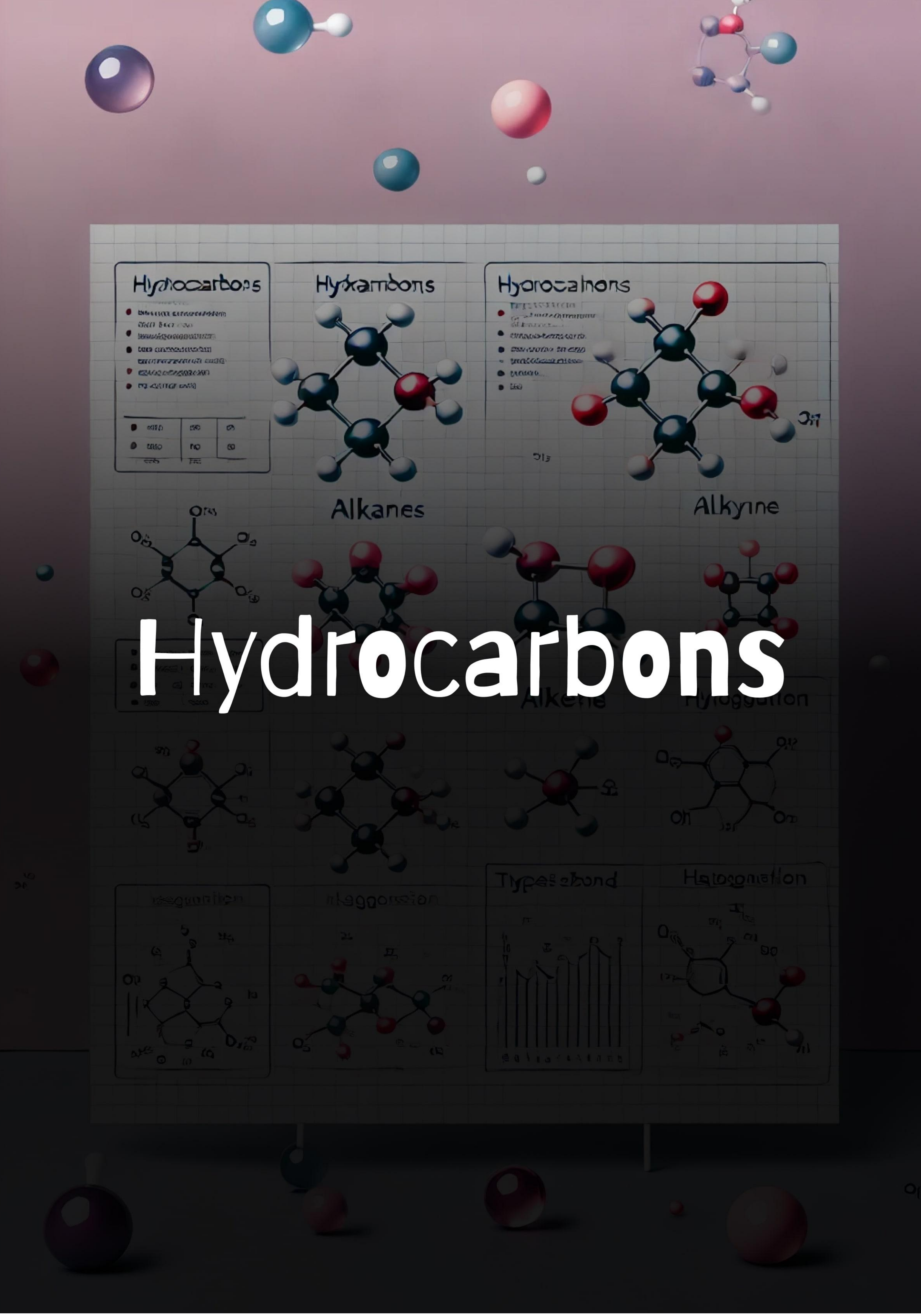


Hydrocarbons

ALKANES

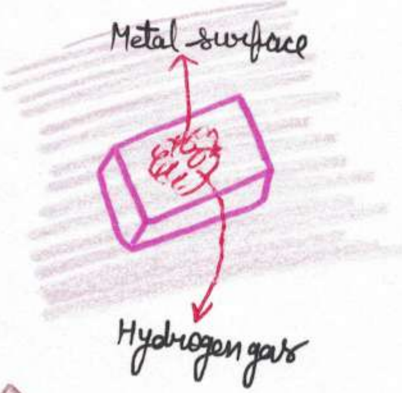
Part-Ist

RATE OF ADSORPTION

OCCLUSION → over surface

i Adsorption of H_2 on the surface of noble metals.

ii Exothermic process; thus, heat is released.

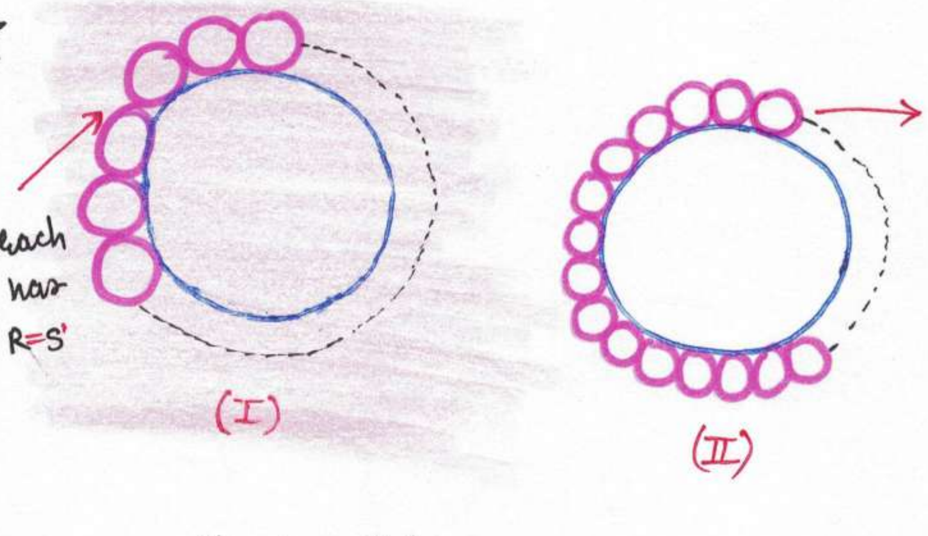


If pressure 'p' is applied on hydrogen gas; then the rate of adsorption ↑.

E.g

QUE Both particles are taken in amount to yield 250g of each which adsorbs better ?

ANS..



each has R = 1'

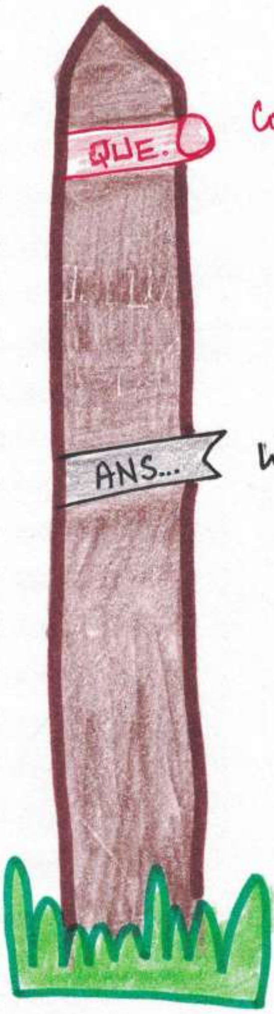
No. of particles on 'I' = x

No. of particles on "II" = y

No. of particles = y > x

Thus, we've more no. of particles on the similar case on (II) rather than (I). Thus, (II) has a better adsorption rate.

$$\boxed{\text{Adsorption} \propto \frac{1}{\text{size}}}$$



Compare the rate of adsorption for:-

$CH_2=CH_2$ (a)

$CH_2-CH=CH_2$ (b)

$CH_2-CH=CH-CH_3$ (c)

$CH_3-CH=CH-CH_2-CH_3$ (d)

We know,

$$\text{Rate of adsorption} \propto \left(\frac{1}{\text{size}}\right)$$

Thus, size will be d > c > b > a → smallest size

d → largest size

Rate of adsorption → a > b > c > d

$$\text{Adsorption Rate} \propto \frac{1}{\text{crowding}} \propto \frac{1}{\text{stability}}$$

Compare rate of adsorption for :-

a.

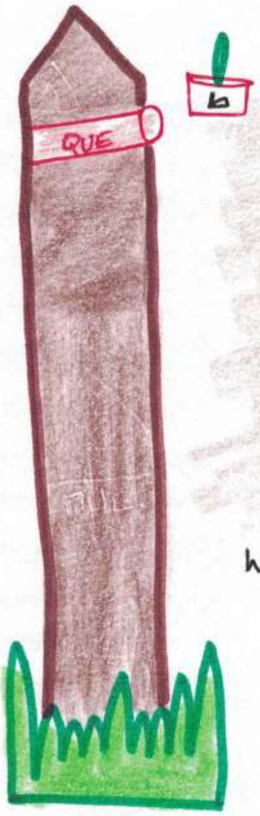
(a)

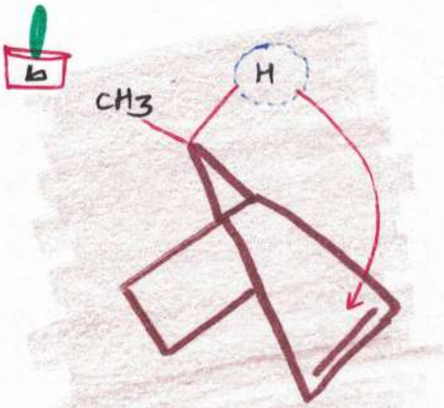
(b)

size = b > a

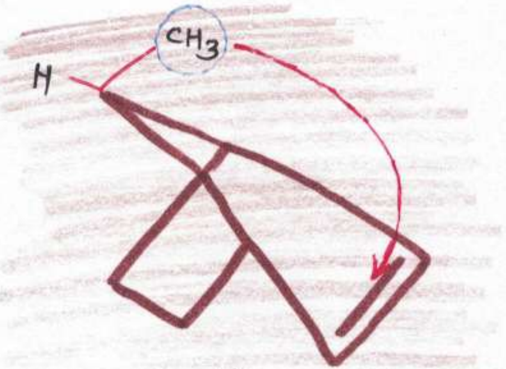
Rate = a > b

we know, $\text{Adsorption} \propto \frac{1}{\text{size}}$





(a)



(b)

we know adsorption $\propto \frac{1}{\text{crowding}}$

crowding on (b) > (a)

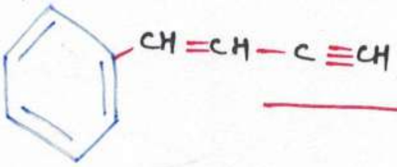
Rate (a) > (b)

PART- II DEGREE OF UNSATURATION

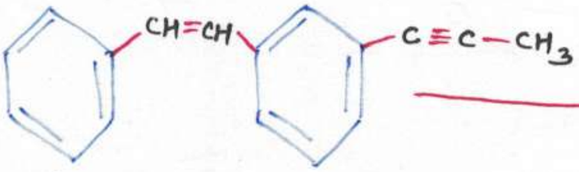
(i) $D.U = \sum(\text{Double bonds} + \text{Rings})$

E.g.

$\longrightarrow D.U. = \underbrace{3}_{\text{Double bonds}} + \underbrace{1}_{\text{Rings}} = 4$



$\longrightarrow D.U = \underbrace{6}_{\text{Double bonds}} + \underbrace{1}_{\text{Rings}} = 7$



$\longrightarrow D.U = \underbrace{9}_{\text{Double bonds}} + \overset{\text{Rings}}{2} = 11$

(ii) Any general compound ;

$$C_xH_yN_zO_pX_q \longrightarrow D.U = (x+1) - \left(\frac{y+q-z}{2}\right)$$

(Independent of oxygen)

E.g.

i $CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow D.U = (5+1) - \left(\frac{8+0-0}{2}\right)$

↳ Here, $x = 5$
$y = 8$
$z = 0$
$p = 1$
$q = 0$

$D.U = 6 - 4$

$\boxed{D.U. = 2}$

ii $C_{10}H_6N_4 \longrightarrow D.U = (10+1) - \left(\frac{6+0-4}{2}\right)$

↳ Here, $x = 10$
$y = 6$
$z = 4$
$p = 0$
$q = 0$

$D.U = 11 - 1$

$\boxed{D.U = 10}$

Reduction reaction
redox reaction

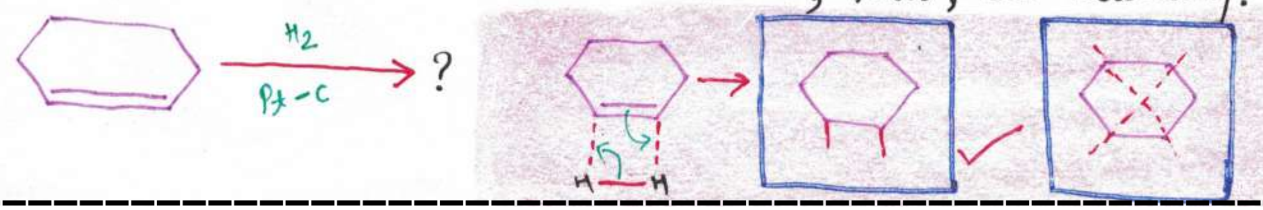
a. **Reduction by $H_2/Pd-c$, $H_2/Pt-c$, $H_2/Ni-c$** - (All three do the same work.)

E.g. (i) $CH_2=CH_2 \xrightarrow[Pd-c]{H_2} CH_3-CH_3$

MECHANISM

Both 'H' are attached on the same side ; thus, cis addition.

(ii)

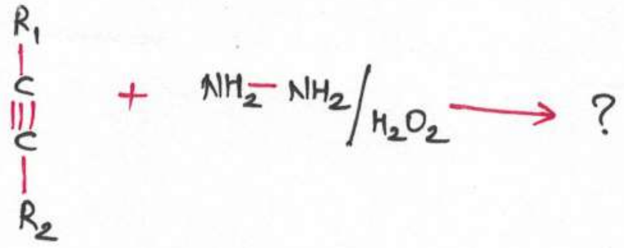


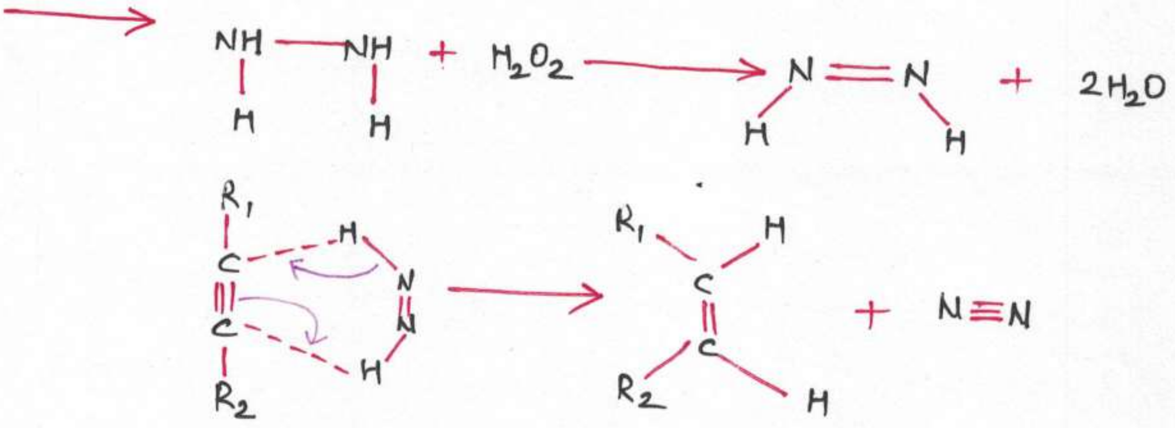
Mechanism was important to know because both hydrogens are attached on the same side.

Transfer hydrogenation by NH_2-NH_2/H_2O

MECHANISM

(i)



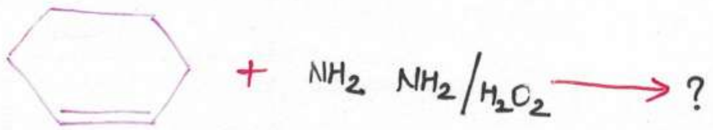


$$NH_2-NH_2 + H_2O_2 \longrightarrow HN=NH + 2H_2O$$

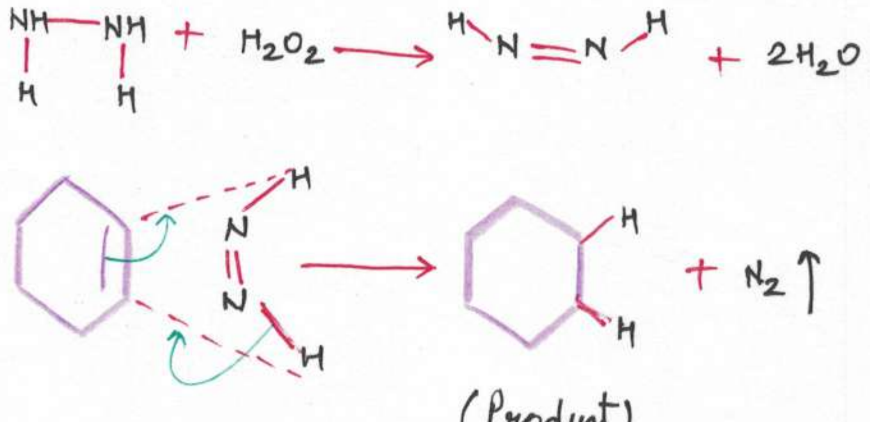
(Product)

Both 'H' are on the same side
Thus, $\boxed{\text{cis addition}}$

(ii)



MECHANISM



$$NH_2-NH_2 + H_2O_2 \longrightarrow HN=NH + 2H_2O$$

(Product)

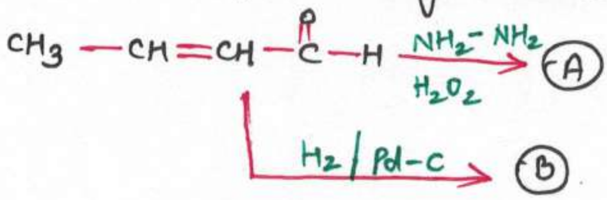
Thus, transfer hydrogenation is a redox type reaction.

The compound in the question is reduced

Nitrogen is oxidised from (−2) to (zero).

IMPORTANT NH_2-NH_2/H_2O_2 only reduces carbon - Carbon bonds.

E.g.

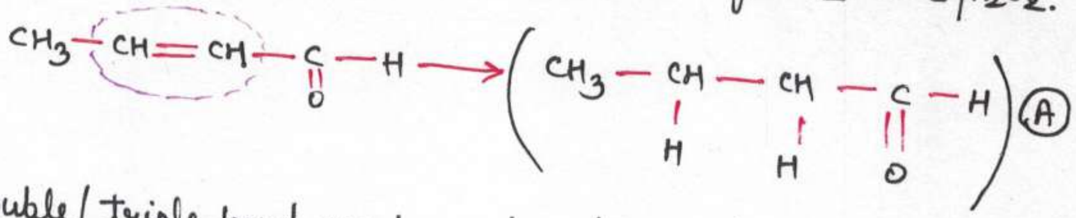


$CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-H \xrightarrow[H_2O_2]{NH_2-NH_2}$ Ⓐ

$\xrightarrow{H_2/Pd-C}$ Ⓑ

PART Ⓐ:- only carbon - carbon bonds are reduced by NH_2-NH_2/H_2O_2.

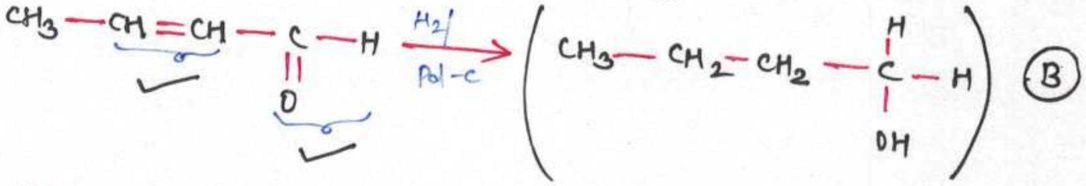
Thus,



$CH_3-CH=CH-\underset{O}{\underset{\|}{C}}-H \longrightarrow \left(CH_3-\underset{H}{\underset{|}{CH}}-\underset{H}{\underset{|}{CH}}-\underset{O}{\underset{\|}{C}}-H\right)$ Ⓐ

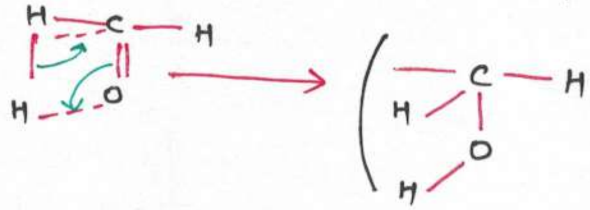
PART Ⓑ:- Every double/triple bond can be reduced by $H_2/Pd-C$.

Thus,



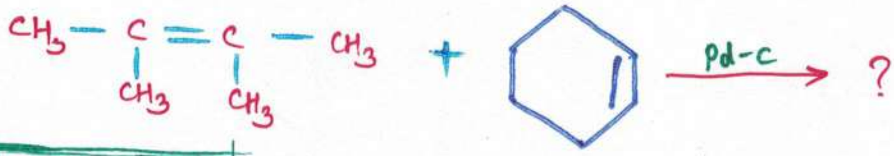
$CH_3-CH=CH-\underset{O}{\underset{\|}{C}}-H \xrightarrow[Pd-C]{H_2/} \left(CH_3-CH_2-CH_2-\overset{H}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-H\right)$ Ⓑ

MECHANISM



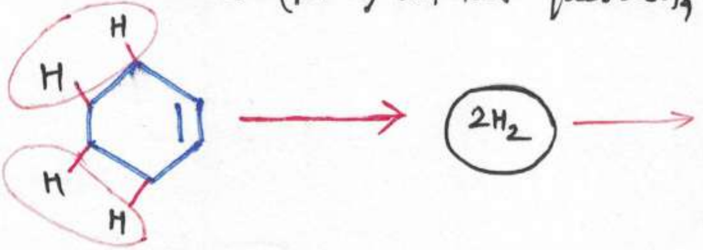
BY CYCLOHEXENE AND Pd-C

QUE

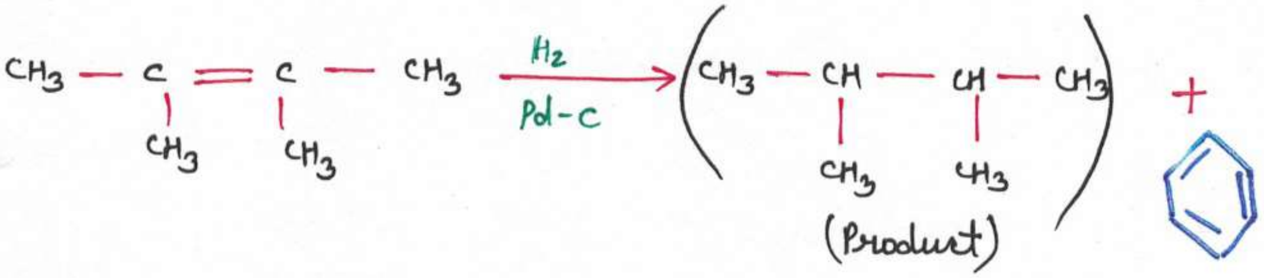


ANS...

MECHANISM we know that $H_2/Pd-C$ is a good reducing agent. we have (Pd-c) in the question; we need to generate (H_2).



