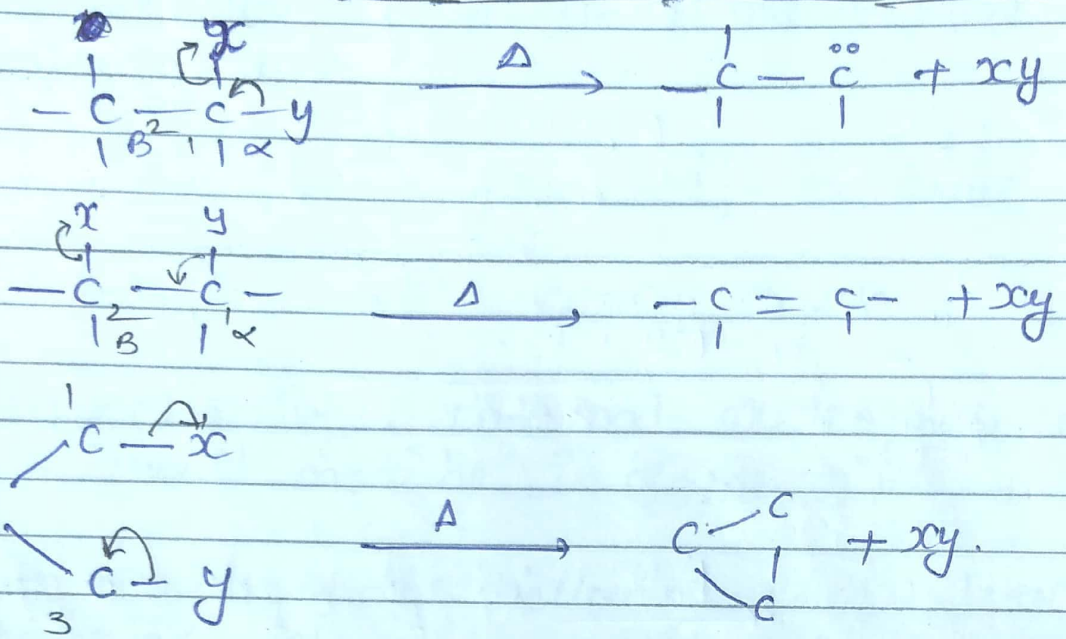
H-W (Ex: 0-1 ⇒ 31 to 71) 1 hour. Time.

18/08/17

Elimination Reaction



- It is endothermic process occure only on Heating

* Types of Elimination :

(1) 1,1 - / α,α - / 1 - / α - Elimination → Carben form

(2) 1,2 - / α,β - / 2 - / β - Elimination ⇒ Alkene/Alkyne.

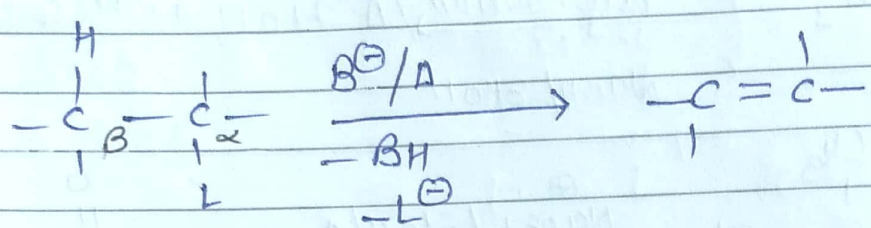
(3) 1,3 - Elimination Rxn
(4) 1,4 - " "
(5) 1,5 " "
(6) 1,6 " "
} Cyclic Elimination ⇒ Cyclic form

19/08/17

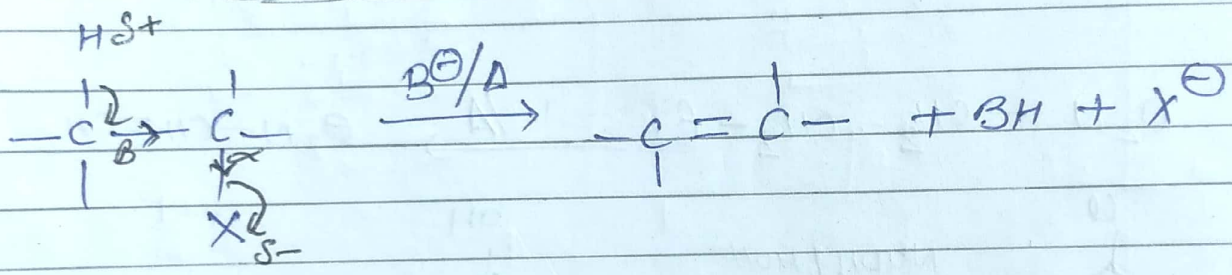
Elimination Rx

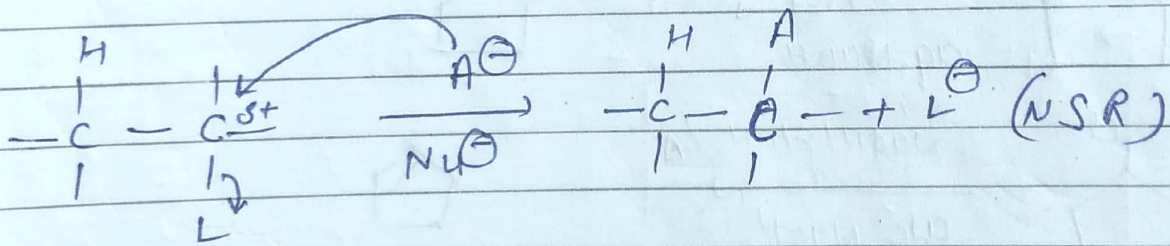
* **β Elimination Rxⁿ :-**
That elimination in which one gp depart from α and other group depart from β are known as β elimination Rxⁿ.

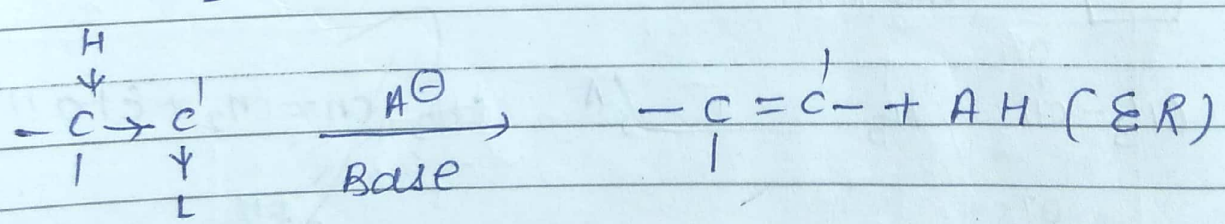
Ex:1

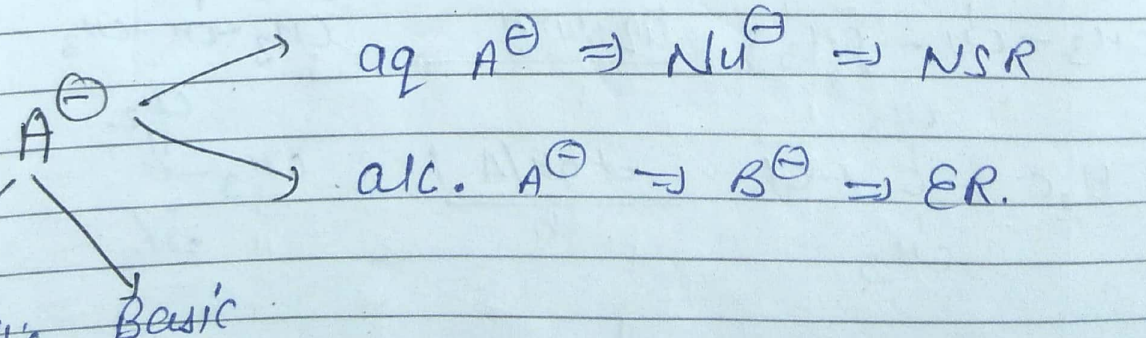


Ex: 1 Dehydrohalogination of alkyl Halide :









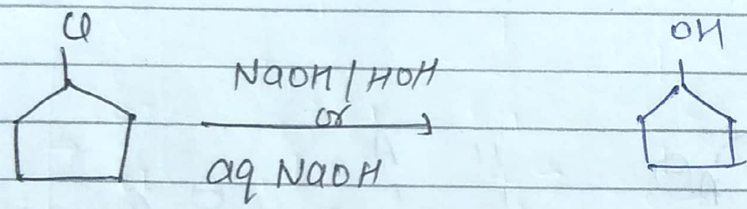
Que:1 $CH_3-CH_2(Cl) \xrightarrow[\text{or } NaOH/H_2O]{aq\ NaOH} CH_3-CH_2(OH)$ (NSR)

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

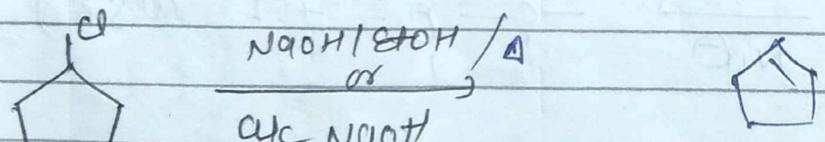
(3) $CH_3-C(CH_3)(CH_3)-Cl \xrightarrow[ER]{Na^{\oplus}OEt^{\ominus}/EtOH/\Delta} H_3C-C(=O)-CH_3$

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

(5)



(6)



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

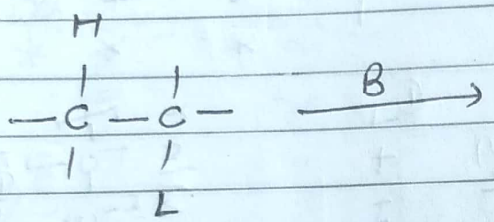
(8) $CH_3-CH(OTs)-CH_3 \xrightarrow{aq\ NaOH} CH_3-CH(OH)-CH_3$

(9) $H_3C-C(CH_3)(CH_3)-Cl \xrightarrow[E_1]{EtOH/\Delta} CH_3-C(=CH_2)-CH_3$

* Mech^{n} of β elimination :-

It occur by following three Mech^{4}.
Depending upon

(1) E_1-Mech^{n} :-
(2) E_2-Mech^{n} :-
(3) E$_{1cB}$ - Mech^{m}



E_1^* ⇒ make + first

H (acid – C.B.)

$$-\overset{H}{\underset{|}{C}}-\overset{|}{\underset{L}{C}}- \xrightarrow[-BH,\ -L^{\ominus}]{B^{\ominus}} -\underset{|}{C}=\overset{|}{C}-$$

E_1 – Mech^n

* Unimolecular elimination Mech^n

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

R.I carbocation

$\rightarrow -\underset{|}{C}=\overset{|}{C}-$ (major) E_1 Product

$-\overset{H^{\oplus}}{\underset{|}{C}}-\overset{B}{\underset{|}{C}}-$ S_N1 Product (MINOR)

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

* $m = 1$, $O = 1$

* Favoured by weak base

Eg: EtOH, NH_3

E_2 – mech^n

* $B^{\ominus}$ - - - - - - - - -

* $-\overset{H}{\underset{|}{C}}{}^{\delta-}-\overset{\delta+}{\underset{L^{\delta-}}{C}} \xrightarrow[slow]{B^{\ominus}} \left[-\overset{H\ \delta+}{\underset{\delta-}{C}}\cdots\overset{|}{\underset{L\ \delta-}{C}}-\right]$ T.S

$\rightarrow -\underset{|}{C}=\overset{|}{C}- + BH + L^{\ominus}$

$-\underset{|}{C}-\overset{B}{\underset{|}{C}}-$

S_N2 – Product Minor

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

* $m = 2$, $O = 2$

* Favoured by strong / moderate base

Eg: alc. KOH, alc. KOR, alc. NaOH, alc. NaOR, $NaNH_2$, RNH_2, KOH, NaOH

E_1CB – Mech^n

• Unimolecular elimination by formation of conjugate base

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

C.B (R.I) or carbanion.

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

* Favoured by strong Base

Eg: alc. KOH

E_1

* favoured By Polar Protic Solvant PPS (Et–OH), NH_3 etc)

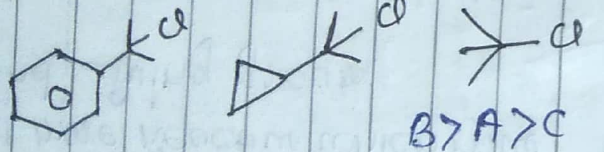
* favoured by good living group

Que: $H_3C-C(CH_3)_2-Cl$ $H_3C-CH(CH_3)-Cl$ H_3C-CH_2-Cl

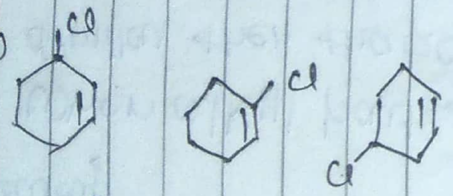
R.O: a > b > c
$3° > 2° > 1°$

* Those comp. are more Reactive towards $E_1 Rx^n$ of which carbocation is more stable.

* Reactivity toward E_1 Rxn ∝ Stability of $C^{\oplus}$ ∝ +m/+H/+I effect

Q.2)


B > A > C

Q.3)


1 > 3 > 2

$E_1 Rx^n$ ∝ 3° stable.

E_2

* favoured by Polar aprotic solvant PAS (→ Dmf, dmso, Acetone, ether)

* favoured by GLG or modrate living group

* Reactivity toward of Cmp. E_2 R_x^n:
∝ stability of Alkene
∝ Acidic nature of $C_\beta - H$

Q. $H_3C-C(CH_3)_2-Cl$ (most Reactive) $H_3C-CH(CH_3)-Cl$ CH_3-CH_2-Cl (Least Reactive)

↓ $H_2C=C(CH_3)-CH_3$ most stable   ↓ $H_2C=CH-CH_3$ ↓ $H_2C=CH_2$ least stable

E_1CB

* favoured by PAS.

* favoured by poor living gp PLG ($-F$, $-O-\overset{O}{\overset{\|}{C}}-R$)

* Condition for E_1CB:
1) Living group should be poor living gp / very poor living gp.
⇒ $-F$, $-O-\overset{O}{\overset{\|}{C}}-CH_3$ ($-OAc$)
2) $-m/-H/-I$ gp at C_β (conj. Base) ('H' of CB should be highly Acidic)

H.W: Q-1 71-

It occur mainly in 3° alkyl halide

* When alkyl part is similar then that comp. will more reactive which have good living group.

* When alkyl gp is similar then

Reactivity of comp ∝ L.N. of L.G.

Q.

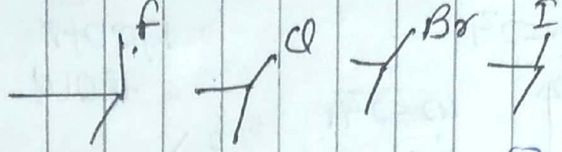
$CH_3-C(CH_3)_2-F$ $\quad$ $H_3C-C(CH_3)_2-Cl$

$CH_3-C(CH_3)_2-Br$ $\quad$ $CH_3-C(CH_3)_2-I$

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

RO = 4 > 3 > 2 > 1

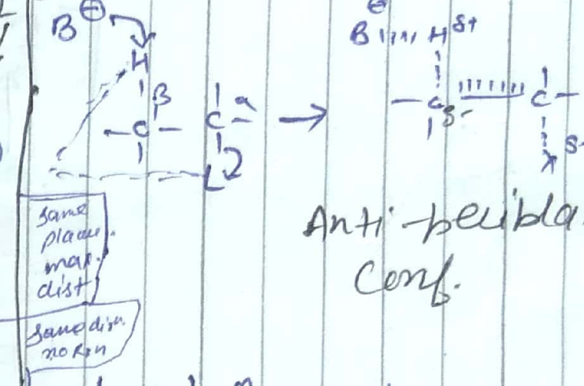
Reactivity of comp. ∝ L.N of L.G.

Q. 

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

R.O ⇒ 4 > 3 > 2 > 1

favourable condition for E_2 Rx^n :



Anti-periplanar Conf.

* Hydrogen C_β carbon and living gp of C_β should be anti to each other: ~~this~~ ~~Conf.~~ should be anti to each other and in same plane this conf. necessary to ~~SN~~ E_2 reaction is known as **anti periplanar conf.**

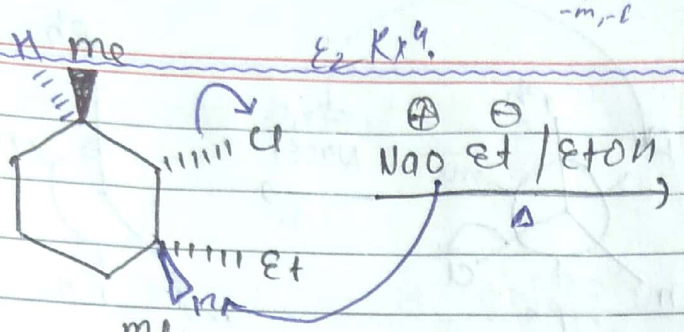
Test syllabus
$Nu^{\ominus}$ SR.
Titomerism, Relationship. SN^1 and SN^2.
E.P.St. R
Carbocation

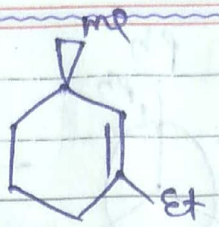
Weak Neutral Base → Cation Stable ⇒ E_1
in Strong Base → E_1cB, E_2

Weak ethanol amonia base.

Erethro → cis like

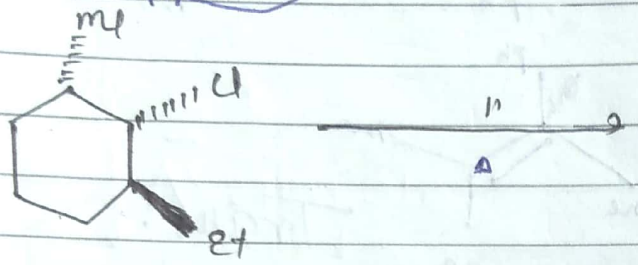
(1) E_2 Rxn.

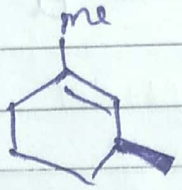




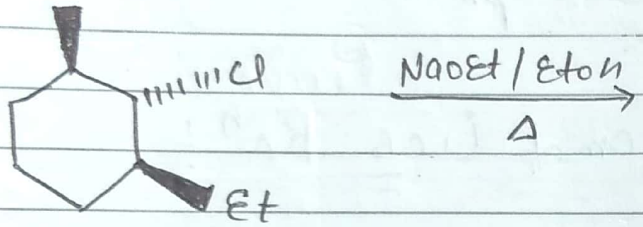
fixed no Rotation

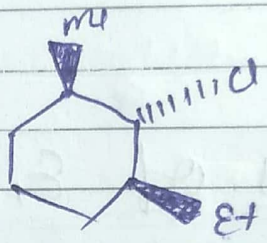
(2)





(3)

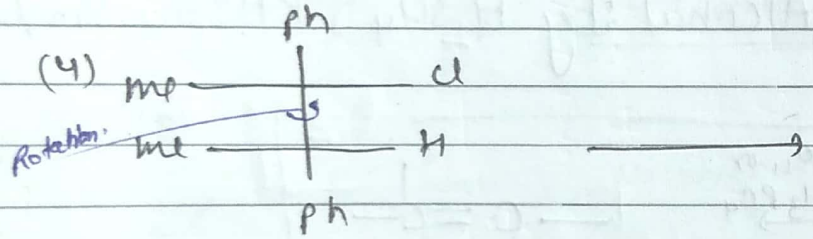




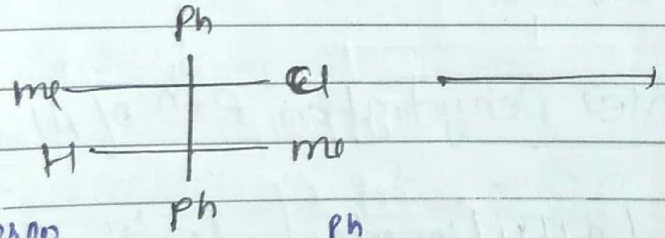
No Rxn.

