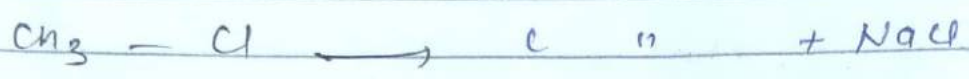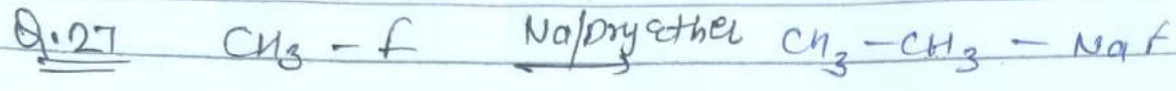
When there are different halogen and same `R.gp`
then Reactivity order

$$R - I > R - Br > R - Cl > R - af$$

Q.28

     $CH_3 - Cl$ $\xrightarrow[Dry\ ether]{Cu\ or\ Ag}$ $CH_3 - CH_3 + CuCl / AgCl$

     (2e⁻)   (2:1)   (Ullmann Rxⁿ).

(20) $CH_3 - Cl$ $\xrightarrow[zn\ /\ Dry\ ether]{mg\ /Dr\ ether\ or}$ $CH_3 - CH_3 + mgCl_2 / znCl_2$

         2:1   (frankland Reaction)

(30) ⬡—Cl $\xrightarrow{Na\ (Dry\ ether}$ ⬡—⬡   (fitting Rxⁿ)
       $→ Ph°$

(31) $CH_3 - Cl + $ ⬡—Cl $\xrightarrow{Na/Dry\ ether}$
       $CH_3°$ $Ph°$
               $Ph - CH_3 + CH_3 - CH_3 +$
               $Ph - Ph$ (wurtz fitting Rxn).
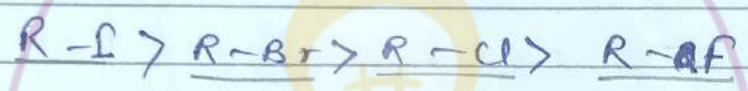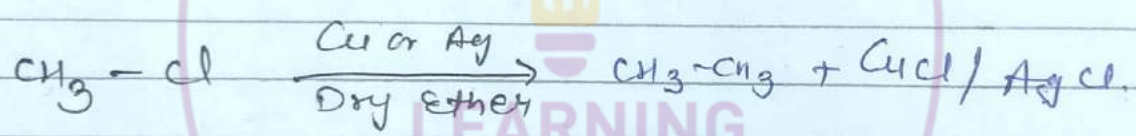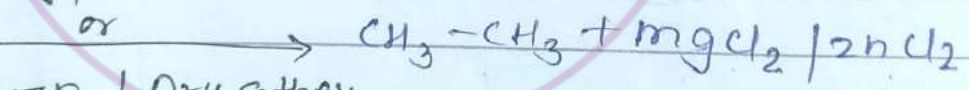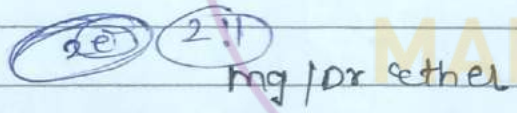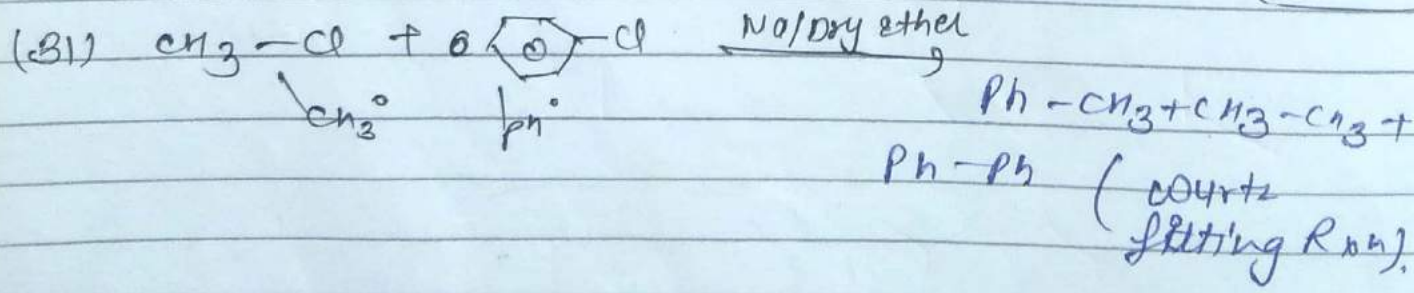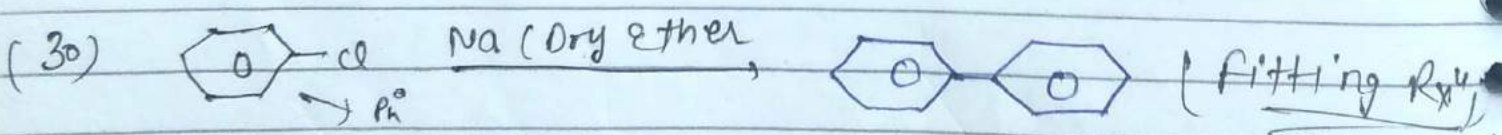
* सावधानी ! In Frankland Rxⁿ Ratio of R−X and zinc or mg should be 2:1 if they are taking in 1:1 then we get grignard Reagent (organometallic compound in the place of alkane).

$$R - X \xrightarrow[1:1]{mg \ or \ zn/ether} RmgX \ / RznX$$
(Grignard Reagent)
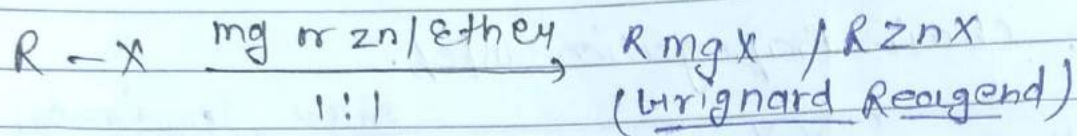
* Addition of HBr with alkenes and alkynes in the presence of Peroxide :-

OR

~~Anti - markonic addition of~~
Anti - markonikoff's Addition of HBr !

OR

kharaush effect / per-oxide effect :-

Markonic Rule

$$H_3C - CH = CH_2 \xrightarrow{HBr} CH_3 - \overset{Br}{CH} - CH_3$$

$$\downarrow H^+$$

$$CH_3 - \overset{\oplus}{CH} - CH_3 \quad \overset{\ominus}{Br} \nearrow$$

R.I (Carbocation)

* $CH_3 - CH = CH_2 \xrightarrow{HBr/ROOR} CH_3 - CH_2 - \overset{Br}{CH_2}$ (anti markonic)
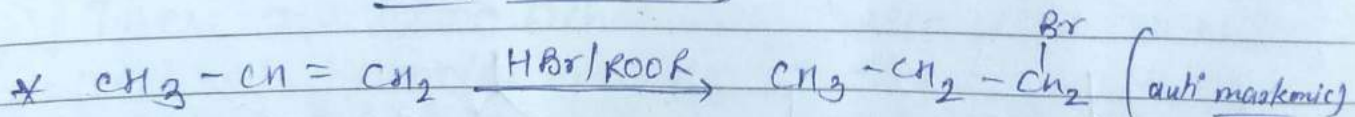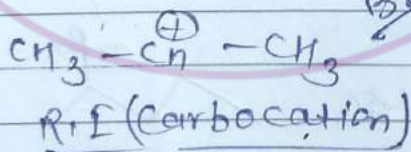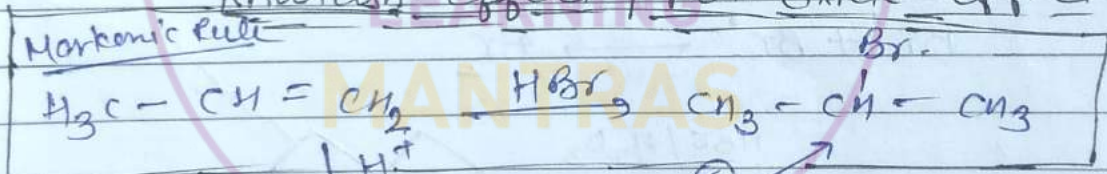
(Antimaykonic of Method)

• Mechᵐ : F.R.M.
* completed in 3 steps.