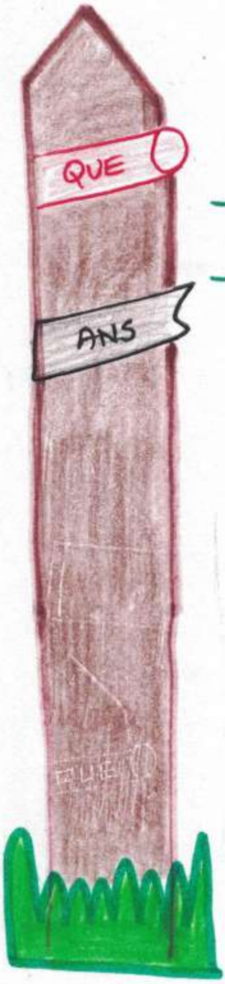
Thus, we've got 'H_2' here. Pd-c is already given.



$$CH_3-\underset{CH_3}{\underset{|}{C}}=\underset{CH_3}{\underset{|}{C}}-CH_3 \xrightarrow[Pd-C]{H_2} \left(CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_3\right) +$$

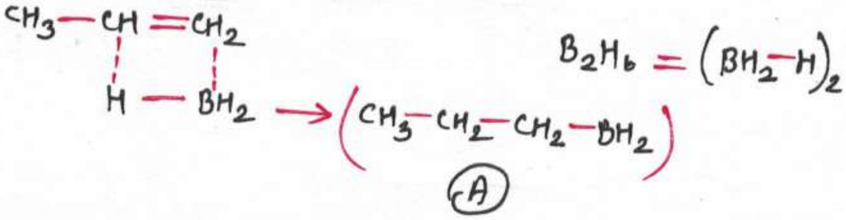
(Product)

Hydroboratio-n Reactions



$CH_3-CH=CH_2 + B_2H_6 \longrightarrow$ Ⓐ $\xrightarrow[CH_3COOH]{\text{dil } H_2SO_4 \text{ or}}$ Ⓑ

MECHANISM :-

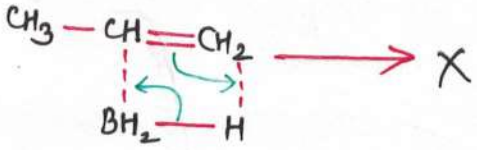


$$\underset{H-BH_2}{CH_3-CH=CH_2} \longrightarrow \left(CH_3-CH_2-CH_2-BH_2\right)$$

Ⓐ

$B_2H_6 = (BH_2-H)_2$

But,



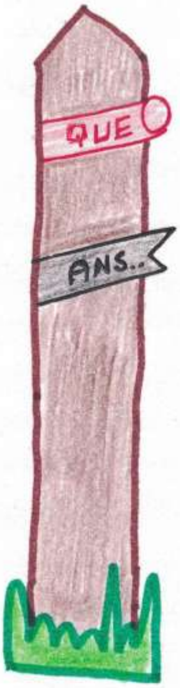
$$\underset{BH_2-H}{CH_3-CH=CH_2} \longrightarrow \times$$

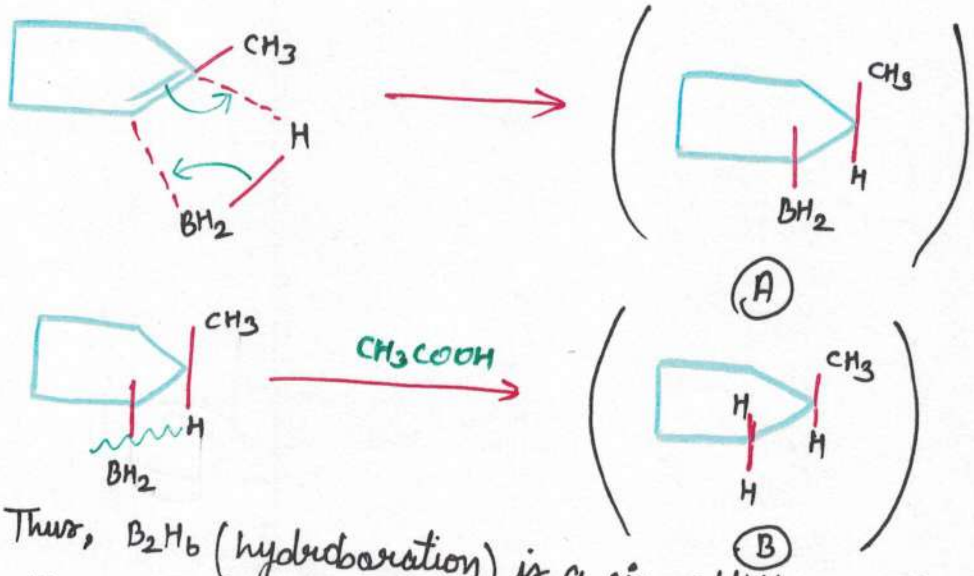
because $-BH_2$ is a crowded group and would go to the less crowded site.

$$CH_3-CH_2-CH_2 \wr BH_2 \xrightarrow[CH_3COOH]{\text{dil } H_2SO_4 \text{ or}} \left(CH_3-CH_2-CH_2-H\right)$$

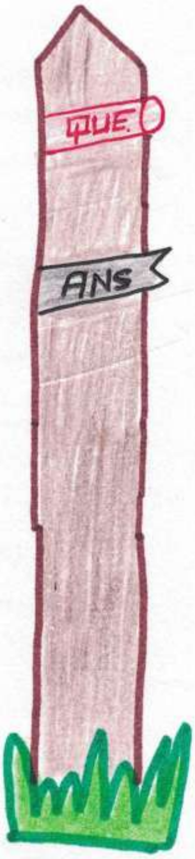
Ⓑ

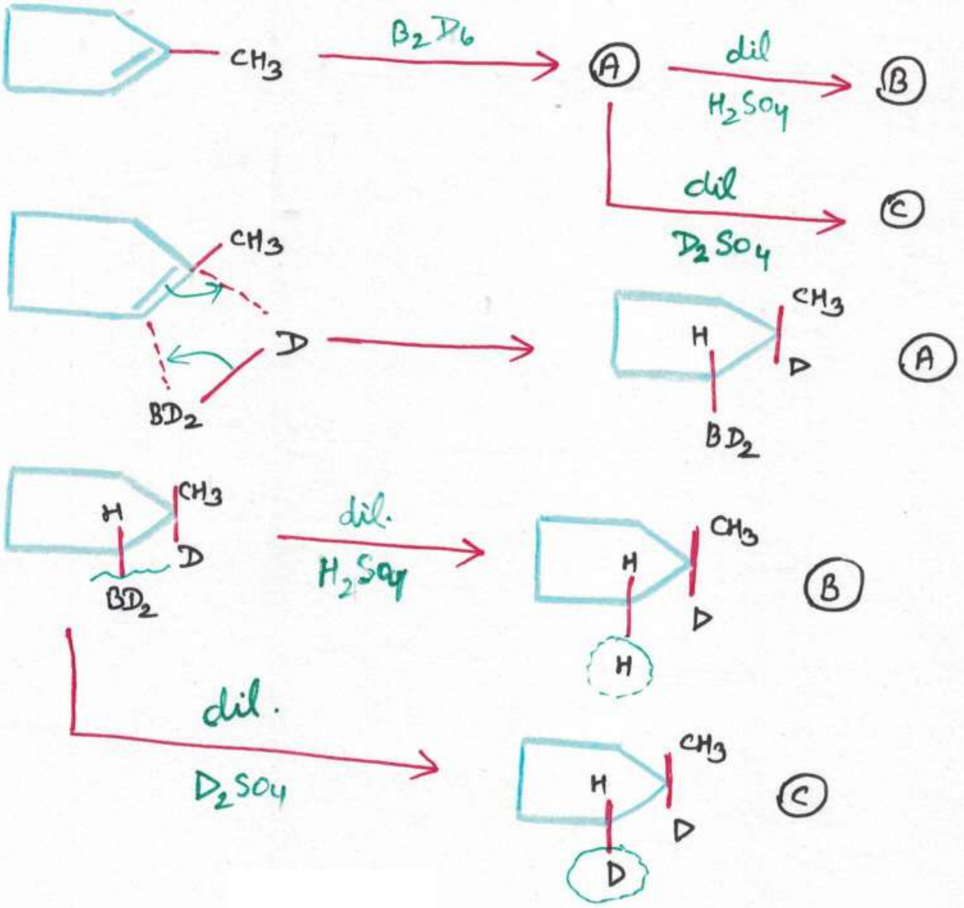
(dil H_2SO_4 or CH_3COOH) replace $-BH_2$ by $-H$

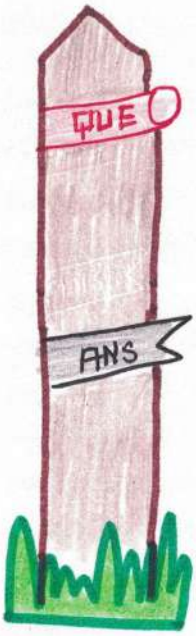


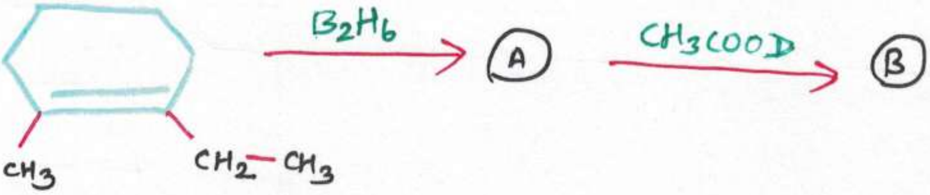


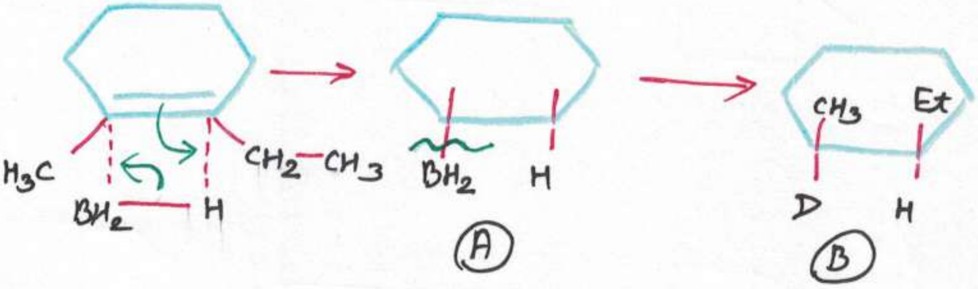
Thus, B_2H_6 (hydroboration) is a cis addition as $(-BH_2)$ and $(-H)$ attach on the same side.











GRIGNARD REAGENT

Difference between Mg/et$_2$O and Mg/THF

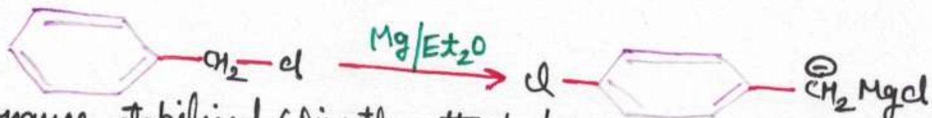
et$_2$O = $CH_3-CH_2-O-CH_2-CH_3$

THF = Tetrahydro furan

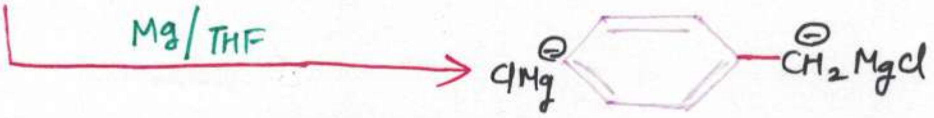
} Aprotic

- $R-X + Mg/et_2O \longrightarrow R^{\ominus}MgX$
- Mg/Et$_2$O can only break the non-resonance stabilised bonds while Mg/THF can break any type of C–X bond.

E.g.



Resonance stabilised (Directly attached to the ring)



- ☐ only the non-resonance (weak bonds) are broken by Mg/Et_2O.
- ☐ Non-resonance (weak) and in-resonance (strong) bonds can be broken by Mg/THF.

E.g. $Cl-CH_2-CH_2-CH=CH-Cl \xrightarrow[Et_2O]{Mg/} ClMg\,\overset{\ominus}{C}H_2-CH_2-CH=CH-Cl$

$\xrightarrow{Mg/THF} ClMg\,\overset{\ominus}{C}H_2-CH_2-CH-\overset{\ominus}{C}H=\overset{\ominus}{C}H\,MgCl$

IMPORTANT POINTS

a. Grignard reagent is organometallic in nature.

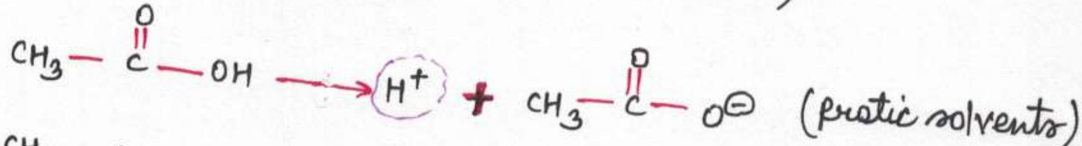
ORGANOMETALLIC – when carbon is directly attached to a metal.

E.g. Grignard reagent, Frankland reagent.

b. Grignard reagent is only stable in the aprotic solvents, It is unstable in protic solvents.

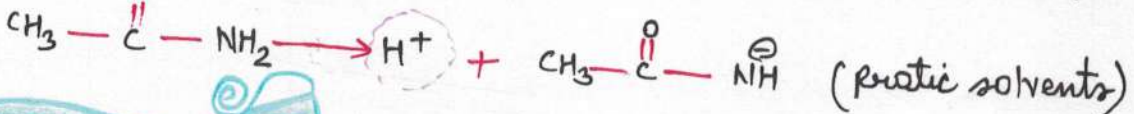
a. **PROTIC SOLVENTS** = The solvents which can readily donate $H^{\oplus}$ are termed as protic solvents.

E.g. $H_2O \longrightarrow H^+ + O^-H$ (Protic solvents)



$CH_3-\overset{O}{\overset{\|}{C}}-OH \longrightarrow H^+ + CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus}$ (protic solvents)

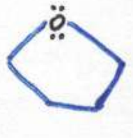
$CH_3-CH_2-OH \longrightarrow H^+ + CH_3-CH_2-O^{\ominus}$ (Protic solvents)



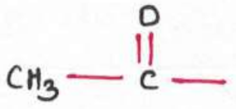
$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \longrightarrow H^+ + CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{N}H$ (protic solvents)

APROTIC SOLVENTS = The solvents which can't readily donate $H^{\oplus}$ are termed as aprotic solvents.

E.g. THF



$\longrightarrow$ can't give $H^{\oplus}$ (Aprotic solvents)



$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow$ can't give $H^{\oplus}$ (Aprotic solvent)

Et$_2$O: $CH_3-CH_2-O-CH_2-CH_3 \longrightarrow$ can't give $H^{\oplus}$ (Aprotic solvent)

☐ Grignard reagent is only stable in the aprotic solvents. In aprotic solvents, grignard reagent doesn't exist.

(i) $R^{\ominus}MgX + \underset{(Protic)}{H_2O} \longrightarrow R-H + Mg(OH)X$

$R-H \longrightarrow$ Grignard reagent is destroyed.

MECHANISM

$H_2O \longrightarrow H^+ + O^-H$

$\underset{H^{\oplus}}{R^{\ominus}}MgX \longrightarrow R-H + Mg(OH)X$

(ii) $R^{\ominus}MgX + \underset{(Protic)}{CH_3OH} \longrightarrow R-H + Mg(OH)X$

(iii) $R^{\ominus}MgX + \underset{(Protic)}{NH_3} \longrightarrow R-H + Mg(NH_2)X$

→ Thus, grignard reagent is only stable in aprotic solvents. It doesn't exist in the protic solvents.

Reduction by LiAlH$_4$, Frankland Reagent

REDUCTION BY LiAl$_4$

(i) LiAlH$_4$ gives 4 $H^{\ominus}$ which are used for reduction of the alkyl halides to Alkanes.

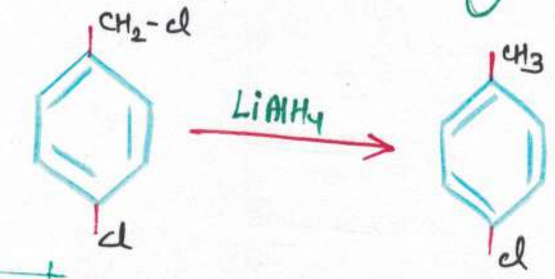
(ii) $R-X + LiAlH_4 \longrightarrow R-H$ (only aliphatic are reduced; not aromatic)

MECHANISM :- $R-X + H^{\ominus} \longrightarrow R-H$
(from $LiAlH_4$) (alkane or any hydro-carbon)

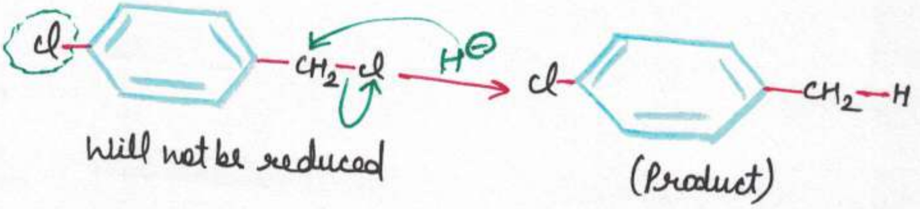
(iii) E.g. a. $CH_3-CH_2-Cl + LiAlH_4 \longrightarrow ?$

MECHANISM :- $CH_3-CH_2-Cl + H^{\ominus} \longrightarrow (CH_3-CH_2-H)$
ethane

b.



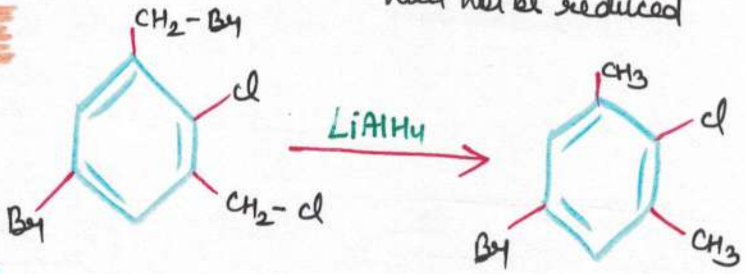
MECHANISM



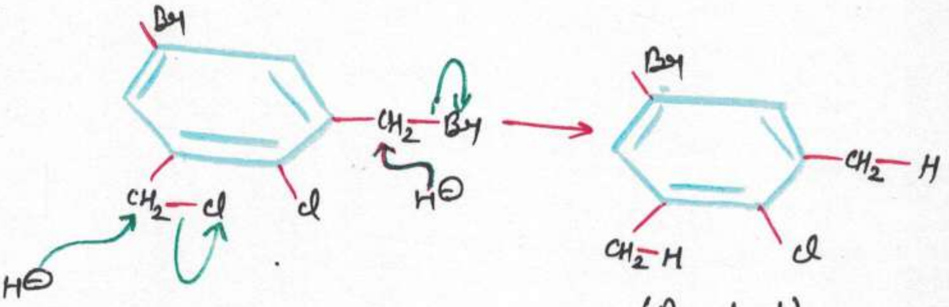
Will not be reduced

(Product)

(iv)



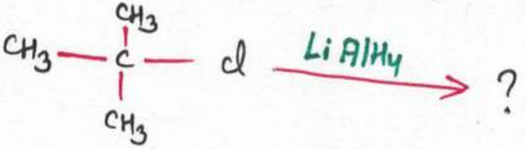
MECHANISM



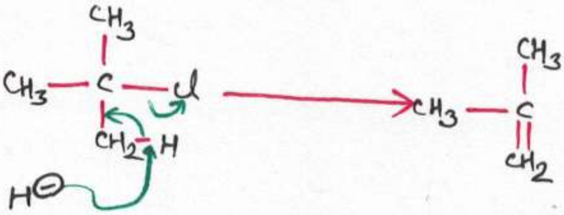
(Product)

(v) The tertiary alkyl halides give an alkane as a major product on reductio

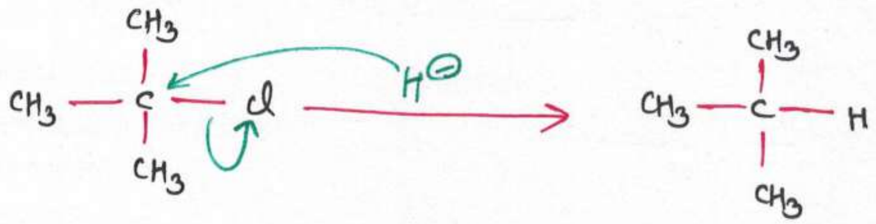
E.g.



$$(CH_3)_3C-Cl \xrightarrow{LiAlH_4} ?$$



(Alkene is the major product)

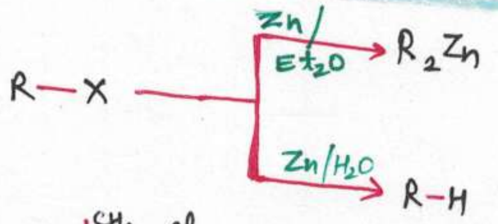


(Alkane is the minor product)

FRANKLAND REAGENT

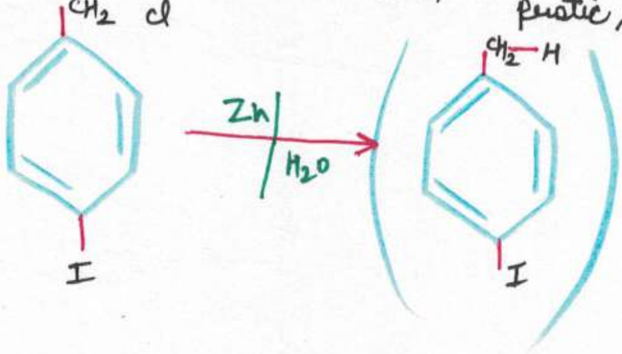
1. 'R_2Zn' is known as Frankland reagent.
2. It is an organometallic compound (carbon is attached to metal).
3. As discussed in the 'Grignard Reagent' video; it is stable only in aprotic solvents.

FORMATION OF FRANKLAND REAGENT



(Frankland reagent gets destroyed in protic solvents)

E.g.



REDUCTION BY P+HI OR HOT HI

(i) (P+HI) or (hot HI) both do the same work.

(ii) Only reduces alkyl iodides. Not other kinds of halides.

MECHANISM :- $R-I \xrightarrow{H-I} R-H + I_2$

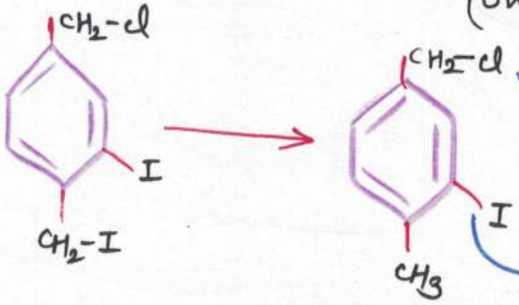
E.g.

a. $CH_3-CH_2-I \xrightarrow{P+HI} \left(\underset{\text{ethane}}{CH_3-CH_2-I}\right)$

b. $CH_3-CH_2-Cl \xrightarrow{P+HI}$ (No reaction)

(only alkyl iodides can be reduced)

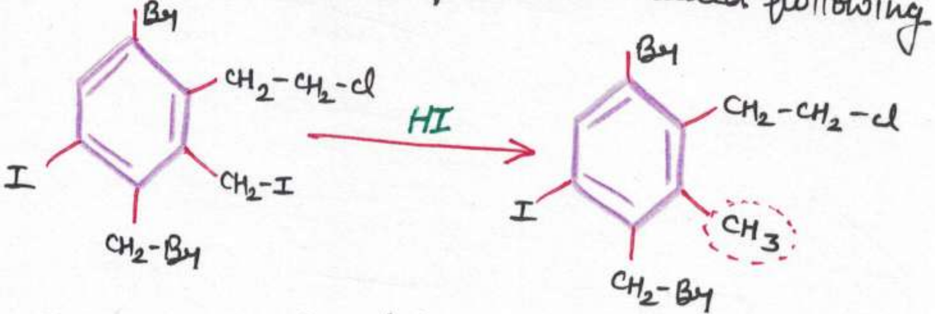
c.



(Not reduced as not an alkyl iodide)

It is an aromatic or resonance stabilised bond. Not broken

d. No. of moles of HI required to reduced following compound are?



(1mole)

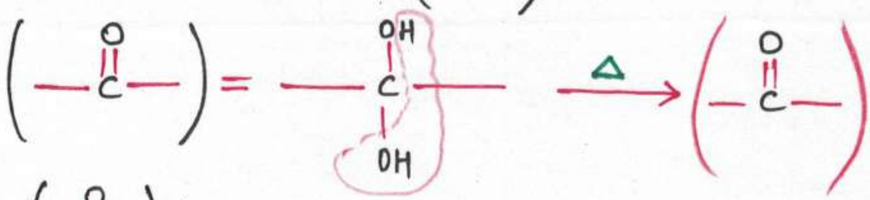
REDUCTION OF ALCOHOLS AND CARBONYL COMPOUND BY (P+HI)

MECHANISM :- $\underset{\text{(Alcohol)}}{R-OH} + HI \longrightarrow R-I + HI \longrightarrow \underset{\text{(Product)}}{R-H}$

(i) Thus, reduction of '1mole' of $-OH$ requires 2 moles HI.

(ii) Remember that if we've $\left(-\overset{O}{\overset{\|}{C}}-\right)$; it can be written in alcohol form.

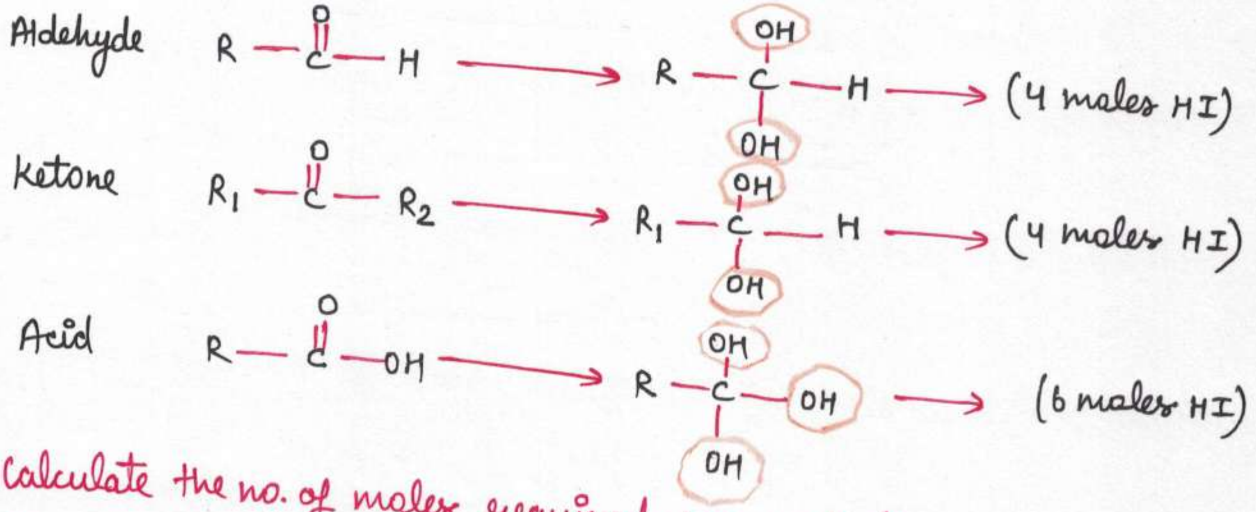
E.g.



$$\left(-\overset{O}{\overset{\|}{C}}-\right) = -\overset{OH}{\underset{OH}{\overset{|}{\underset{|}{C}}}}- \xrightarrow{\Delta} \left(-\overset{O}{\overset{\|}{C}}-\right)$$

one $\left(-\overset{O}{\overset{\|}{C}}-\right)$ has two (–OH) groups; thus, we requires 4 moles (P+HI).

(iii)



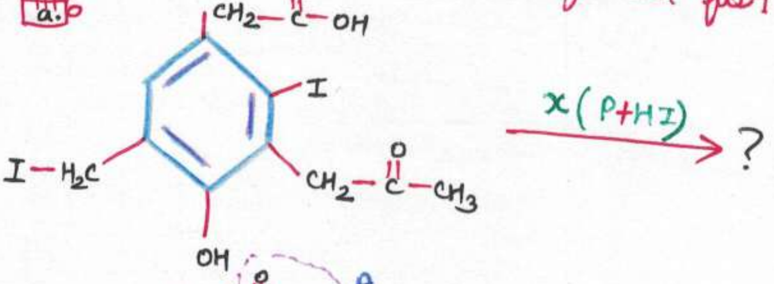
Aldehyde $R-\overset{O}{\overset{\|}{C}}-H \longrightarrow R-\overset{OH}{\underset{OH}{\overset{|}{\underset{|}{C}}}}-H \longrightarrow$ (4 moles HI)

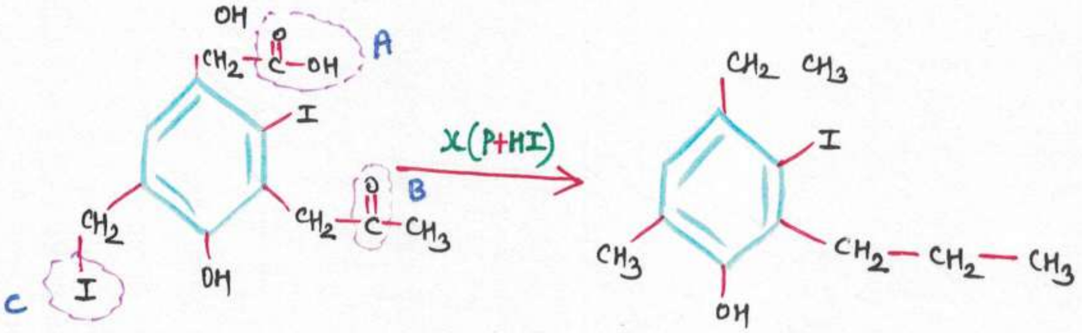
Ketone $R_1-\overset{O}{\overset{\|}{C}}-R_2 \longrightarrow R_1-\overset{OH}{\underset{OH}{\overset{|}{\underset{|}{C}}}}-H \longrightarrow$ (4 moles HI)

Acid $R-\overset{O}{\overset{\|}{C}}-OH \longrightarrow R-\overset{OH}{\underset{OH}{\overset{|}{\underset{|}{C}}}}-OH \longrightarrow$ (6 moles HI)

Q. Calculate the no. of moles required for reduction :-

a.