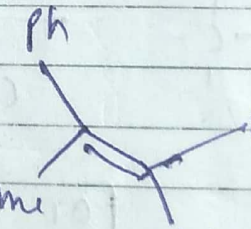
Rotation.

(4)



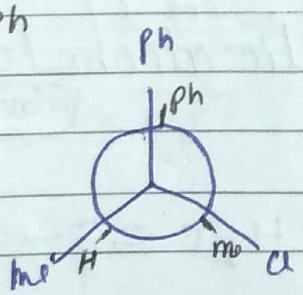
(5)



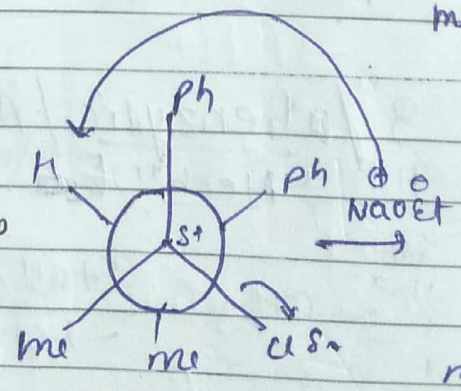


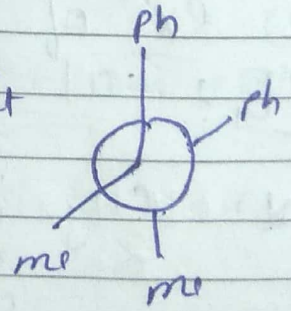
Cis

Threo Isomer



60°





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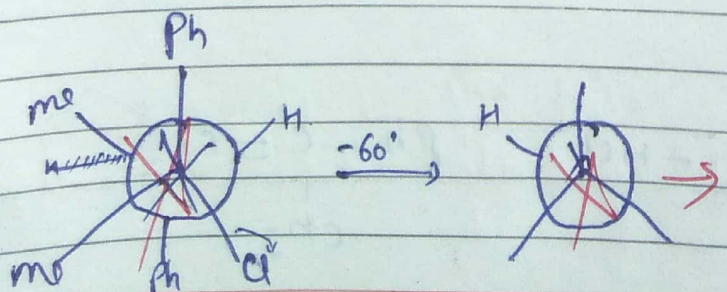

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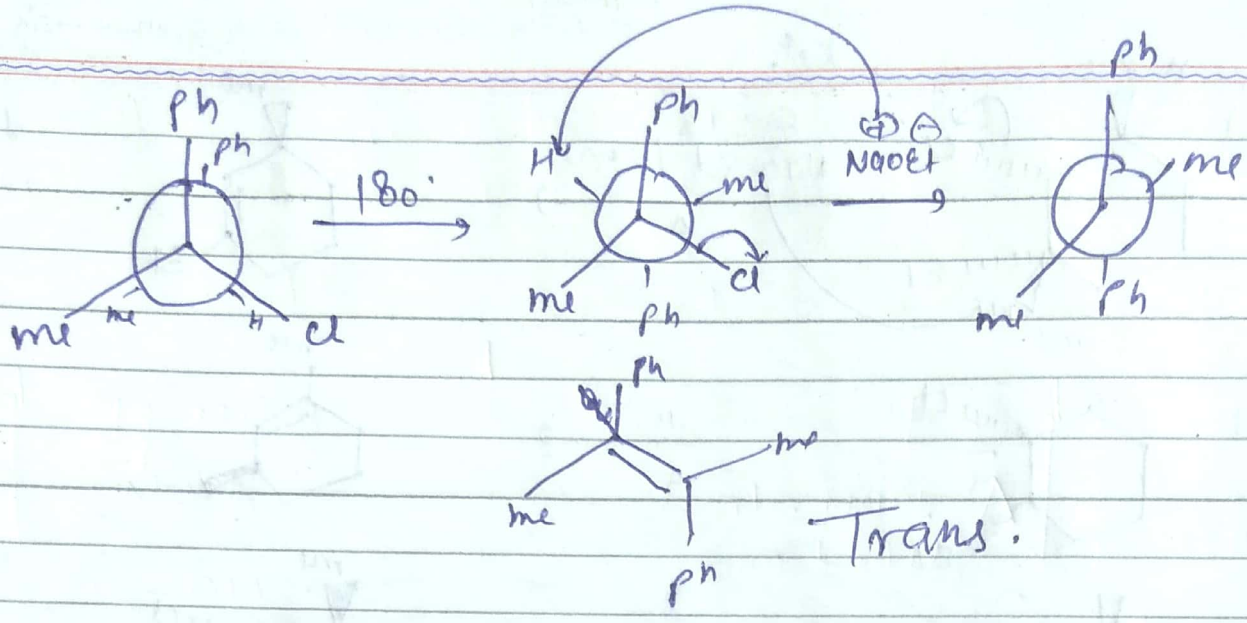


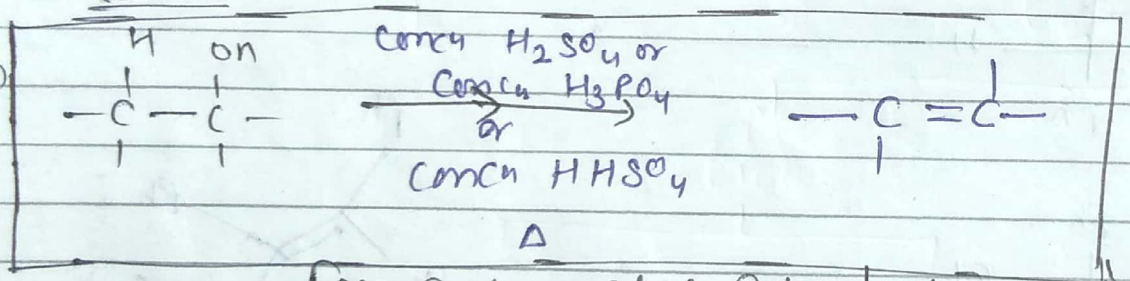
Trans.

* Examples of E_1, E_2 and E_1cB Rxn :-

(E_1)

(1) Dehydration of Alcohal by H_2SO_4, $KHSO_4$ and H_3PO_4 :-

(1) (a)



For Detail See Dehydration Rx^n of Alcohol

(2) Rx^n of 3°/Benzylic/Allylic alcohol with EtOH

Meh E_1 : at HI : Meoh : E_1 (make alkene)

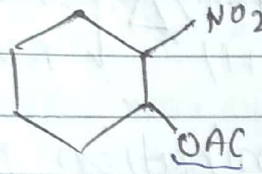
(i) $CH_3-C(Cl)(CH_3)-CH_3 \xrightarrow[-HCl]{EtOH/\Delta} H_2C=C(CH_3)-CH_3$

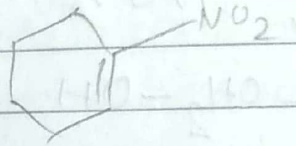
(ii) $Ph-C(Cl)(CH_3)-CH_3 \xrightarrow{-HCl} Ph-C(CH_3)=CH_2$

Rest Rx^{n} always E_2.

* Examples of E1cB :

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

(2) 

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

(3) $Ph-CH_2-\underset{F}{\underset{|}{CH}}$ $\xrightarrow{NaOEt/EtOH/\Delta}$

(4) $\underset{H}{\overset{F}{\diagdown}}C=C\underset{F}{\overset{F}{\diagup}}$ $\xrightarrow{NaOEt/EtOH}$ $\overset{F}{\underset{F}{\diagdown}}C=C$

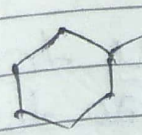
Rest other Elimination is E_2

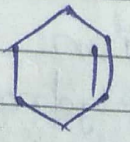
* Examples of E_2 - Rxn :

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

(2) $D_3C-CH_2-Cl \xrightarrow[r_2]{KOH/\Delta} D_2C=CH_2 + HOH + KCl$

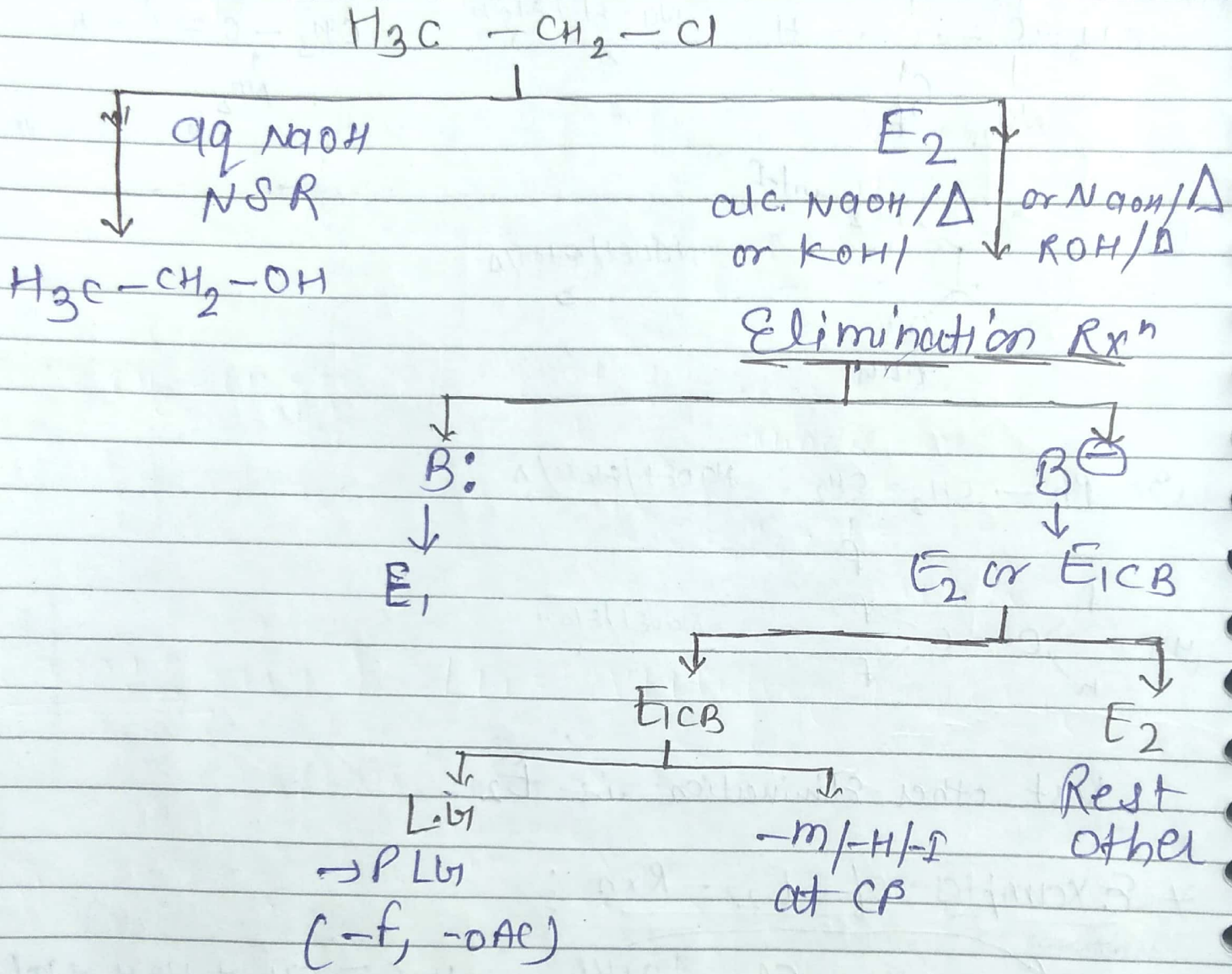
Slow Rx^{n} $\quad r_1$ & r_2 - order

(3) 

$\xrightarrow{NaOEt}$  $+ EtOH + NaCl.$

aq NO heat → Substitution

* Orientation in Elimination Rxn :-



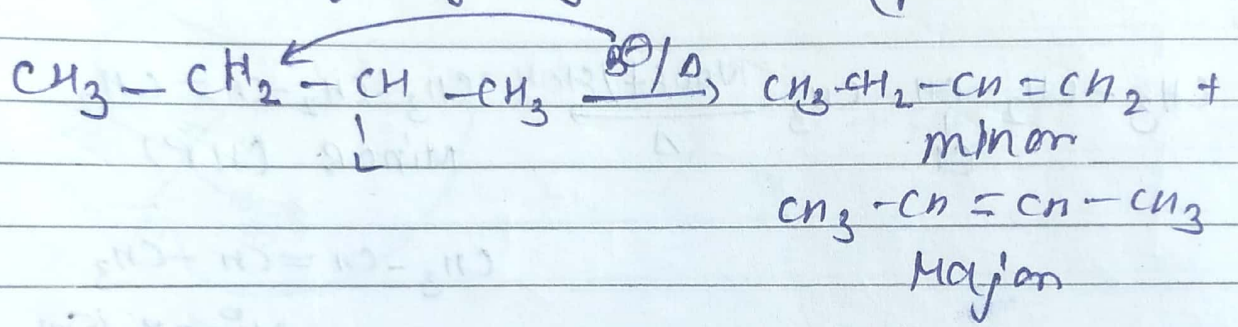
* $CH_3 - \underset{\beta}{CH_2} - \underset{L}{\underset{|}{CH}} - \underset{\beta'}{CH_3} \xrightarrow[ER]{B^{\ominus}/\Delta} CH_3 - CH = CH - CH_3 + CH_3 - CH_2 - CH = CH_2$

In Elimination Rxn 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.

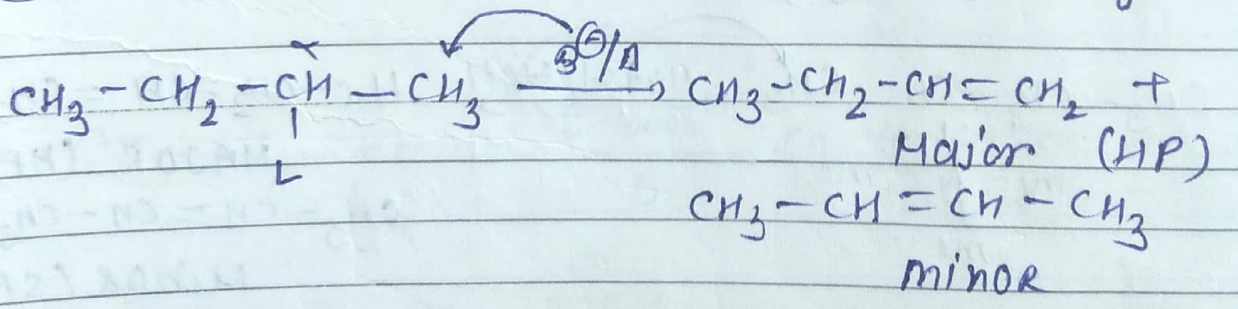
(1) Saytzeff's Rule
(2) Hafmann Rule

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



* Hafmann Rule :-

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



* for E_1 Mechⁿ :- ⇒ Saytzeff's Rule (SR)
* for E_1cB Mechⁿ :- ⇒ Hafmann Rule. (HR).
* for E_2 Mechⁿ :- Both (~~OR~~ :- SR + HR).
  - ↓ In most of the case
  - ↳ In '4' Cases

Case:- Haf

(1) When L.Gr is VPLGr (very Poor Living gr).

[-F, -O-C(=O)-CH3 (-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 LGr = VLLGr (very Large Living gr).

($-\overset{\oplus}{N}R_3$, $-\overset{\oplus}{S}R_2$)

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

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

me_3N.

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

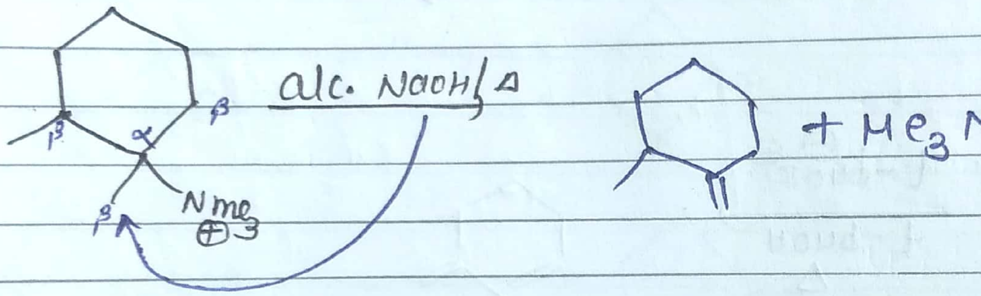
$+ me_2S$

Ex: $CH_3-CH_2-\underset{\underset{Et}{|}}{\overset{\overset{CH_3}{|}}{CH}}$ … $CH_3-CH_2-CH(CH_3)-CH(N^{\oplus}(Me)_2Et)-CH_2-CH_3$ $\xrightarrow{NaOEt/EtOH/\Delta}$ $H_3C-CH_2-CH=CH_2$ + (Major)

$CH_3-CH=CH-CH_3$ (minor)

$\longrightarrow$ $CH_3-CH(CH_3)-CH(N(CH_3)_2)-CH_3$ + $H_2C=CH_2$

(4)



alc. NaOH/Δ

+ Me_3N

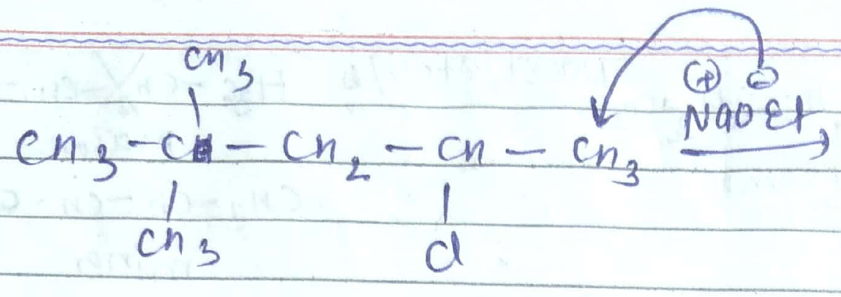
Case: 3 When Base is large size Base

Ex: (t-BuO$^{\ominus}$K$^{\oplus}$ = $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O^{\ominus}K^{\oplus}$)

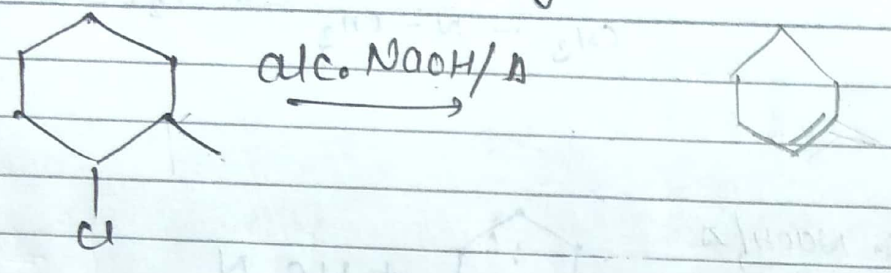
Q. $CH_3-\overset{\beta}{CH_2}-\underset{Cl}{\overset{\alpha}{CH}}-\overset{\beta'}{CH_3}$ $\xrightarrow[\Delta]{t-BuO^{\ominus}K^{\oplus}}$ $CH_3-CH_2-CH=CH_2$ (Major) + $CH_3-CH=CH-CH_3$

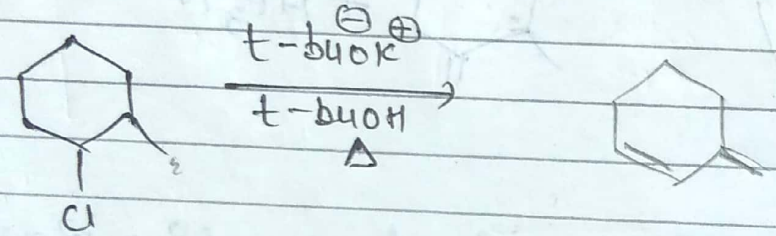
$CH_3-CH_2-\underset{Cl}{CH}-CH_3$ $\xrightarrow{Na^{\oplus}O^{\ominus}Et}$ " + $CH_3-CH=CH-CH_3$ (MAJOR)