* **Step: 1** (Chain Initiation Step)

$$R - \overset{\frown}{O - O} - R \longrightarrow R - \overset{..}{O} + R - \overset{.}{O}$$

$$R - \overset{.}{O} + H \overset{\frown}{-} Br \longrightarrow R - OH + Br^{\cdot}$$

Step: 2 Chain Propagation Step:

$$H_3C - \underset{b}{CH} = \underset{a}{CH_2} + Br^{\cdot} \longrightarrow$$

on 'a' → $CH_3 - \overset{.}{CH} - CH_2 - Br$ $\alpha H = 5$ (M.S)

'b' → $CH_3 - \overset{.}{CH} - \overset{.}{CH_2}$ $\alpha H = 1$ (L.S)

$$CH_3 - \overset{\frown}{\overset{.}{CH} - CH_2} Br + H \overset{\frown}{-} Br \longrightarrow CH_3 - CH_2 - CH_2 Br + Br^{\cdot}$$
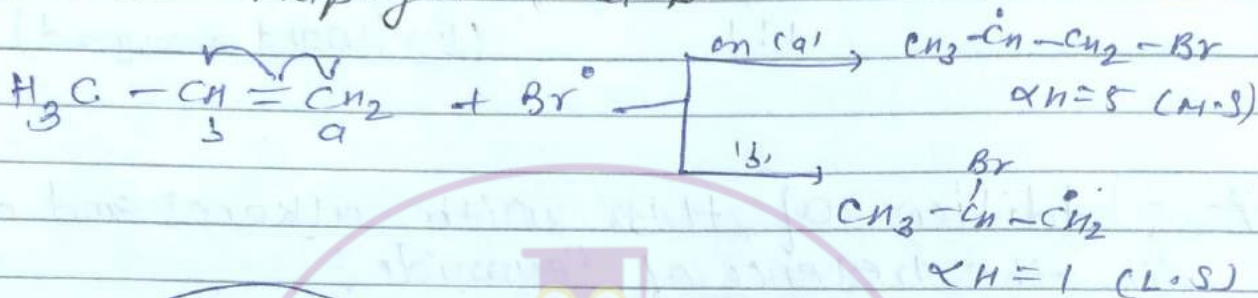
Step III: Chain Termination Step:

$$Br^{\cdot} + Br^{\cdot} \longrightarrow Br_2$$

(1)

(2)

(3)

(4) [structure diagram] $\xrightarrow{HBr/ROOR}$ [structure with Br]

$\xrightarrow{HBr}$ [bracketed structures with Br, X]   [structure with Br]
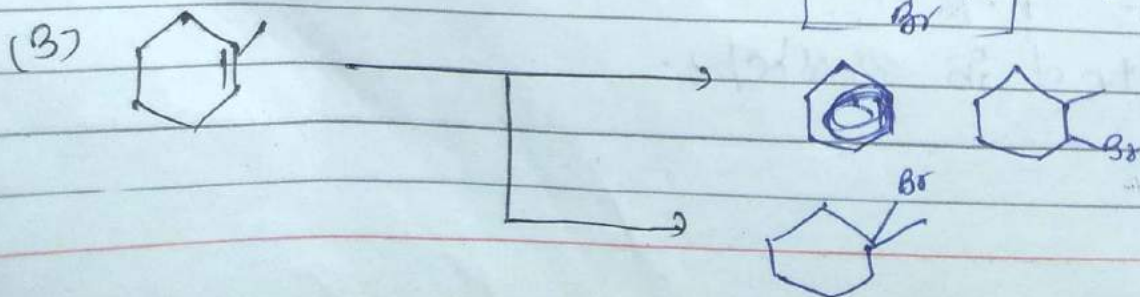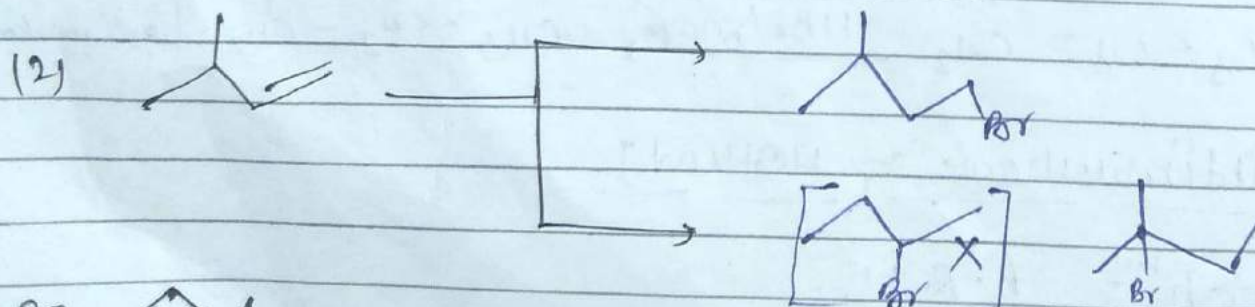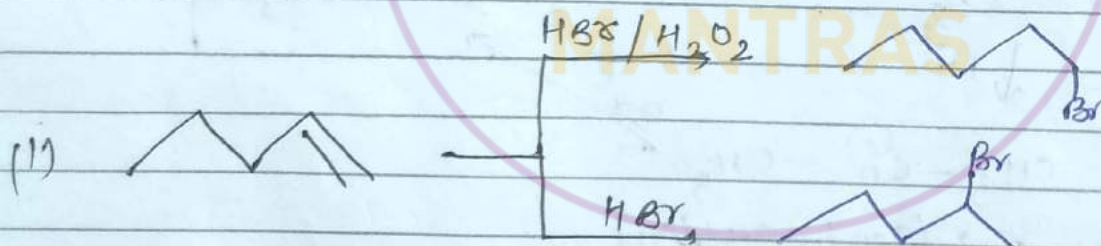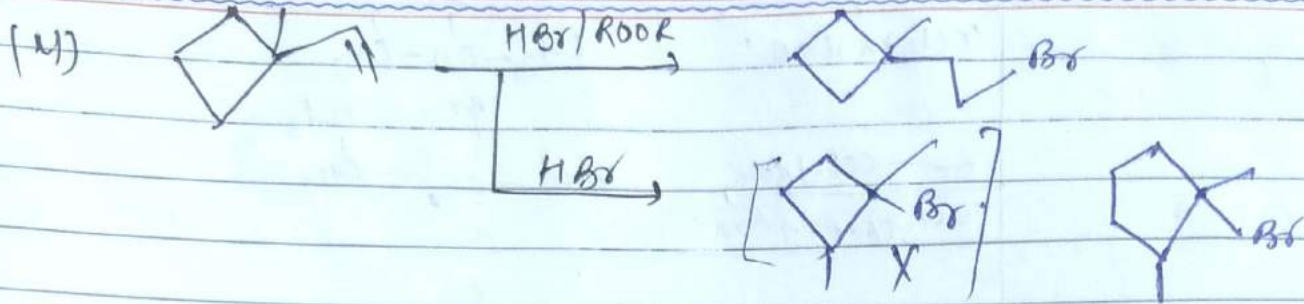
* Important Note :-

(1) In the Presence of Peroxide addition of HBr with alkene becomes by/occur by free Radical Mech^n.

(2) In this Rx^n Rearrangement not occur.