For A ⟶ 6 moles (P+HI)

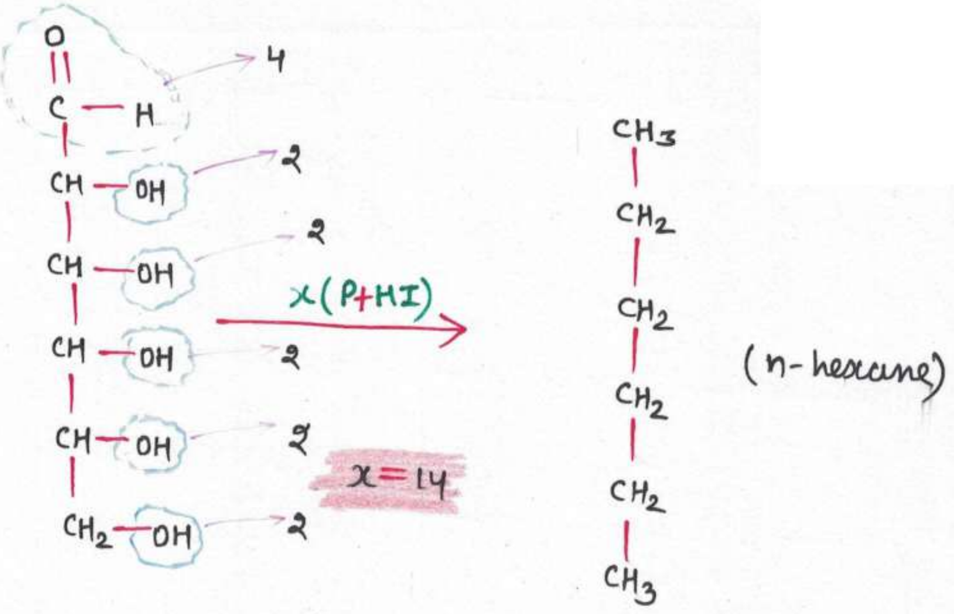
For B ⟶ 4 moles (P+HI)

For C ⟶ 1 moles (P+HI)

Thus, $x = 11$

Rest bonds are aromatic in nature (directly attached to the ring) & hence, can't be reduced.

Glucose

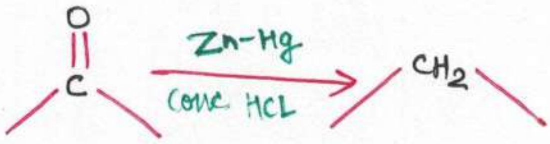


CLOMENSON'S REDUCTION

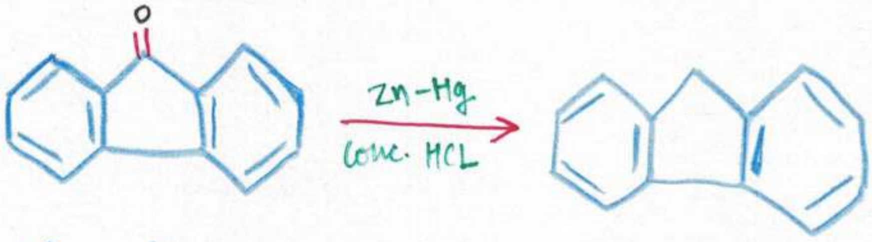
(i) Reagent used is (Zn/Hg /conc. HCL).

(ii) Done in the acidic medium.

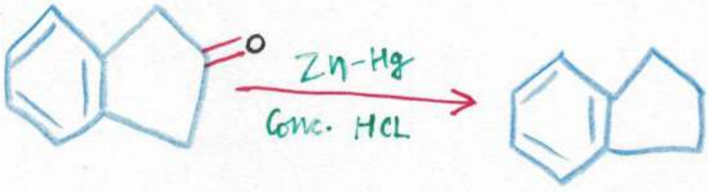
(iii) Works some on the carbonyl compounds as (P+HI)



Eg. a.



b.

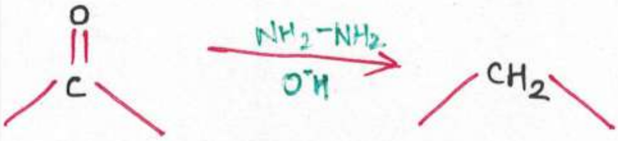


WOLFF KISHER'S REDUCTION

(i) Reagent used is (NH_2-NH_2/O^-H)

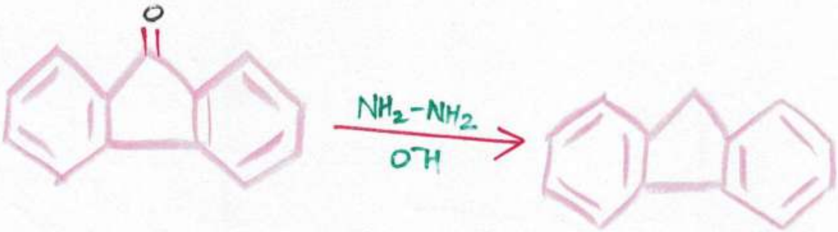
(ii) It is done in basic medium.

(iii) Works same on carbonyl compounds as (P+HI)

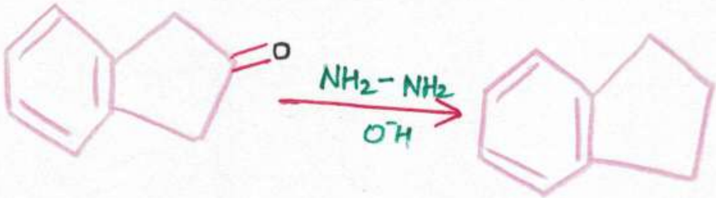


E.g.

a

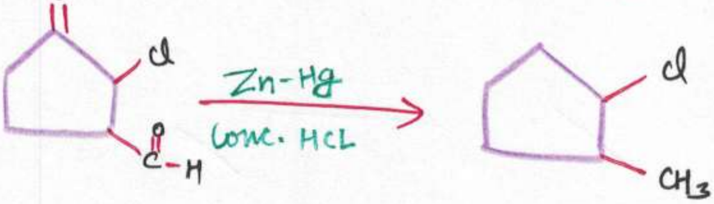


b.

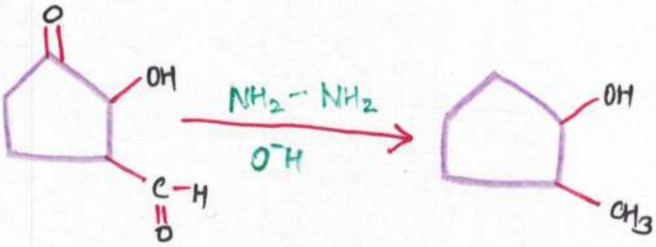


Write the products formed on reduction :-

i



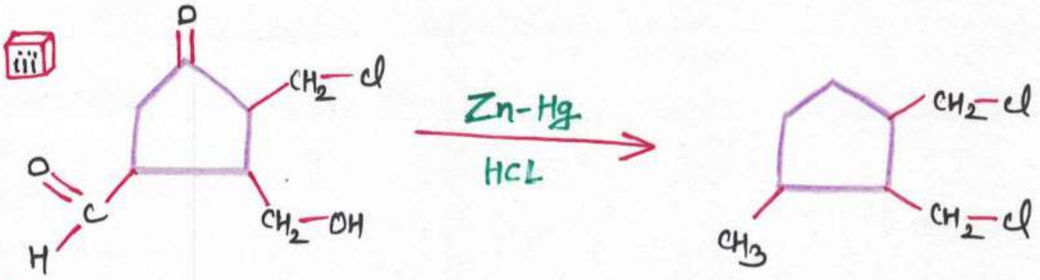
ii



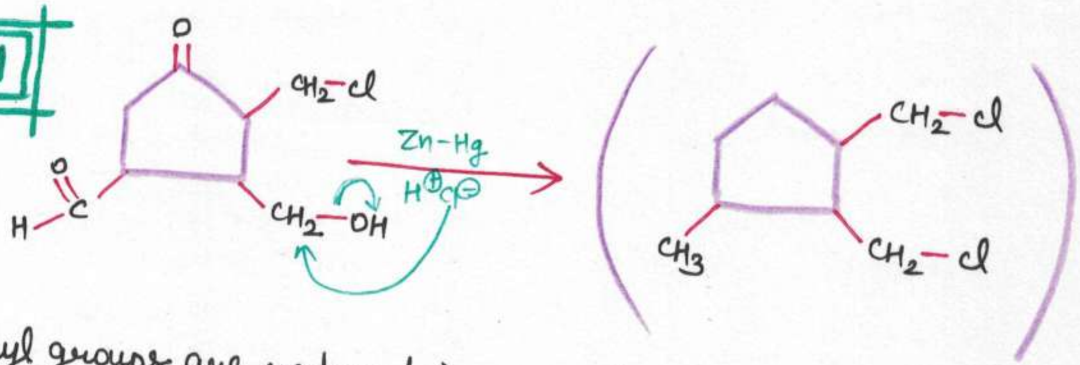
In i, no effect on 'Cl' as it is acidic medium.

In ii, no effect on 'OH' as it is basic medium.

iii



MECHANISM

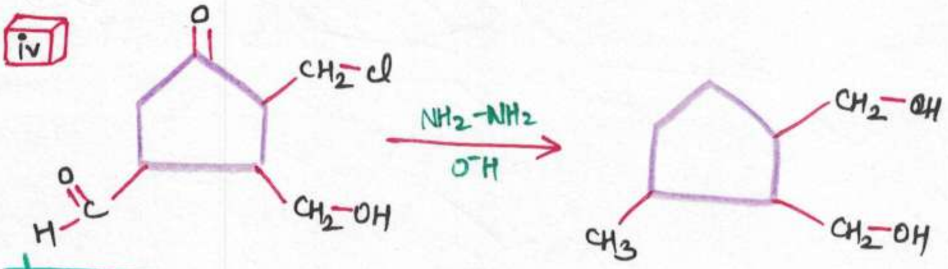


a. The carbonyl groups are reduced in a regular manner.

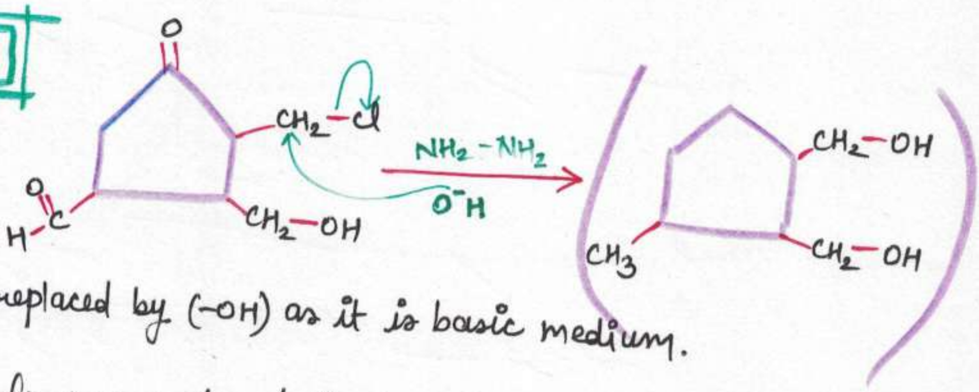
b. (-OH) is basic in nature. It is replaced by (-Cl).

c. No effect on the (-Cl) present initially in the question as it is acidic medium.

iv



MECHANISM



a. (-Cl) is replaced by (-OH) as it is basic medium.

b. The carbonyls are reduced in the similar manner.

c. No effect on the (-OH) present initially as the reaction is in basic medium.

WURTZ REACTION

i) Reagent used as Na/et_2O.

ii) Any metal always tends to donate electrons. $Na \rightarrow Na^+ + e^-$

iii) **MECHANISM** :-

$$2(R-X) + Na/et_2O \longrightarrow ?$$

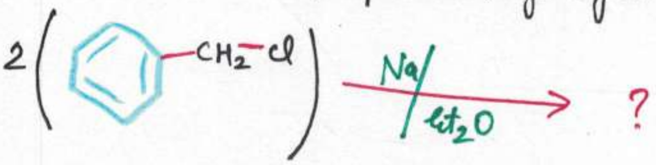
$$Na \longrightarrow Na^+ + e^-$$

$$R-X + e^{\ominus} \longrightarrow R^{\ominus}$$

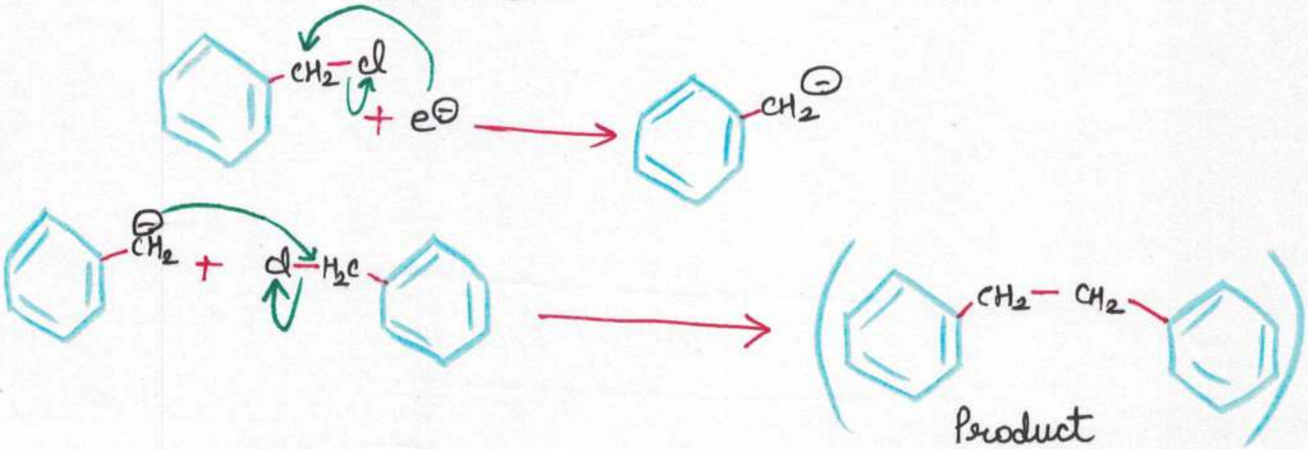
$$R^{\ominus} + R-X \longrightarrow (R-R)$$

(Thus, it is used for the preparation of symmetrical alkanes).

Eg i)



Mechⁿ :- Na Na⁺ e⁻



ii $2(CH_3-CH_2-Cl) \xrightarrow[Et_2O]{Na} ?$

MECHANISM :- $CH_3-\overset{\ominus}{C}H_2 \quad CH_3-CH_2-Cl$

$\rightarrow (CH_3-CH_2-CH_2-CH_3)$

Product

⊙ Viscinal halides give a double bond with Na/Et₂O

E.g (i) $Cl-CH_2-CH_2-Cl \xrightarrow[Et_2O]{Na} (CH_2=CH_2)$

MECHANISM :- $Na \rightarrow Na^+ + e^-$

$Cl-CH_2-CH_2-Cl + e^{\ominus} \rightarrow Cl-CH_2-\overset{\ominus}{C}H_2$

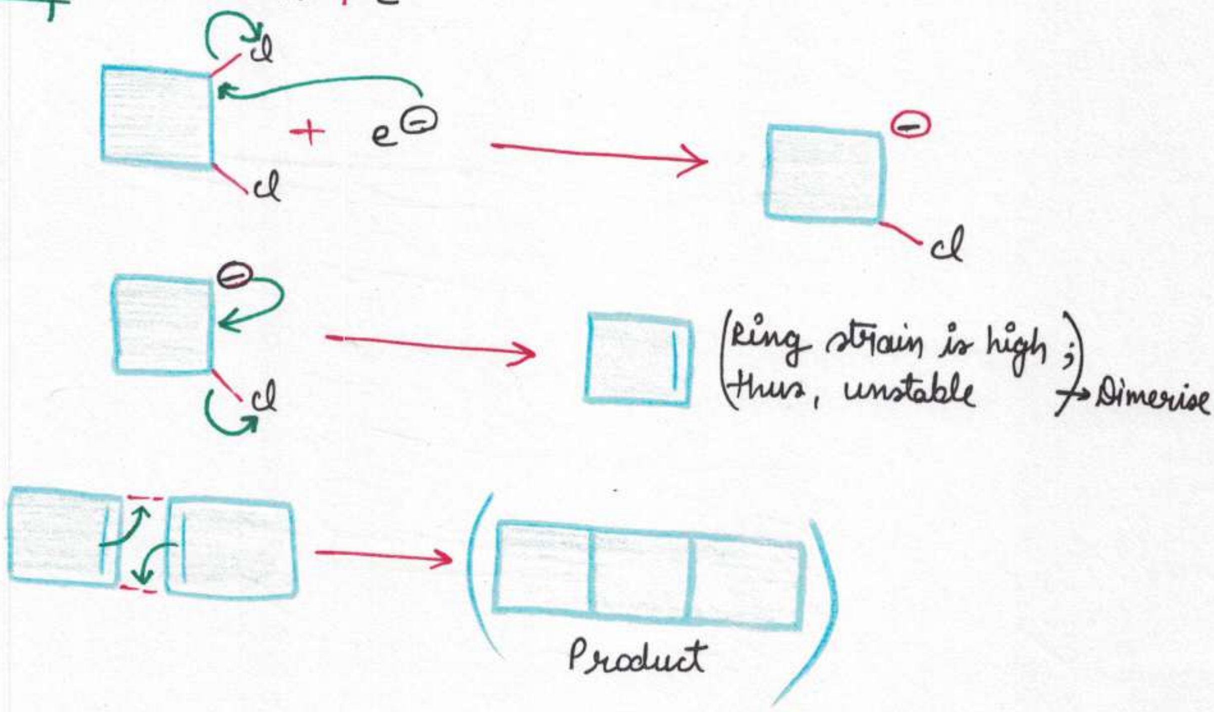
$\overset{\ominus}{C}H_2-CH_2-Cl \rightarrow (CH_2=CH_2)$

Product

(ii)

MECHANISM

$Na \rightarrow Na^+ + e^-$



(Ring strain is high; thus, unstable) → Dimerise

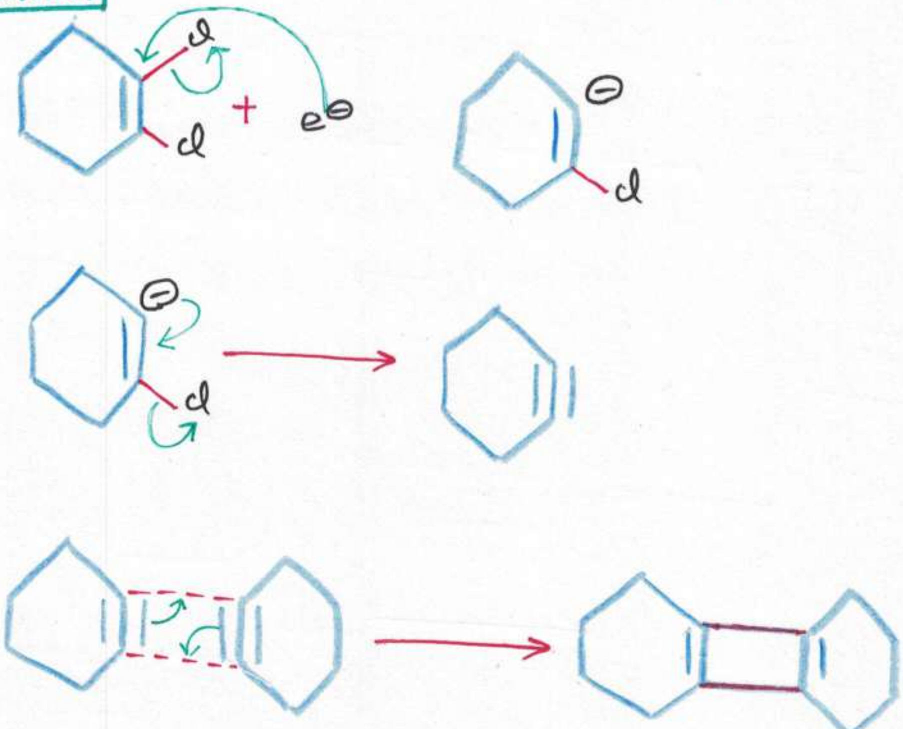
Product

☐ The compounds in which the ring strain is high tend to dimerise to release the ring and hence, become stable.

(iii)

MECHANISM

$Na \rightarrow Na^+ + e^-$



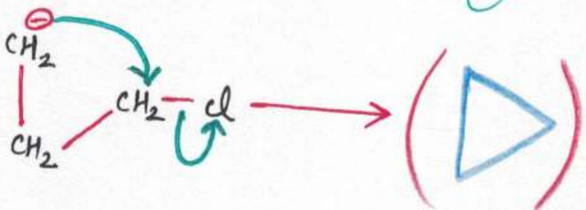
(Product)

(i) $Cl-CH_2-CH_2-CH_2-Cl \xrightarrow[Et_2O]{Na} ?$

MECHANISM

$Na \rightarrow Na^+ + e^-$

$Cl-CH_2-CH_2-CH_2-Cl + e^{\ominus} \rightarrow Cl-CH_2-CH_2-\overset{\ominus}{C}H_2$



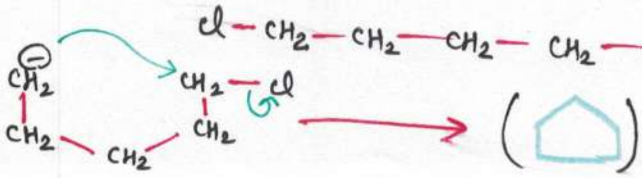
(Product)

(ii) $Cl-CH_2-CH_2-CH_2-CH_2-CH_2-Cl \xrightarrow[Et_2O]{Na} ?$

MECHANISM

$Na \rightarrow Na^+ + e^-$

$Cl-CH_2-CH_2-CH_2-CH_2-CH_2-Cl + e^{\ominus} \rightarrow Cl-(CH_2)_4-\overset{\ominus}{C}H_2$

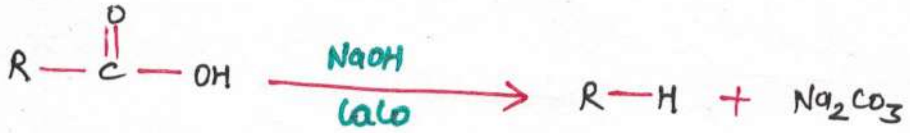


Product

DECARBOXYLATION OF CARBOXYLIC ACIDS

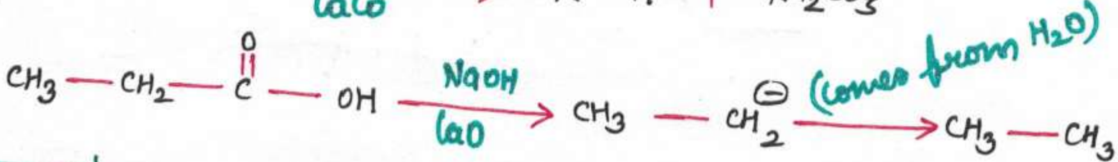
(i) Reagent used is NaOH/ CaO.

(ii) Some compounds decarboxylate on heating only; discussed in the later part of the video.



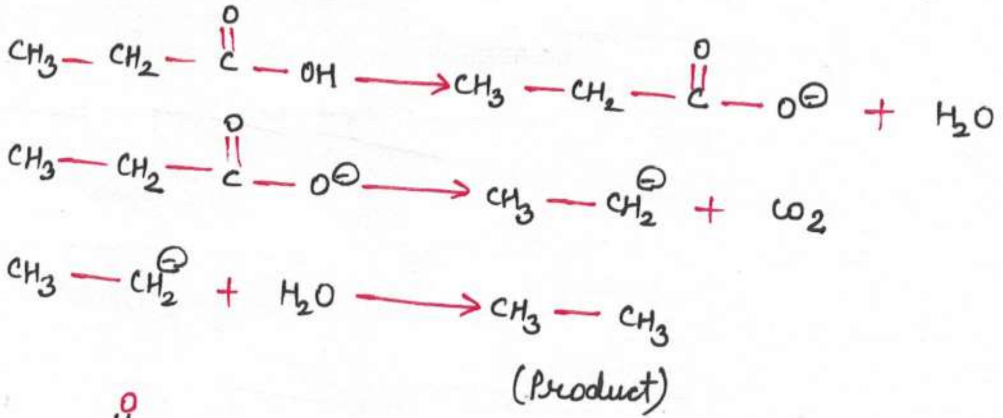
$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[CaO]{NaOH} R-H + Na_2CO_3$$

E.g.



$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[CaO]{NaOH} CH_3-\overset{\ominus}{C}H_2 \xrightarrow{\text{(comes from } H_2O)} CH_3-CH_3$$

MECHANISM

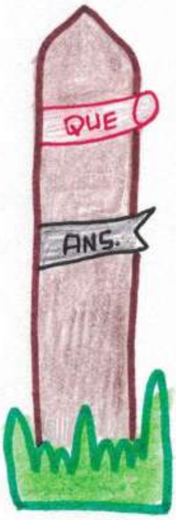


$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH \longrightarrow CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O^{\ominus} + H_2O$$

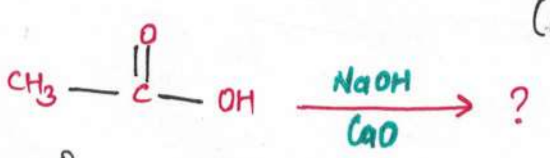
$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O^{\ominus} \longrightarrow CH_3-\overset{\ominus}{C}H_2 + CO_2$$

$$CH_3-\overset{\ominus}{C}H_2 + H_2O \longrightarrow CH_3-CH_3$$

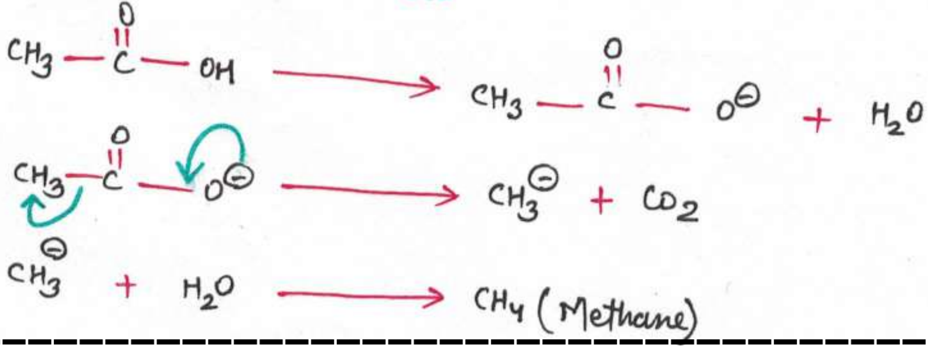
(Product)



(i)



$$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[CaO]{NaOH} ?$$



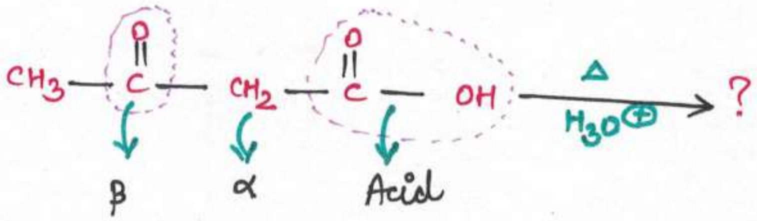
$$CH_3-\overset{O}{\overset{\|}{C}}-OH \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus} + H_2O$$

$$CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus} \longrightarrow \overset{\ominus}{C}H_3 + CO_2$$

$$\overset{\ominus}{C}H_3 + H_2O \longrightarrow CH_4 \text{ (Methane)}$$

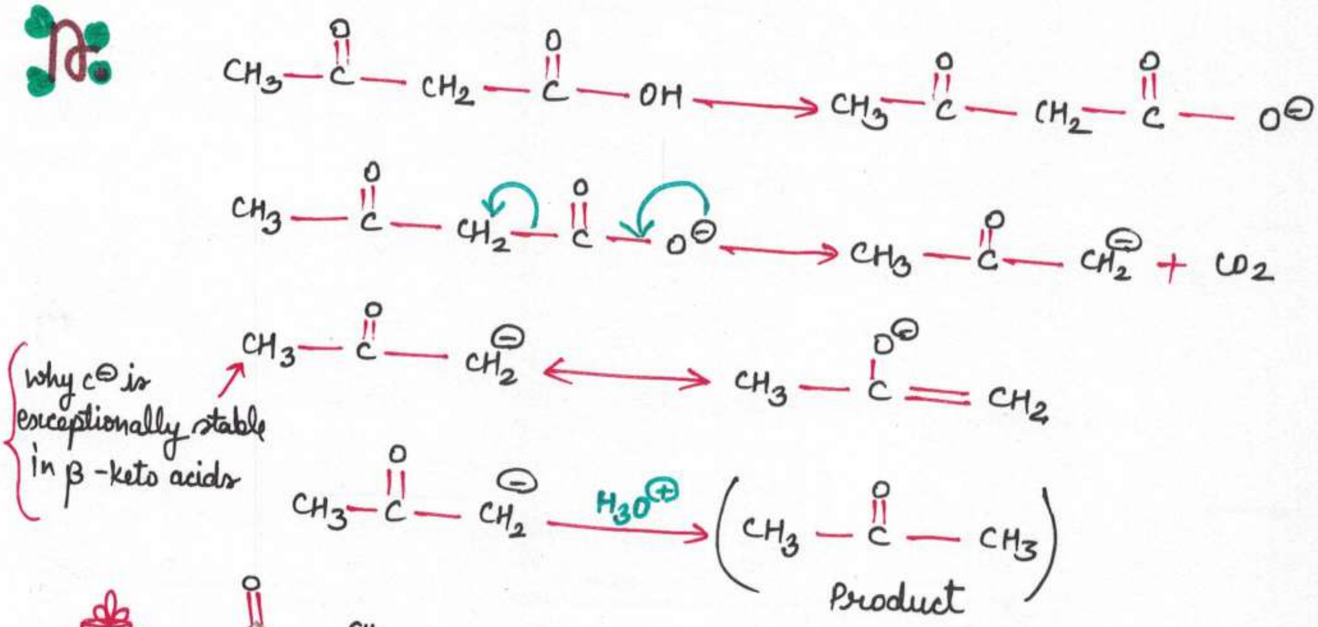
- Thus, we see that the intermediate formed is a carbanion.
- β-keto acids decarboxylate on heating as the C⊖ formed is in resonance.