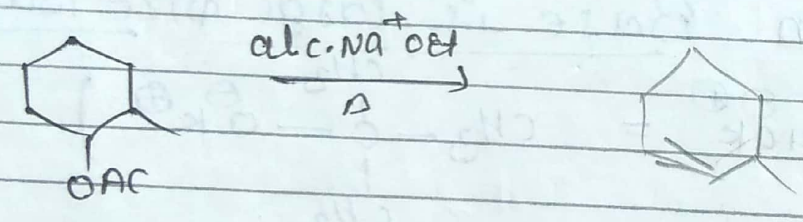
Case: 4 When their is crowding around H Responsible for Sed. Product then also elimination occur by Halfmann Rule

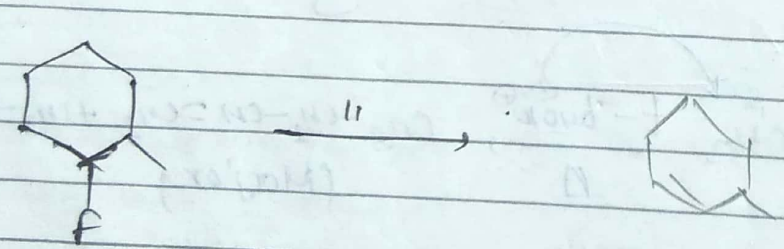


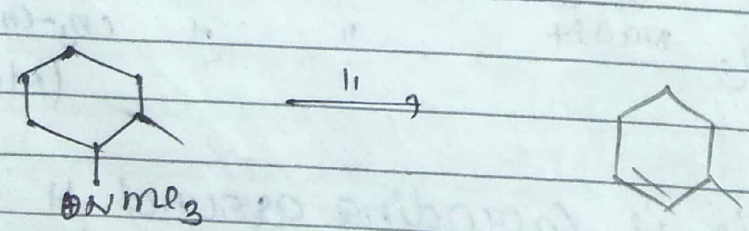
* Q. Complete following Rxn :

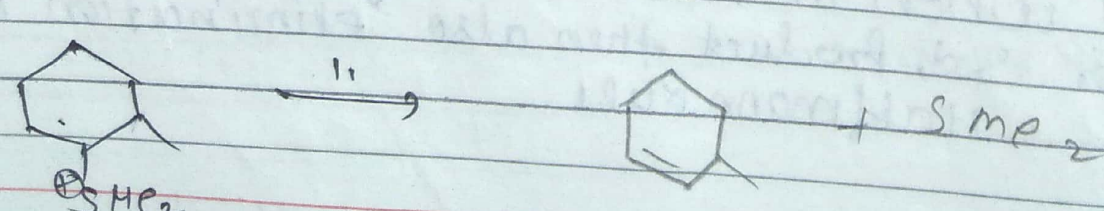
(1) 

(2) 

(3) 

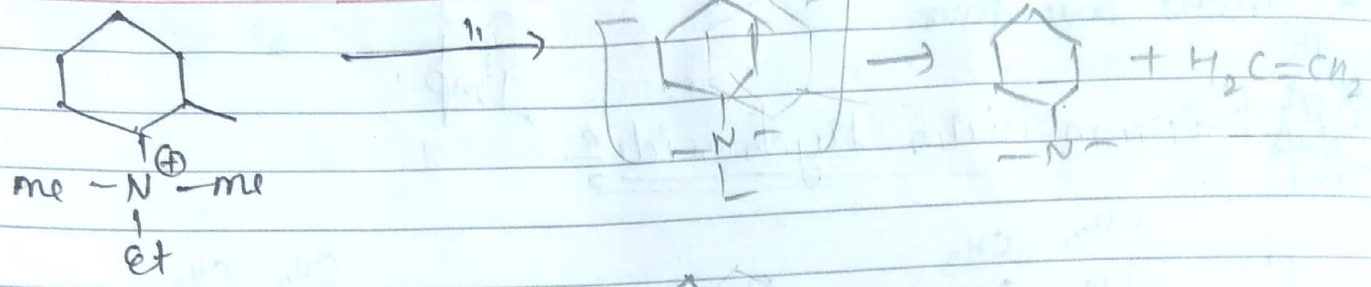
(4) 

(5) 

(6) 

H.W ÷ Race ÷ 13 [illegible] Not done by me.

(7)



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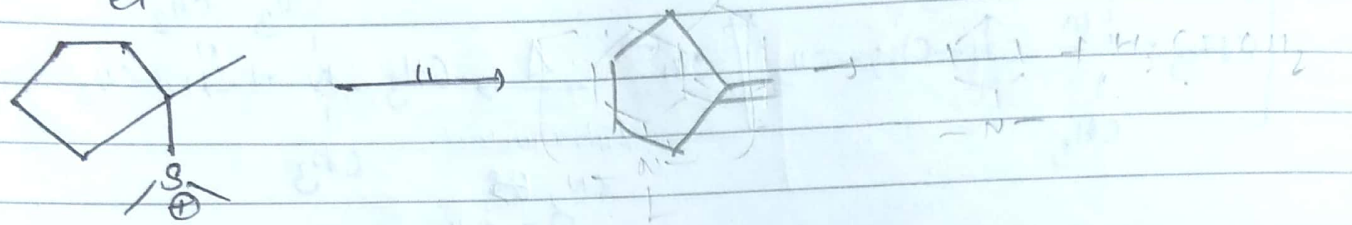
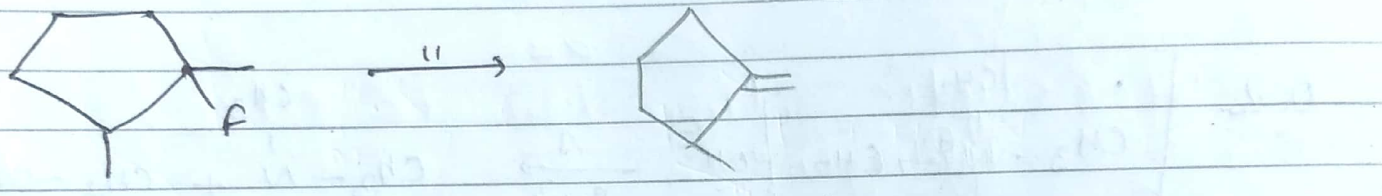
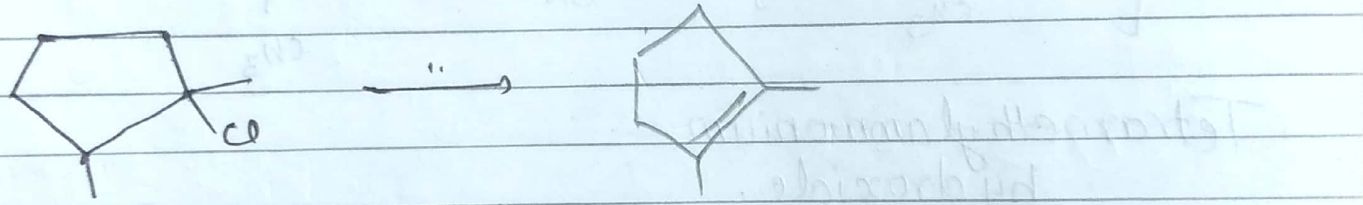


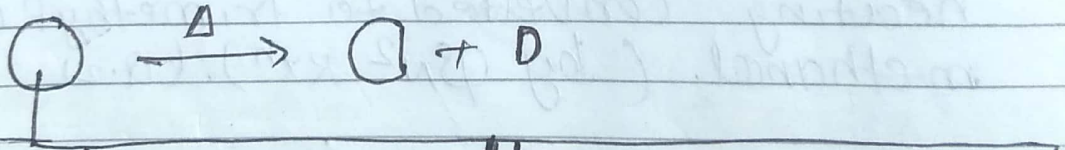
(9)



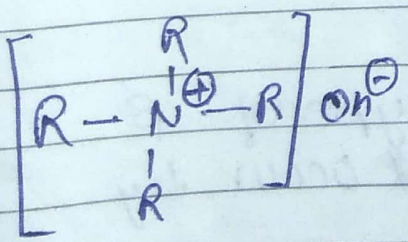
(10)



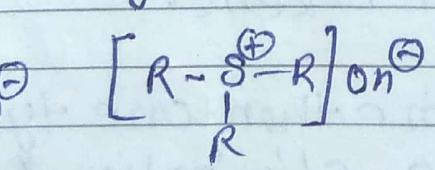
* Pyrrolytic/Thermal Elimination Reaction:



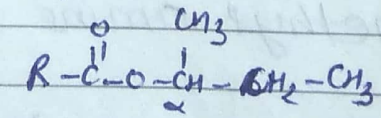
4° Ammonium Hydroxide



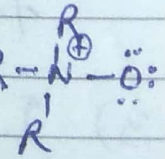
3° Sulfonium hydroxide



Ester having β–H

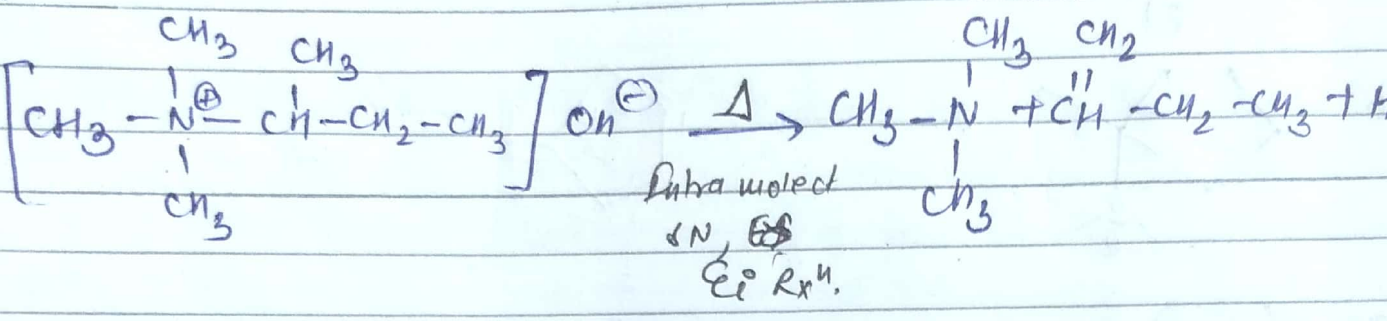


3° Amine oxide.



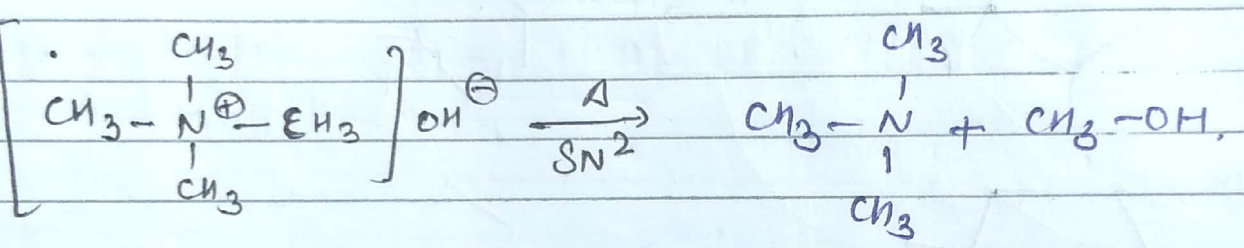
* There are four

4° - Ammonium hydroxide ⇒



Intramolecular S_Ni Rx^n.

Q.2



Tetramethylammonium hydroxide.

(1) When all alkyl gp are methyl gp. then on heating converted to trimethyl amine and methanol. (by S_N2 Rx^n). (Q.2)

2) when any alkyl gp larger the alkyl gp then 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.

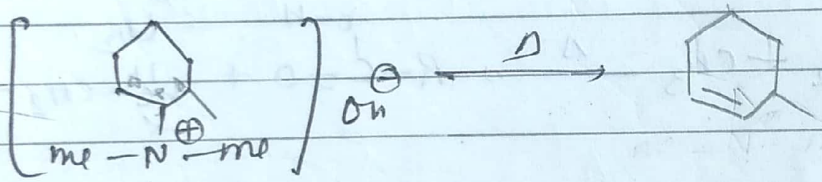
*3° Sulfonium hydroxide:-

In 3° sulfonic hydroxide Pyrolatic Elimination Rxn is similar to 4° ammonium hydroxide

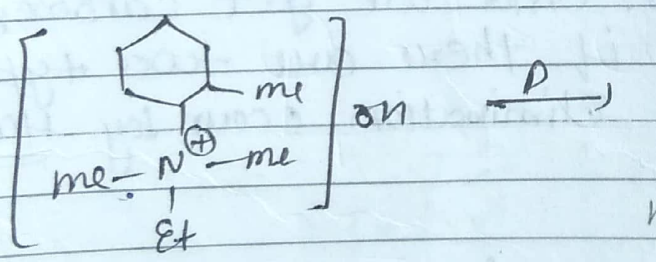
(2) $[CH_3-\overset{\oplus}{S}(CH_3)_2]\,OH^{\ominus} \xrightarrow[SN^2]{\Delta} CH_3-\underset{CH_3}{S} + CH_3-OH$

(1) $CH_3-\overset{\oplus}{S}(CH_3)-CH(CH_3)-CH_2-CH_3\,]\,OH^{\ominus} \xrightarrow[E_i\ Rxn]{\Delta} CH_3-\underset{CH_3}{S} + CH_2=CH-CH_2-CH_3 +$ Hon.

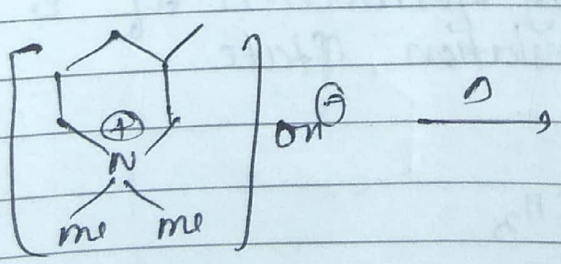
Q.1



(2)



(3)



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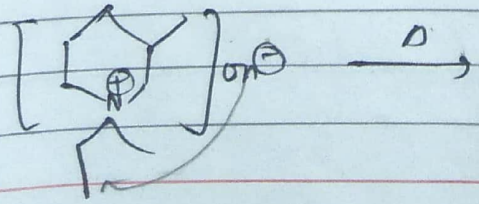

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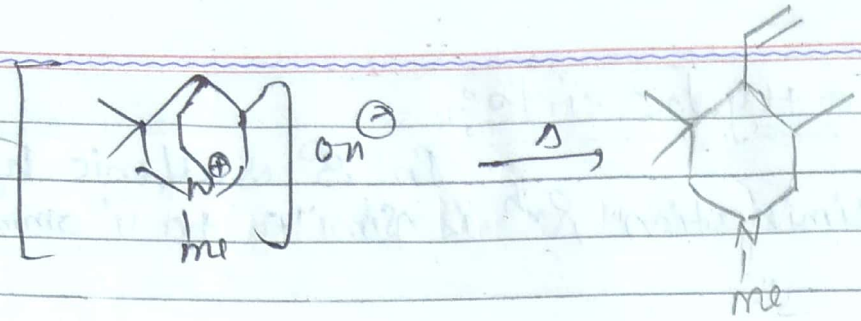
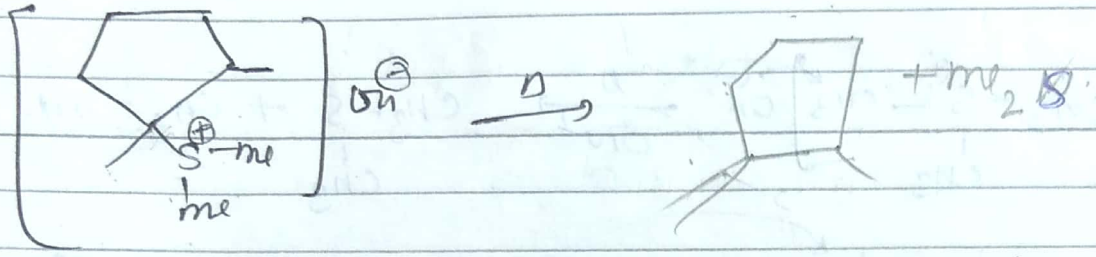
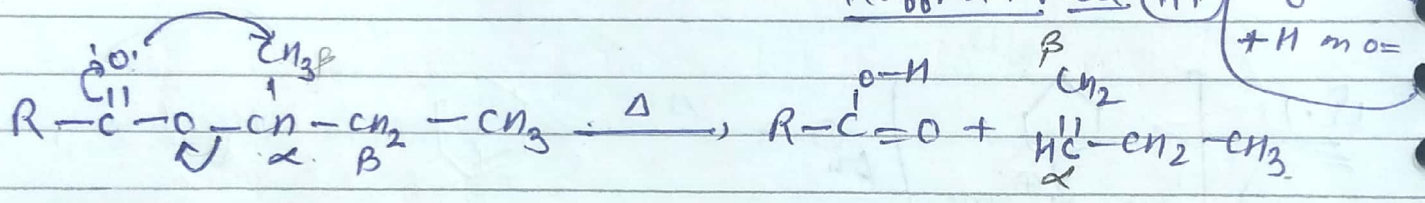


(6)



Pyrrolytic elimination in ester having β-Hydrogen:

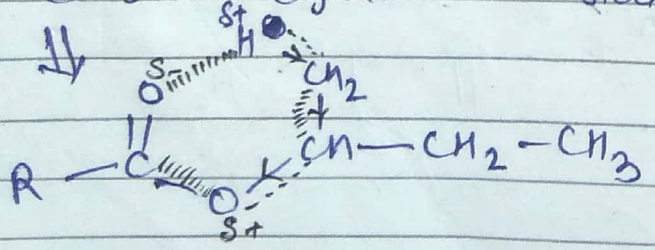
Hoffman Rule (HR)



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 Hoffmann Rule

Mech^{n}:

This Rx^{n} occur by formation of 6 member cyclic Transition state



6 M-CTS

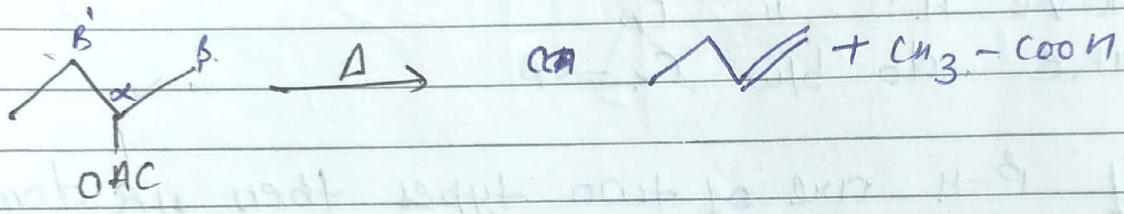
Syn elimination

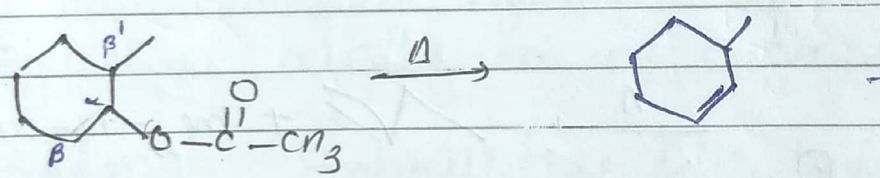
TTMP (Trioxo to make Product) (formation)

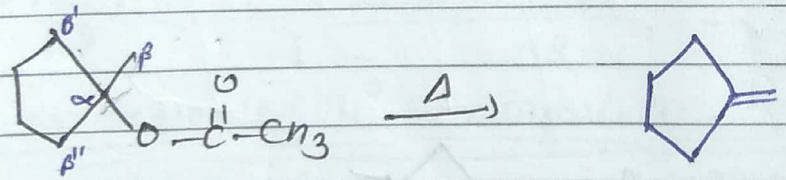
- Remove $R-COO^{\ominus}$ from C_α.
  Remove $H^{\oplus}$ " C_β.
  make db b/w $C_\alpha - C_\beta$

- If β-H are of 4°, 3° type then H R dominate.