(4) there is no effect of peroxide addition of HF, HCl, HF. [But only on HBr]

* | $CH_3 - CH = CH_2 \xrightarrow{HCl/H_2O_2} CH_3 - \overset{Cl}{\underset{}{CH}} - CH_3$ | [HI weak Bond. large amount of I]

Que:7: $CH_3 - CH \equiv CH \xrightarrow[2eq]{HBr/ROOR} CH_3 - CH_2 - \overset{Br}{\underset{Br}{C}} - H$
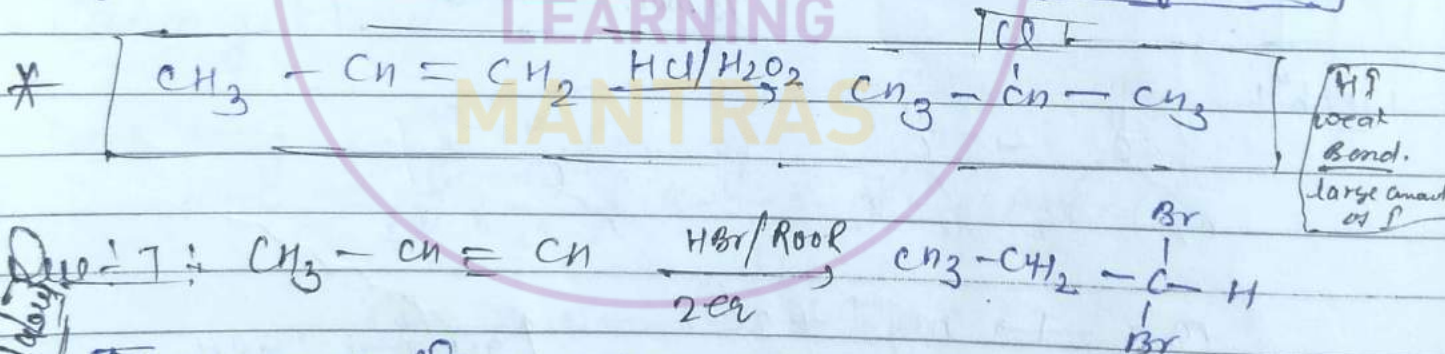
Out of syllabus

There are some other comp. also upon which effect of peroxide are some these are Haloform (H−CX$_3$). Cl−CCl$_4$, Br−CCl$_3$, I−CCl$_3$, $CH_3 - S - H$.

$\xrightarrow[Br^\circ + ROR - R - \overset{\cdot}{O}]{H-Br/ROOR.} CH_3 - \overset{H}{\underset{}{CH}} - \overset{Br}{\underset{}{CH_2}}$

* $CH_3 - \underset{b}{CH} = \underset{a}{CH_2}$ $\xrightarrow[\cdot CX_3 + ROH + RO\cdot]{H-CX_3/ROToR.} CH_3 - \overset{H}{\underset{}{CH}} - \overset{CX_3}{\underset{}{CH_2}}$

$l - CCl_3 / ROOR$ $\overset{I}{\underset{}{C}} \quad \overset{CCl_3}{\underset{}{|}}$

$\cdot CCl_3 + ROl + RO\cdot$ $CH_3 - \overset{|}{C}H - \overset{|}{C}H_2$

          $\overset{Br}{|} \quad \overset{CCl_3}{|}$

$Br - CCl_3 / ROOR$ $CH_3 - CH_2 - \overset{|}{C}H_2$

$\cdot CCl_3 + RO Br + ROo\cdot$

          $\overset{Cl}{|} \quad \overset{CCl_3}{|}$

$Cl - CCl_3 / ROOR$ $CH_3 - CH_2 - \overset{|}{C}H_2$

$\cdot CCl_3 + ROCl + RO\cdot$

          $\overset{H}{|} \quad \overset{SR}{|}$

$H - S - \overset{\ominus}{R} / ROOR$ $CH_3 - \overset{|}{C}H - CH_2$

$R - S + ROH + RO\cdot$

☆☆☆ ** Pinacol formation!

            $\overset{OH}{|} \quad\quad \overset{OH}{|}$

$\underset{R_1}{\overset{O}{\underset{}{\parallel}}} \overset{}{C} \underset{R_2}{} \xrightarrow{mg(Hg)/H_2O} \underset{R_1 \quad R_2 \quad R_1 \quad R_2}{\overset{}{C} - \overset{}{C}}$

$m - mol.$ $n/2 \, mol.$ Pinacol

Mech":

   $\underset{R_1 \quad R_2}{\overset{O}{\underset{}{\parallel}} C} + \underset{R_1 \quad R_2}{\overset{O}{\underset{}{\parallel}} C} \longrightarrow \underset{R_1 \quad R_2 \quad R_1 \quad R_2}{\overset{OH \quad OH}{\underset{}{|} \quad |} \overset{}{C} - \overset{}{C}}$

$mg \longrightarrow mg^{++} + 2e^{\ominus}$

           $\uparrow 2H - \overset{\frown}{O} - H \; ; \; 2OH$

$\underset{R_1 \quad R_2 \quad R_1}{\overset{O\ominus}{\underset{}{|}} \overset{}{C}\cdot} \quad \underset{B_2}{\cdot\overset{O\ominus}{\underset{}{|}} \overset{}{C}} \longrightarrow \underset{R_1 \quad R_2 \quad B_1 \quad R_2}{\overset{}{C} - \overset{}{C}}$

Que!' 1) $CH_3 \underset{CH_3}{\overset{O}{\underset{}{\overset{\parallel}{C}}}} \xrightarrow{mg(H_2)/H_2O} \underset{CH_3 \quad CH_3 \quad CH_3 \quad CH_3}{\overset{OH \quad\quad OH}{\underset{}{|} \quad\quad |} \overset{}{C} - \overset{}{C}}$

2) $CH_3 \underset{Ph}{\overset{O}{\underset{}{\overset{\parallel}{C}}}} \xrightarrow{Mg(Hg)/H_2O} \boxed{A} \xrightarrow{Dil \, Acid} \boxed{B} \; \underset{Ph}{\overset{O \quad CH_3}{\underset{}{} CH_3 - \overset{\parallel}{C} - \overset{|}{C} - Ph}}$

$\underset{Ph \quad Ph}{\overset{OH \quad OH}{\underset{}{|} \quad |} CH_3 - \overset{}{C} - \overset{}{C} - CH_3}$

(3)
$$\text{H}-\overset{O}{\overset{||}{C}}\overset{*}{-}\text{CH}_2-\text{CH}_2-\overset{O}{\overset{||}{C}}\overset{*}{-}\text{H} \longrightarrow$$ (cyclopentane with two OH groups)

(4) $$\text{me}-\overset{O}{\overset{||}{C}}\overset{*}{-}\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\overset{O}{\overset{||}{C}}\overset{*}{-}\text{CH}_3 \longrightarrow$$ (cyclohexane with two OH groups)

$$\xrightarrow{\text{Dil } H_2SO_4}$$

Out of Syllabus

✗ ★ A ~~Hund's~~ Hunsdicker Reaction :

$$\boxed{R-\overset{O}{\overset{||}{C}}-\overset{\ominus}{O}\overset{\oplus}{Ag} \xrightarrow{Br_2/\Delta} R-Br + AgBr + CO_2(\uparrow).}$$

Silver salt of
Carboxylic acid

Mech^n :

$$R-\overset{O}{\overset{||}{C}}-\overset{\ominus}{\ddot{O}}\overset{\oplus}{Ag} \xrightarrow{Br-\overset{\frown}{Br}} R-\overset{O}{\overset{||}{C}}-\ddot{\overset{..}{O}}-\ddot{\overset{..}{Br}}: + AgBr(\downarrow)$$
                                                                        ppt

$$R^\bullet + CO_2(\uparrow) \longleftarrow R-\overset{O}{\overset{||}{C}}-\overset{..}{O}^\bullet + Br^\bullet$$

$$\downarrow Br^\bullet$$
$$R-Br$$

① $$CH_3-COOAg \xrightarrow{Br/\Delta} CH_3-Br + CO_2(\uparrow) + AgBr$$

② (cyclopentane)$-COOH \xrightarrow{AgOH (A)} \xrightarrow{Br_2} B) \longrightarrow (O) + (O)$
                                                              has   Light Yellow ppt