Q. i



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[H_3O^{\oplus}]{\Delta} ?$$

S.



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-O^{\ominus}$$

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-O^{\ominus} \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H_2 + CO_2$$

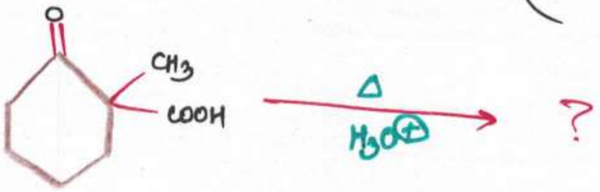
$$CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H_2 \longleftrightarrow CH_3-\overset{O^{\ominus}}{\overset{|}{C}}=CH_2$$

$$CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H_2 \xrightarrow{H_3O^{\oplus}} \left(CH_3-\overset{O}{\overset{\|}{C}}-CH_3\right)$$

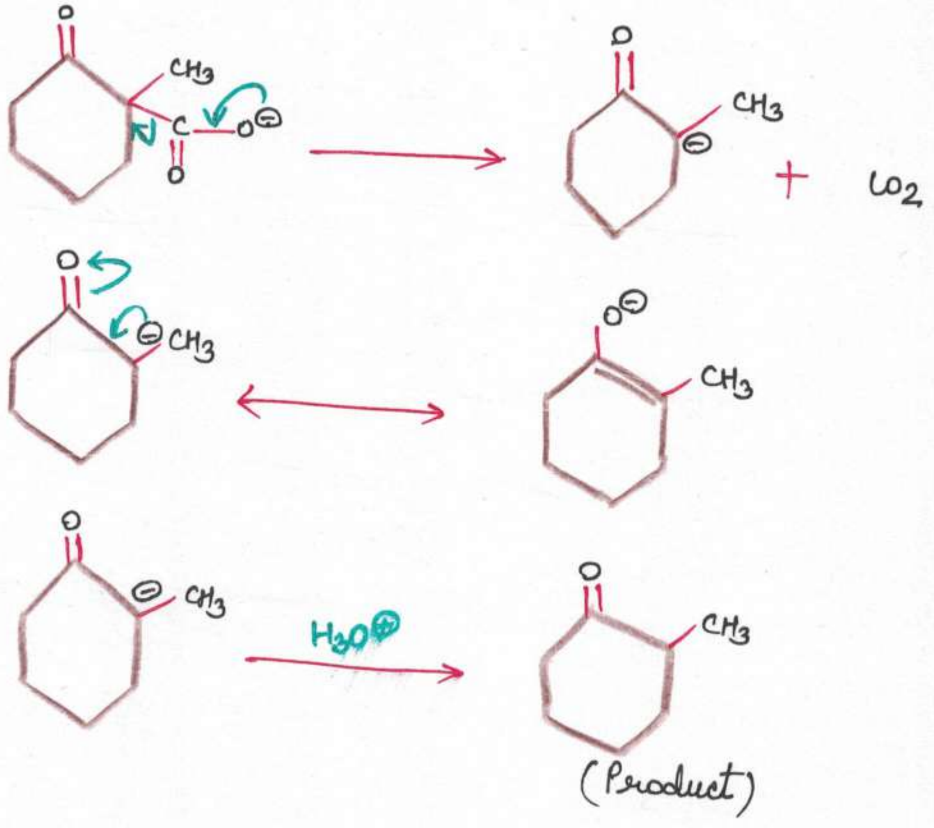
Product

why C⊖ is exceptionally stable in β-keto acids

ii

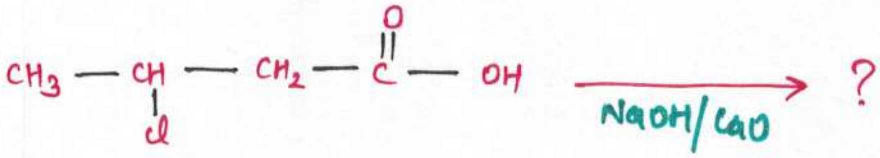


MECHANISM



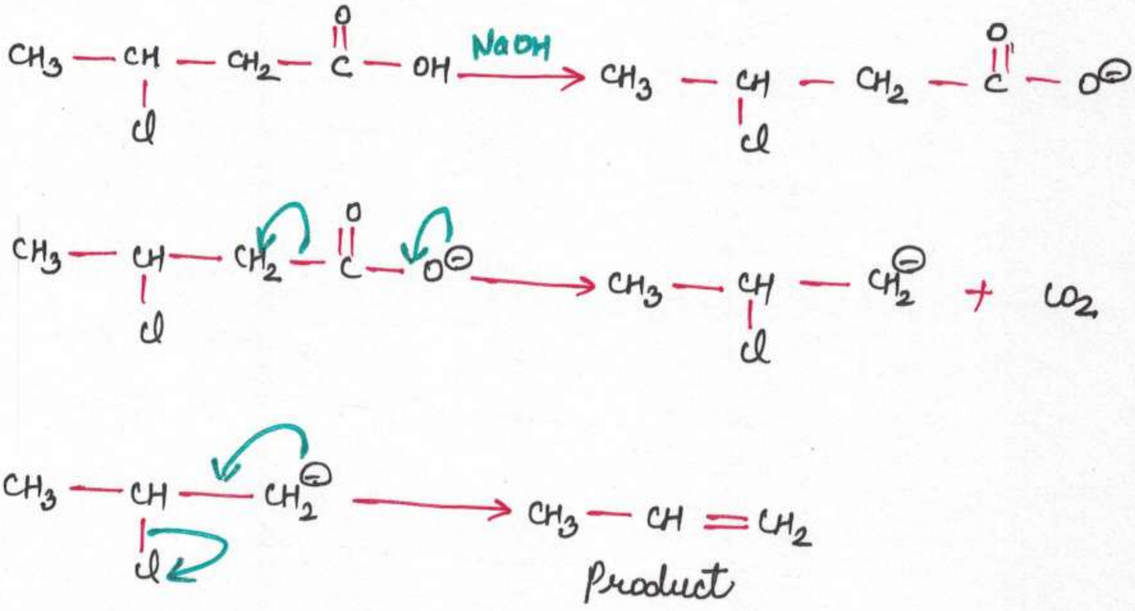
(Product)

Q 1



$$CH_3-\underset{Cl}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[NaOH/CaO]{} ?$$

1.A:



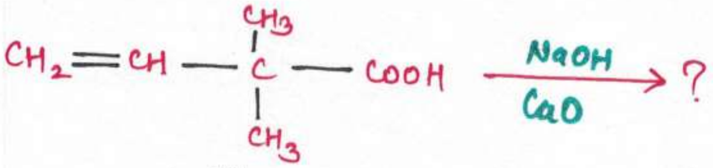
$$CH_3-\underset{Cl}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{NaOH} CH_3-\underset{Cl}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-O^{\ominus}$$

$$CH_3-\underset{Cl}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-O^{\ominus} \longrightarrow CH_3-\underset{Cl}{CH}-\overset{\ominus}{CH_2} + CO_2$$

$$CH_3-\underset{Cl}{CH}-\overset{\ominus}{CH_2} \longrightarrow CH_3-CH=CH_2$$

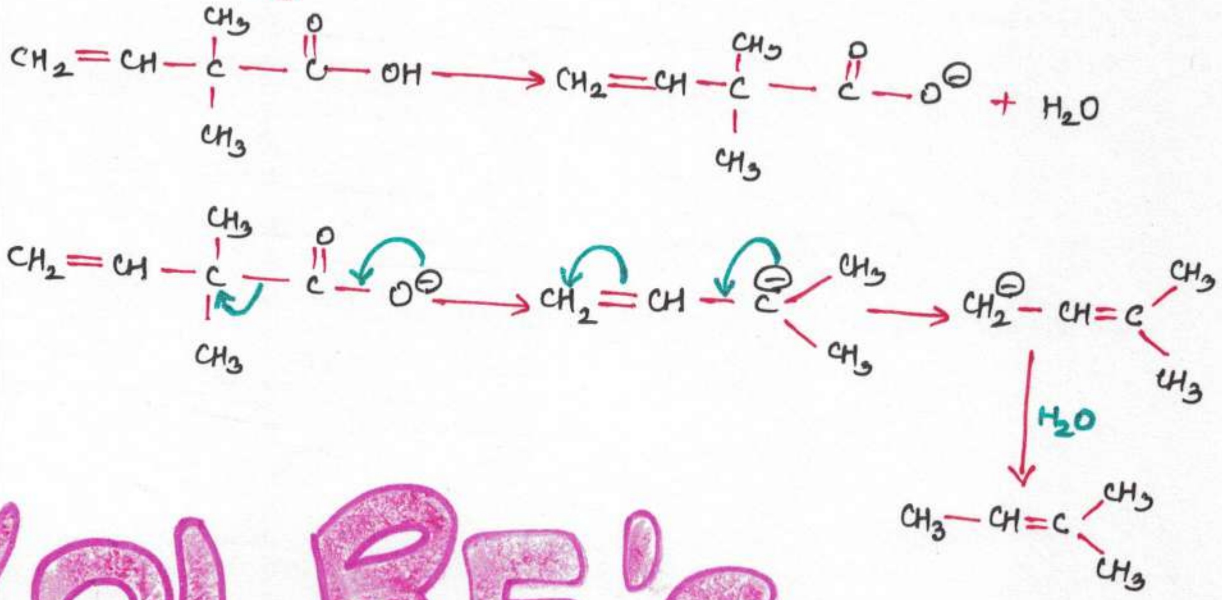
Product

2.



$$CH_2=CH-\underset{CH_3}{\overset{CH_3}{C}}-COOH \xrightarrow[CaO]{NaOH} ?$$

2.A.



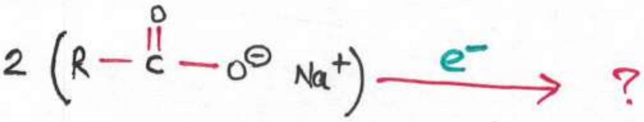
$$CH_2=CH-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-OH \longrightarrow CH_2=CH-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-O^{\ominus} + H_2O$$

$$CH_2=CH-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-O^{\ominus} \longrightarrow CH_2=CH-\overset{\ominus}{C}{<}^{CH_3}_{CH_3} \longrightarrow \overset{\ominus}{CH_2}-CH=C{<}^{CH_3}_{CH_3} \xrightarrow{H_2O} CH_3-CH=C{<}^{CH_3}_{CH_3}$$

KOLBE'S

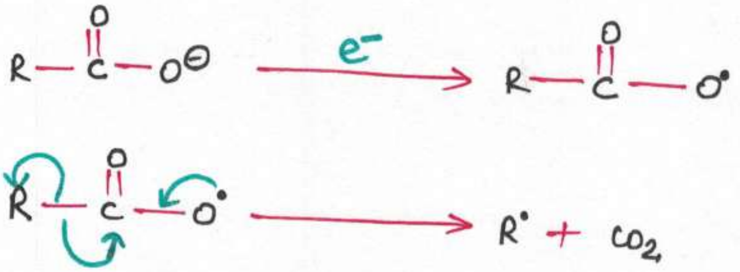
electrolysis

Q



$$2\left(R-\overset{O}{\overset{\|}{C}}-O^{\ominus}\ Na^{+}\right) \xrightarrow{e^-} ?$$

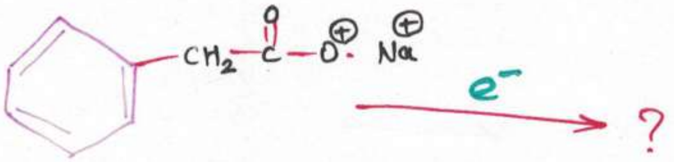
Ans.



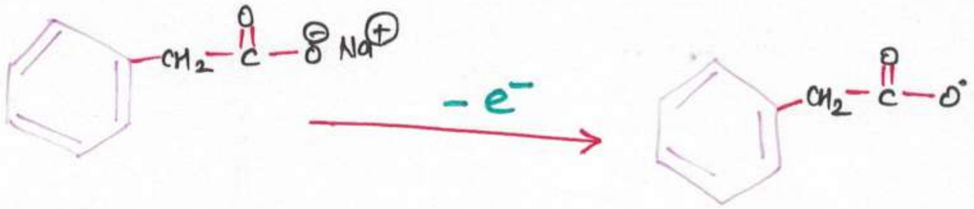
(some for the second mole of the question)

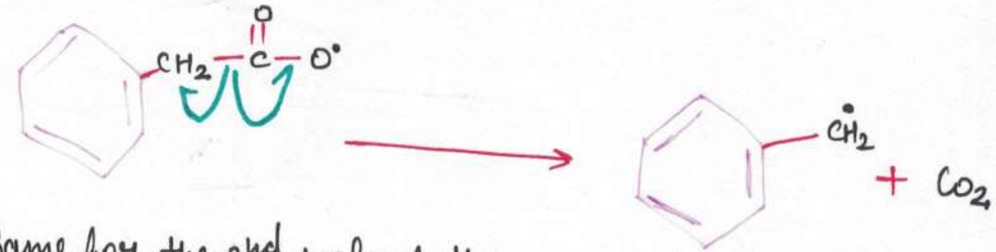
Product

QUE. (i)



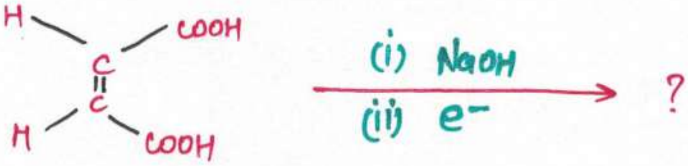
ANS (i)





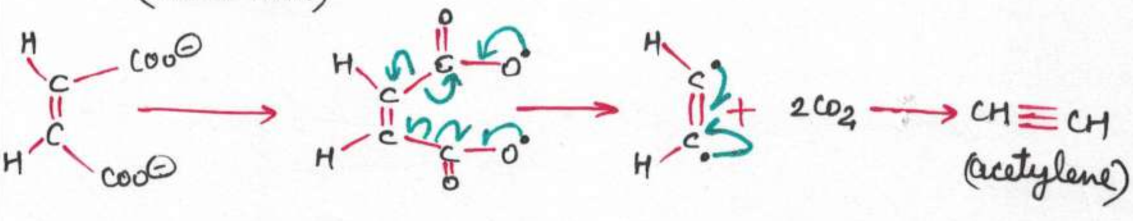
(Same for the 2nd mole of the compound)

QUE



(Maleic acid)

ANS



⊙ Same reaction for fumaric acid on kolbe's electrolysis.

COREY HOUSE REACTIONS

i) $R-X + Li/et_2O \longrightarrow (A) \longrightarrow (B) \longrightarrow (C)$

MECHANISM

$$R-X + Li \longrightarrow \underset{(A)}{R^{\ominus}Li^{\oplus}}$$

$$2R^{\ominus}Li^{\oplus} + CuI \longrightarrow Li^{+}\underset{(B)}{[R-Cu-R]} + LiI$$

$$R_2CuLi + R'-X \longrightarrow \underset{(C)}{(R-R')}$$

Thus corey House reactions can be used in the preparation of the symmetrical and asymmetrical alkanes.

$$\begin{tikzcd} CH_3-X + Li/et_2O \arrow[r] & (A) \arrow[r, "CuI"] & (B) \arrow[r, "CH_3-CH_2-X"] \arrow[dr, "CH_3-X"'] & (C) \\ & & & (D) \end{tikzcd}$$

$$CH_3-X + Li/et_2O \longrightarrow \underset{(A)}{\overset{\ominus}{C}H_3\ Li^{\oplus}}$$

$$\overset{\ominus}{C}H_3\ Li^{+} + CuI \longrightarrow \underset{(B)}{[(CH_3)_2CuLi]}$$

$$(CH_3)_2CuLi \xrightarrow{CH_3-CH_2-X} CH_3-CH_2-CH_3 \quad (C)$$

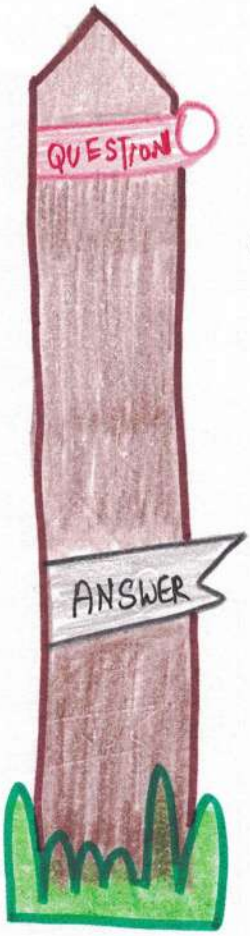
Asymm.

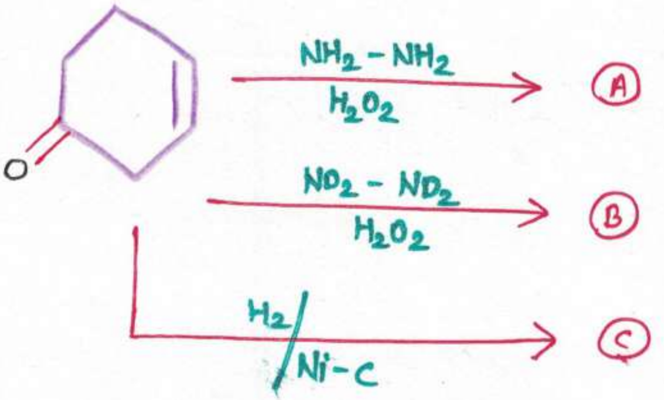
$$(CH_3)_2CuLi \xrightarrow{CH_3-X} CH_3-CH_3 \quad (D)$$

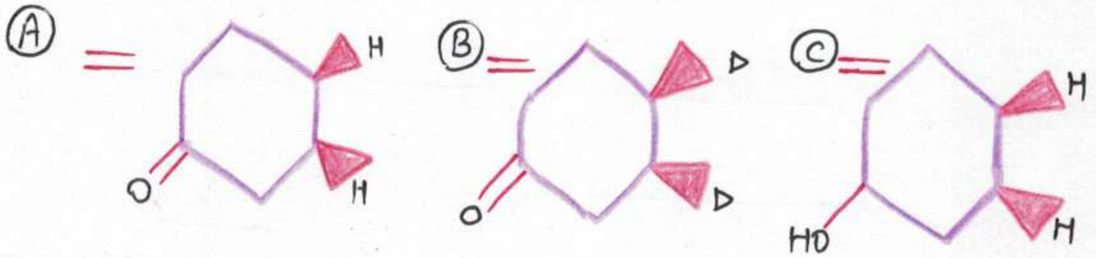
symm.

QUESTION

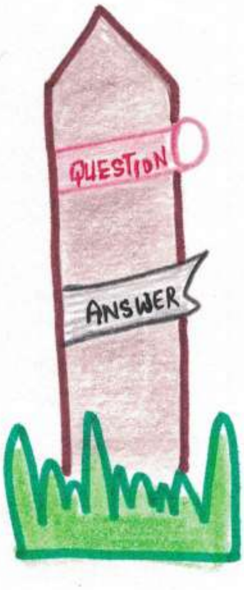
FOR QUICK REVISION

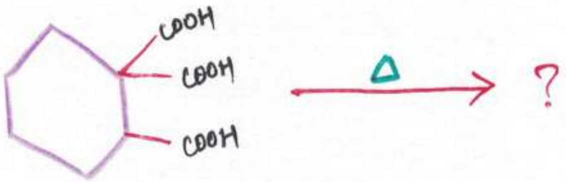


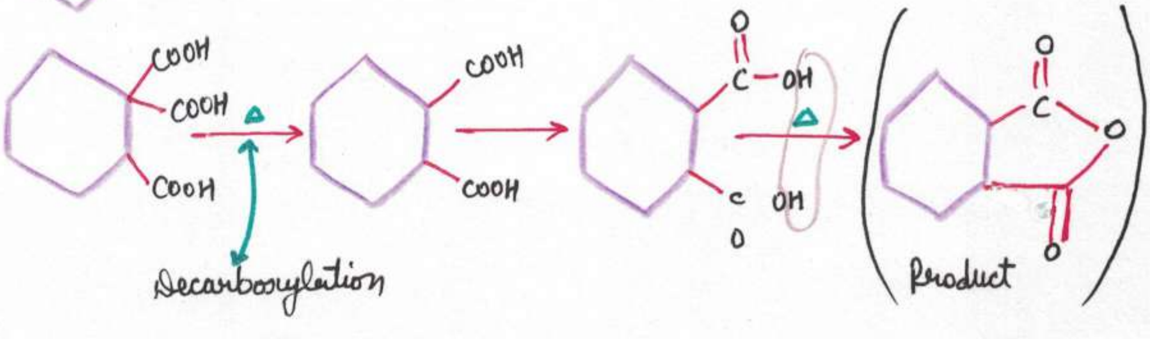




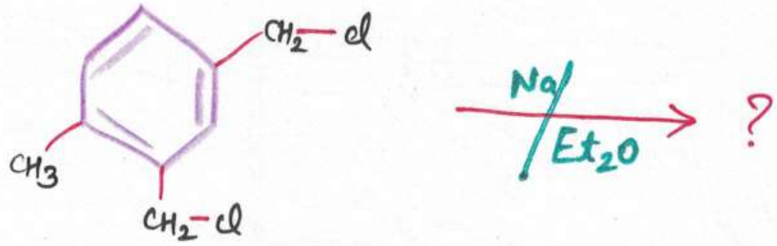
Cis addition, thus, attached on the same side.



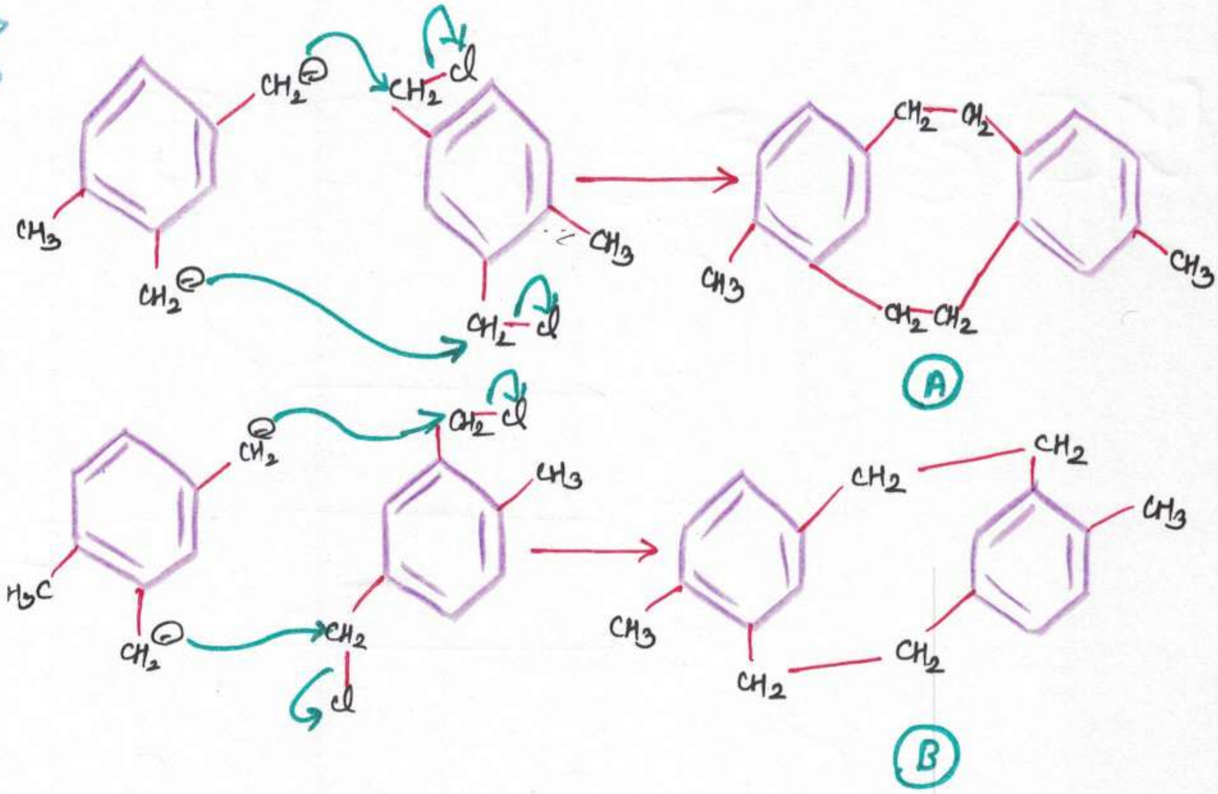




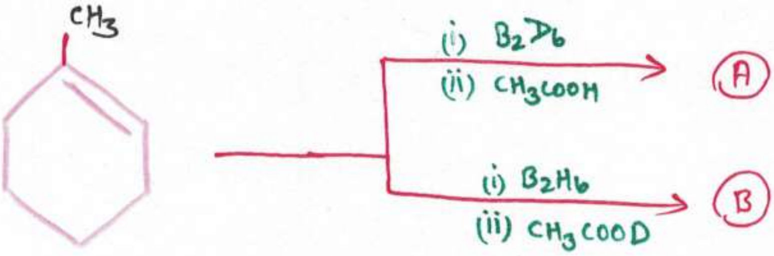
Question



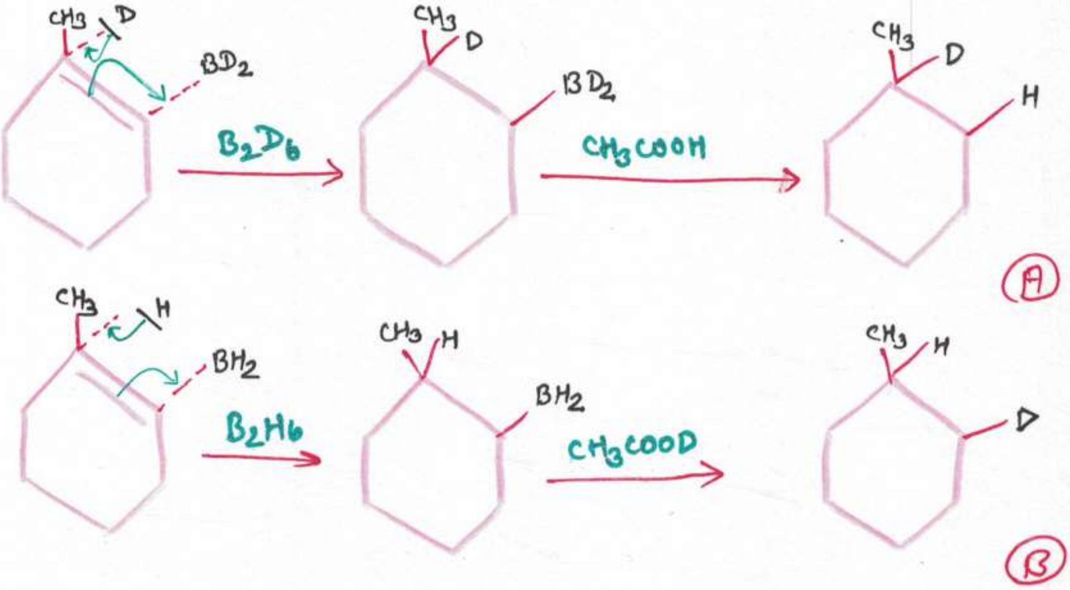
ANSWER



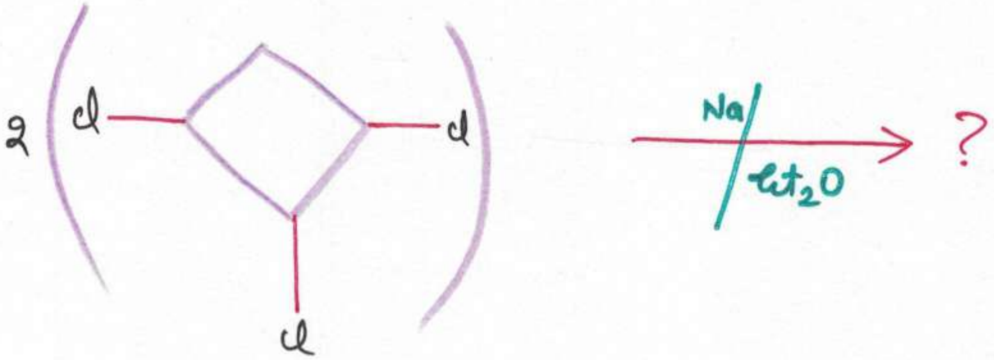
Q.