Qu:

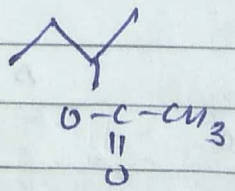
(1) 

(2) 

(3) 

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

$CH_3-COO^{\ominus}Ag^{\oplus}$
silver salt of Acid
(silver acetate)



(5) $Cl-CH_2-CH_2-CH_2-CH_2-Cl$

$\downarrow CH_3-COOAg$ (xs)

(A) $CH_3-COO-\overset{\alpha}{CH_2}-\overset{\beta}{CH_2}-\overset{\beta}{CH_2}-\overset{\alpha}{CH_2}-O-\overset{O}{\overset{\|}{C}}-CH_3$

$\downarrow \Delta$

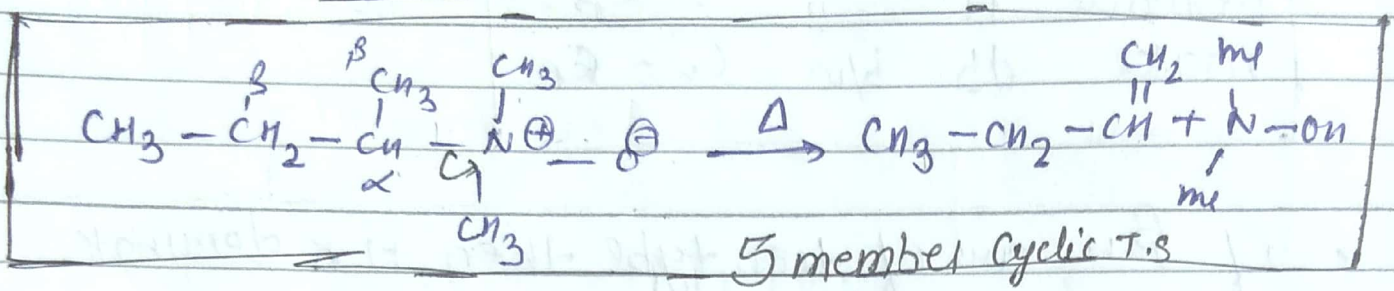
(B) + (C) $H_2C=CH-CH=CH_2$ + $2\,CH_3-COOH$.

Acid.

* Pyrolytic Elimination on 3° - Amine Oxide :

OR

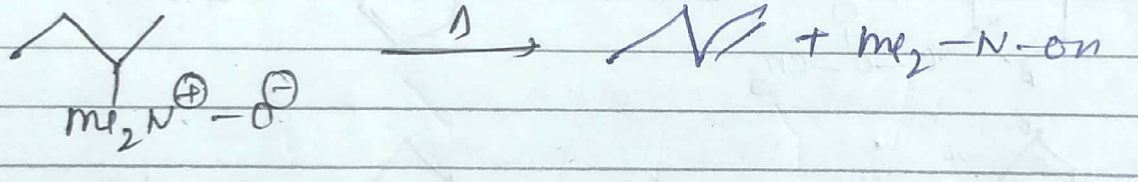
(Cope - Elimination)



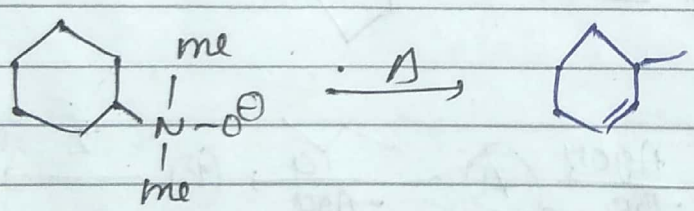
- + THP
  Remove $N^{\oplus}$ from C_α
  Remove H^+ " C_β
  make db b/w $C_\alpha - C_\beta$

- If $^\beta$-H are of two types then HR dominate.

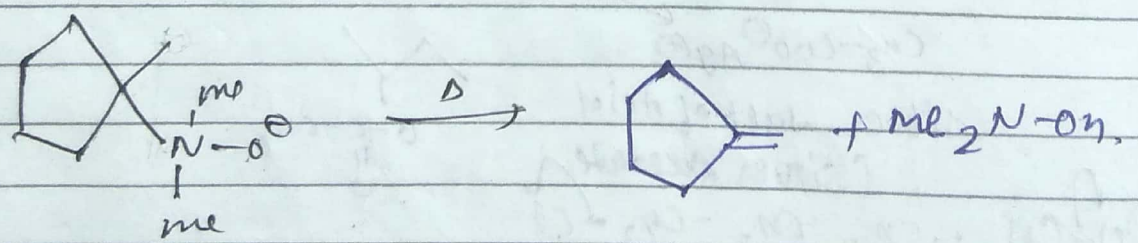
Qu:



(ii)



(iii)



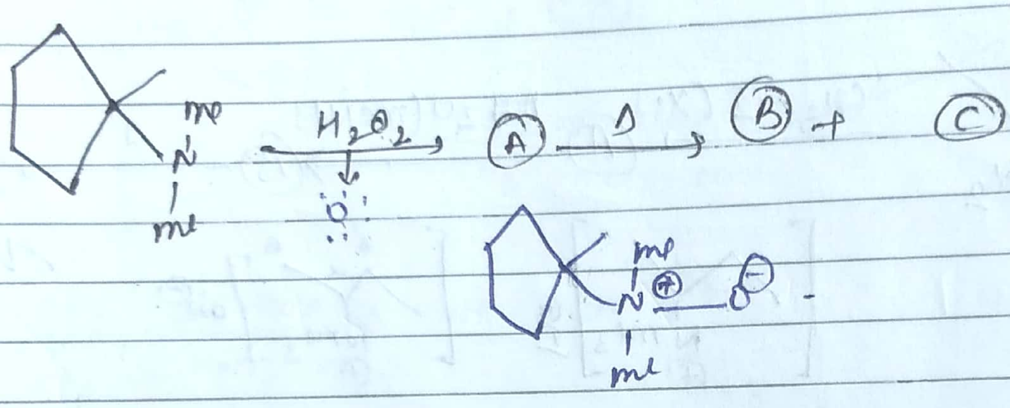
Not

Halfman

Note: 3° Ammine oxide can be prepared by Rx^n of 3° Ammine with H_2O_2 or Ag_2O or CH_2/Ag

$$R_3N: \xrightarrow[\ddot{O}: + H_2O]{H_2O_2} R_3\overset{\oplus}{N}-\overset{\ominus}{N}$$

Q.



* 4° Amino Amonium Hydroxide can be prepared by Exastive alkilation of amines or Amonium.

* Haffman Exhaustive Alkylation of NH_3:

OR.

Formation of 4°- Ammonium hydride:

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

4°- Ammonium halide

* $H_3N: + \overset{\delta+}{R}-\overset{\delta-}{X} \rightarrow [H-\overset{H}{\underset{H}{N}}{}^{\oplus}-R]X^{\ominus} \xrightarrow{-HX} R-\ddot{N}H_2 \xrightarrow[-HX]{R-X}$

1° Amine

$R-\ddot{N}H-R \xrightarrow{R-X}$ $\xrightarrow[-HX]{R-X}$ $R_3\ddot{N} \xrightarrow{R-X} [R-\overset{R}{\underset{R}{N}}{}^{\oplus}-R]X^{\ominus}$

2° Amine, 2° Amine, 3° amine

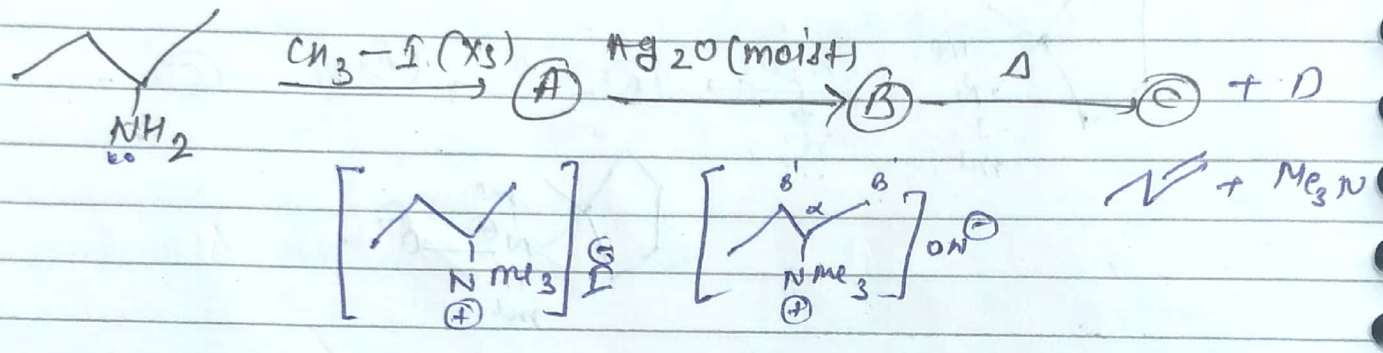
$H_3N: + R-H \Rightarrow$ Remove H and Br. and make $R-\overset{R}{\underset{R}{\overset{|}{N}}}-R$

$$\left[R-\overset{R}{\underset{R}{\overset{|}{N}}}-R\right]X^{\ominus} \xrightarrow[Ag_2O]{moist} \left[R_4N^{\oplus}\right]OH^{\ominus} + AgX$$

* Key point ⇒

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

Q.



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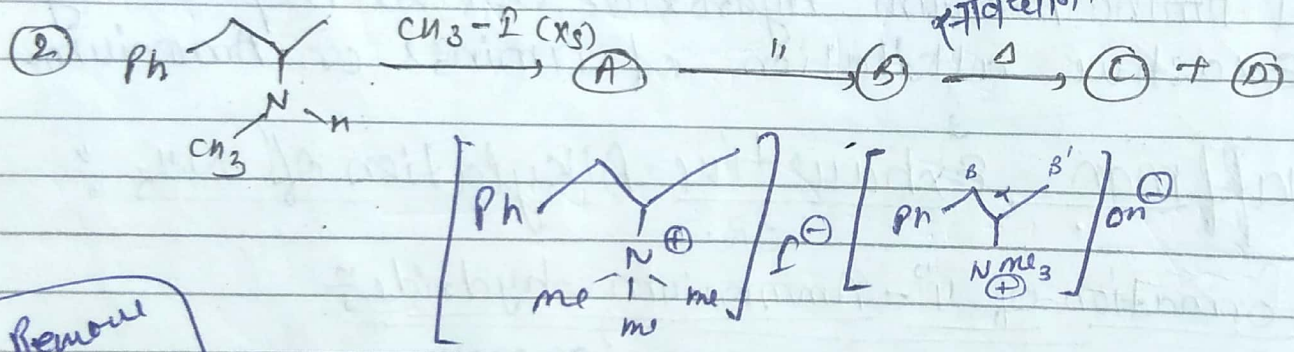


Remove H. Resonance bond make Conjugation

Saytzeff

During elimination Rx^n if one side β carbon gives Conjugated compound and other side not then always Rx^n occur in such a way by which Conjugated comp. form.

No Rule follow

Hw ⇒ 2:00 —
H.W: Rau: 14 ex: 10

* Double elimination Rxn:

$CH_3-CH(Cl)-Cl$ —alc. KOH/Δ, −HOH, −KCl→ $H_2C=C(Cl)-H$ —NaOH, −NaCl, −H_2O; KOH (s)/Δ −KCl, −OH; $NaNH_2$/Δ −NaCl, −NH_3; KNH_2/Δ −KCl, −NH_3→ $H-C\equiv C-H$

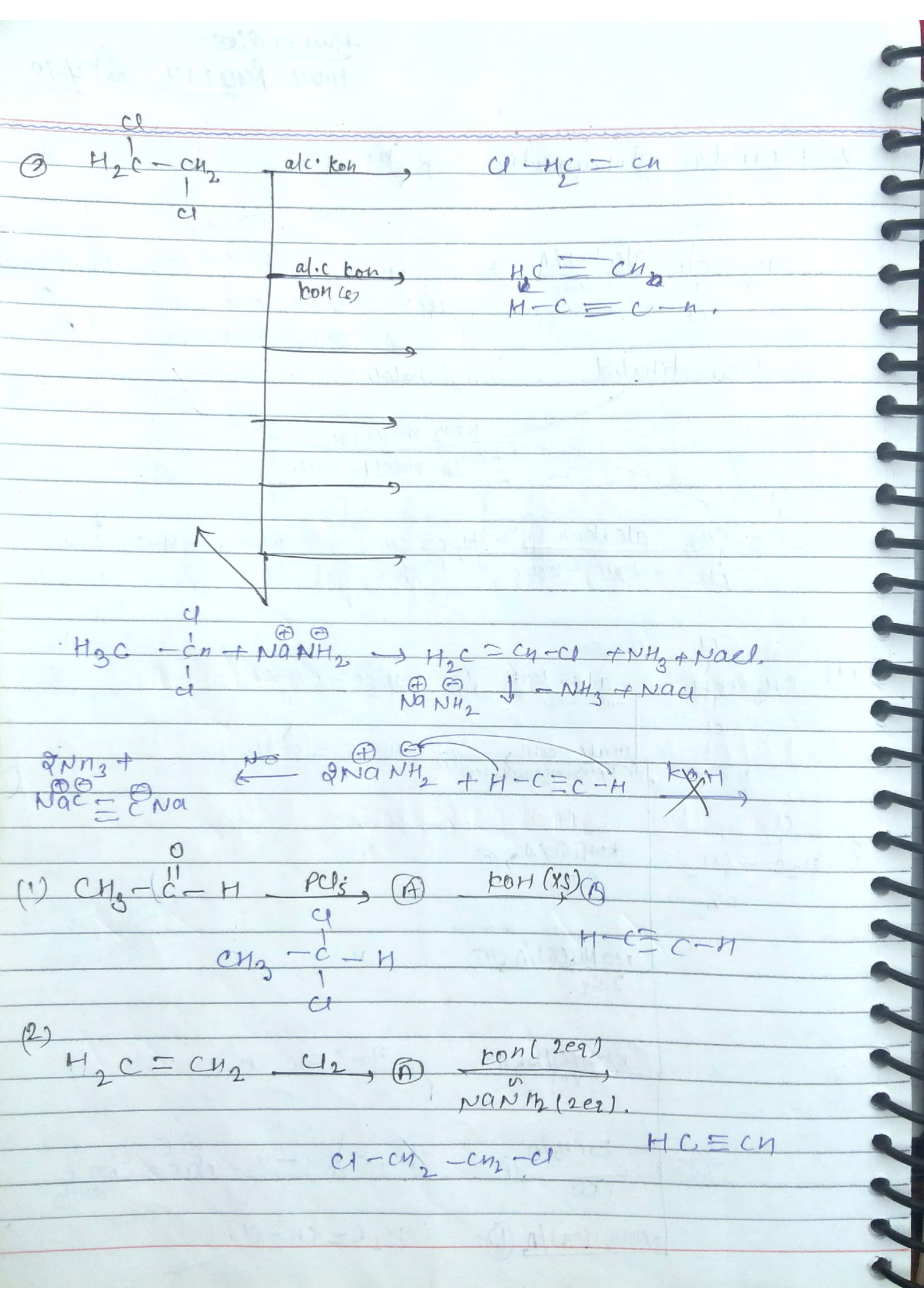
Gem-dihalid — Vinyl halide

(direct: KNH_2 or $NaNH_2$, −NH_3, −KCl / −NaCl.)

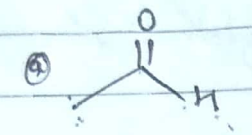
$H_2C(Cl)-CH_2(Cl)$ —alc. KOH, −HOH, −KCl→ $H_2C=CH(Cl)$ —"→ $H-C\equiv C-H$

(1) $CH_3-CH(Cl)(Cl)$ or (2) $H_2C(Cl)-CH_2(Cl)$

- —alc. KOH, −HOH −KCl→ (A) $H_2C=CH-Cl$
- —(i) alc. KOH (ii) KOH(s) or $NaNH_2$(1eq)→ (B) $H-C\equiv C-H$.
- —KOH(S)/Δ, 2eq→ (C) "
- —$NaNH_2$(S)/Δ, 2eq→ (D) "
- —KOH(S)/Δ, (XS)→ (E) $H-C\equiv C-H$
- ☆ —$NaNH_2$/Δ, (XS)→ (F) H–C≢C–H (crossed out) $Na^{\oplus}\,{}^{\ominus}C\equiv C^{\ominus}Na^{\oplus}$ + $2NH_3$
- —$NaNH_2$(1eq)/Δ→ (G) $H_2C=CH-Cl$.


(3)
alc. KOH
alc. KOH
KOH (s)
NaNH2
NaNH2
NaNH2 (2eq)

Q3 Convert



$\xrightarrow{(A)}$ $H-C\equiv C-H$

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

(4) $CH_3-\underset{\underset{Cl}{|}}{\overset{Cl}{\overset{|}{C}}}-H \xrightarrow[xs]{NaNH_2} (A) \xrightarrow[xs]{CH_3-I} (B)$ $CH_3-C\equiv C-CH_3 + 2NaI$

$Na^{\oplus}\,C^{\ominus}\equiv C^{\ominus}\,Na^{\oplus}$

(5) Convert

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

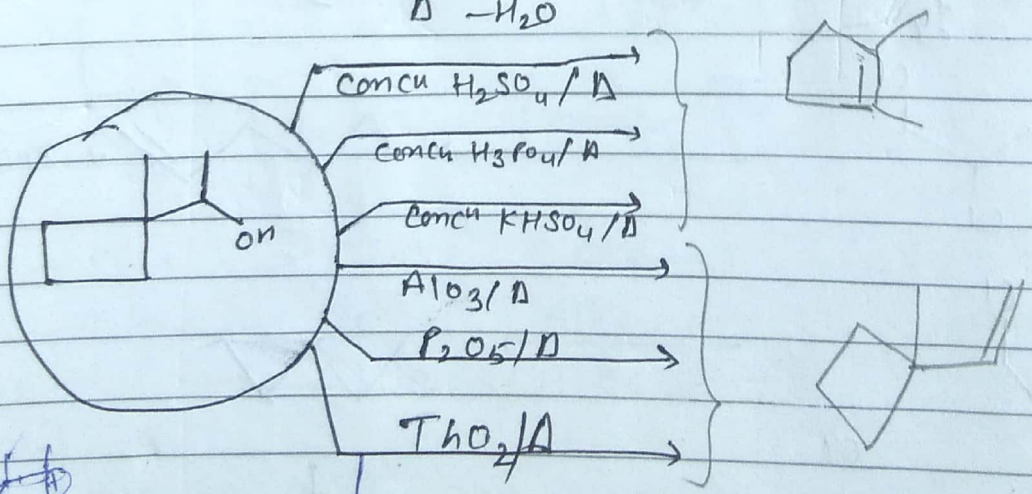
* Dehydration Rxn :-

$-\underset{|}{\overset{H}{C}}-\underset{|}{\overset{OH}{C}}- \xrightarrow[\text{or } P_2O_5 \text{ or } SOCl_2 \,(E2)]{\text{Conc}^n\ H_2SO_4 \text{ or } H_3PO_4 \text{ or } KHSO_4\,(E1)} -\underset{|}{C}=\underset{|}{C}-$

$ThO_2.\ (E_{1cB})$

$\Delta\ -H_2O$

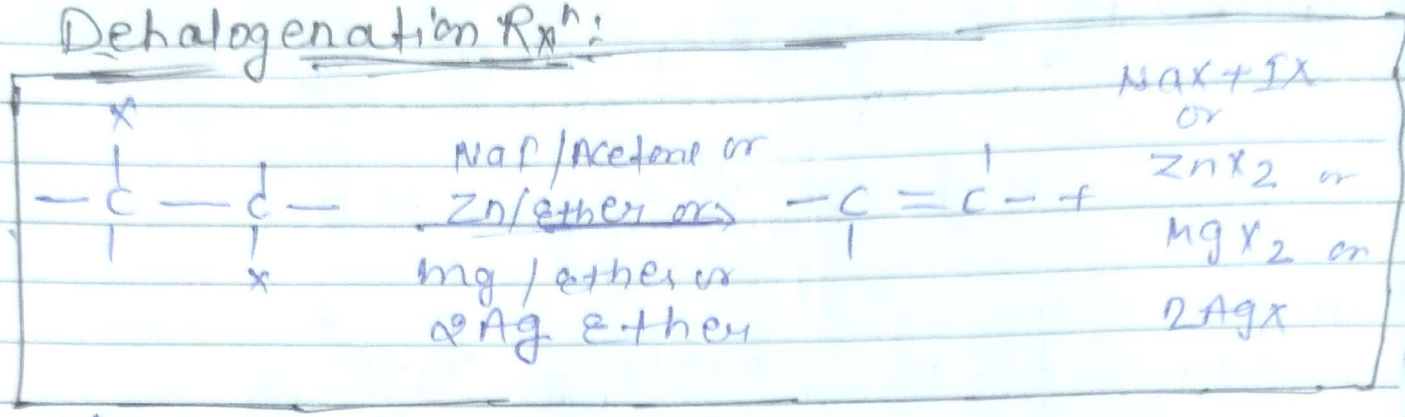
Q.