(cyclopentane)$-\overset{\ominus}{COOAg}^\oplus$ (cyclopentane)$-Br + CO_2(\uparrow)$
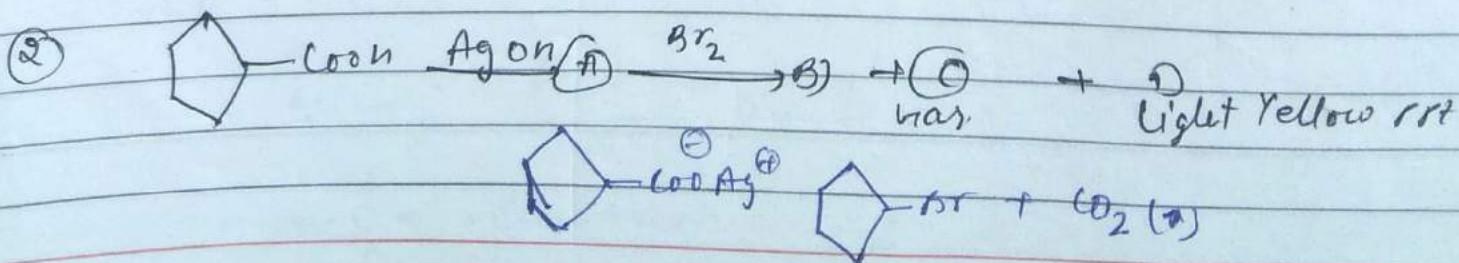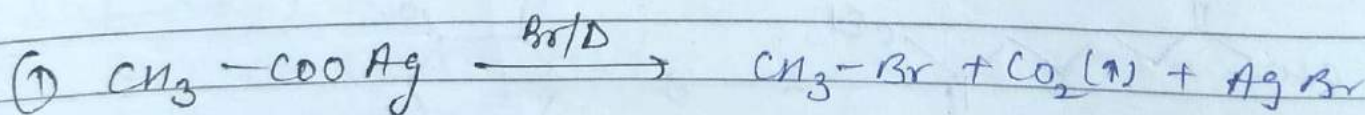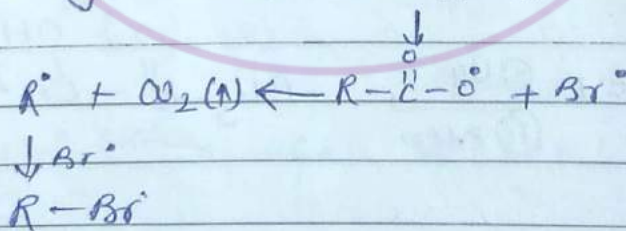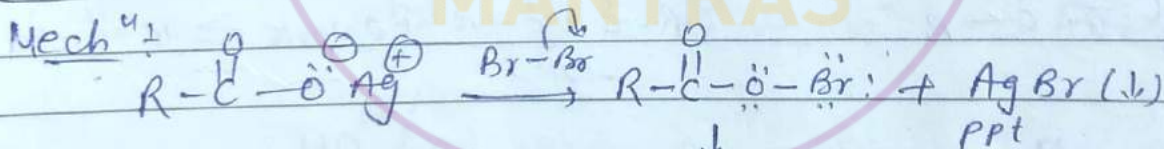
✻ Acyloin Condensation Rxⁿ:

$$R-\overset{O}{\overset{||}{C}}-OR' \xrightarrow{Na/R-OH} R-\overset{O}{\overset{||}{C}}-\overset{OH}{\overset{|}{C}H}-R$$

n-mol   n/2 mol

ester   Acyloin (α·Hydroxy c.c)

Mechⁿ:

$$2R-\overset{O}{\overset{||}{C}}-OR \xrightarrow[2Na^+ + 2e^⊖]{2Na} R-\overset{\overset{⊖}{O}Na^⊕}{\overset{|}{C}}-OR + \cdot\overset{\overset{⊖}{O}Na^⊖}{\overset{|}{C}}-R \xrightarrow{Na^⊖} R-\overset{\overset{⊖}{O}Na^⊕}{\overset{|}{C}}-\overset{|}{\overset{|}{C}}-R$$
$$\overset{|}{OR} \quad\quad \overset{|}{OR}$$

$$\downarrow$$

$$\overset{⊖}{O}Na^⊕ \quad \overset{⊖}{O}Na^⊕$$
$$R-\overset{|}{C}-\overset{|}{C}-R \xleftarrow{} \xleftarrow{2Na \rightleftharpoons 2Na^⊕ + 2e^⊖} R-\overset{O}{\overset{||}{C}}-\overset{O}{\overset{||}{C}}-R$$

$$\downarrow$$

$$\overset{⊖}{O}Na^⊕ \quad \overset{⊖}{O}Na^⊕$$
$$R-\overset{|}{C}=\overset{|}{C}-R \xrightarrow{2H-O-R} R-\overset{|}{C}=\overset{|}{C}-R + 2NaOR \rightleftharpoons R-\overset{O}{\overset{||}{C}}-\overset{OH}{\overset{|}{C}H}$$
$$\text{enol}$$

Q. $$CH_3-\overset{O}{\overset{||}{C}}-OEt \xrightarrow[\text{(ii) EtOH}]{\text{(i) Na}} CH_3-\overset{O}{\overset{||}{C}}-\overset{OH}{\overset{|}{C}H}-CH_3$$

Q.

★ Imp
★★★
★
★★ **Halogenation:**

$$-\overset{\mid}{\underset{\mid}{C}} - H + X_2 \xrightarrow{hv \text{ or } \Delta} -\overset{\mid}{\underset{\mid}{C}} - X + HX$$

SP^3
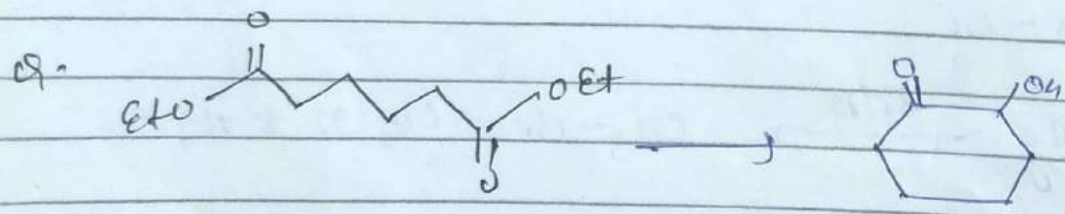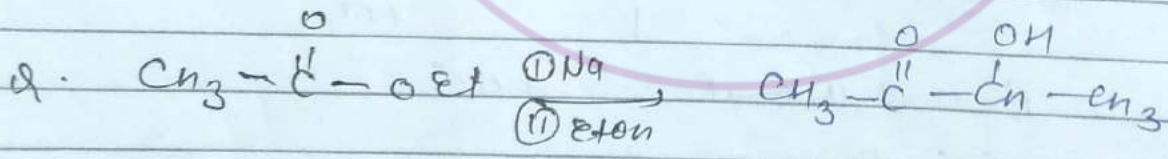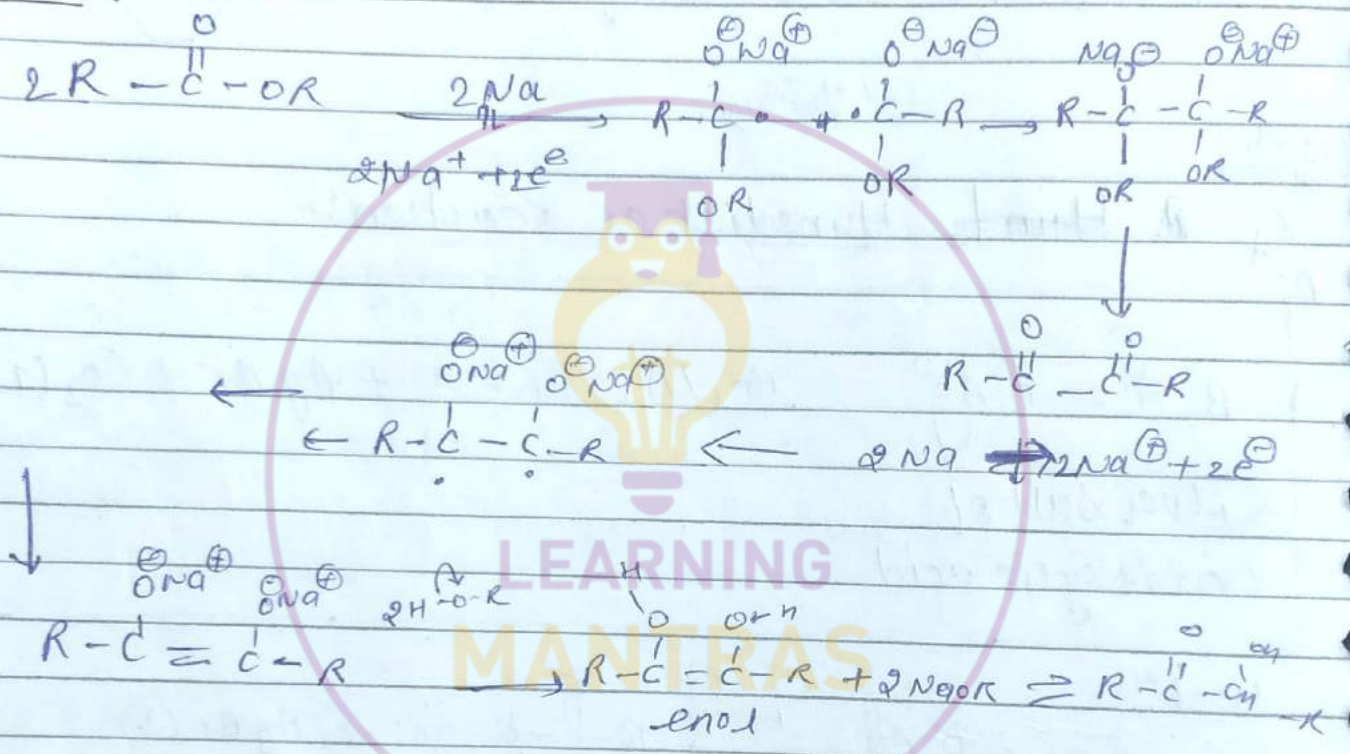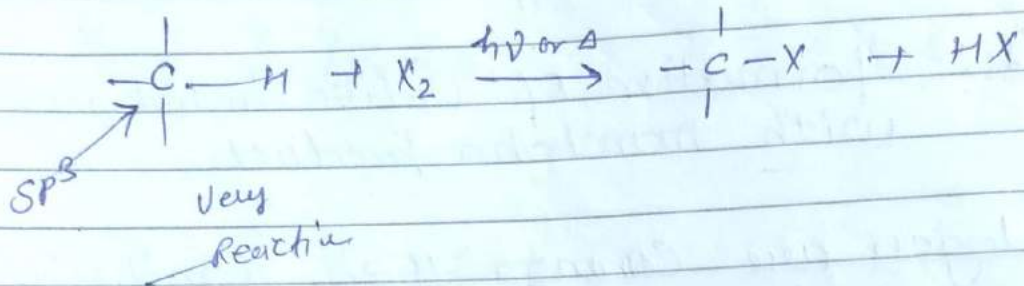
Very
Reactive