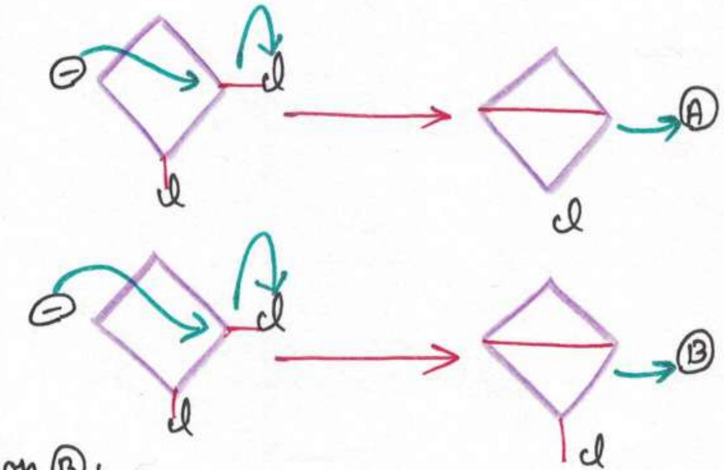
A.



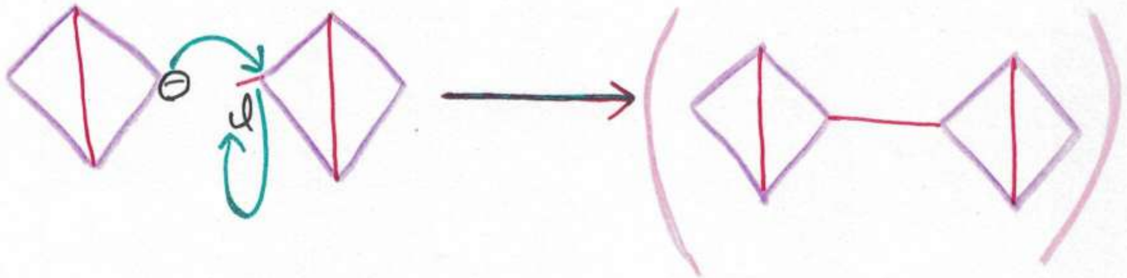
Q.



A.



Now Ⓐ on Ⓑ ;



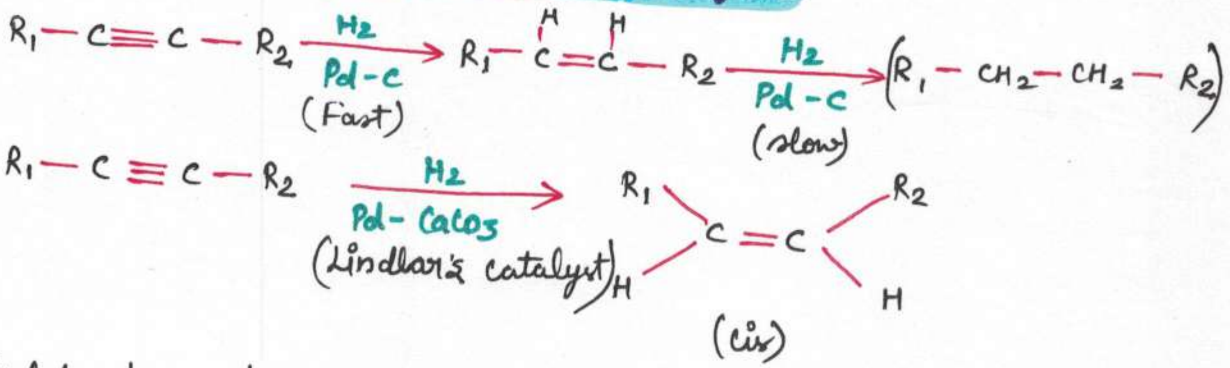
ALKENES

organic begins here.........

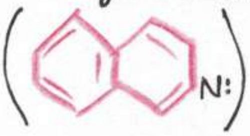
PREPARATION

FROM ALKYNES

A. By Catalytic hydrogenation of Alkynes

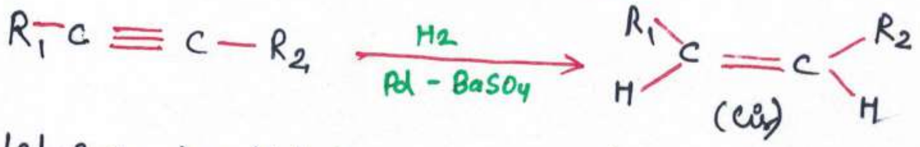


The CaCO3 here contains 'S' or 'Pb(OAc)$_4$' or Isoquinolen they act as catalyst poisoners.



- Lindlar's catalyst only converts the alkynes to alkenes. there is no further reduction.
- If the contaminants like "S" etc are not present, then it act as the (H_2/Pd-C) giving red reduction to alkanes.

B. By Using Rosenmund reduction



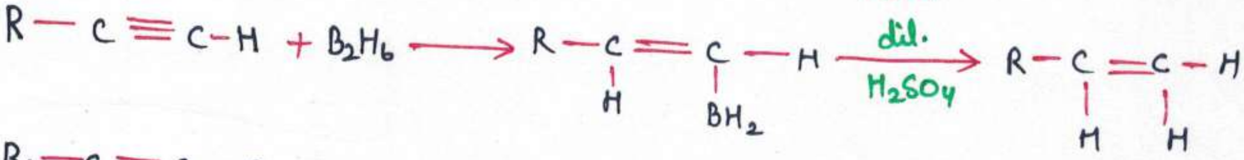
H_2/Pd-BaSO$_4$ is called Rosenmund catalyst having the 'S', Pb(OAc)$_4$, Isoquinolene on it.

only reduction till alkene.

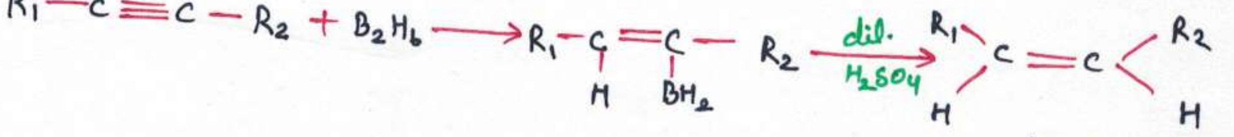
- ☐ The above reactions are stereoselective as cis is formed of the so many isomers, Cis is formed as major.

C. By hydroboration

- ☐ $R-CH=CH_2 + B_2H_6 \longrightarrow R-CH_2-CH_2-BH_2 \xrightarrow[H_2SO_4]{dil} (R-CH_2-CH_3)$

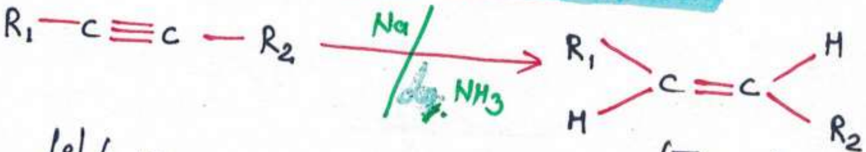


$R-C\equiv C-H + B_2H_6 \longrightarrow R-\underset{H}{C}=\underset{BH_2}{C}-H \xrightarrow[H_2SO_4]{dil.} R-\underset{H}{C}=\underset{H}{C}-H$

- ☐ 

(cis)

D. By Birch Reduction of alkynes

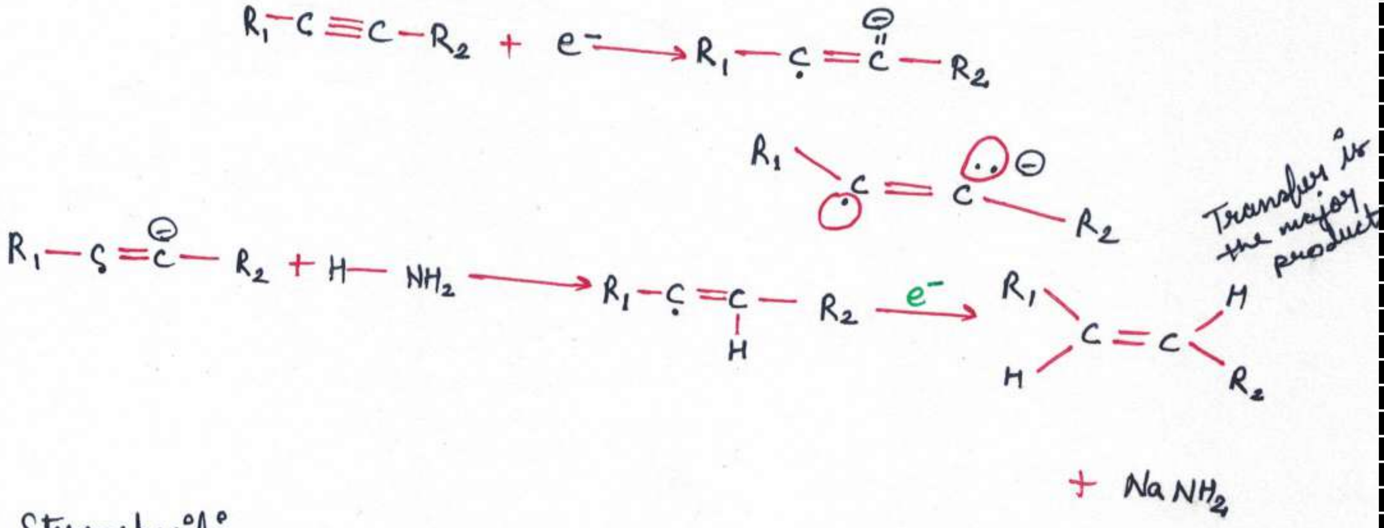
- ☐ 

(Trans)

Li/liq NH_3 — Also Birch redn

MECHANISM

$2Na \longrightarrow 2Na^+ + 2e^-$



- ☐ Stereospecific.

All $E_1 \rightarrow$ (Trans)

- only terminal alkens further undergo Birch Reduction.

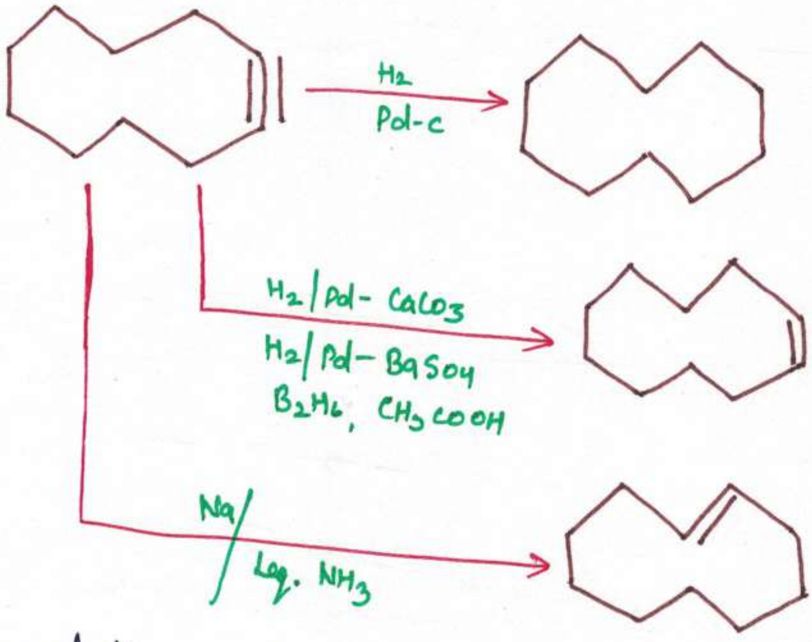
$$R_1-CH=CH_2 \longrightarrow (R_1-CH_2-CH_3)$$

$$R-CH=CH-R \longrightarrow N.R.$$

- Terminal alkynes don't undergo Birch Reduction. They form salts here

$$R-C\equiv C-H + Na/liq.\ NH_3 \longrightarrow R-C\equiv C^{\ominus}\ Na^{\oplus} + H_2\uparrow$$

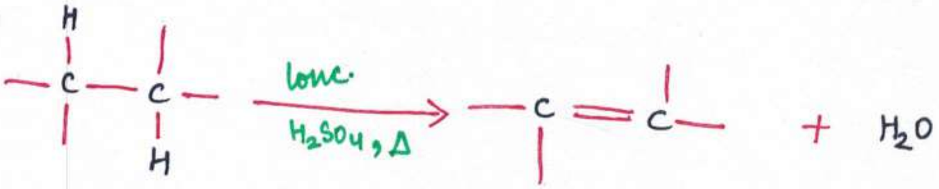
- Ammoniated e⁻ is the actual Birch reagent.



Stereoselective reaction.

ii

By dehydration of alcohols

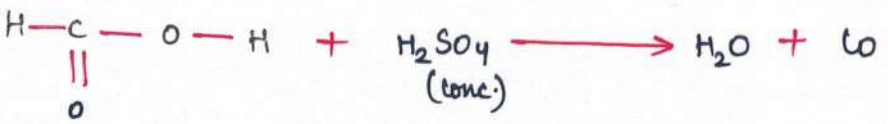


$$-\overset{H}{\underset{|}{C}}-\overset{|}{\underset{H}{C}}- \xrightarrow[H_2SO_4,\ \Delta]{Conc.} -\underset{|}{C}=\overset{|}{C}- + H_2O$$

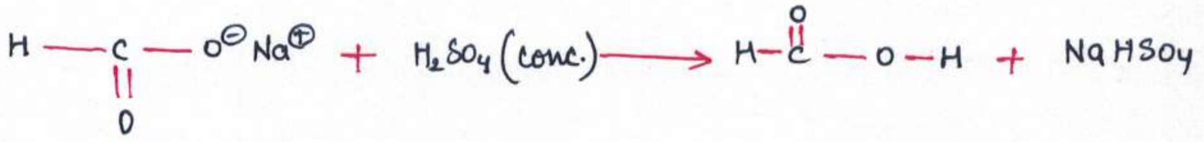
Conc. H_2SO_4 has a very high tendency to undergo hydration due to H-bonding tendency.

General formula of carbohydrate $C_x(H_2O)_y$

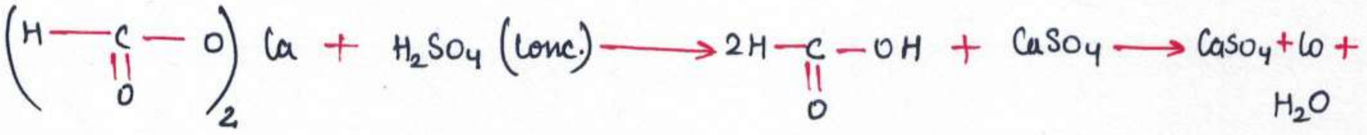
IMPORTANT

☐ 

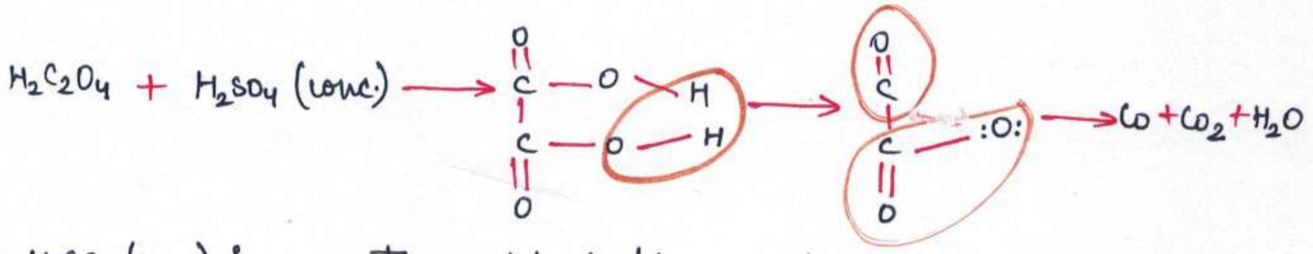
$H-\underset{\underset{O}{\|}}{C}-O-H + \underset{(conc.)}{H_2SO_4} \longrightarrow H_2O + CO$

☐ 

$H-\underset{\underset{O}{\|}}{C}-O^{\ominus}Na^{\oplus} + H_2SO_4(conc.) \longrightarrow H-\overset{\overset{O}{\|}}{C}-O-H + NaHSO_4$

☐ 

$\left(H-\underset{\underset{O}{\|}}{C}-O\right)_2 Ca + H_2SO_4(conc.) \longrightarrow 2H-\underset{\underset{O}{\|}}{C}-OH + CaSO_4 \longrightarrow CaSO_4 + CO + H_2O$

☐ 

$H_2C_2O_4 + H_2SO_4(conc.) \longrightarrow (COOH)_2 \longrightarrow CO + CO_2 + H_2O$

H_2SO_4 (conc.) is very strong dehydrating agent.

☐ $Na_2C_2O_4 + H_2SO_4(conc.) \longrightarrow H_2C_2O_4 + Na_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO + CO_2$

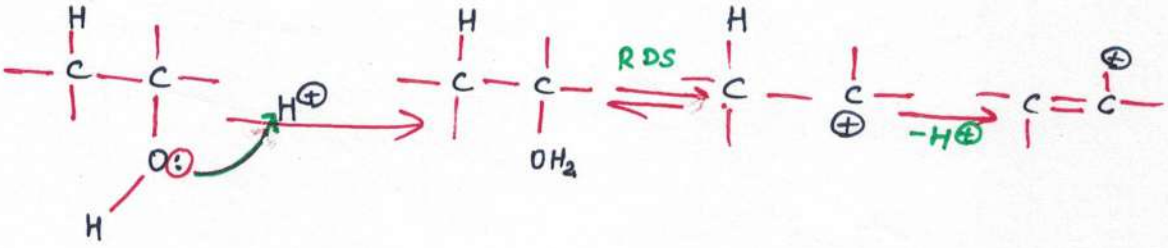
☐ $C_6H_{12}O_6 \longrightarrow C_6(H_2O)_6 \xrightarrow[(conc.)]{H^{\oplus}} 6C + 6H_2O$

(Black)

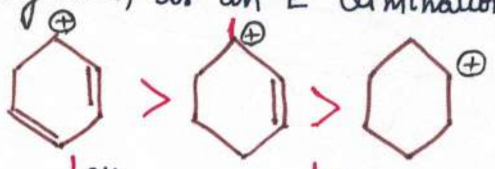
$C_{12}H_{22}O_{11} \longrightarrow C_{12}(H_2O)_{11} \xrightarrow[(conc.)]{H^{\oplus}} 12C + 11H_2O$

(Sucrose)

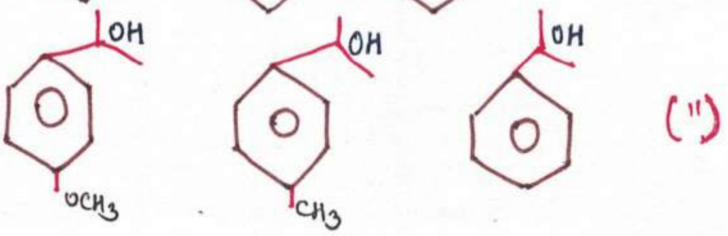
MECHANISM



☐ Dehyration is an E elimination (Trans elimination).

☐ 

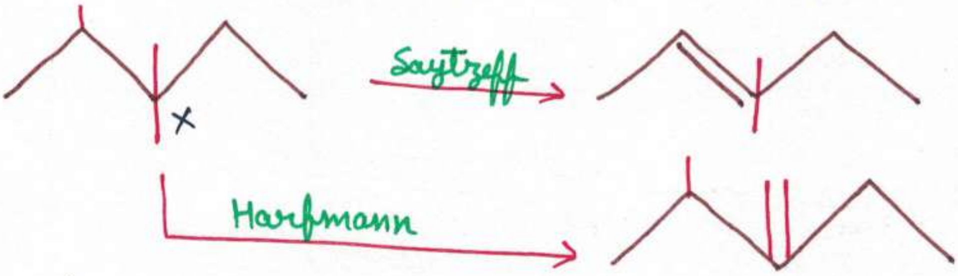
(Dehydration)

☐ 

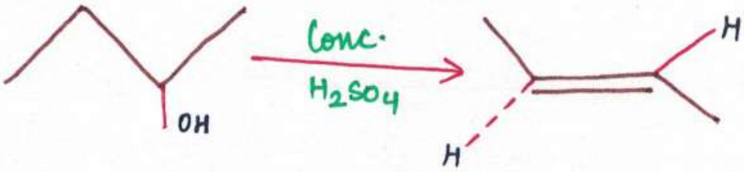
Major alkene is saytzeff (more stable) → More substituted

Major alkene is Harfmann (less stable) → Least stable (more acidic –H)

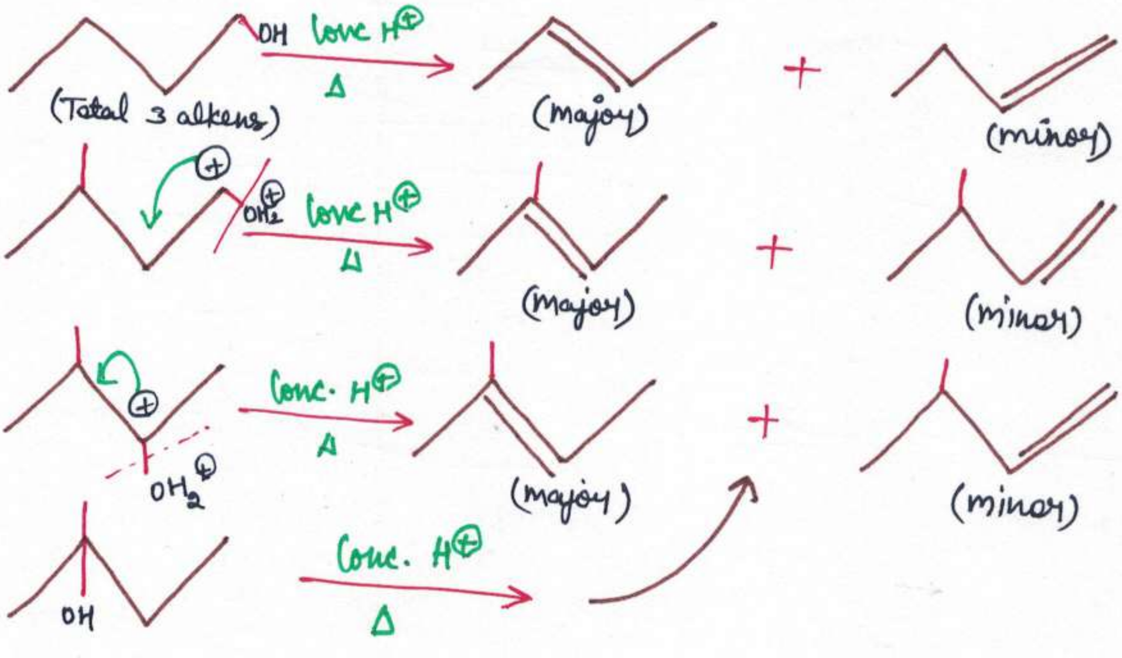
In Saytzeff Elimination, the rate of removal of hydrogen is t > s > p.



All E_1 elimination are saytzeff elimination.

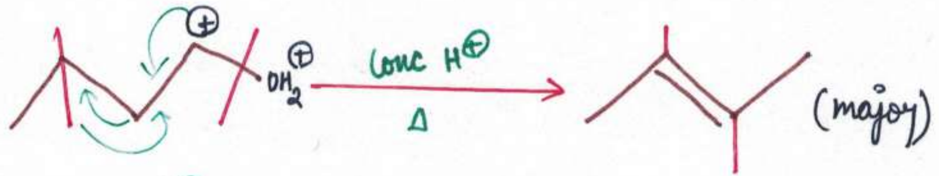


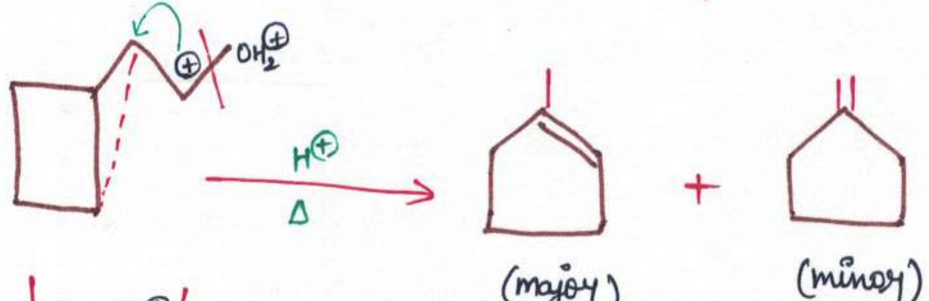
(Trans is major)

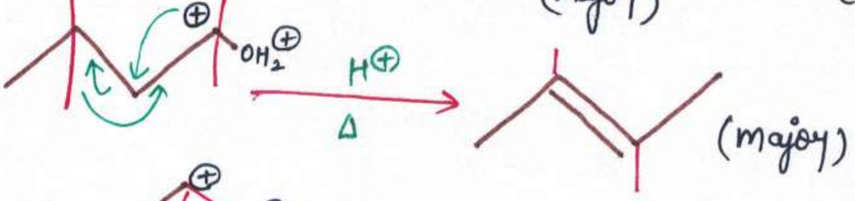


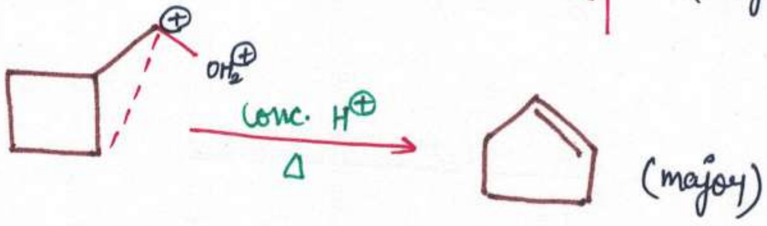
As they form the same intermediate, thus, same product is formed.