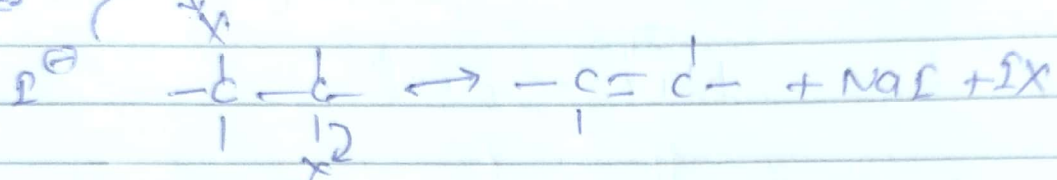
F

Rearrangement Not occur

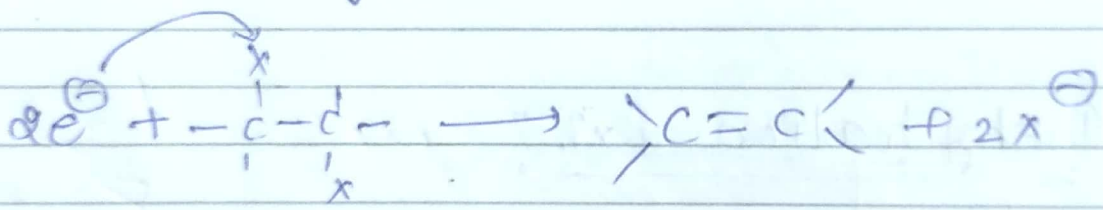
* Dehalogenation Rxn:



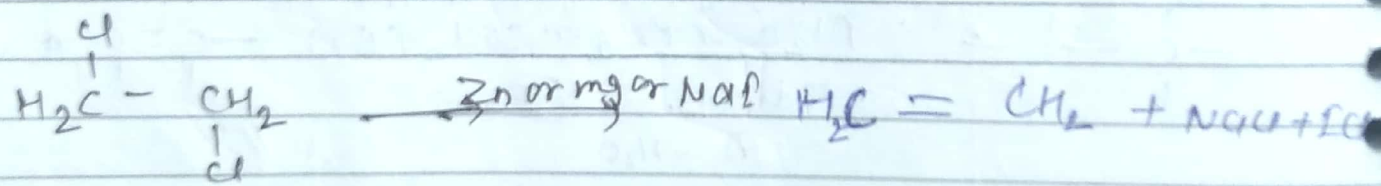
Mechⁿ



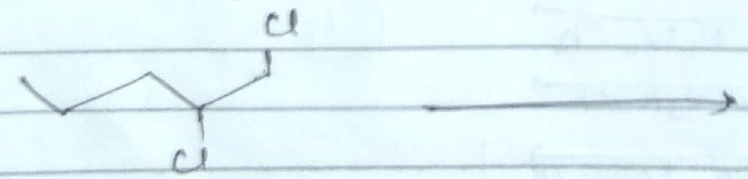
(1) with Zn/Mg/2Ag ($Zn \rightarrow Zn^{++} + 2e^{\ominus}$)



Q.1



(2)



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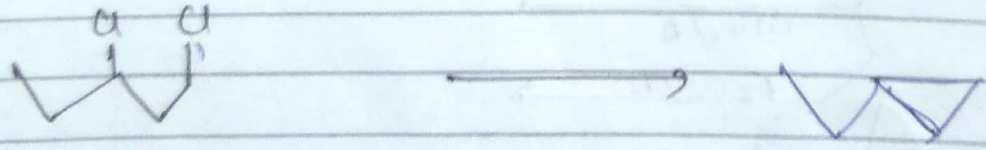

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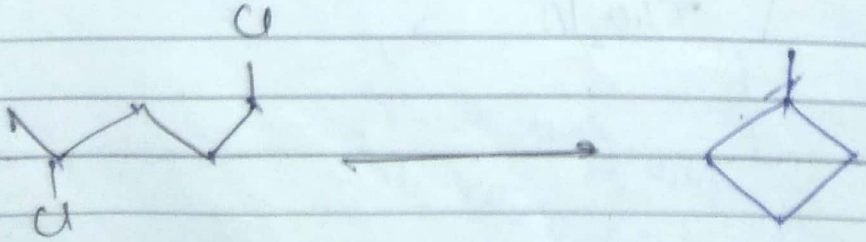
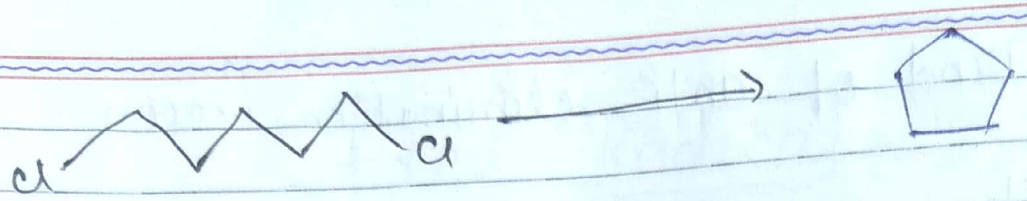
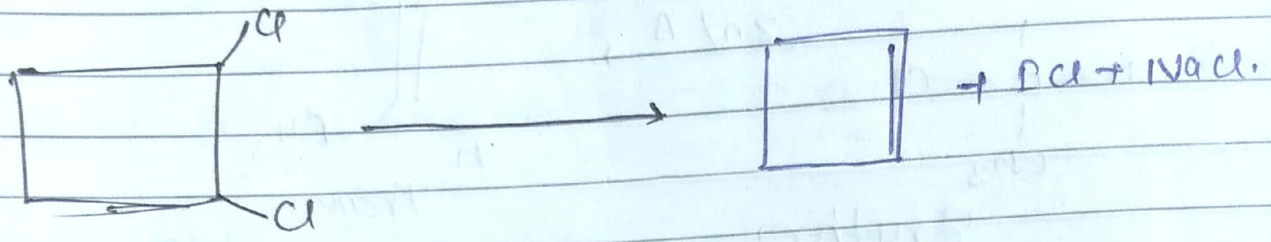
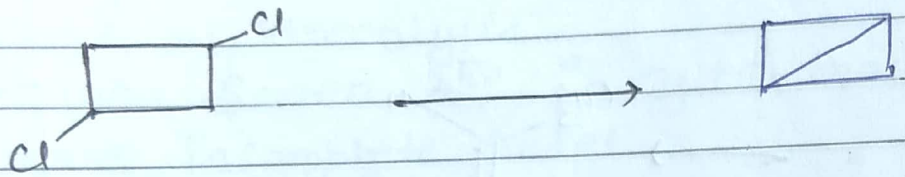


1,1 → Dimer.

(5) 

(6) 

(7) 

(8) $Cl-CH_2-CH_2-Cl \xrightarrow{Zn/\text{ether}/\Delta} CH_2=CH_2 + ZnCl_2$

(9) $CH_3-CH(Cl)_2 \xrightarrow{Ag/\Delta} CH_3-\dot{C}H \rightarrow CH_3-C\equiv CH$

$CH_3-\ddot{C}H \quad CH_3-CH$

$CH_3-CH=CH-CH_3$

(10) $CH_3-C(Cl)_2-Cl \xrightarrow{Ag/\Delta} CH_3-C\equiv C-CH_3$

$CH_3-\dot{C}: \quad :\dot{C}-CH_3$

* 1,1-DH → Dimer (Alkene)

* 1,1-TH → " (Alkyne)

1,2- → Alkene/Alkene

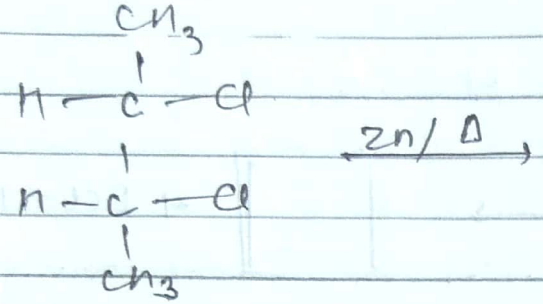
1,3-, 1,4-, 1,5-, 1,6- DH → cyclic compound

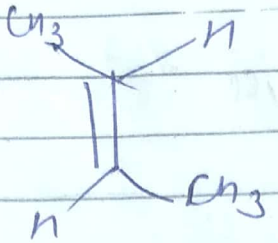
1,7 → Polymer

1,n →

* It is a kind of anti elimination process

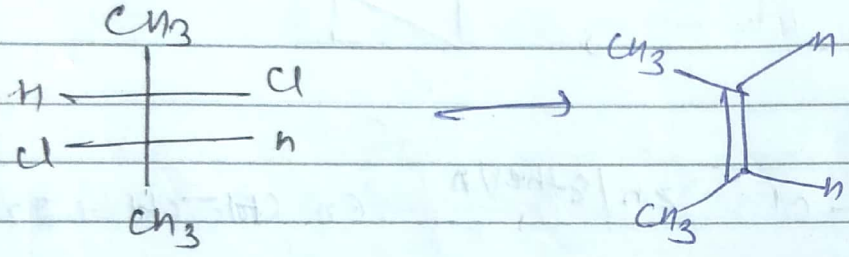
Q.

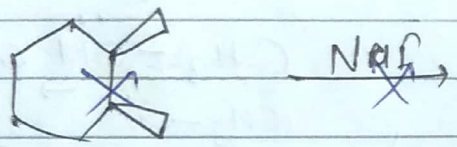


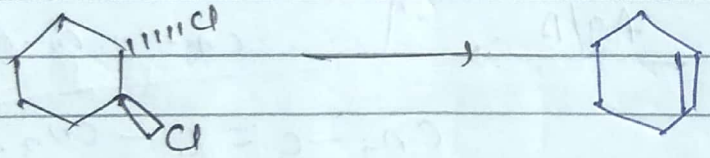


Trans

Erythro







H.W Ex :- 2 :- 1 to 16. # 11

* Free - Radical *

$\dot{C}H_3$ (sp^2) $CH_3-\dot{C}H_2$ (sp^2) $H_2C=\dot{C}H$ (sp^2) $\dot{N}a$ $\dot{K}$, 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
* TGP (Trigonal Planar (when sp^2 hybridised)).
* have one unhybridised p-orbital with one unpair $e^{\ominus}$ lie ⊥ to sigma bond.

* Rx^n's involving free Radicals :

(1) Kolbe's Electrolysis :

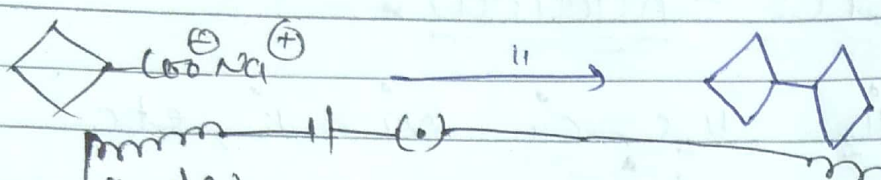
(Sod./Pot. of C.A) $\xrightarrow{\text{Electrolysis}}$ $\underbrace{HC + CO_2}_{\text{At anode}} + \underbrace{NaOH + H_2(\uparrow)}_{\text{At cathode}}$

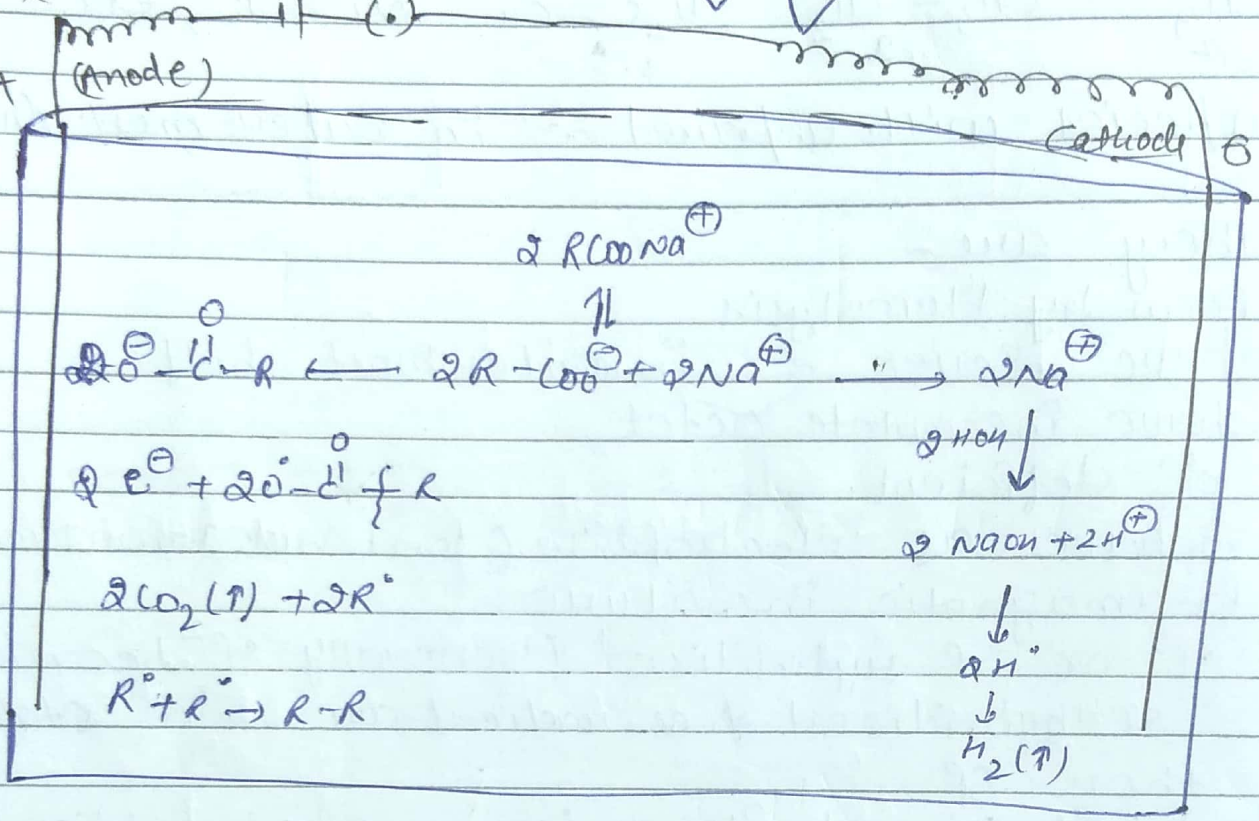
$2R-COO^{\ominus}Na \xrightarrow{\text{Electrolysis}} R-R + 2CO_2(\uparrow) + 2NaOH + H_2(\uparrow)$.

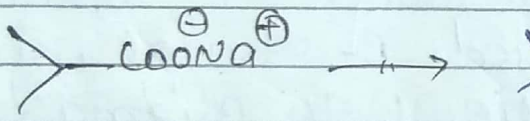
① $CH_3-COO^{\ominus}Na^{\oplus} \xrightarrow{H_2O}$ $CH_3-CH_3 + H_2 + H_2 + H_2$

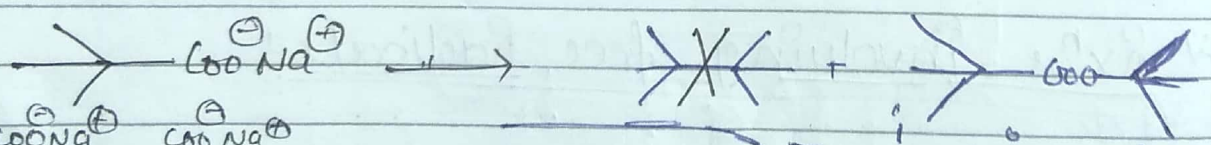
(4) $Ph-COO^{\ominus}Na^{\oplus}$ ⟶ $Ph-Ph$ + ...

2 $CH_3-CH_2-COO^{\ominus}Na^{\oplus}$ ⟶ $CH_3-CH_2-CH_2-CH_3$ + ... + ... + ...

3 

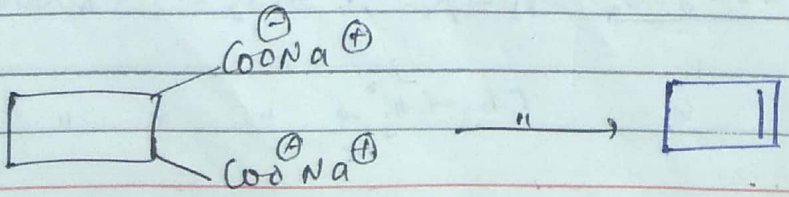


(5) 

(6) 

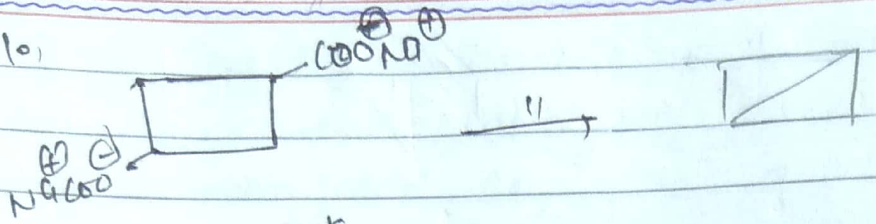
(7) H_2C-CH_2 ⟶ $H_2C=CH_2$ + ...