* $X_2 \neq F_2$ or $I_2 \rightarrow$ less Reactive

* $X_2 = Cl_2$ or Br_2 (Generally)

$X_2 = F_2 \gg Cl_2 > Br_2 \gg I_2$

* Rx^n occur on SP^3 - Hybridised -C.

Mech^n: FRM $\Rightarrow$ completed in three steps.
   (i) CIS (ii) CPS (iii) CTS.

Step:1 CIS:

$$X \overset{\curvearrowright}{\frown} X \xrightarrow[\text{or}]{hv} X^\circ + X^\circ \Rightarrow \text{Endothermic}$$

$\Delta \begin{pmatrix} 300°C \text{ or} \\ \text{above} \end{pmatrix}$

~~Step 1 : CPS~~   Step - CPS

$$-\overset{\mid}{\underset{\mid}{C}} \overset{\curvearrowright}{\frown} H + X^\circ \xrightarrow{slow} -\overset{\mid}{\underset{\mid}{C}} \cdot + HX \qquad EXO$$

~~Step CPS :~~

$$-\overset{\mid}{\underset{\mid}{C}} \cdot + X - X \xrightarrow{fast} -\overset{\mid}{\underset{\mid}{C}} - X + X^\circ \qquad EXO$$

Step 3: CTS

$$X^\circ + X^\circ \xrightarrow{fast} X_2$$

$$-\overset{\mid}{\underset{\mid}{C}} \cdot \quad \cdot \overset{\mid}{\underset{\mid}{C}} - \xrightarrow{fast} -\overset{\mid}{\underset{\mid}{C}} - \overset{\mid}{\underset{\mid}{C}} -$$
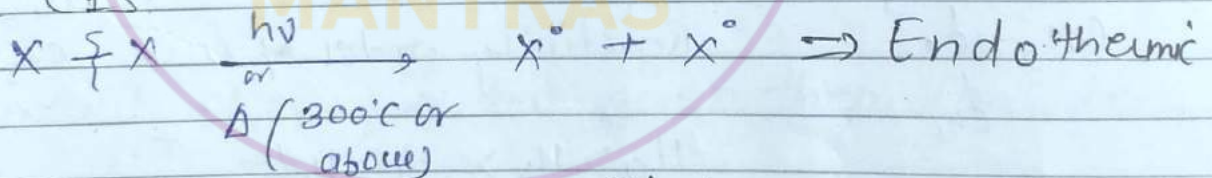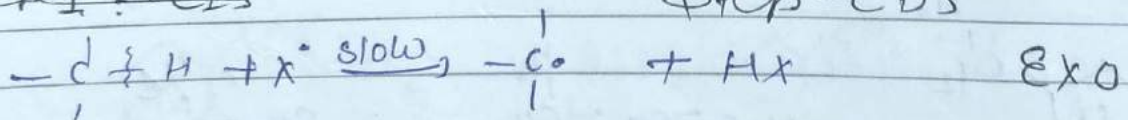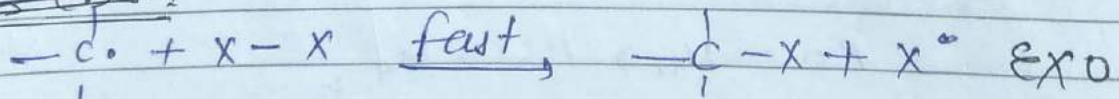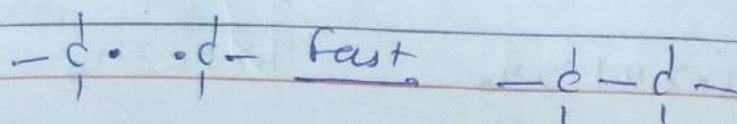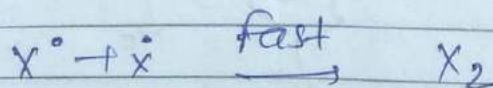
* **Merit :** → overall Rx^n is exothermic.
　　　　　└→ Takes very less time.

* **Demerits:** formation of ~~Unlike~~ Unchaha product
　　　　　with manchaha product.

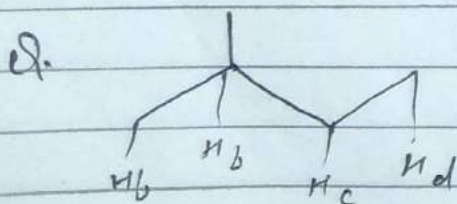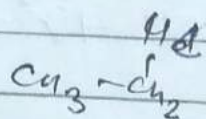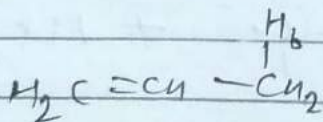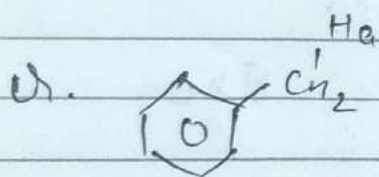If halogen are common then Reactivity of
　Halogen toward halogination
　depends on free radical

| Reactivity of 'H' towards $\propto$ Stability of |
| Halogenation Rx^n 　　　 f·R (RS) formed |

d.
$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \cancel{} H_a \qquad CH_3 - CH - H_b \qquad CH_3 - CH_3 - H_c$$

$$\downarrow \qquad \qquad\qquad\qquad\qquad\qquad CH_3 - H_d$$

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\bullet \qquad \text{Reactivity order of H} \qquad \downarrow \qquad CH_3\bullet$$

$$H_a > H_b > H_c > H_d$$

b.

（ring with O, $\overset{H_a}{CH_2}$ ）　$H_2C = CH - \underset{H_b}{CH_2}$　$CH_3 - \underset{H_d}{CH_2}$

$$RO \to H_a > H_b > H_c$$

c.