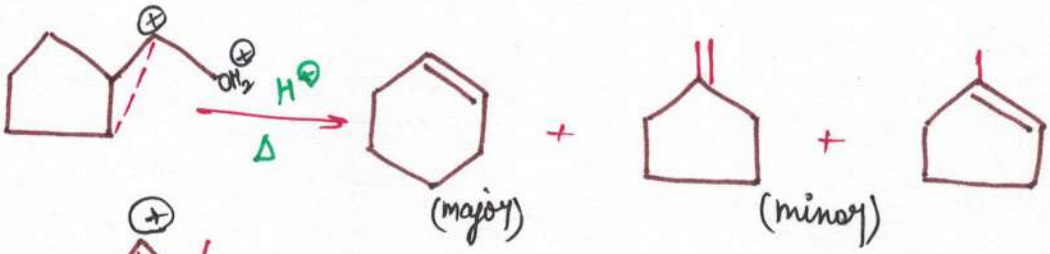
(Major)

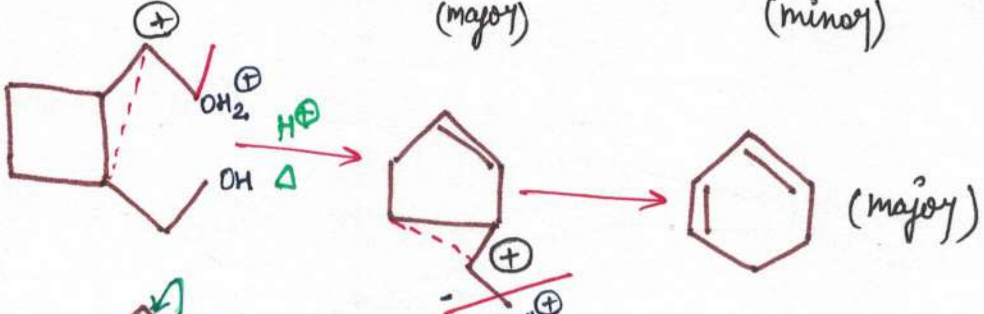

OH2⊕
Conc H⊕
Δ
(major)

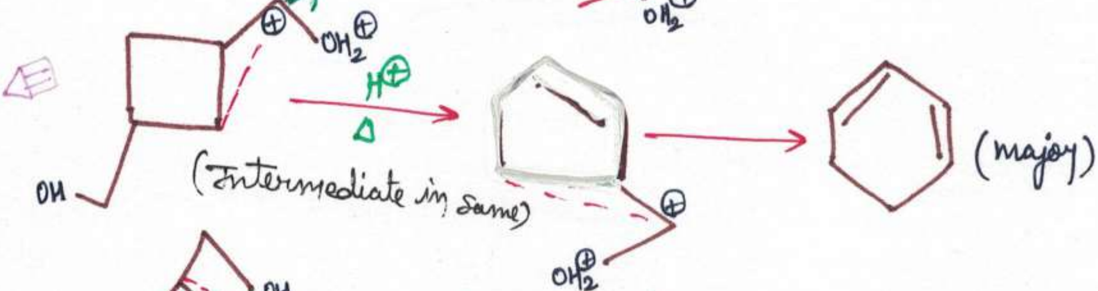

OH2⊕
H⊕
Δ
+
(major)
(minor)

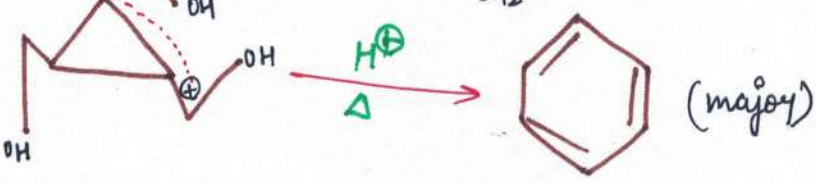

OH2⊕
H⊕
Δ
(major)

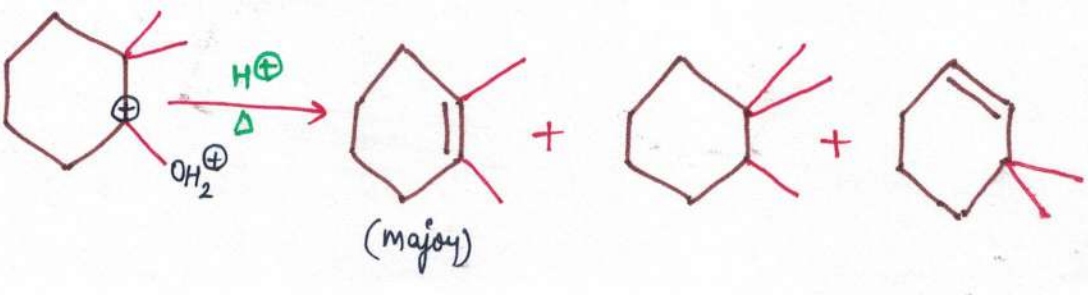

OH2⊕
Conc. H⊕
Δ
(major)

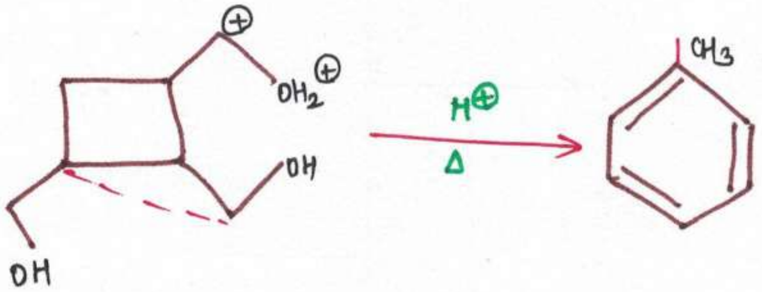

OH2⊕
H⊕
Δ
+
+
(major)
(minor)


OH2⊕
OH
H⊕
Δ
OH2⊕
(major)

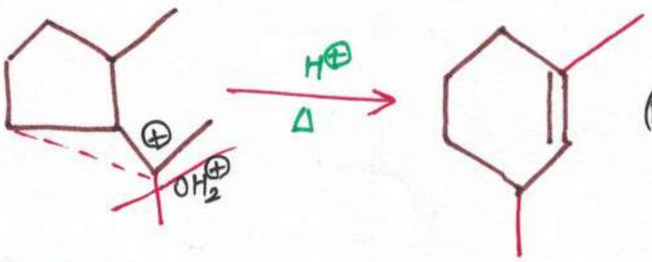

OH2⊕
H⊕
Δ
OH
(Intermediate in same)
OH2⊕
(major)


OH
OH
OH
H⊕
Δ
(major)

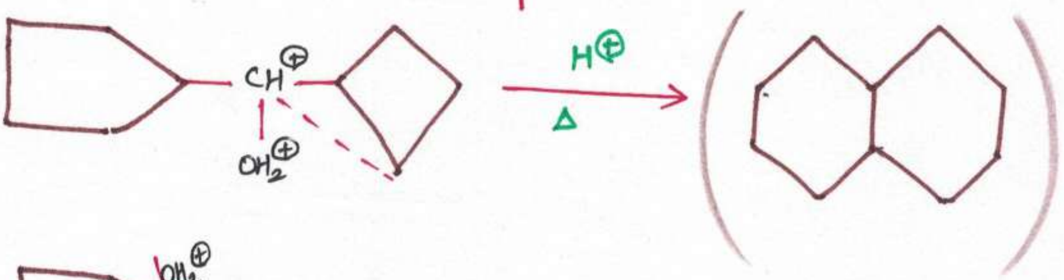

OH2⊕
H⊕
Δ
+
+
(major)

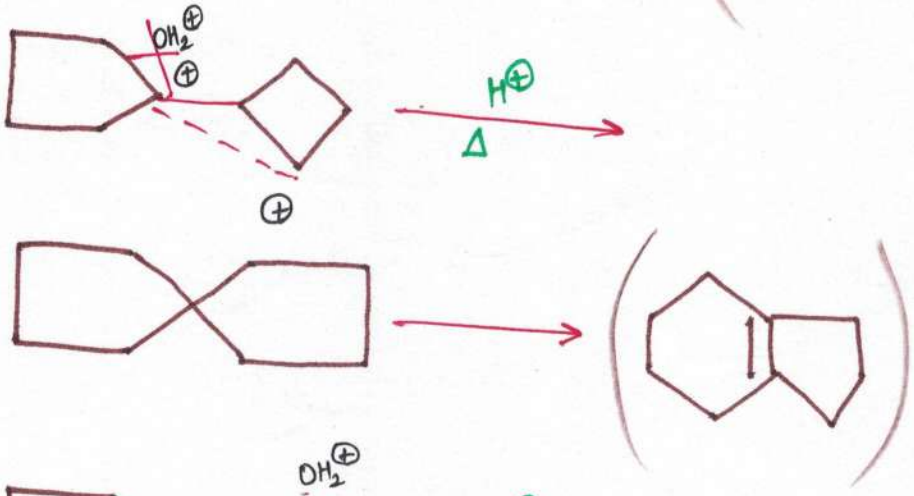


(Toulene)
(majoy)

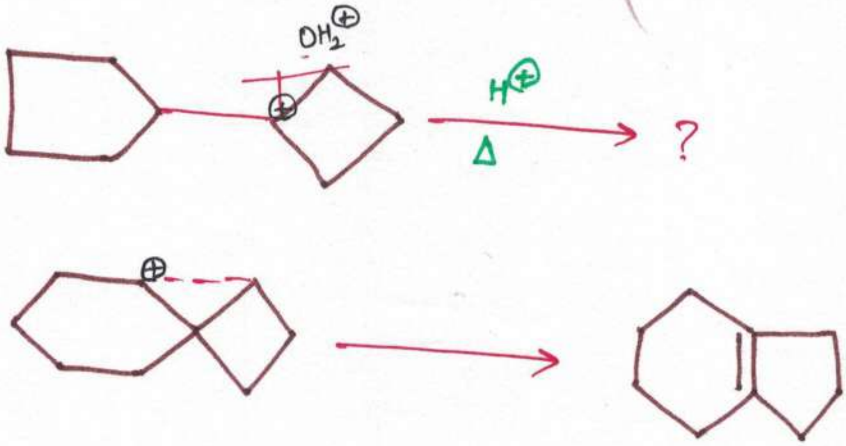


(majoy)



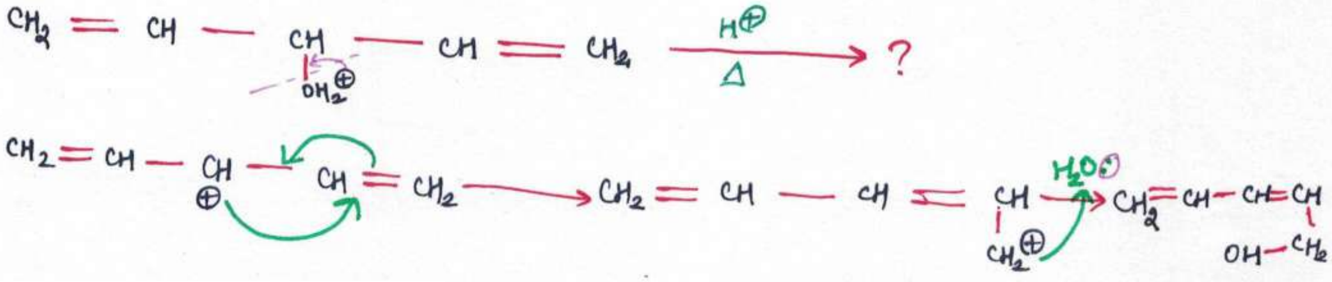


(majoy)



(mgjor)

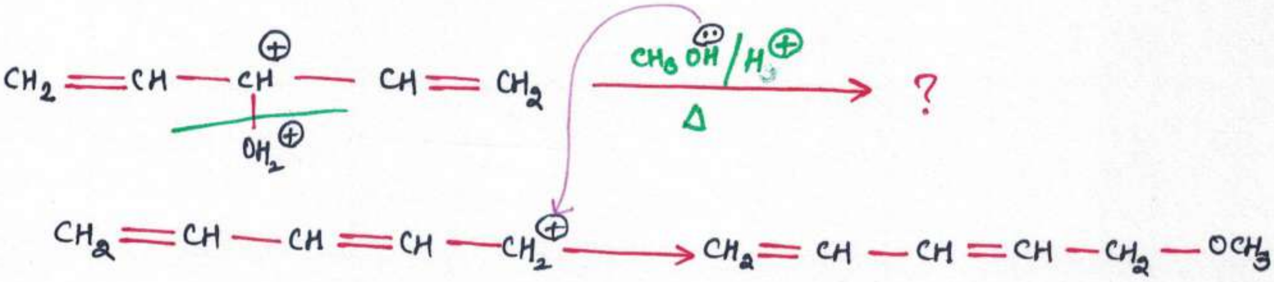
☐



$CH_2=CH-\underset{OH_2^{\oplus}}{CH}-CH=CH_2 \xrightarrow[\Delta]{H^{\oplus}} ?$

$CH_2=CH-\underset{\oplus}{CH}-CH=CH_2 \longrightarrow CH_2=CH-CH=\underset{CH_2^{\oplus}}{CH} \xrightarrow{H_2O^{\cdot\cdot}} CH_2=CH-CH=\underset{CH_2-OH}{CH}$

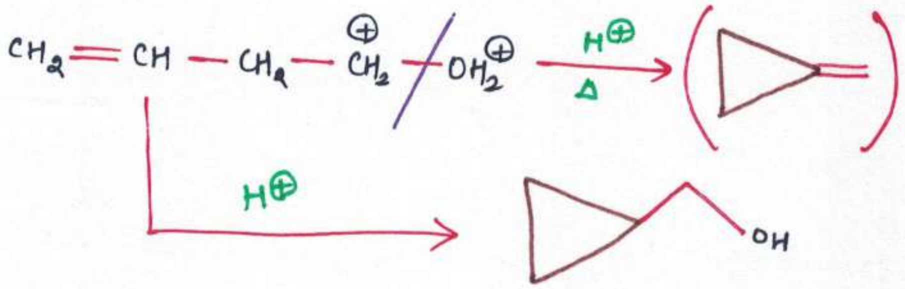
H.W



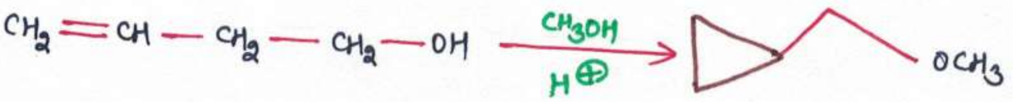
$CH_2{=}CH{-}\underset{OH_2^{\oplus}}{\overset{\oplus}{CH}}{-}CH{=}CH_2 \xrightarrow[\Delta]{CH_3\ddot{O}H/H^{\oplus}} ?$

$CH_2{=}CH{-}CH{=}CH{-}\overset{\oplus}{CH_2} \longrightarrow CH_2{=}CH{-}CH{=}CH{-}CH_2{-}OCH_3$

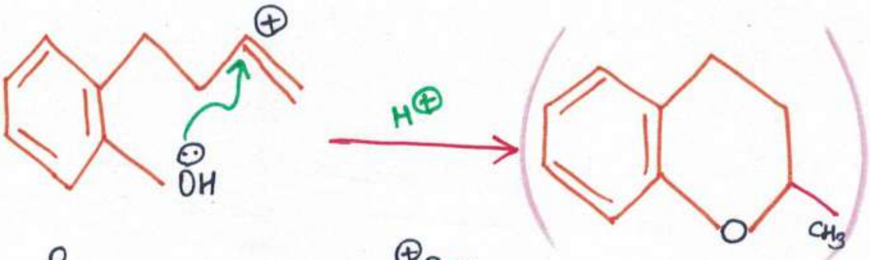
IMPORTANT



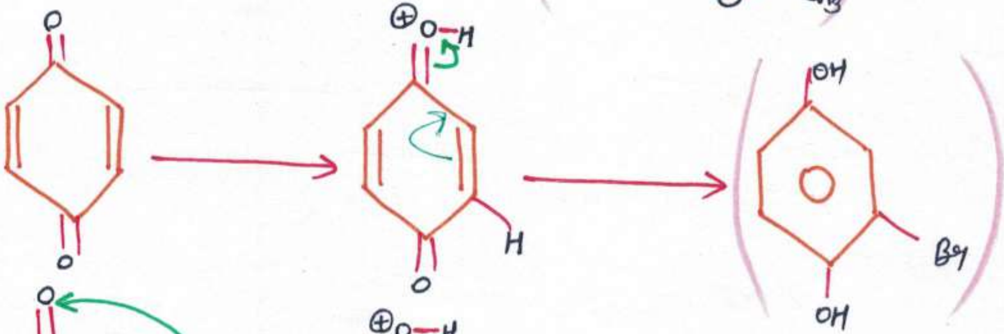
H.W



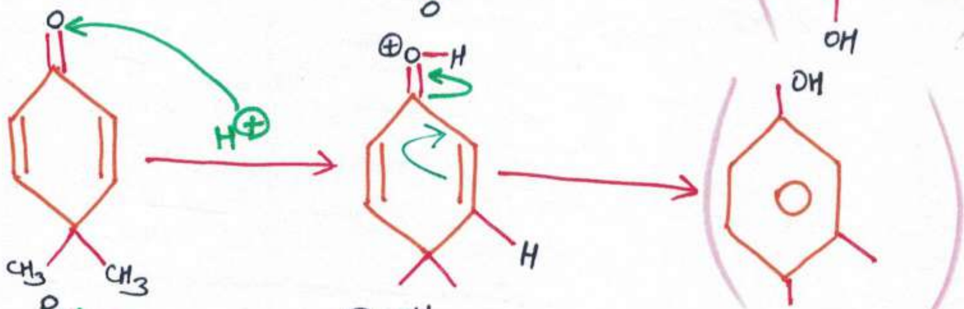
H.W



H.W

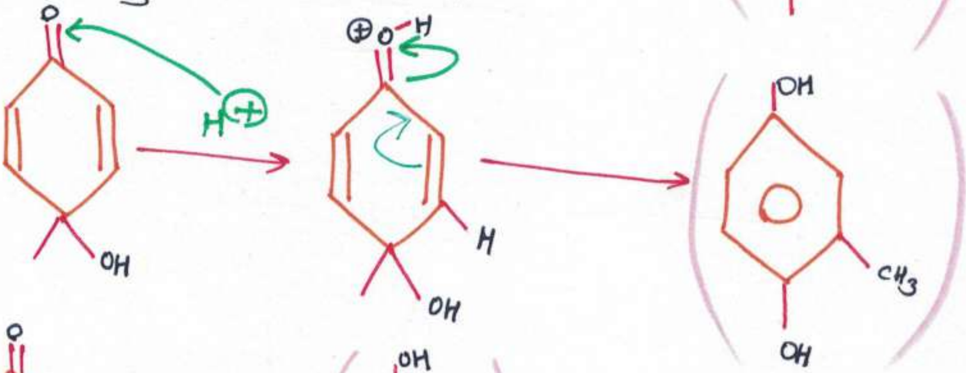


H.W

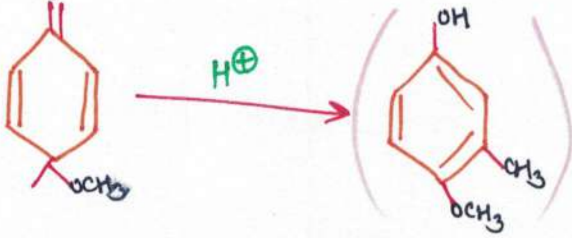


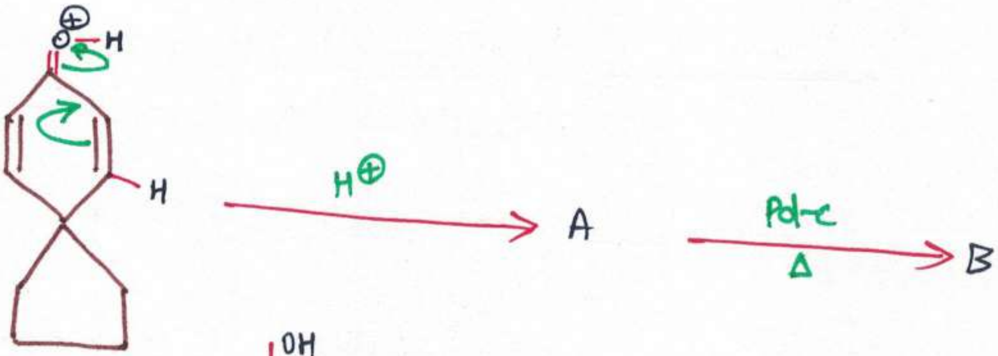
(major)

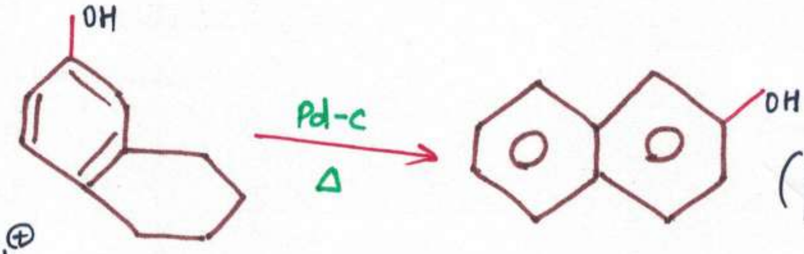
H.W



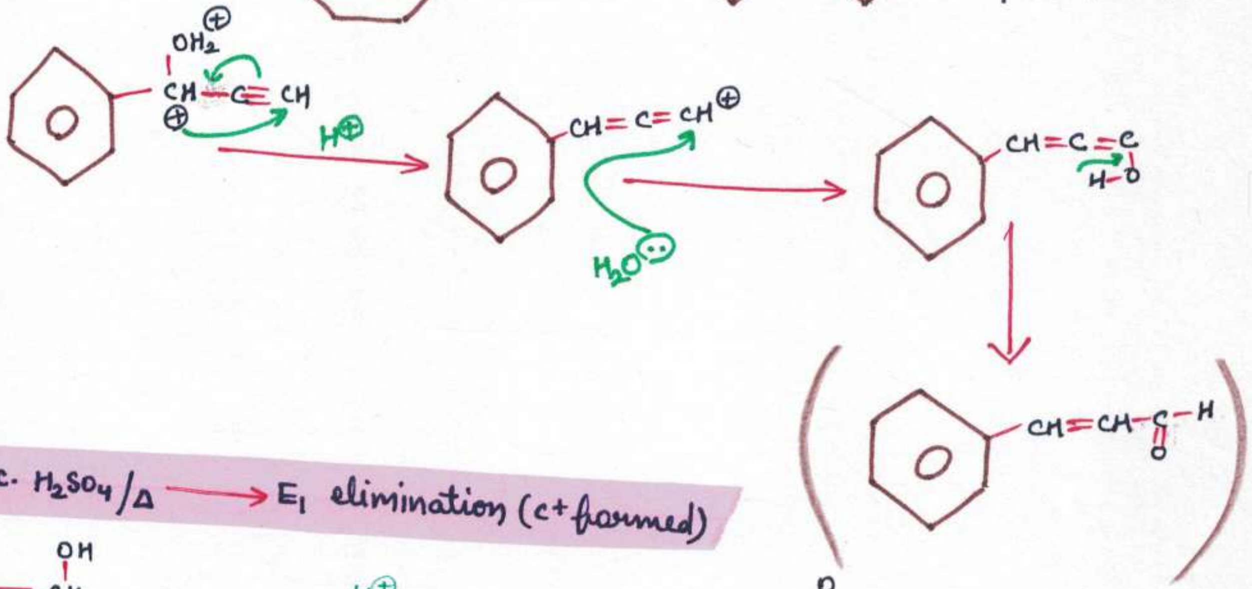
H.W







(β-napthol)

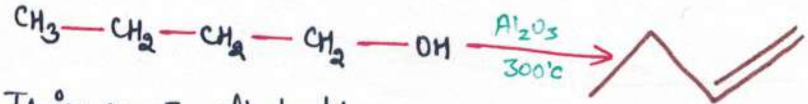


Conc. H_2SO_4/Δ → E_1 elimination (c+ formed)

$$R-\overset{OH}{\underset{|}{CH}}-C\equiv CH \xrightarrow{H^{\oplus}} R-CH=CH-\overset{O}{\overset{\|}{C}}-H$$

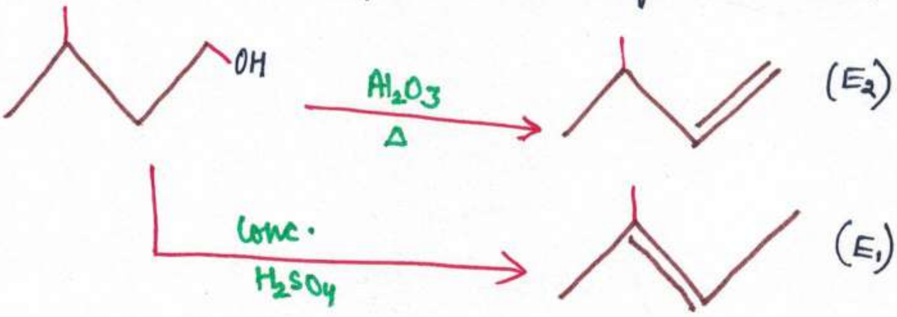
[a.] DEHYDRATION WITH Al_2O_3

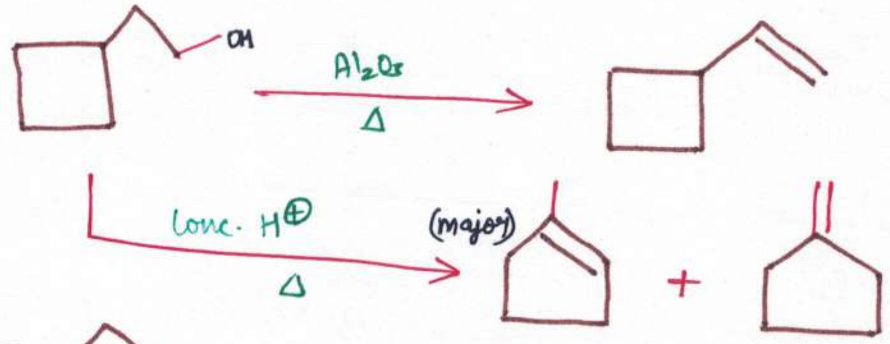
- $R-CH_2-CH_2-OH \xrightarrow[300°C]{Al_2O_3} (R-CH=CH_2)$