(8) $H_2C=CH_2$ ⟶ $CH_2=CH$

(9) 

1.7 Polymer

(10)



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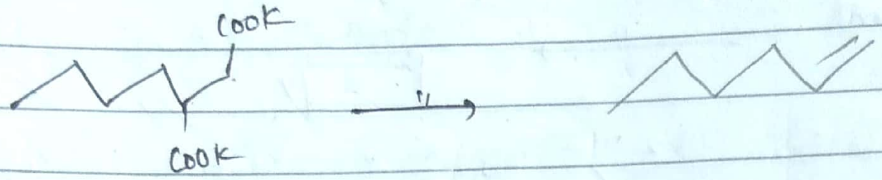

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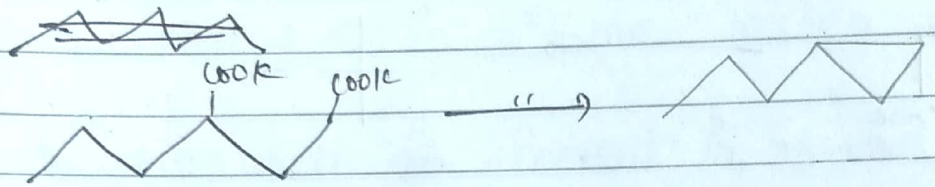

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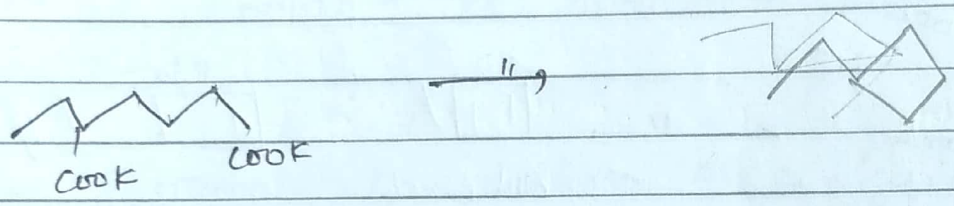

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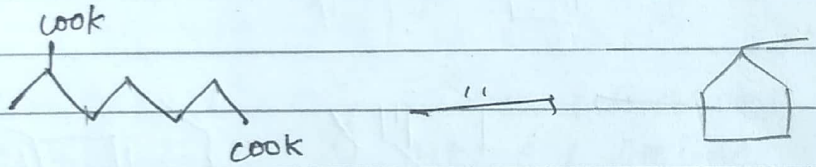

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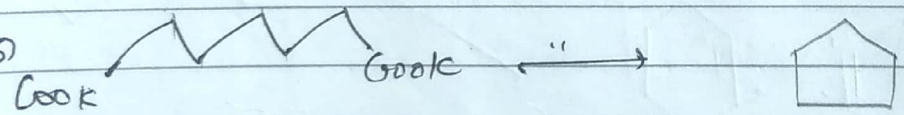

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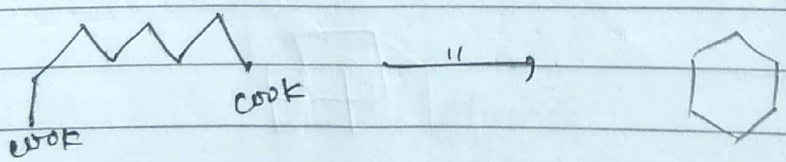

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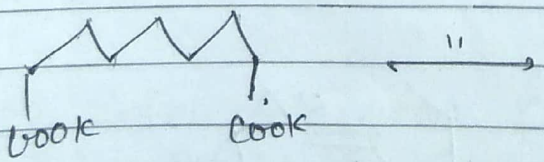
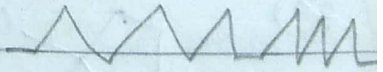
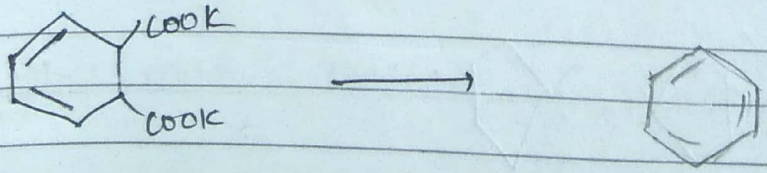


Polymer

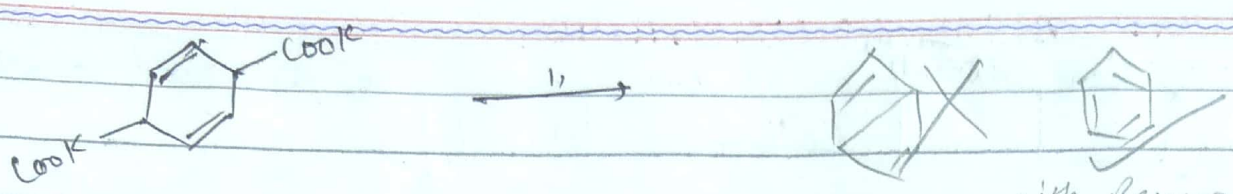


(18)



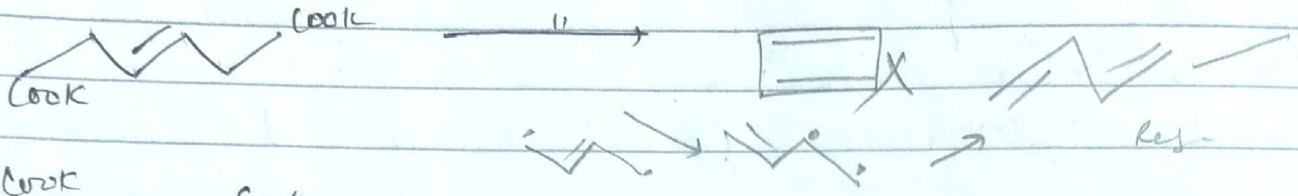
8 membered → 3 Bond.

(19)



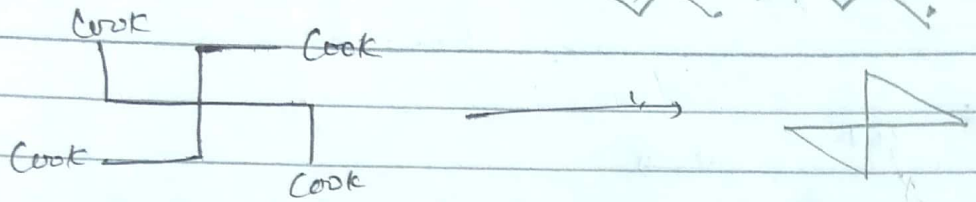
with Resonance.

(20)



Res-

(21)



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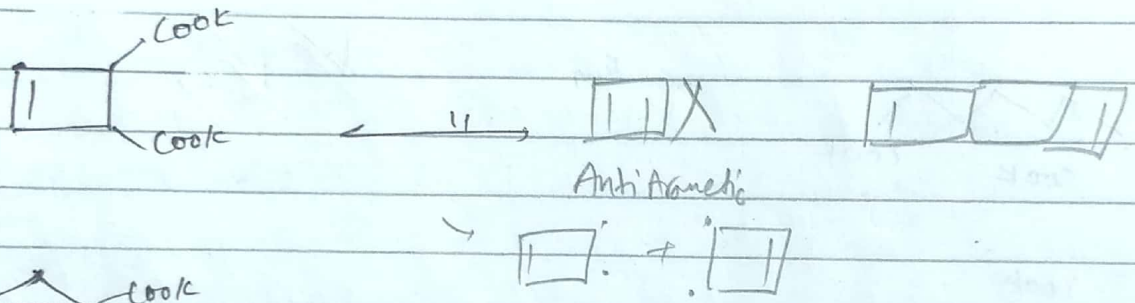
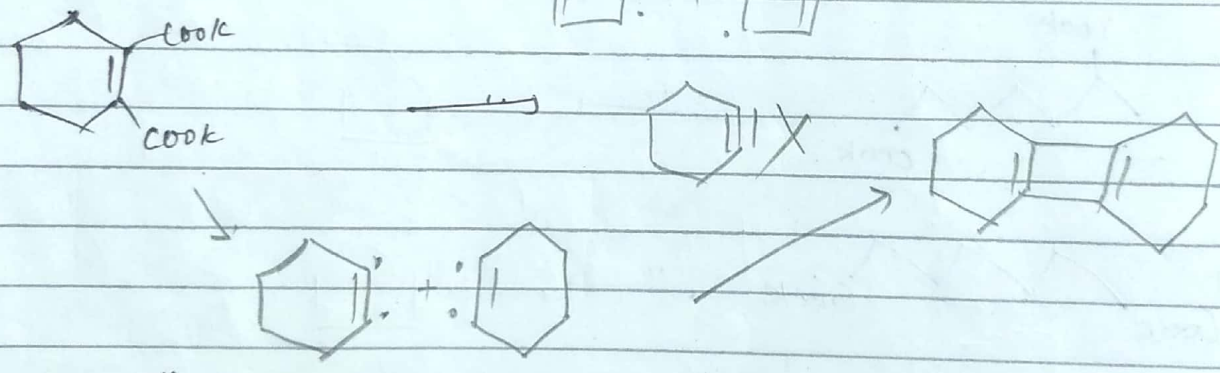


Anti Aromatic

(23)



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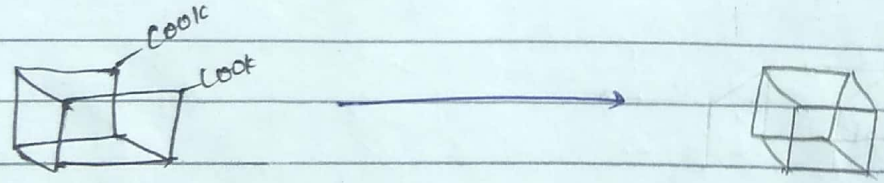

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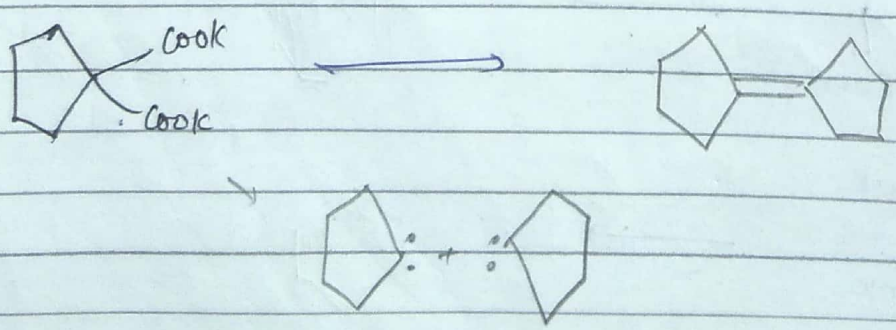


* Key Points :- When aquas sodium and Pot. salt of acid is electrolysed then we get alkane (Hydrocarbon) and CO_2 gas anode and NaOH + H_2(gas) at Cathode

* 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 → Dimer (Alkene)
  1,2 - Disalt → Alkene / Alkyne.
  1,3 - , 1,4 - , 1,5 - , 1,6 - } " → Cyclic Compound.
  1,7 , 1,n } " → Polymer.

* By Intermolecular Kolbe's electrolysis symmetrical alkene with even carbon can be prepare.

* By this method methane can not form.

Remove H Cathode

1 cor Formic (anode and cathode Remove H)

Q. which of the following alkane can be prepared by Colbe's electrolysis effectively

(i) methane CH_4 ✗

(ii) C—C ✗ ✓ — mid cut: For (sym) formic

(iii) C—C—C ✗

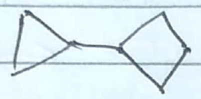
(iv) C—C—C—C ✓

(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 KE

(11) $CH_3-COO^{\ominus}K^{\oplus}$ $\quad$ $CH_3-CH_2-COO^{\ominus}K^{\oplus}$ $\longrightarrow$ $CH_3-CH_2-CH_3$ + CH_3-CH_3 + C—C—C—C

$\dot{C}H_3$ $\quad$ $CH_3-\dot{C}H_2$

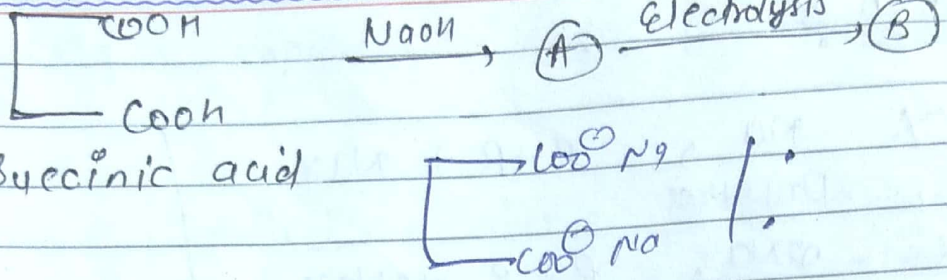
$\dot{C}H_3 + \dot{C}H_2CH_3$
$\dot{C}H_3 + \dot{C}H_3$ $\quad$ $Et^{\circ} + Et^{\circ}$

★ **Cross K E :** The KE in which both salt are different is known as Cross KE.

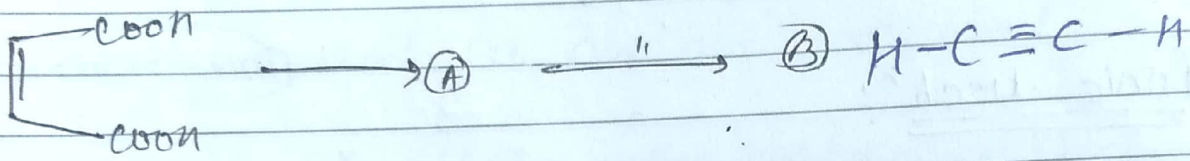
★★ Q8) $H-COO^{\ominus}K^{\oplus}$ $\longrightarrow$ $H_2(\uparrow) + CO_2(\uparrow)$ (A) + $KOH + H_2O$ (C)

$\downarrow$ $H^{\oplus}$

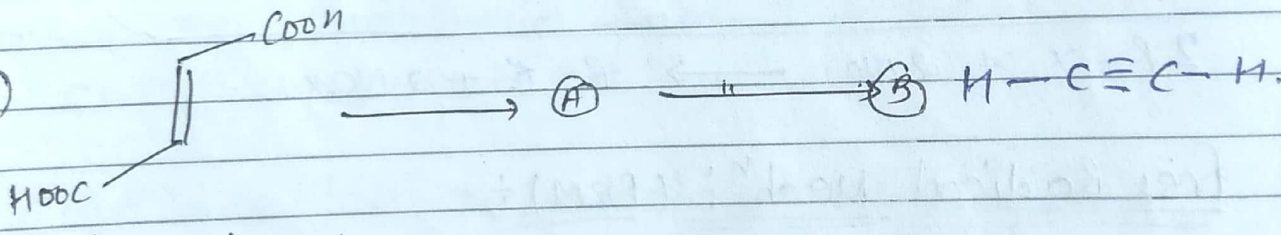
* Salt of formic Acid (Sod. or Pota. formate) give H(gas) on both electrode.

(29) 

Succinic acid

(30) 

Maleic acid

(31) 

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.

(1) Rx – 2 NaX

(1) Ionic Mechⁿ :

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

Nucleophile (carbanion RI)

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

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

(2) free Radical Mechⁿ : (FRM) :

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

$$R^{\bullet} + R^{\bullet} \longrightarrow R-R$$

* 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 Rxn is known as IMWR (Intramolecular wurtz Rxn)

* In IMWR Product is either alkene or alkyne or cyclic compounds. By ~~Intra~~ Inter molecular wurtz Rxn Alkane with even carbon and symetrical 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 Rxn is known as CWR (cross wurtz Rxn).

* CWR are less important for us.

* If alkyl halide is 3° alkyl halide then in the Place of combination Rxn disproportation Rxn occur and we get alkane + alkene.

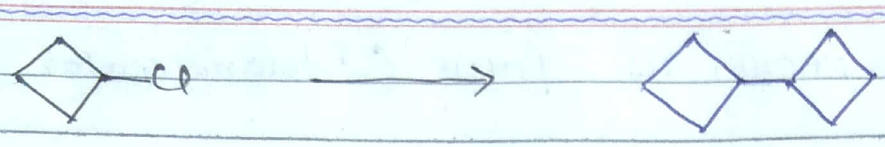
* Solvent for this Rxn should be dry ether or dry PAS (Polar aprotic Saluant).

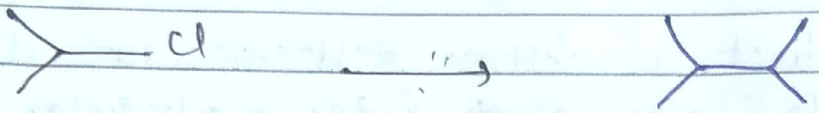
Q.1) $2CH_3 + Cl \xrightarrow[\text{Dry ether}]{Na} CH_3 - CH_3$

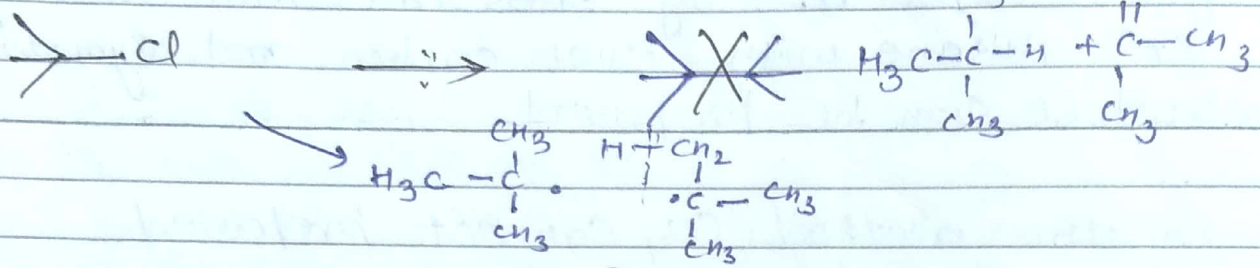
$\rightarrow 2CH_3^{\bullet} + 2NaCl$

(2) $CH_3 - CH_2 + Cl \longrightarrow CH_3 - CH_2 - CH_2 - CH_3$

2 same → 2 diff. comb., called disproportionation

(3) 

(4) 

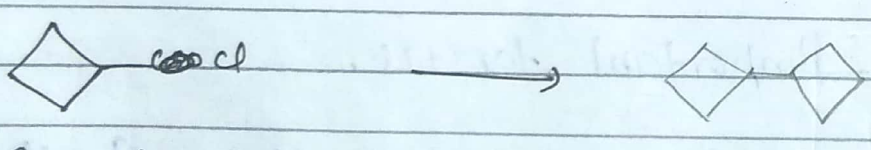
(5) 

(6) $CH_2(Cl)-CH_2(Cl) \longrightarrow CH_2=CH_2$

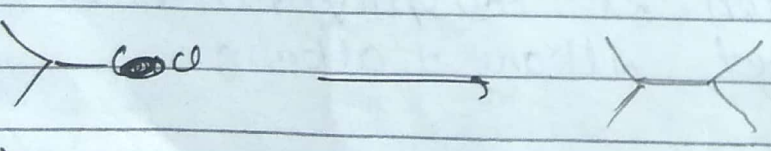
* ~~3° alkyl~~ Q. 7, 8 ---- 26.

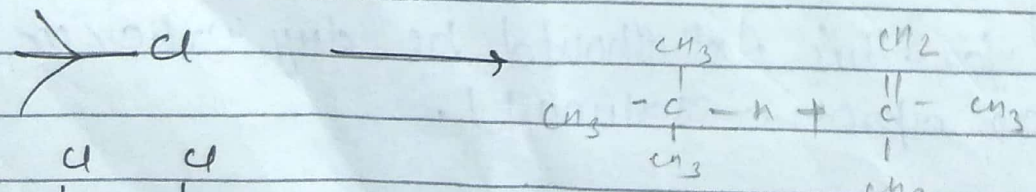
Q. 7 $CH_3-Cl \longrightarrow$

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

(9) 

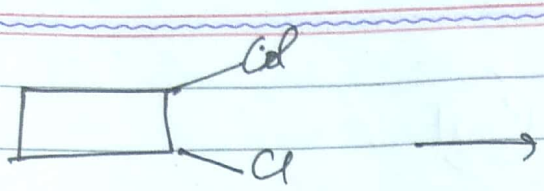
(10) $Ph-Cl \longrightarrow Ph-Ph$

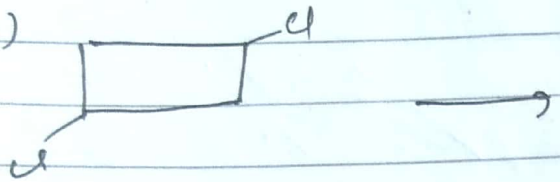
(11) 

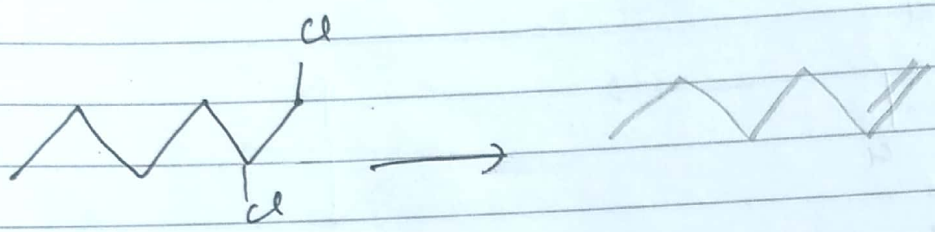
(12) 

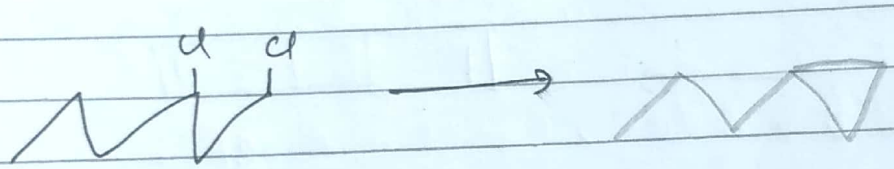
(13) $H_2C(Cl)-CH_2(Cl) \longrightarrow CH_2=CH_2$

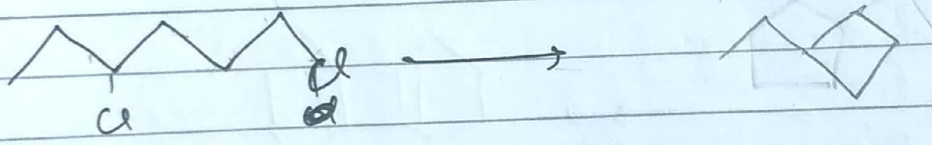
(14) $H_2C(Cl)=CH_2(Cl) \longrightarrow CH \equiv CH$

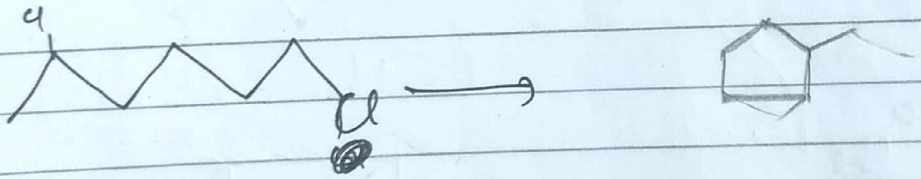
15) 

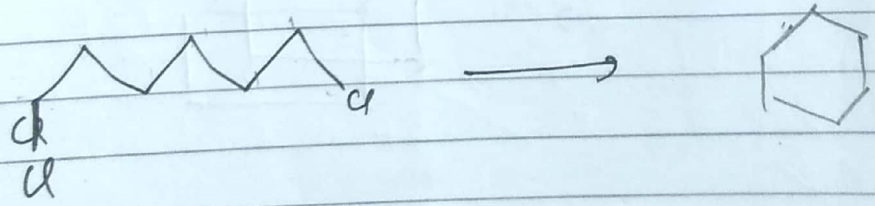
16) 

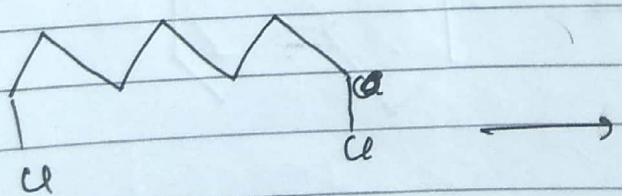
17) 

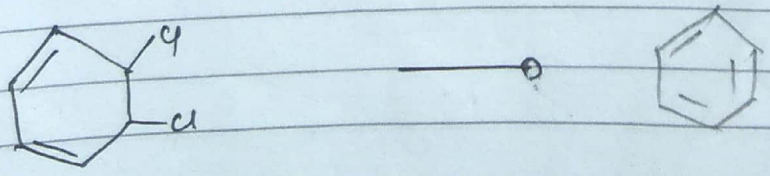
18) 

19) 

20) 

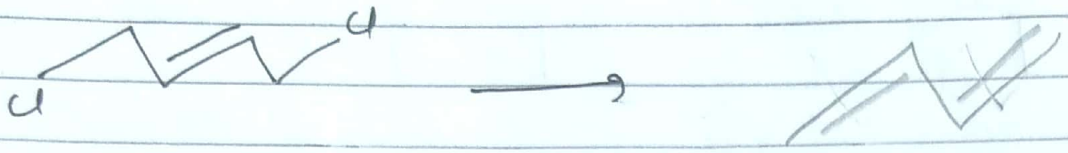
21) 

22) 
Polymers.