（structure with H_b, H_c, H_d） 　Cl 　（ring with O, H_b, H_c, H_a）

$$H_b > H_c > H_d > H_a \qquad\qquad H_b > H_c > H_a$$

* fluorination :

$$H - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - H \quad \xrightarrow{\;F_2/h\nu \text{ or } \Delta\;} \quad C_{black} + 4HF$$

* Chlorination : $X_2 = Cl_2$

(*) $\quad -\overset{|}{\underset{|}{C}} - H + Cl_2 \quad \xrightarrow{\;h\nu/\Delta\;} \quad -\overset{|}{\underset{|}{C}} - Cl + HCl$

(1) $\quad CH_4 - Cl_2 \quad \xrightarrow[1.eq.]{\;h\nu \text{ or } \Delta\;} \quad CH_3 - Cl + HCl \;(\text{mono chlori-}$
$\qquad\qquad\qquad\quad 1:1 \qquad\qquad\qquad\qquad\qquad \text{nation})$

(2) $\quad CH_4 + \underset{XS}{Cl_2} \quad \xrightarrow{\;\;\;\;\;\;\;\;\;\;} \quad CCl_4 + 4HCl \;(\text{Poly}$
$\qquad\qquad\qquad\quad 1:XS \qquad\qquad\qquad\qquad \text{chlorination})$

(3) $\quad CH_4 + Cl_2 \quad \xrightarrow{\;\;\;\;\;\;\;\;\;\;} \quad CCl_4 + 4HCl$
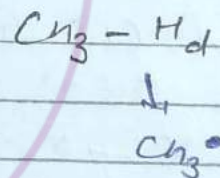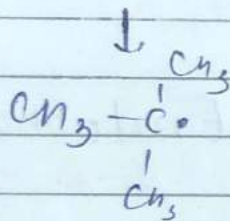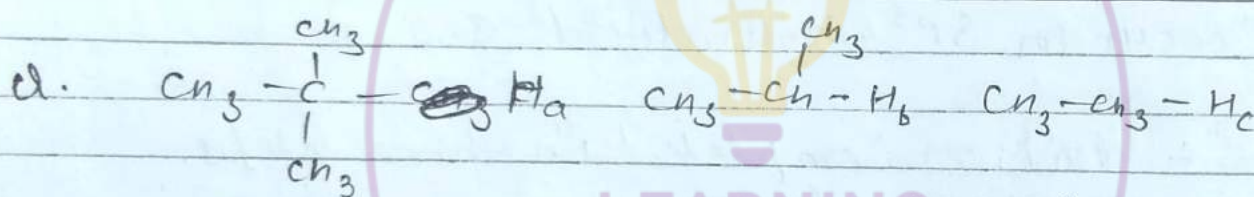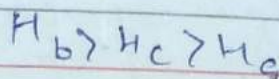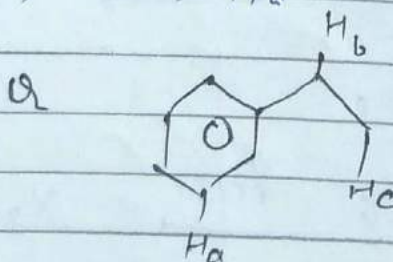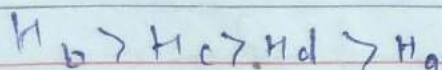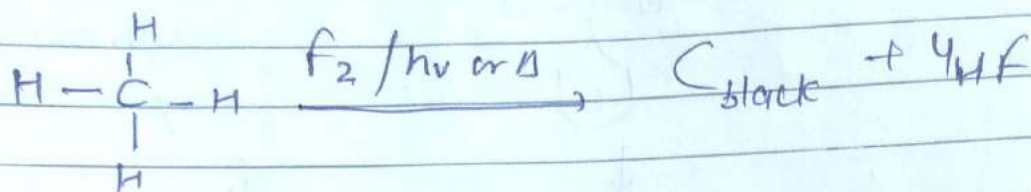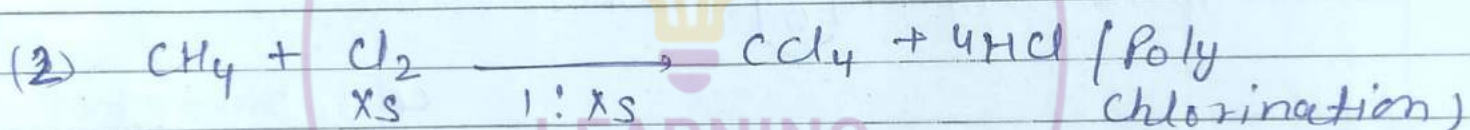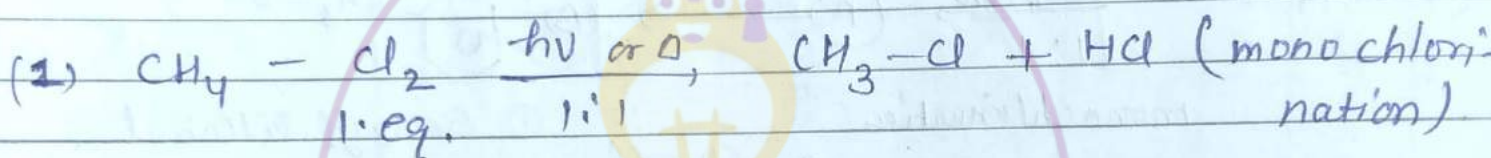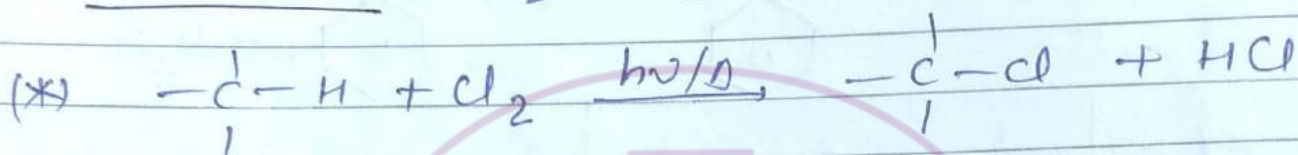
*** If amount of Cl_2 is not given then consider
Cl_2 as excess.**

(4) $+ Cl_2 \xrightarrow[1:1]{\;\;\;\;\;} $

$\qquad$ Toluene $\qquad\qquad\qquad\qquad$ Benzyl chloride.

(5) $\xrightarrow{\;Cl_2/h\nu\;}$

(6) $\quad$ Toluene $\xrightarrow{\;Cl_2\;}$

⑥ Toluene $\xrightarrow[\text{chlorination}]{Cl_2/h\nu}$ (A) $\xrightarrow{aq\ NaOH}$ (B)

COOH

Benzoic acid

⑦ Toluene $\xrightarrow[1:1 \text{ monochlorination}]{Cl_2/h\nu}$ (A) $\xrightarrow{aq\ NaOH}$ (B)

CH_3-OH

Benzyl alcohol

*⑧ $CH_3-CH_2-CH_3 \xrightarrow[1:1]{Cl_2/h\nu \text{ or } \Delta} CH_3-CH_2-CH_2 + CH_3-\overset{Cl}{\underset{|}{CH}} + CH_3$

1-Cl   2-Cl

⑨ $\overset{CH_3}{CH_3-\underset{3°}{\overset{|}{CH}}-\underset{2°}{CH_2}-\underset{1°}{CH_2}} \xrightarrow[1:1]{Cl_2/h\nu} Cl-CH_2-\overset{CH_3}{\underset{*}{\overset{|}{CH}}}-CH_2-CH_2 +$