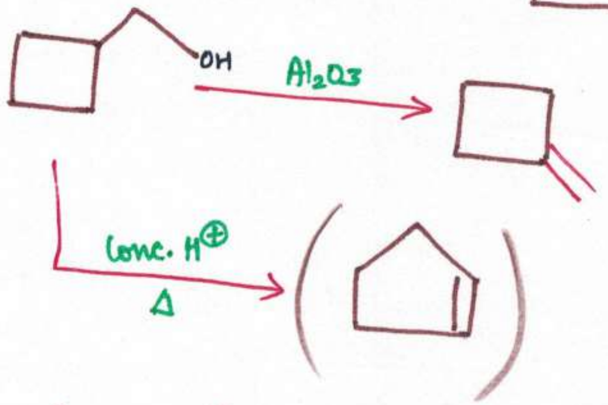
- 

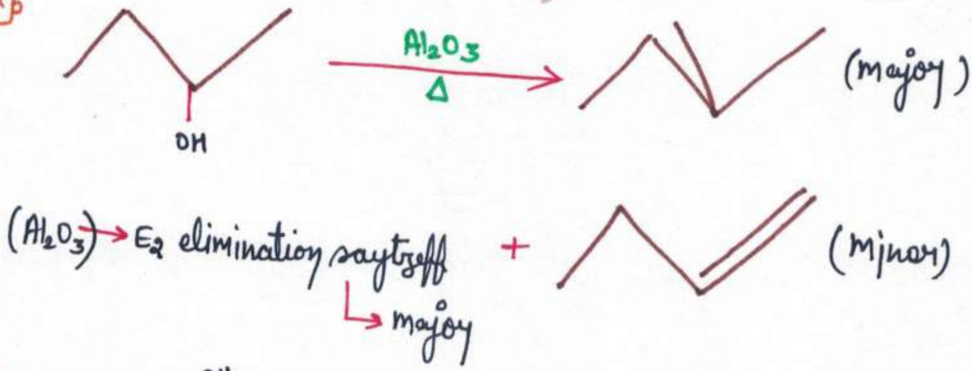
  $CH_3-CH_2-CH_2-CH_2-OH \xrightarrow[300°C]{Al_2O_3}$

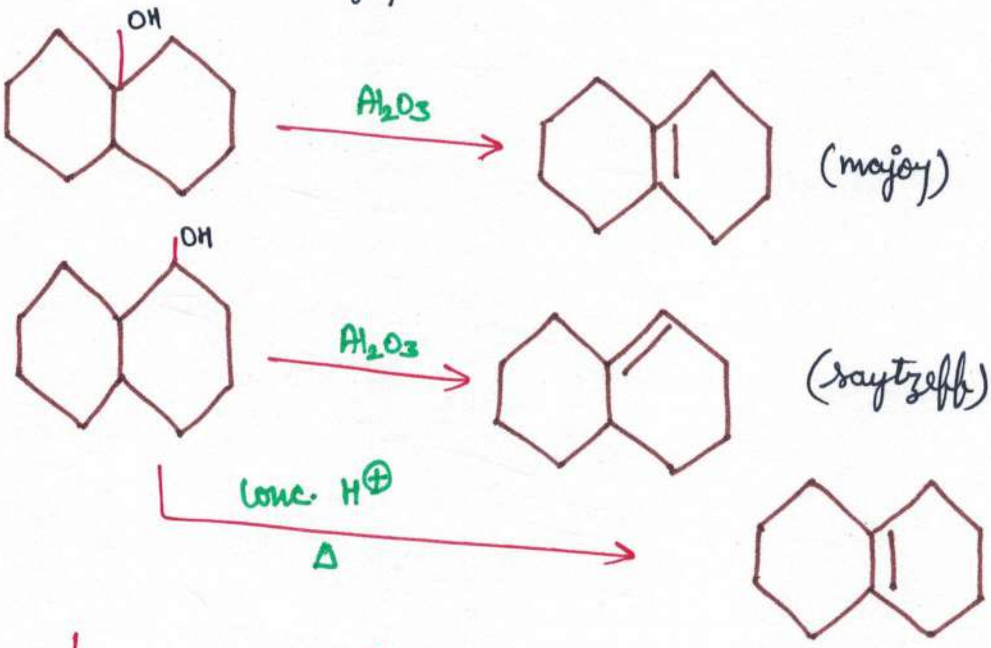
- It is an E_2 elimination No rearrangement occurs.

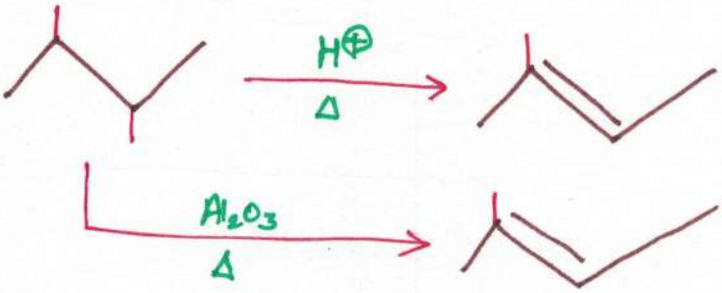



OH
Al_2O_3
Δ
Conc. $H^{\oplus}$
Δ
(major)
+


OH
Al_2O_3
Conc. $H^{\oplus}$
Δ

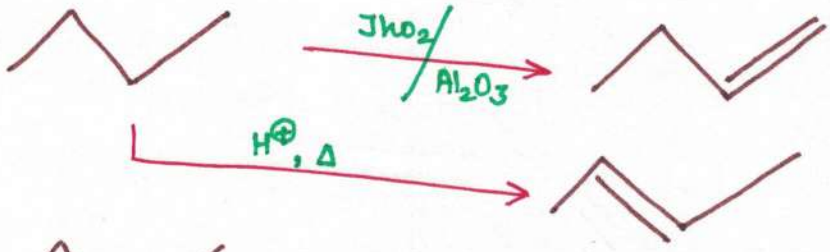

OH
Al_2O_3
Δ
(major)
(Al_2O_3) → E_2 elimination saytzeff
→ major
+
(minor)

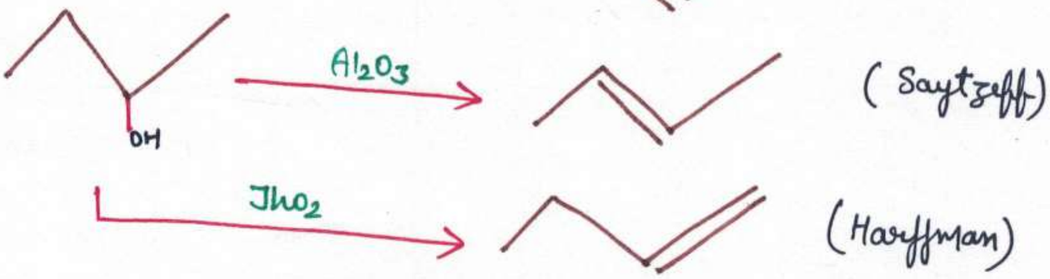

OH
Al_2O_3
(major)
OH
Al_2O_3
(saytzeff)
Conc. $H^{\oplus}$
Δ


$H^{\oplus}$
Δ
Al_2O_3
Δ

[b] DEHYDRATION WITH ThO_2

◎ $ThO_2 \rightarrow E_2$ elimination, Hoffmann → major

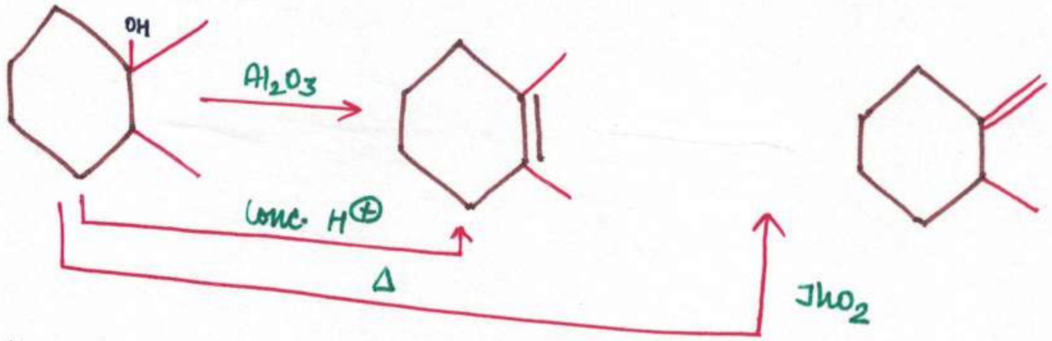
◎ 

◎ 

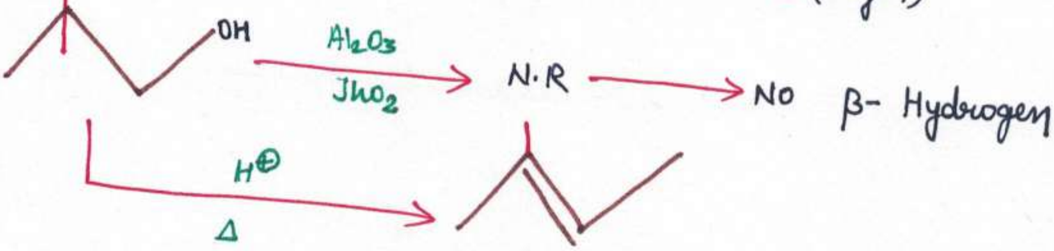
All E_1 → Saytzeff

All E_1CB → Hoffman

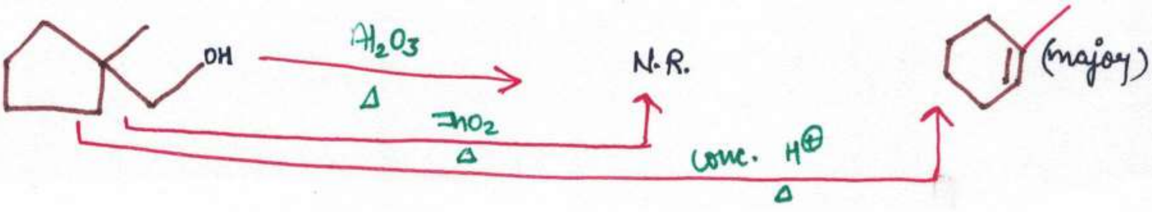
E_2 → can be both saytzeff / Hoffman

▢ 

▲ Hoffmann – always form the least stable → (Major)

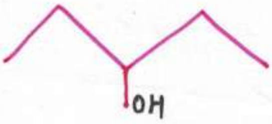
▲ 

For E_2 elimination, β-hydrogen is essential. without it, the reaction isn't possible.

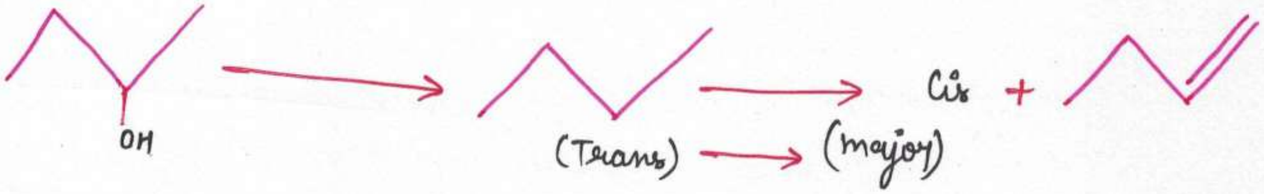
▢ 

A ($C_5H_{12}O$) $\xrightarrow{Al_2O_3}$ only / Pentene

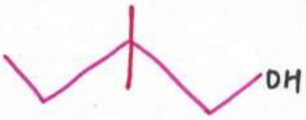
($C_5H_{12}O$) $\xrightarrow{Al_2O_3}$ 2 pentene only



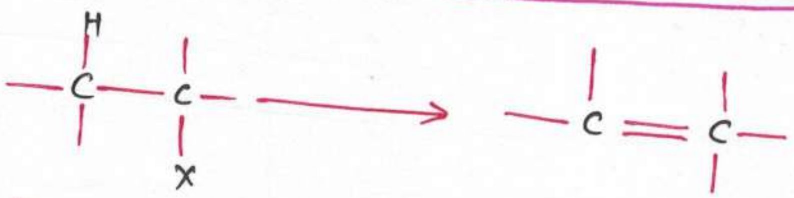
$C_4H_{10}O$ $\xrightarrow[\Delta]{Al_2O_3}$ A + B + C



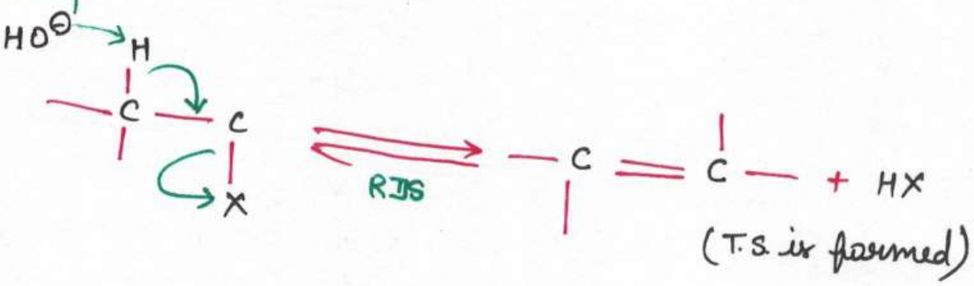
A ($C_6H_{14}O$) $\xrightarrow[\Delta]{Al_2O_3}$ N.R.



[iii] BY DEHYDROHALLOGENATION OF ALKYL HALLIDES



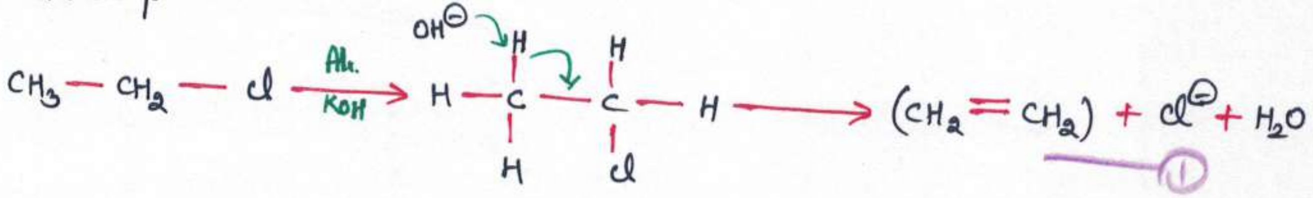
MECHANISM



Rate ∝ Frequency of collisions ∝ $[RX][OH^{\ominus}]$

It is an E_2 elimination (elimination bimolecular).

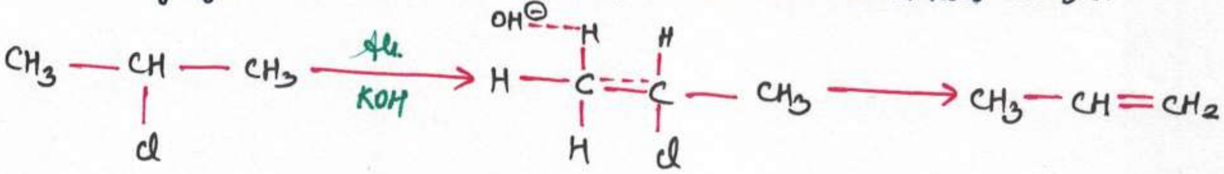
Concerted mechanism. T.S is an intermediate shows -ve entropy of activation. Doesn't show rearrangement shows elemental effect. It is trans elimination.

- 
$CH_3-CH_2-Cl \xrightarrow[KOH]{Alc.} H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}-H \longrightarrow (CH_2=CH_2) + Cl^{\ominus} + H_2O$ ①

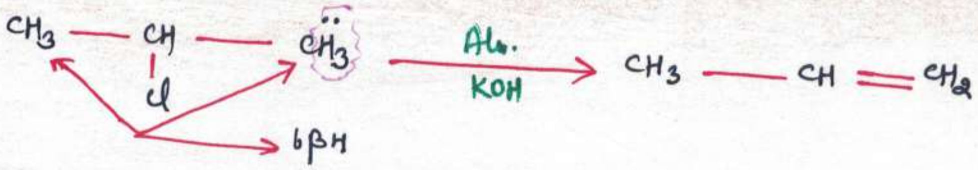
$CH_3-CH_2-CH_2-Cl \xrightarrow[KOH]{Alc.} CH_3-CH=CH_2$ ②

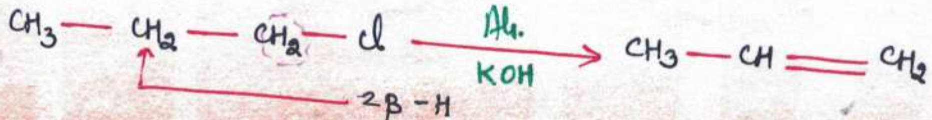
A T.S is a partial alkene, β-hydrogen isotopic effect.

As in ②, more stable T.S ; thus ; ② is faster than ①;

- As basicity of base ↑ thus, reaction tends to eliminate rise.
- 
$CH_3-\underset{Cl}{CH}-CH_3 \xrightarrow[KOH]{Alc.} H-\overset{H}{\underset{H}{C}}\cdots\overset{H}{\underset{Cl}{C}}-CH_3 \longrightarrow CH_3-CH=CH_2$

IMPORTANT NOTE

1. 
$CH_3-\underset{Cl}{CH}-\ddot{C}H_3 \xrightarrow[KOH]{Alc.} CH_3-CH=CH_2$

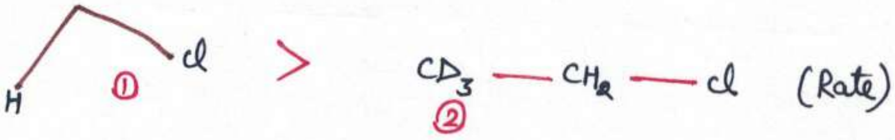
2. 
$CH_3-CH_2-CH_2-Cl \xrightarrow[KOH]{Alc.} CH_3-CH=CH_2$

In 1 and 2 the product is same, but in 1 6 β-H, thus, more frequency of collison in 1 ; thus, the reaction is faster.

Rate of elimination :— 3° > 2° > 1°

Rate ∝ stability of alkene formed, also

∝ Frequency of collisions



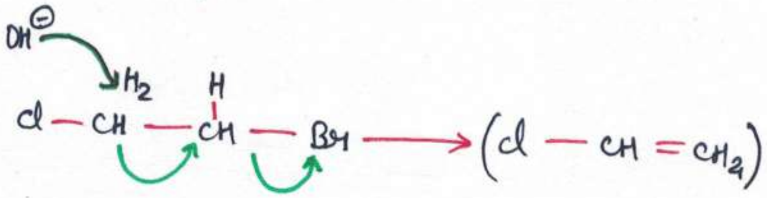
① reacts 7 times faster than ②

As the β-hydrogen is same in both cases.

$C-I > C-Br > C-Cl > C-F$ (Rate)

$Cl-CH_2-CH_2-Br \xrightarrow[OH^{\ominus}]{Alc.} (CH_2=CH-Cl)$

MECHANISM

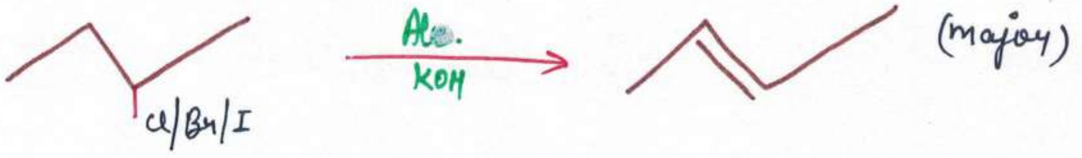


As Ha is more acidic, OH⁻ will attack it.

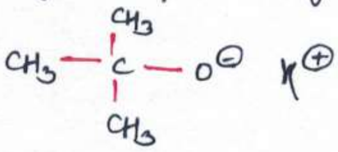
ORIENTATION DEHYDROHALLOGE-NATION

- I = 90% 10%
  Br = 80% 20%
  Cl = 70% 30%
  F = 30% 70%

- In Fluorides (alkyl), the major will always be Harffmann elimination.



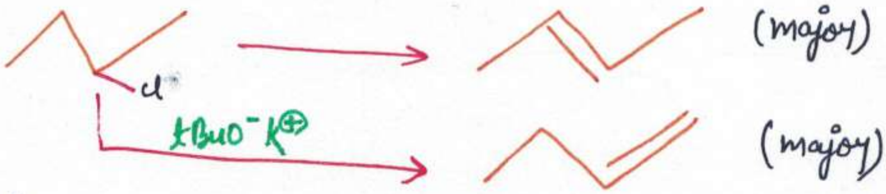
- As the EN of the leaving group ↑, saytzeff ↓, harff. ↑.
- $tBuO^{\ominus}K^{\oplus} \longrightarrow$



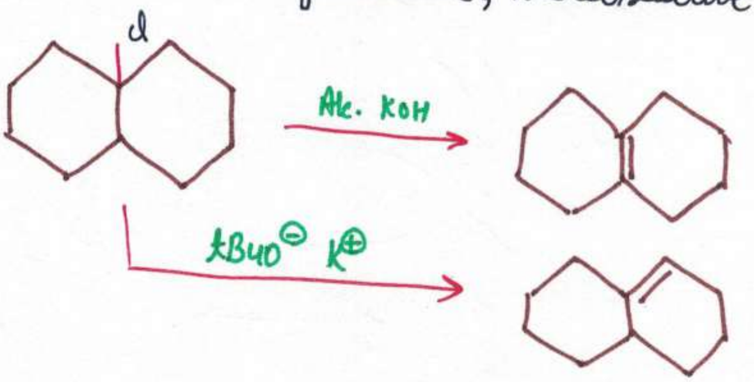
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-O^{\ominus}\;K^{\oplus}$$

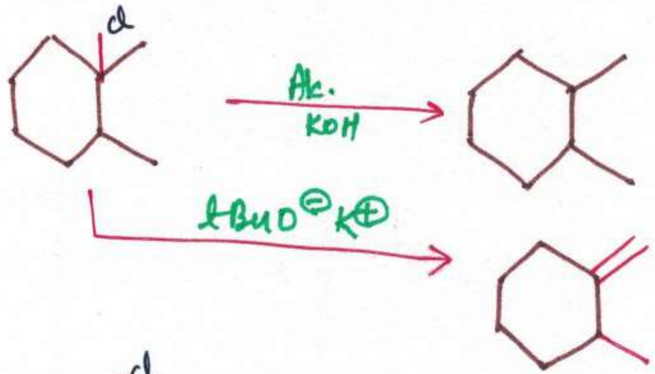
IMP.) As the basicity ↑, thus reactivity of the reagent ↑, thus, the major product will go towards Harffmann ↑.

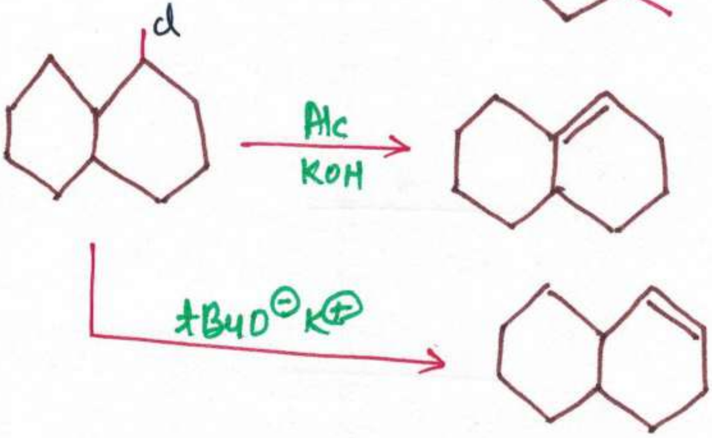
- As crowding around the reagent (base), the product will be Harffmann as major.
-

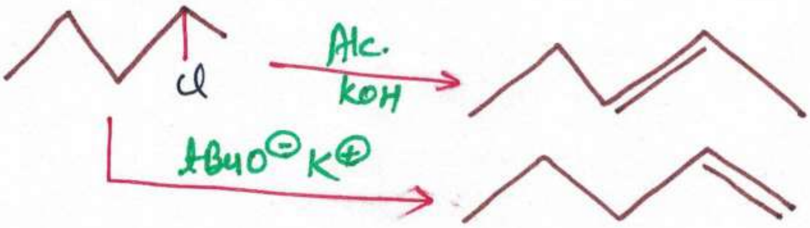


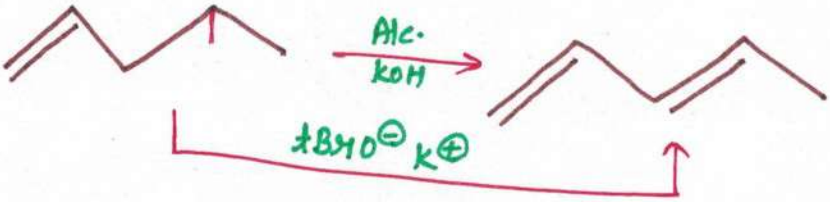
- E2 elimination are regioselective, stereoselective.







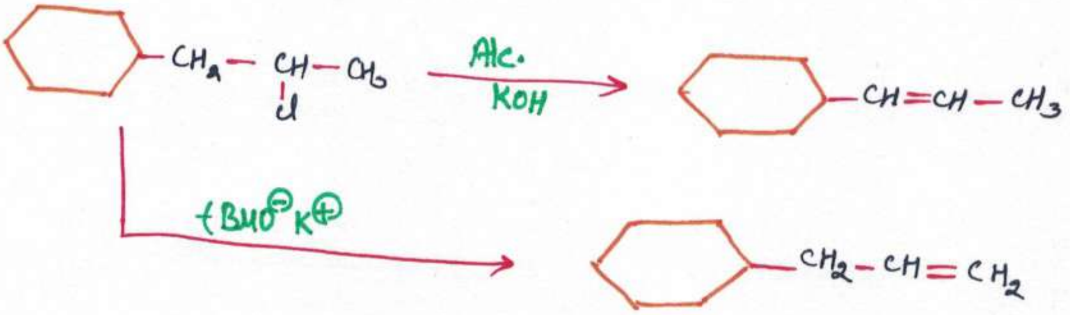


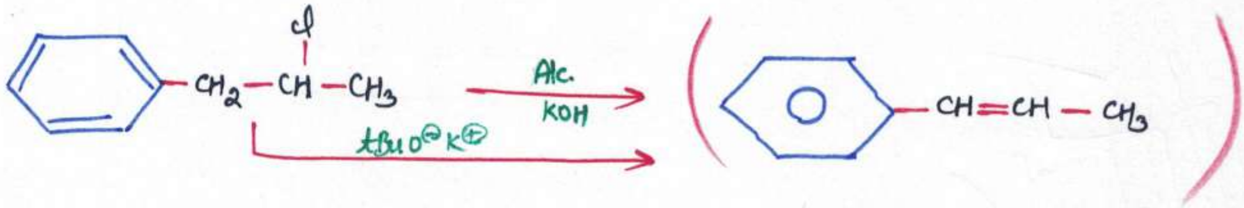


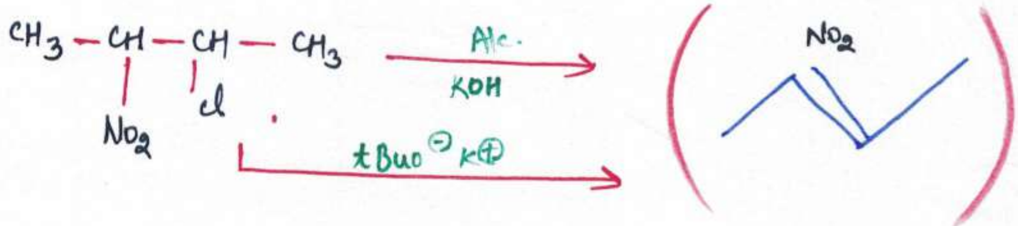
Always the conjugated system is formed as major.