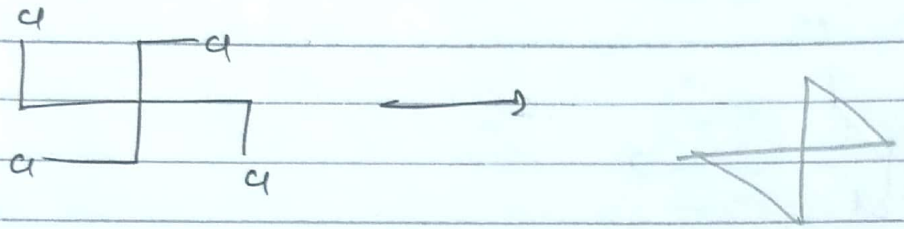
23) 

(24)

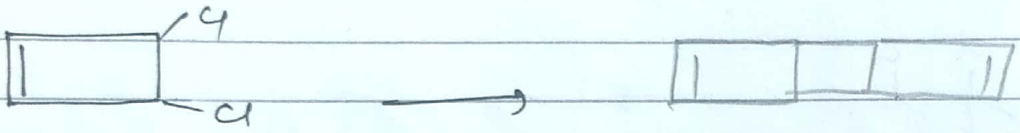
(25)



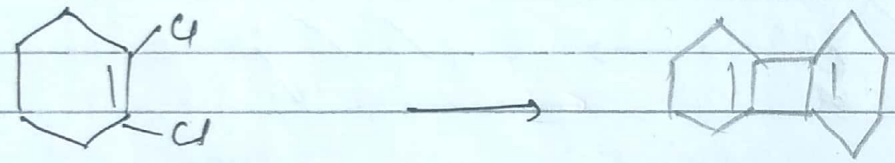
(26)



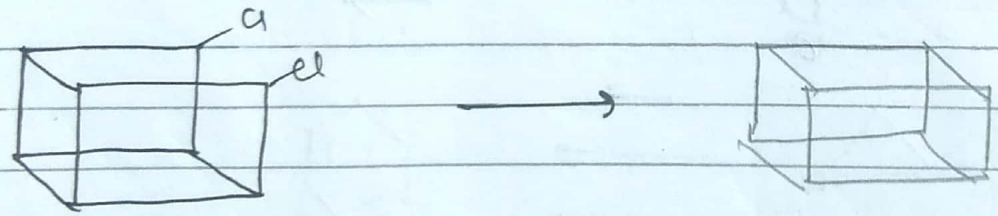
(27)



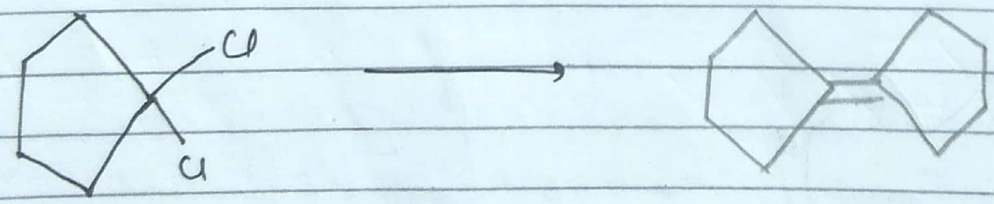
(28)



(29)



(30)



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

$$R-I > R-Br > R-Cl > R-F$$

Q.28

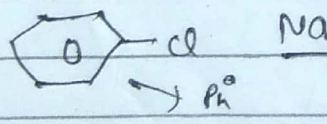
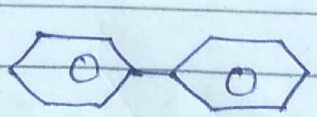
$CH_3-Cl \xrightarrow[Dry\ ether]{Cu\ or\ Ag} CH_3-CH_3 + CuCl/AgCl$ (Ullmann Rxn).

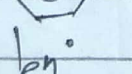
(2e) (2:1)

(2°) $CH_3-Cl \xrightarrow[or\ Zn/Dry\ ether]{Mg/Dry\ ether} CH_3-CH_3 + MgCl_2/ZnCl_2$

2:1

(Frankland Reaction)

(3°)  $\xrightarrow{Na/Dry\ ether}$  (Fitting Rxn)

(3') $CH_3-Cl +  $ $\xrightarrow{Na/Dry\ ether}$ $Ph-CH_3 + CH_3-CH_3 + Ph-Ph$

CH_3° 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).

$$R-X \xrightarrow[1:1]{mg \text{ or } zn/ether} RMgX / RZnX$$
(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

Kharash-effect / Per-oxide effect :-

Markonic rule

$$H_3C-CH=CH_2 \xrightarrow{HBr} CH_3-\overset{Br}{\underset{|}{C}}H-CH_3$$

$$H_3C-CH=CH_2 \xrightarrow{H^+} CH_3-\overset{\oplus}{C}H-CH_3 \xrightarrow{Br^\ominus} CH_3-\overset{Br}{\underset{|}{C}}H-CH_3$$

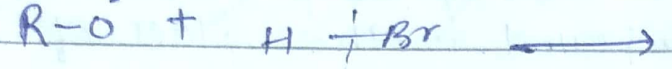
R.I (Carbocation)

* $CH_3-CH=CH_2 \xrightarrow{HBr/ROOR} CH_3-CH_2-\overset{Br}{\underset{|}{C}}H_2$ (anti markonic)

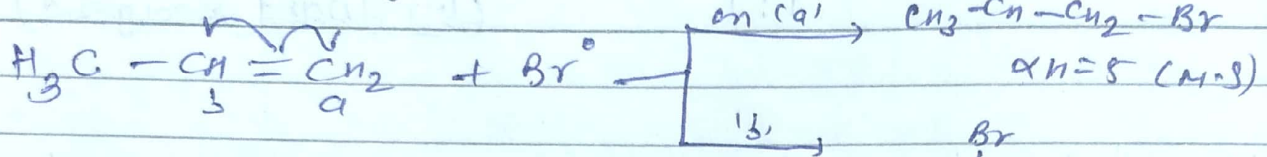
(Antimarkonic of Method)

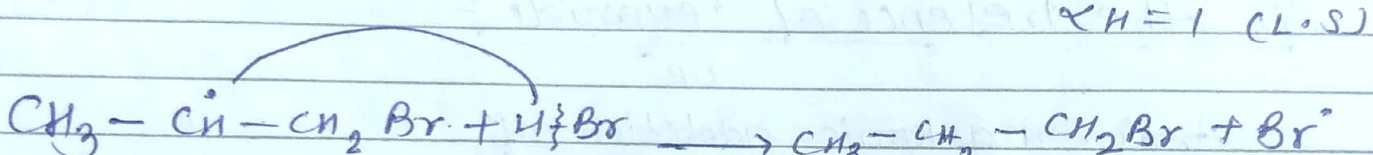
- Mech^m : F.R.M.
- Completed in 3 steps.

* Step: 1 (Chain Initiation Step)

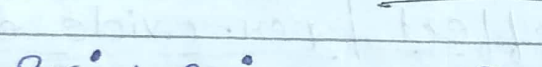


Step: 2 Chain Propogation Step.

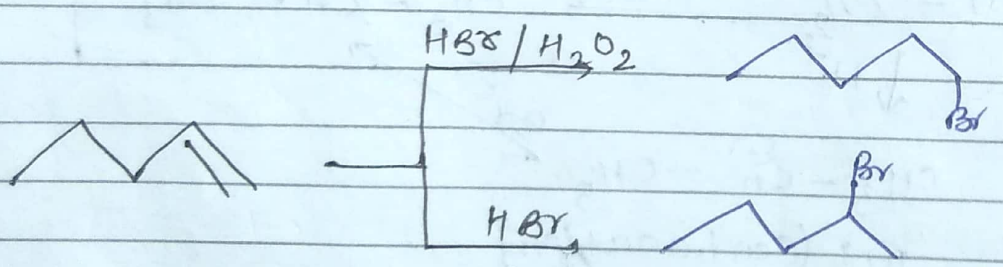




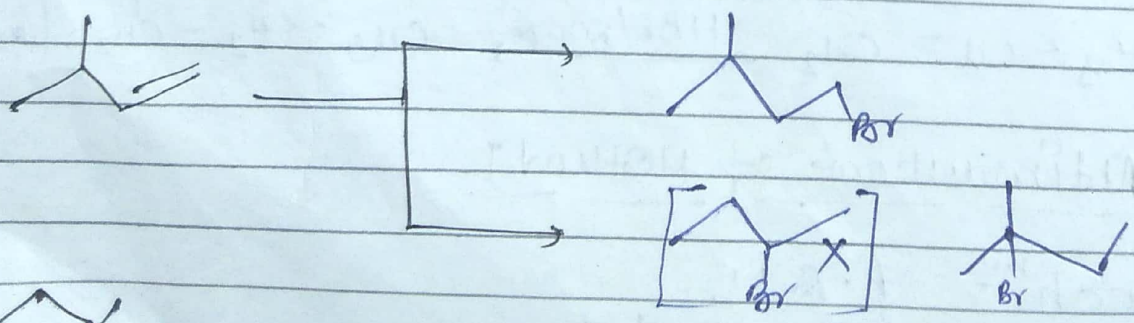
Step III: Chain Termination Step:



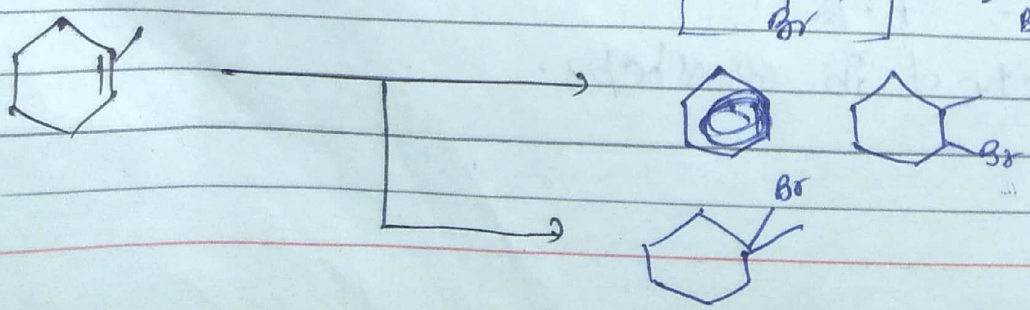
(1)



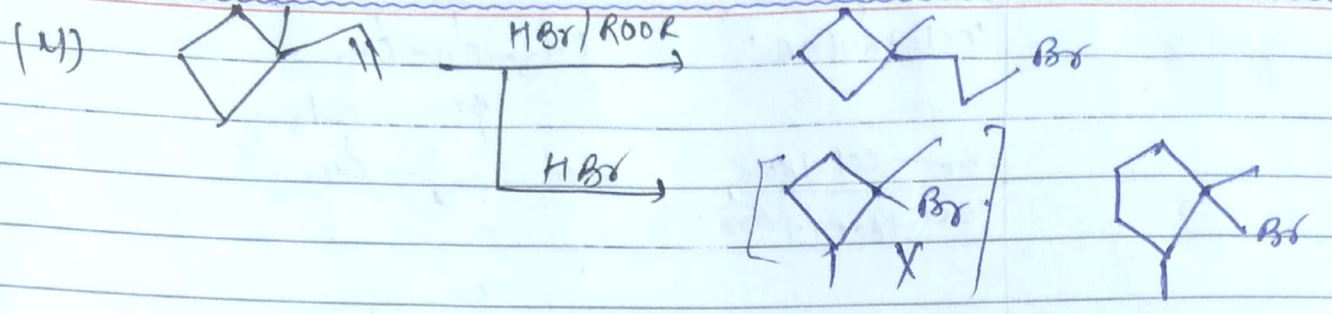
(2)



(3)



(4)



* 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 on addition of HF, HCl, HI. [But only on HBr]

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

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

[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.

$\xrightarrow{H-Br/ROOR}$ $CH_3-\overset{H}{\overset{|}{C}}H-\overset{Br}{C}H_2$

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

* $\underset{b}{CH_3-CH}=\underset{a}{CH_2}$

$\xrightarrow{H-CX_3/RO-OR}$ $CH_3-\overset{H}{\overset{|}{C}}H-\overset{CX_3}{C}H_2$

$^{\bullet}CX_3 + ROH + RO^{\bullet}$

I – CCl_3 / ROOR

$^{\cdot}CCl_3 + ROI + RO^{\cdot}$

$CH_3-CH(I)-CH_2-CCl_3$

Br – CCl_3 / ROOR

$^{\cdot}CCl_3 + ROBr + ROO$

$CH_3-CH(Br)-CH_2-CCl_3$

Cl – CCl_3 / ROOR

$^{\cdot}CCl_3 + ROCl + RO^{\cdot}$

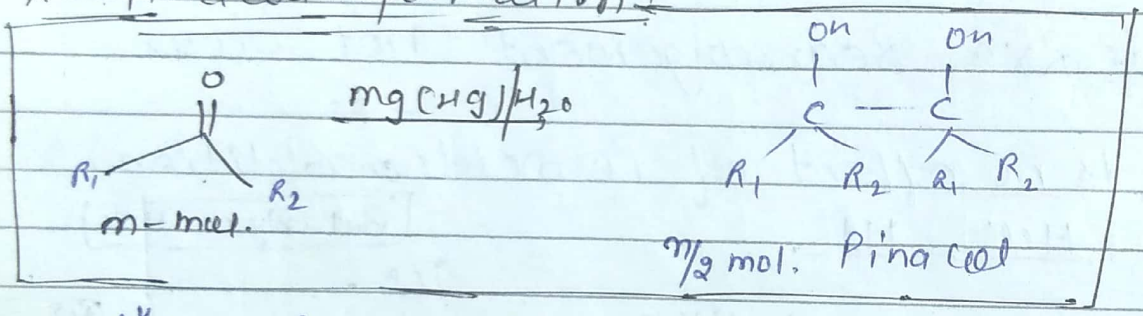
$CH_3-CH(Cl)-CH_2-CCl_3$

H – S – R / ROOR

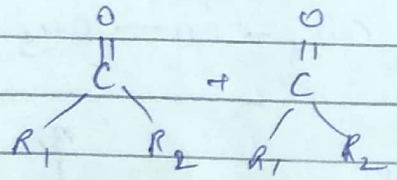
$R-S + ROH + RO^{\cdot}$

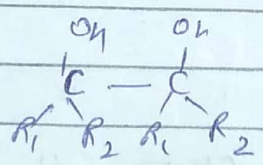
$CH_3-CH(H)-CH_2-SR$

* Pinacol formation :



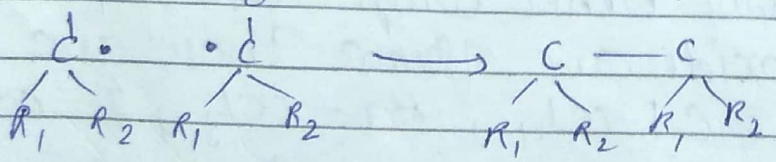
Mech^{n} :

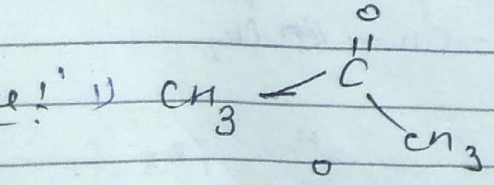


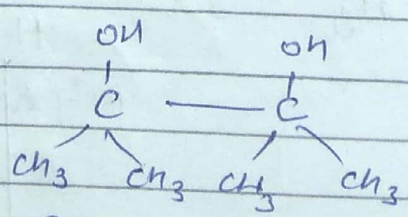


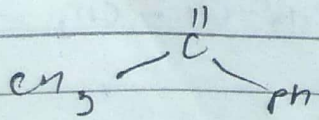
$Mg \rightarrow Mg^{++} + 2e^{\ominus}$

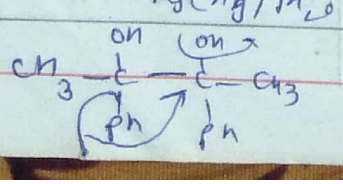
$2H-O-H : 2OH$

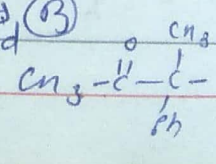


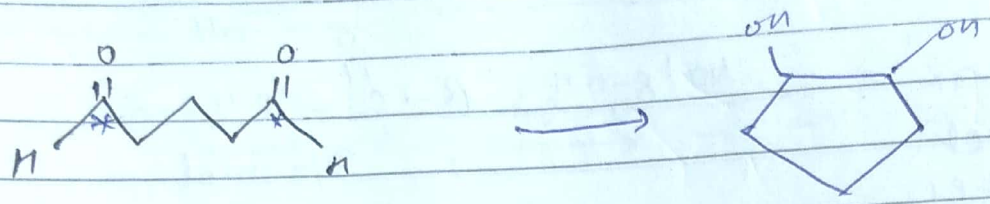
Que : 1) 

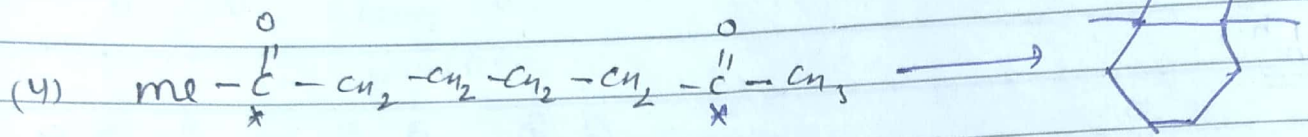
$\xrightarrow{Mg(Hg)/H_2O}$ 

2) 

$\xrightarrow{Mg(Hg)/H_2O}$ (A) 

$\xrightarrow{Dil\ Acid}$ (B) 

(3) 

(4) 

$\xrightarrow{Dil\ H_2SO_4}$

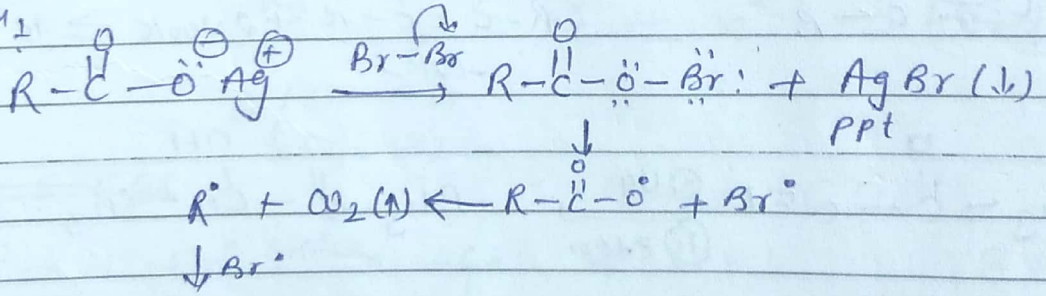
Out of Syllabus

~~Hund~~s Hunsdicker Reaction!