$+ CH_3-\overset{CH_3}{\underset{Cl}{\overset{|}{C}}}-CH_2-CH_3$ ②

$\overset{CH_3}{CH_3-\overset{|}{CH}-CH_2-CH-Cl} + CH_3-\overset{CH_3}{\underset{Cl}{\overset{*|}{CH}}}-\overset{|}{CH}-CH_3$
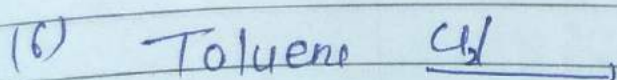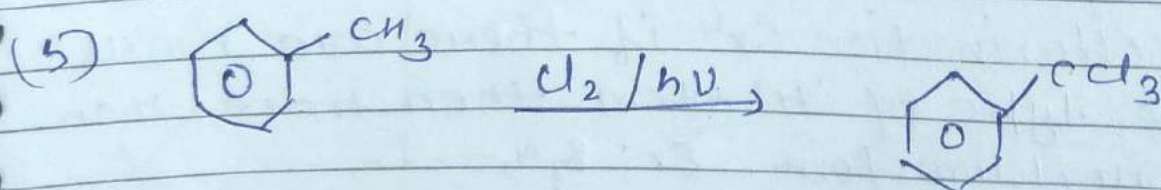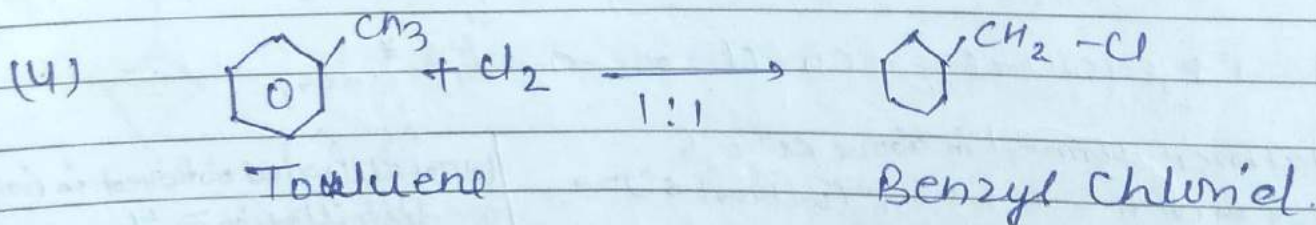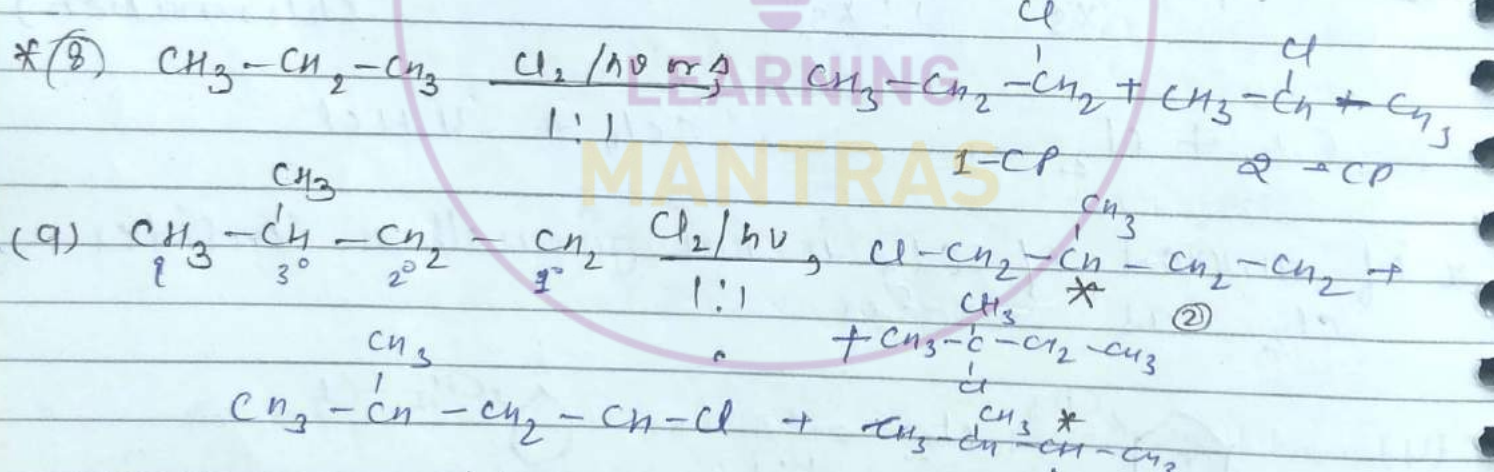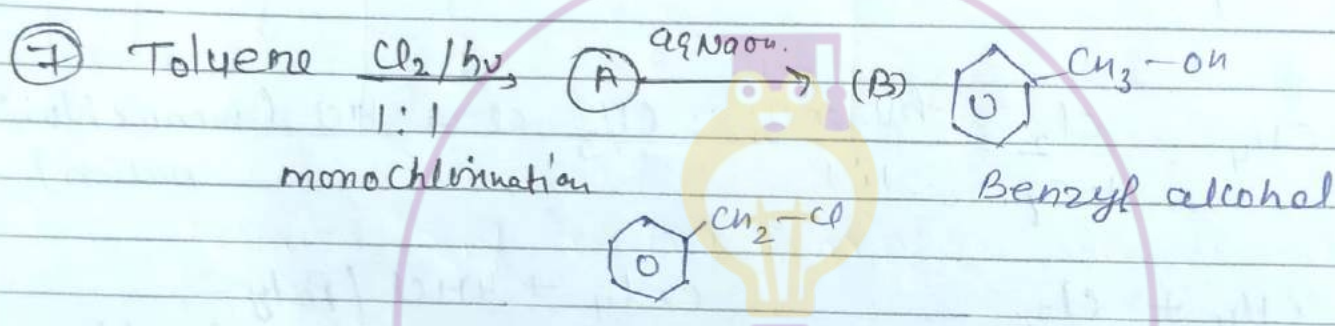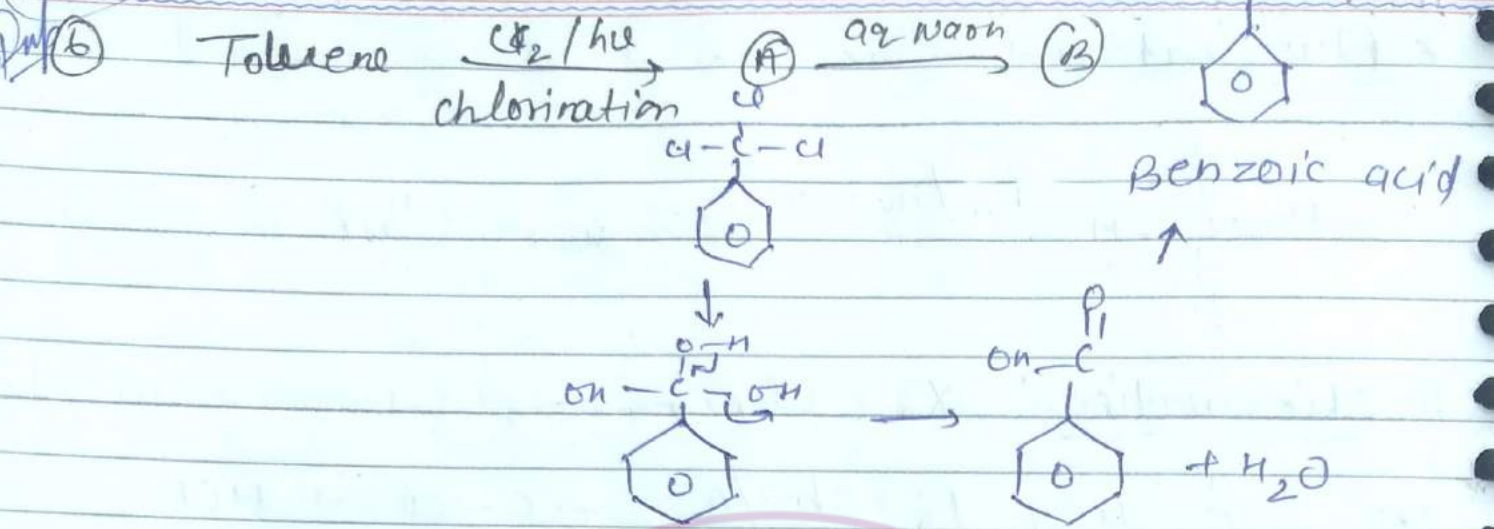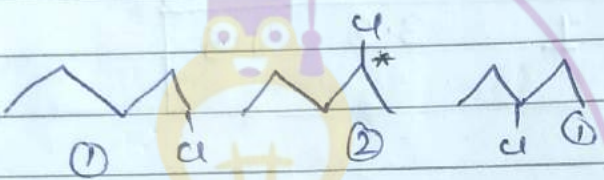
(a) Total mcp formed in above Rxⁿ = 6
(b) Total mcp " " " " (without st) = 4
(c) " " optically active (chiral product) = 4
(d) Total product obtained in fractional distillation = 4.

NOTE: In chlorination Rxⁿ if there are more then one type of 'H' atom then more then one monochloro form. Ex: 8, 9, - - - - - - -

Q. Make Monochloro Product: and decide a,b,c,d in following
molecules

molecules	Product	a	b	c	d
① Ethene.					
(2) n-Butane					
(3) Iso-Butane.					
(4) n-Pentane		4	3	2	3
(5) Isopentane					
(6)					
(7) Cl					
(8) Br					

* Determination of % of mcp (mono chloro Product).

Percentage of Any Isomer = $\dfrac{\text{Relative amount of that Isomer}}{\text{R.A of Total isomer}} \times 100$

Relative amount of Any Isomer = No. of Responsible-H $\times$ R. Reactive.

Types of 'H'	1°	2°	3°
R.R	1	3.8	4.5

Q. Determine % of Product form of on mono chlorination of Propane !

Soln.⁴

$$CH_3 - CH_2 - CH_3 \xrightarrow[1:1]{Cl_2/h\nu \text{ or } \Delta} CH_3 - CH_2 - \underset{\overset{|}{Cl}}{CH_2} + CH_3 - \underset{\overset{|}{Cl}}{CH} - CH_3$$

1-CP (44%)   2-CP 56%
     MINOR   MAJOR
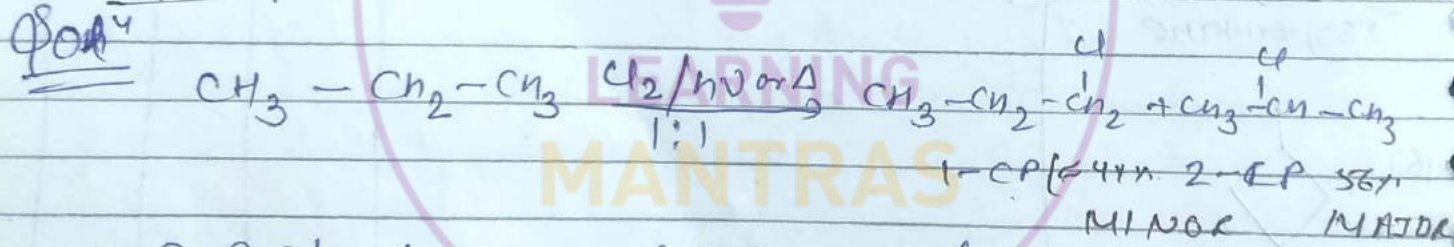
· R.A of 1-C.P = $6.0 \times 1.0 = 6.0$
· R.A of 2-CP = $2.0 \times 3.8 = 7.6$

% of 1.CP = $\dfrac{6.0}{13.6} \times 100 = \dfrac{600}{13.6} \approx 44\%$

% of 2-CP = $\dfrac{7.6}{13.6} \times 100 \approx 56\%$

** अल्केन

Q. Make MCP and decide % of Product of form in isoButane.

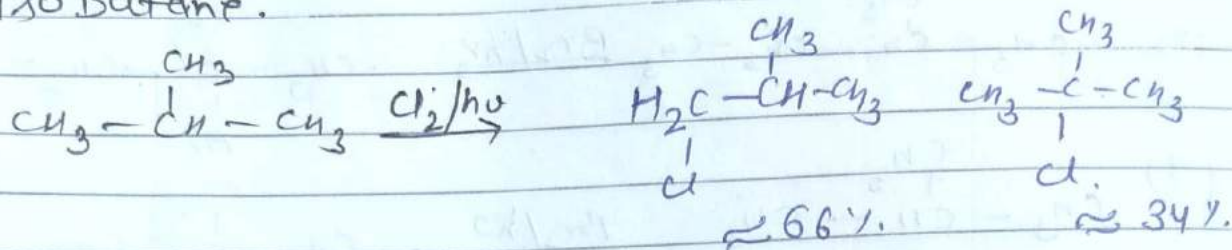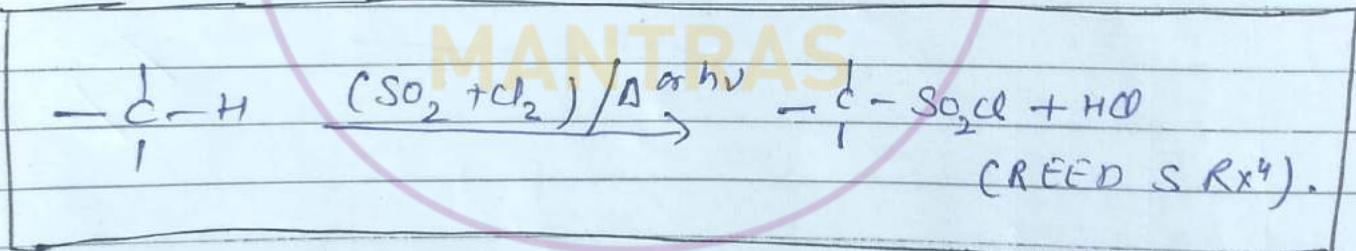$$CH_3 - \overset{\overset{CH_3}{|}}{CH} - CH_3 \xrightarrow{Cl_2/h\nu} \quad H_2C - \overset{\overset{CH_3}{|}}{\underset{Cl}{CH}} - CH_3 \quad CH_3 - \overset{\overset{CH_3}{|}}{\underset{Cl}{C}} - CH_3$$

$$\approx 66\% \qquad\qquad \approx 34\%$$

MCP =   =

Note: Chlorination can also be done by $SO_2 Cl_2$

$$CH_4 \xrightarrow[\downarrow \Delta]{SO_2Cl_2/h\nu \text{ or } \Delta} CH_3 - Cl + HCl + SO_2 (\uparrow)$$

$$Cl_2 + SO_2 (\uparrow)$$
$$\downarrow \Delta$$
$$Cl^\circ + Cl^\circ$$

$$\boxed{- \overset{|}{\underset{|}{C}} - H \xrightarrow{(SO_2 + Cl_2)/\Delta \text{ or } h\nu} - \overset{|}{\underset{|}{C}} - SO_2Cl + HCl \qquad (REED\ S\ Rx^n).}$$
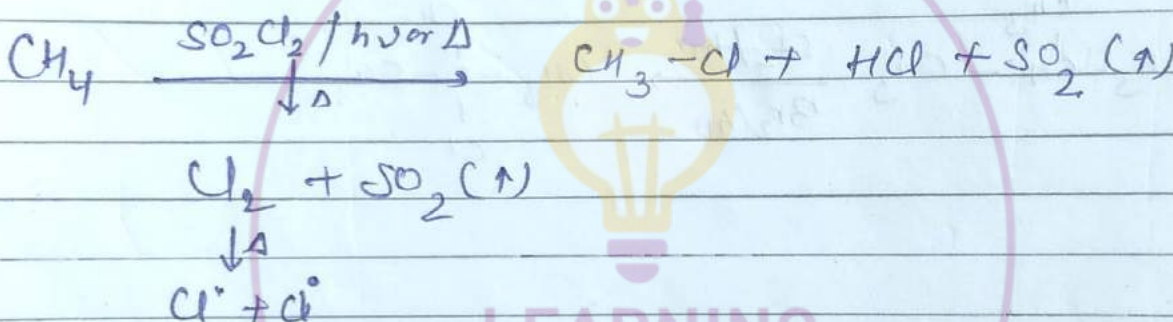
* Bromination : $X_2 = Br_2$
  Mech^n : similar chlorination.
Due to less Reactivity than Bromchlorine
  Bromine is a selecting Bromanitry agent
(i.e if more then Hydrogen present in Comp. then
  it Brominate most Reactive Hydrogen).

(1) $CH_3 - CH_2 - CH_3 \xrightarrow{Br_2/h\nu} CH_3 - \overset{Br}{\underset{}{CH}} - CH_3$

(2) $CH_3 - \overset{CH_3}{\underset{}{CH}} - CH_2 - CH_3 \xrightarrow{Br_2/h\nu} CH_3 - \overset{CH_3}{\underset{Br}{\overset{|}{\underset{|}{C}}}} - CH_2 - CH_3$

(3) $CH_3 - \overset{CH_3}{\underset{}{CH}} - CH_3 \xrightarrow{Br_2/h\nu} CH_3 - \overset{CH_3}{\underset{Br}{\overset{|}{\underset{|}{C}}}} - CH_3$

(4)

$\xrightarrow{Br_2/h\nu}$

Q.5 $CH_3 - \overset{CH_3}{\underset{}{CH}} - CH_3 \xrightarrow[Br_2/h\nu]{Cl_2/h\nu} CH_3 - \overset{CH_3}{\underset{Cl}{\overset{|}{\underset{|}{C}}}} - CH_3$