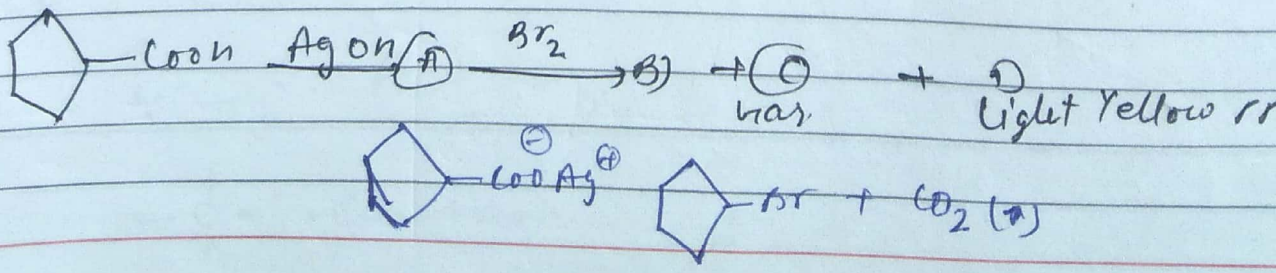
$$R-\overset{O}{\overset{\|}{C}}-O^{\ominus}Ag^{\oplus} \xrightarrow{Br_2/\Delta} R-Br + AgBr + CO_2(\uparrow)$$

Silver salt of Carboxylic acid

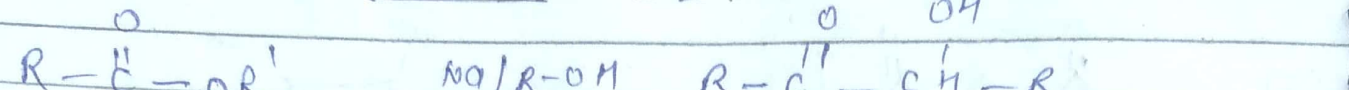
Mech^{n}:



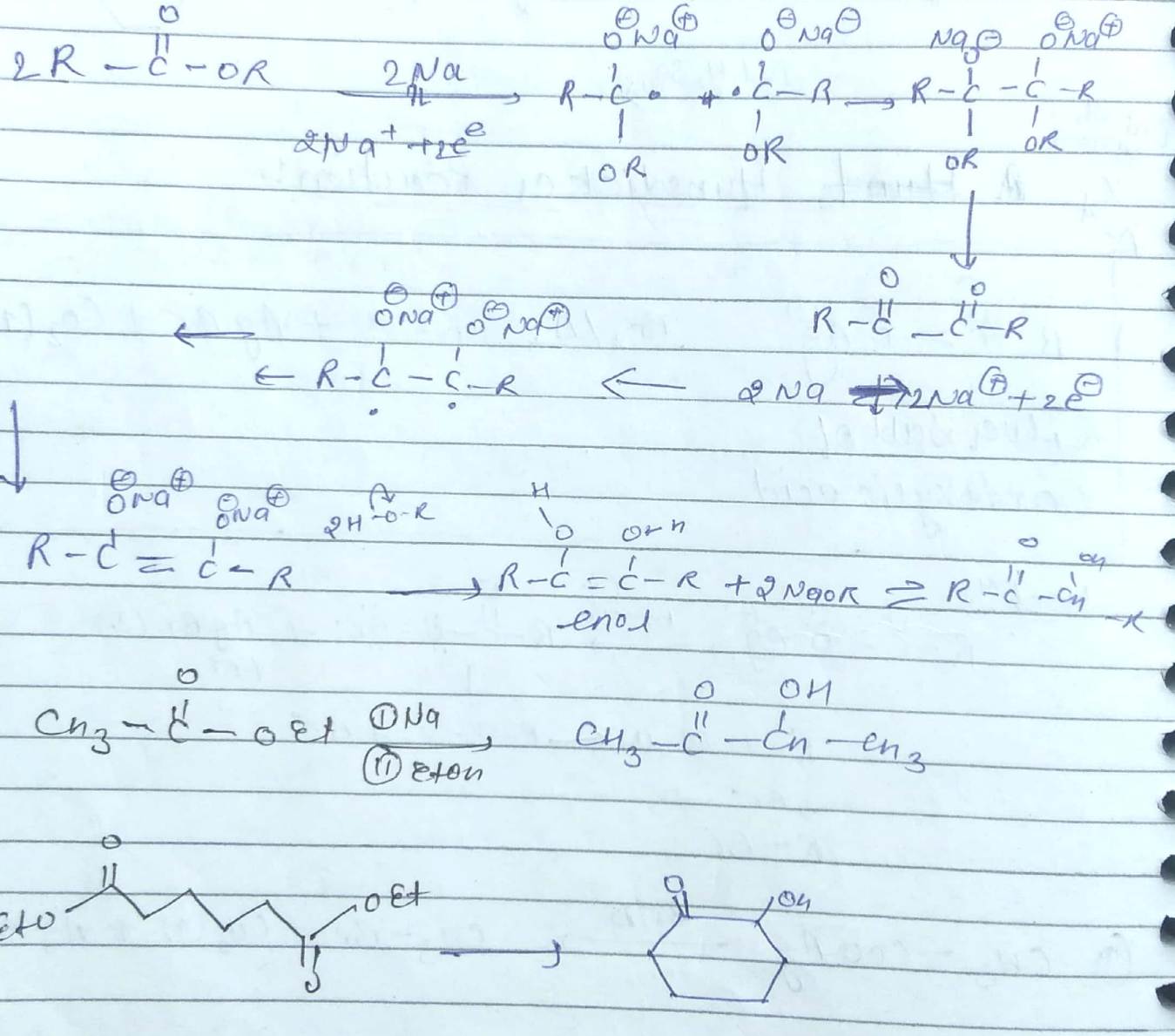
$$CH_3-COOAg \xrightarrow{Br_2/\Delta} CH_3-Br + CO_2(\uparrow) + AgBr$$

(2) 

* Acyloin Condensation Rxn :



Mechⁿ :

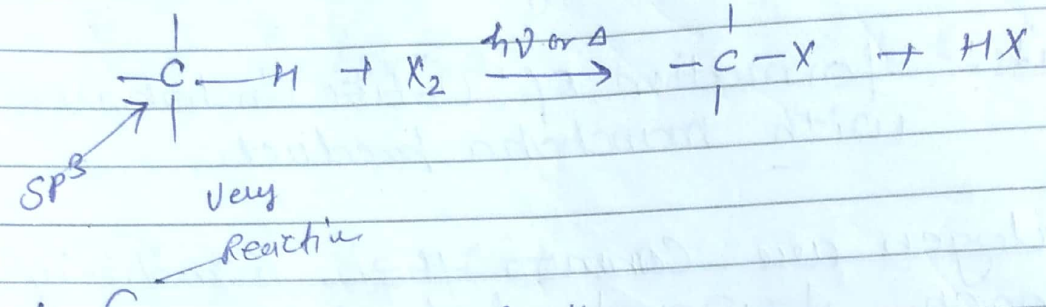


Q. $CH_3-\overset{O}{\overset{\|}{C}}-OEt \xrightarrow[\text{(II) EtOH}]{\text{(I) Na}} CH_3-\overset{O}{\overset{\|}{C}}-\underset{OH}{CH}-CH_3$

Q.

hν Sunlight

Halogenation :



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

* $X_2 = Cl_2$ or Br_2 (Generally)

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

* Rxn occur on SP^3 - Hybridised - C.

Mech^n :- FRM ⇒ Completed in three steps.

(I) CIS (II) CPS (III) CTS.

Step :1 CIS :

$X \overset{|}{-} X \xrightarrow[\text{or } \Delta\ (300^\circ C \text{ or above})]{h\nu} X^\bullet + X^\bullet$ ⇒ Endothermic

~~Step 1 : CPS~~

Step-CPS

$-\overset{|}{C}-H + X^\bullet \xrightarrow{\text{slow}} -\overset{|}{C}^\bullet + HX$ Exo

~~Step CPS :~~

$-\overset{|}{C}^\bullet + X-X \xrightarrow{\text{fast}} -\overset{|}{C}-X + X^\bullet$ Exo

Step 3 : CTS

$X^\bullet + X^\bullet \xrightarrow{\text{fast}} X_2$

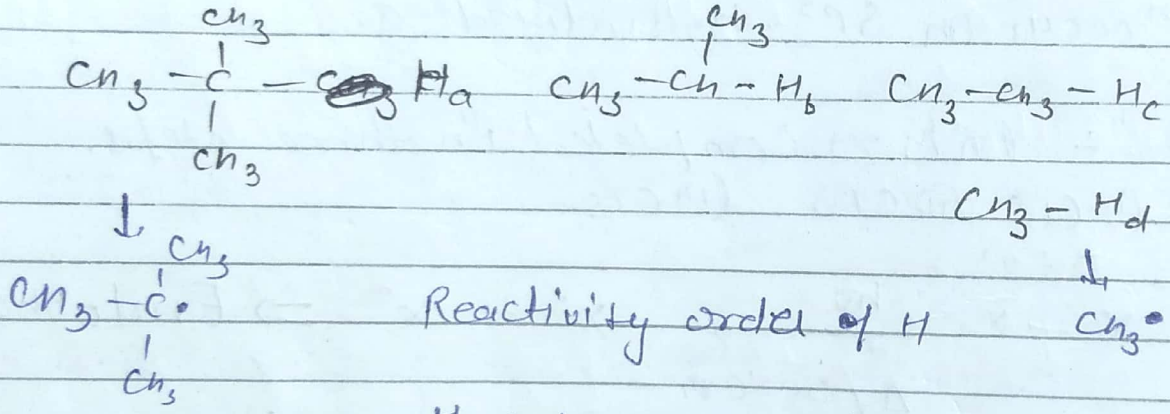
$-\overset{|}{C}^\bullet \; {}^\bullet\overset{|}{C}- \xrightarrow{\text{fast}} -\overset{|}{C}-\overset{|}{C}-$

* Merit :- → Overall Rxn is exothermic.
→ Takes very less time.

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

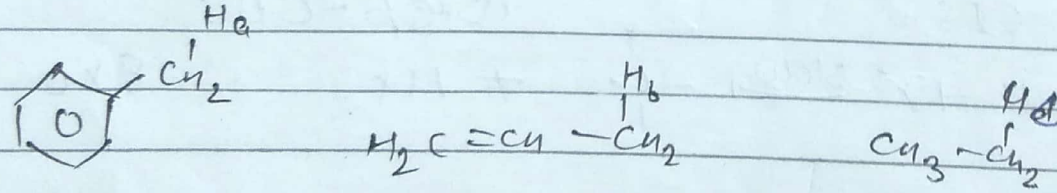
If halogen are common then Reactivity of Halogen toward halogination depends on free radical

Reactivity of 'H' towards Halogenation Rxn ∝ Stability of f.R (RS) formed

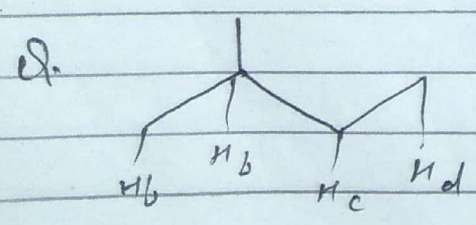
a. 

Reactivity order of H

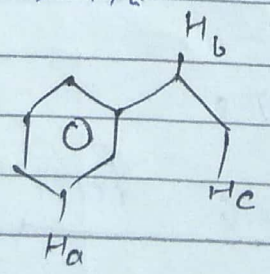
$H_a > H_b > H_c > H_d$

b. 

RO → $H_a > H_b > H_c$

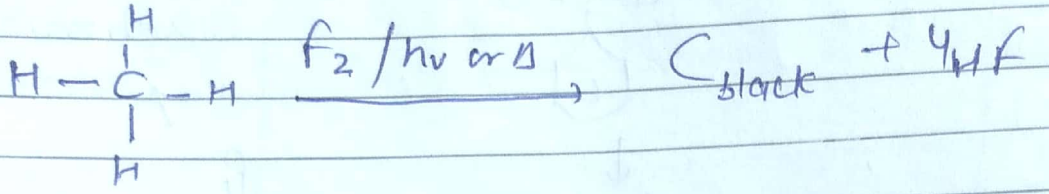
c. 

$H_b > H_c > H_d > H_a$

d 

$H_b > H_c > H_a$

* **Fluorination :**



$$\xrightarrow{F_2/h\nu \text{ or } \Delta} C_{black} + 4HF$$

* **Chlorination :** $X_2 = Cl_2$

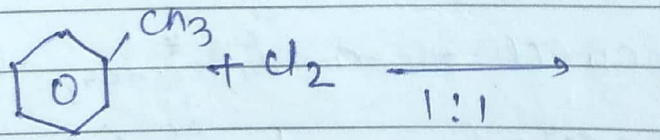
(*) $-\overset{|}{\underset{|}{C}}-H + Cl_2 \xrightarrow{h\nu/\Delta} -\overset{|}{\underset{|}{C}}-Cl + HCl$

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

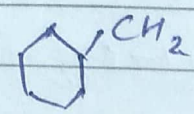
(2) $CH_4 + Cl_2 \longrightarrow CCl_4 + 4HCl$ (Poly chlorination)
xs $\quad 1 : xs$

(3) $CH_4 + Cl_2 \longrightarrow CCl_4 + 4HCl$

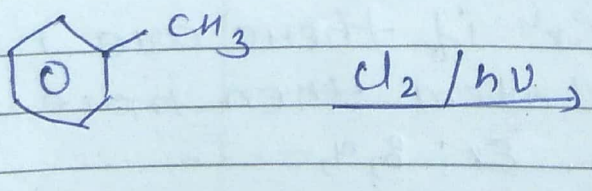
* If amount of CCl_4 is not given then consider Cl_2 as excess.

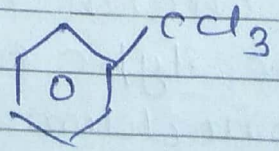
(4) 

$$\xrightarrow[1:1]{}$$



Toluene $\qquad$ Benzyl Chloride

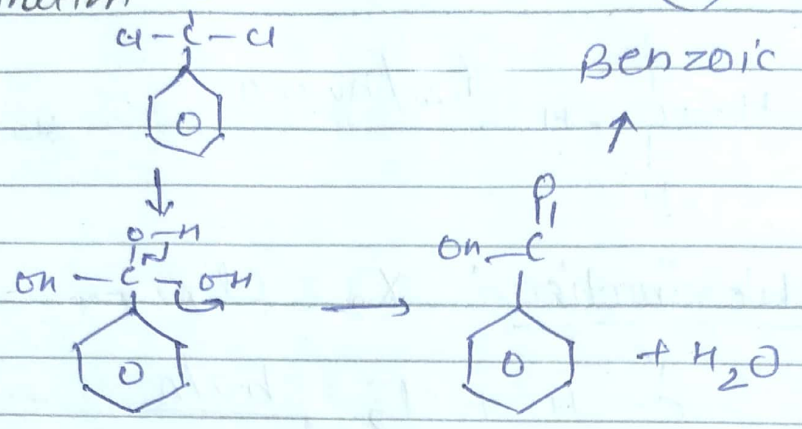
(5) 



(6) Toluene $\xrightarrow{Cl_2}$

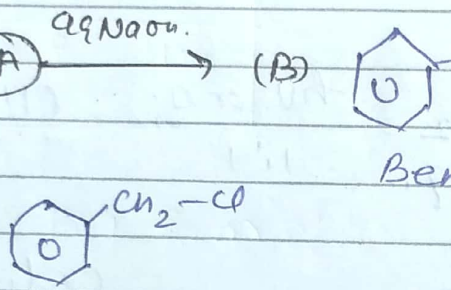
IIT

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



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

monochlorination



Benzyl alcohol

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

1-Cl 2-Cl

(9) $\underset{1^\circ}{CH_3}-\underset{3^\circ}{CH}-\underset{2^\circ}{CH_2}-\underset{1^\circ}{CH_2} \xrightarrow[1:1]{Cl_2/h\nu}$ $Cl-CH_2-\underset{CH_3}{\overset{CH_3}{CH}}-CH_2-CH_2 +$ ②

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

$CH_3-\underset{CH_3}{CH}-CH_2-\underset{Cl}{CH}-Cl + CH_3-\underset{Cl}{\overset{CH_3}{CH}}-\underset{*}{CH}-CH_3$

(a) Total mCP formed in above Rx^n = 6

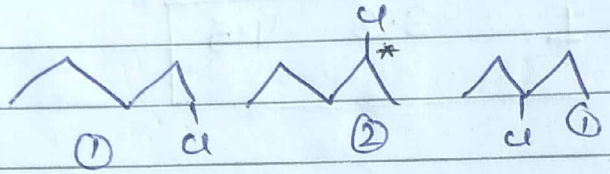
(b) Total mCP " " " (without SI) = 4

(c) " optically active (chiral Product) = 4

(d) Total Product obtained in fractional distillation = 4.

Note: In chlorination Rx^n 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)					
(8)					

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

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

Relative amount of Any Isomer = No. of Responsible-H X 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

$$CH_3-CH_2-CH_3 \xrightarrow[1:1]{Cl_2/h\nu \text{ or } \Delta} \underset{\text{1-CP (44\%) MINOR}}{CH_3-CH_2-\overset{Cl}{\overset{|}{C}}H_2} + \underset{\text{2-CP 56\% MAJOR}}{CH_3-\overset{Cl}{\overset{|}{C}}H-CH_3}$$

- R.A of 1-C.P = 6.0 X 1.0 = 6.0
- R.A of 2-CP = 2.0 X 3.8 = 7.6

$$\% \text{ of } 1\text{-CP} = \frac{6.0}{13.6} \times 100 = \frac{600}{13.6} \approx 44\%$$

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

(2004)

** extra

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

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

$\simeq 66\%$ $\simeq 34\%$

1 CP = =

Note: Chlorination can also be done by SO_2Cl_2

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

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

$$-\underset{|}{\overset{|}{C}}-H \xrightarrow{(SO_2+Cl_2)/\Delta \text{ or } h\nu} -\underset{|}{\overset{|}{C}}-SO_2Cl + HCl$$

(FREED S Rx^n).

* Bromination: $X_2 = Br_2$

Mech^n: similar chlorination.

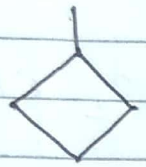
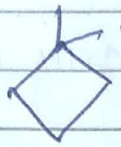
Due to less Reactivity than ~~Br~~ chlorine Bromine is a selecting Brominating agent (i.e if more then Hydrogen Present in Comp. then it Brominate most Reactive Hydrogen).

Sajalya-2
IIIrd flr. 2:30 — 5:30 PM

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

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

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

(4)  $\xrightarrow{Br_2/h\nu}$ 

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