In Saytzeff, orientation depends on stability of alkenes. In Hoffmann, the more acidic β-hydrogen is removed. Orientation in Hoffmann depends on acidic nature of β-H.

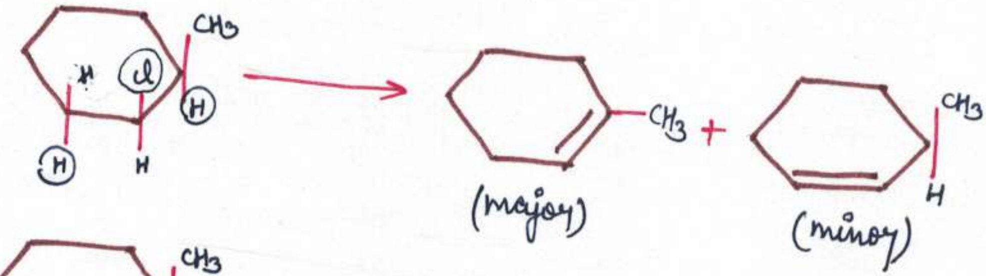
Rule fails but the concept never fails.

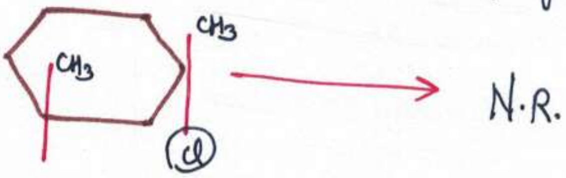


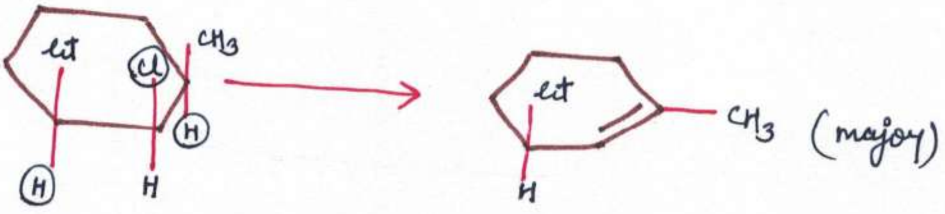




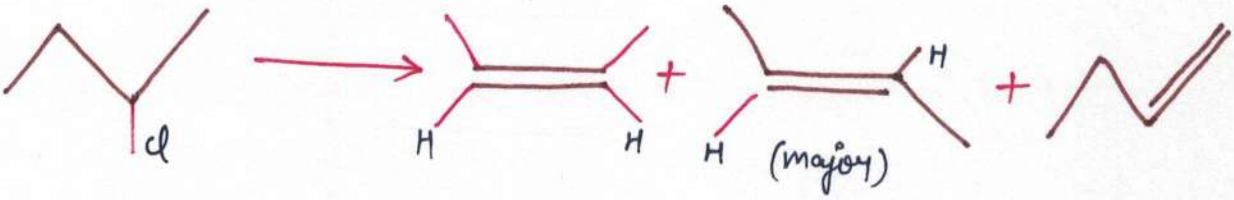
DEHYDROHALLOGENATION — STEREOCHEMISTRY







A (C_4H_9Cl) $\xrightarrow[\text{KOH}]{\text{Alc}}$ B + C + D

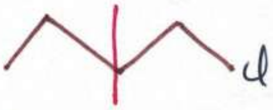


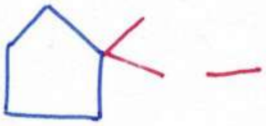
A ($C_5H_{10}Cl$) $\xrightarrow[\text{KOH}]{\text{Alc.}}$ only 1 Pentene

$C_5H_{11}Cl$ $\xrightarrow[\text{KOH}]{\text{Alc.}}$ only 2 pentene

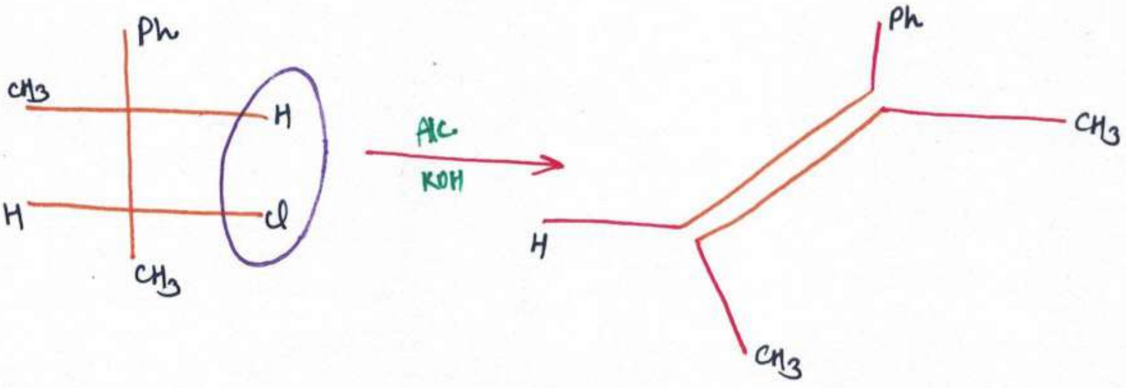
$C_5H_{11}Cl$ $\xrightarrow[\text{KOH}]{\text{Alc.}}$ N.R

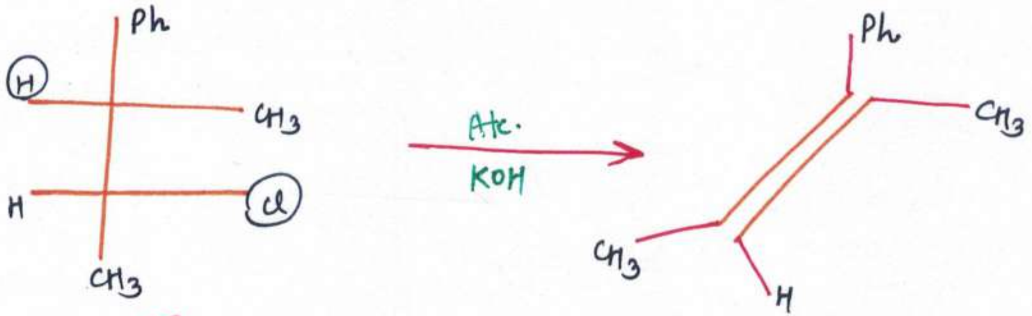
$C_6H_{13}Cl$ $\xrightarrow[\text{KOH}]{\text{Alc.}}$ N.R

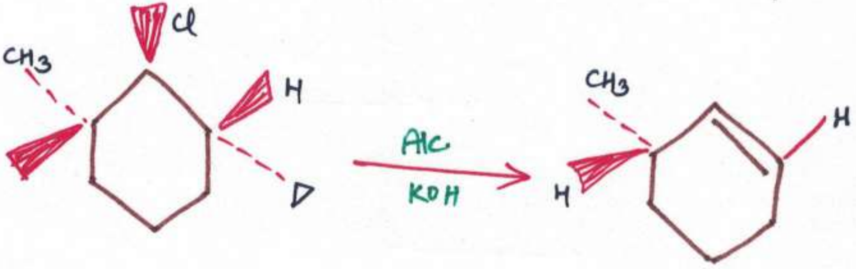




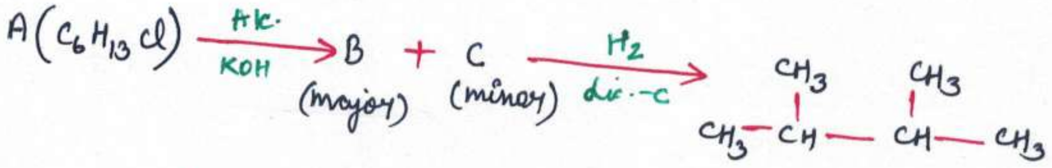
$\xrightarrow[\text{KOH}]{\text{Alc.}}$ N.R.





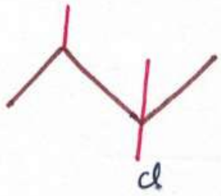


(-DCL occurs)



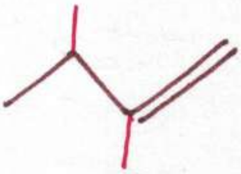
$$\text{A}(C_6H_{13}Cl)\xrightarrow[KOH]{Alc.}\underset{(major)}{\text{B}}+\underset{(minor)}{\text{C}}\xrightarrow[Ni.-C]{H_2}CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_3$$

A →



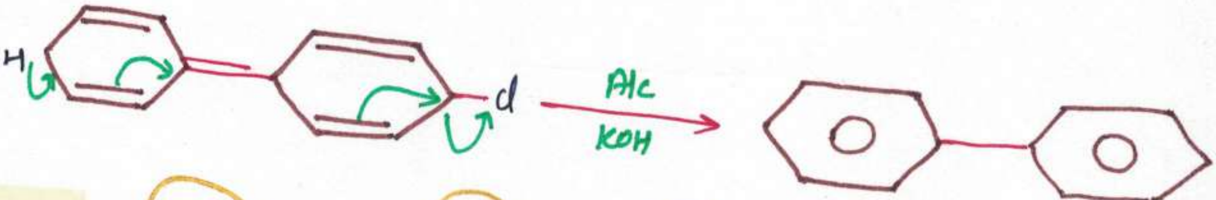
B →

C →

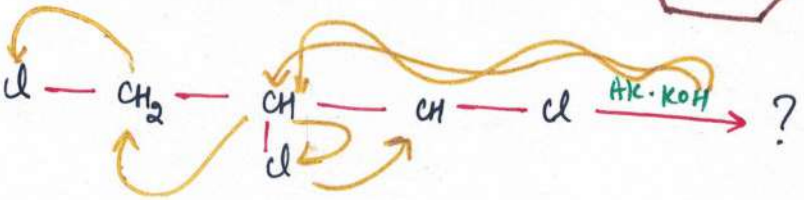


$CH_3-CH=CH-CH_2-Cl\xrightarrow[KOH]{Alc}$?

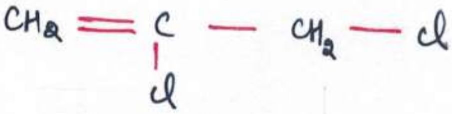
$(CH_2=CH-CH=CH_2)$



IMPORTANT



$$Cl-CH_2-\underset{Cl}{\underset{|}{CH}}-CH-Cl\xrightarrow{Alc.\,KOH}\ ?$$



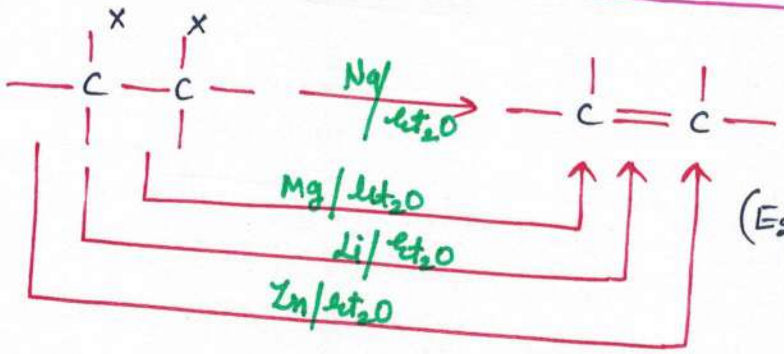
$$CH_2=\underset{Cl}{\underset{|}{C}}-CH_2-Cl$$

IMPORTANT $CH_2=CH-CH_2-Cl \longrightarrow ?$

$CH_2=C=CH_2 \longrightarrow (CH\equiv C-CH_3)$

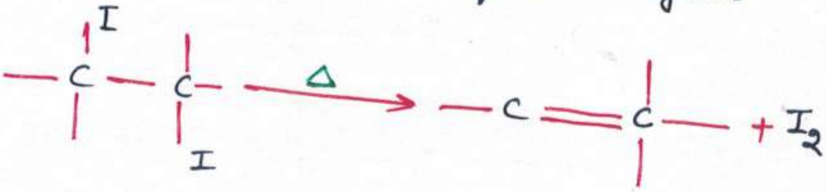
- Any reaction shown by Mg will also be shown by Li. (Diagnal)

[I] DEHALOGENATION OF VISCINAL DIHALIDES



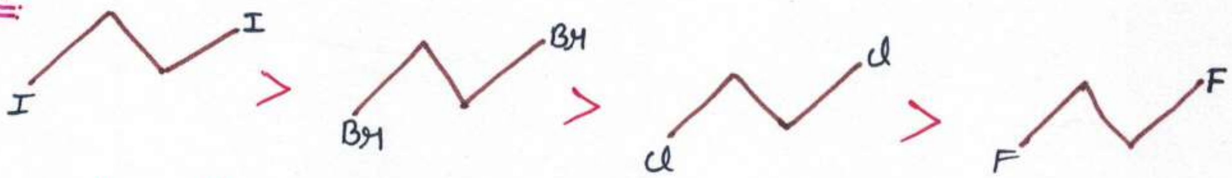
(E₂/Trans)

- Viscinal diodides don't even require catalysts.

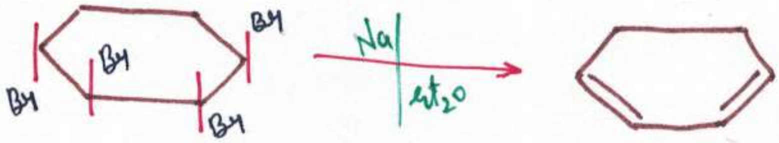


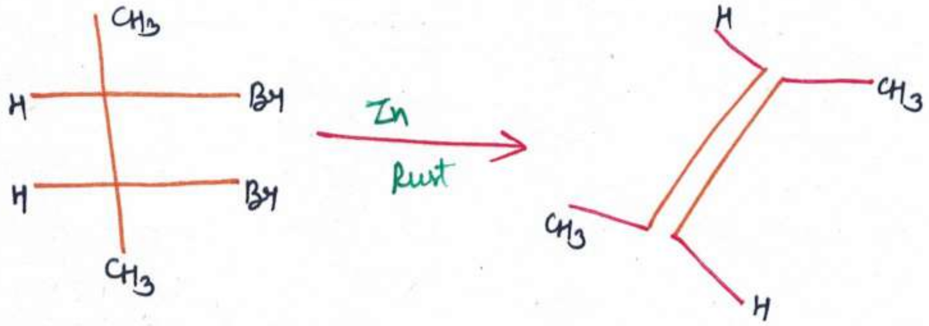
Zn/et₂O is commonly used catalyst

RATE

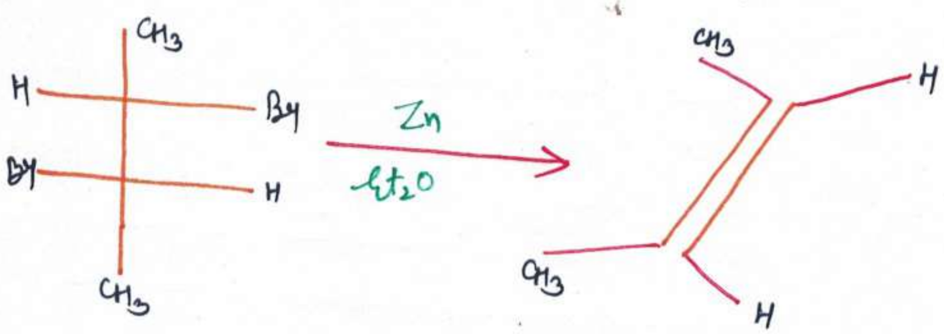


- Anti elimination

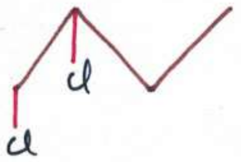


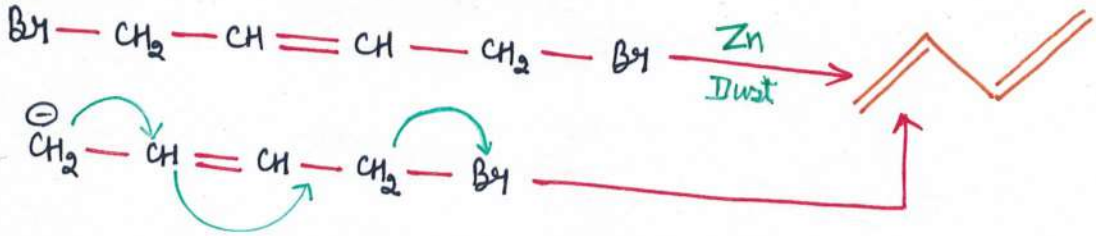


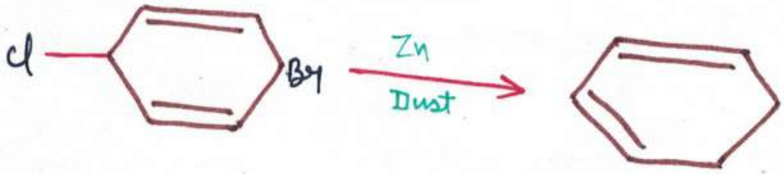
(Stereoselective, stereospecific)



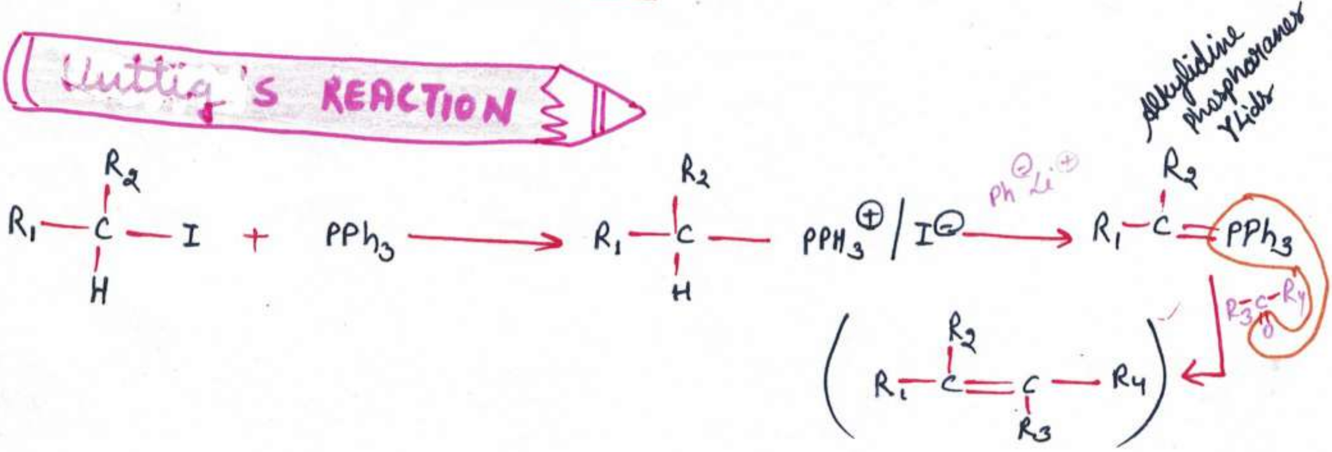
$A(C_4H_8Cl_2) \xrightarrow[\text{Dust}]{\text{Zn}}$ 1 butene







[E] Wittig's REACTION

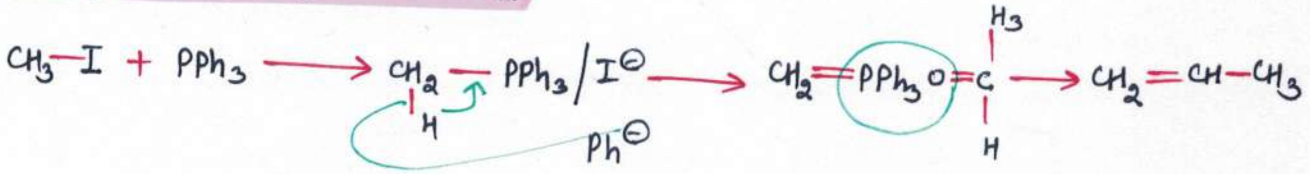


Tertiary / Aryl / Those who don't have α-H don't form ylids.

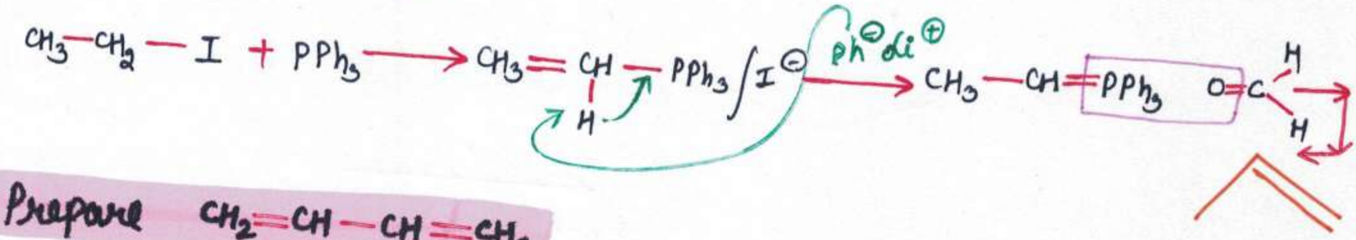
$PPh_3 \rightarrow$ Nucleophilic

Prepare $CH_3-CH=CH_2$

i

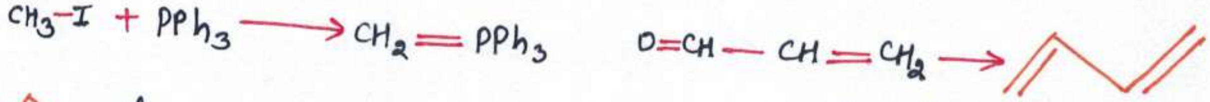


ii



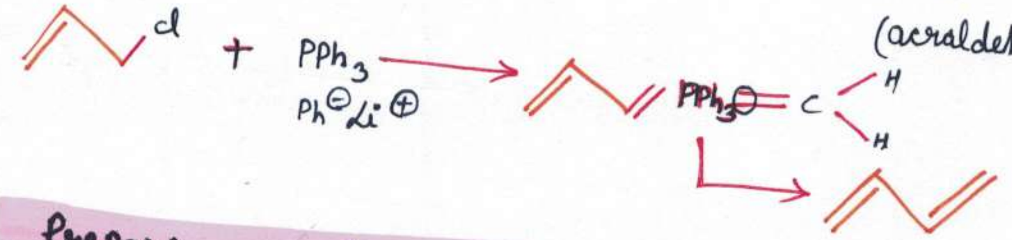
Prepare $CH_2=CH-CH=CH_2$

i

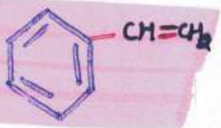


(acraldehyde)

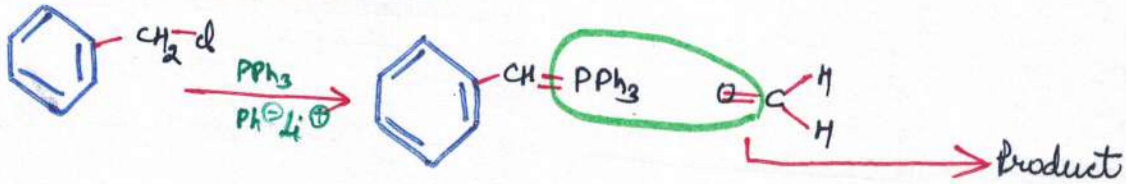
ii



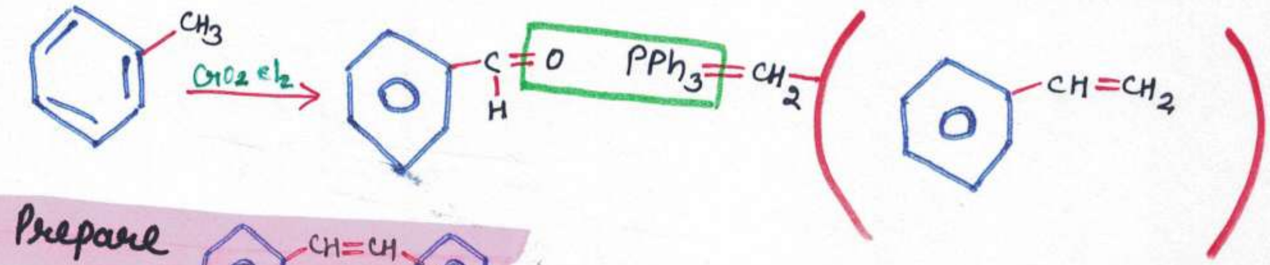
Prepare



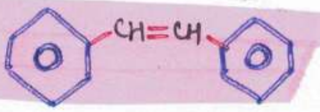
1.



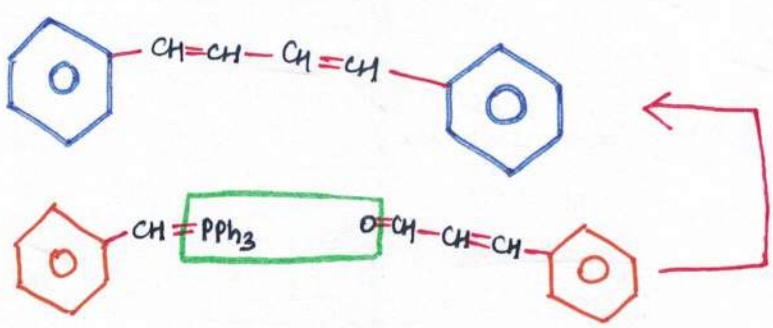
2.

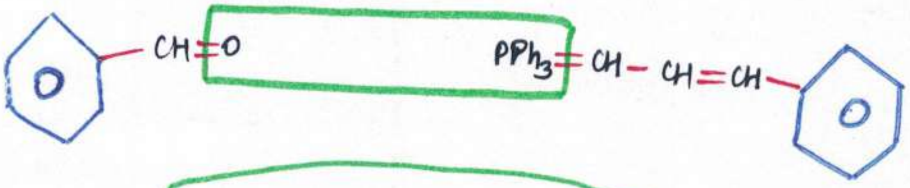


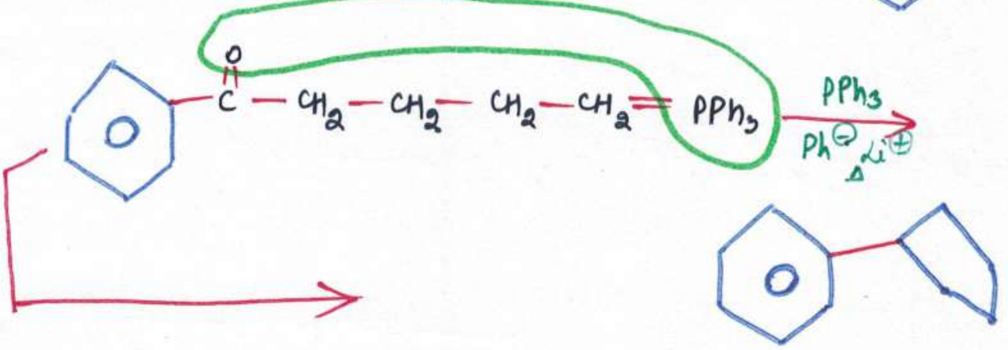
Prepare



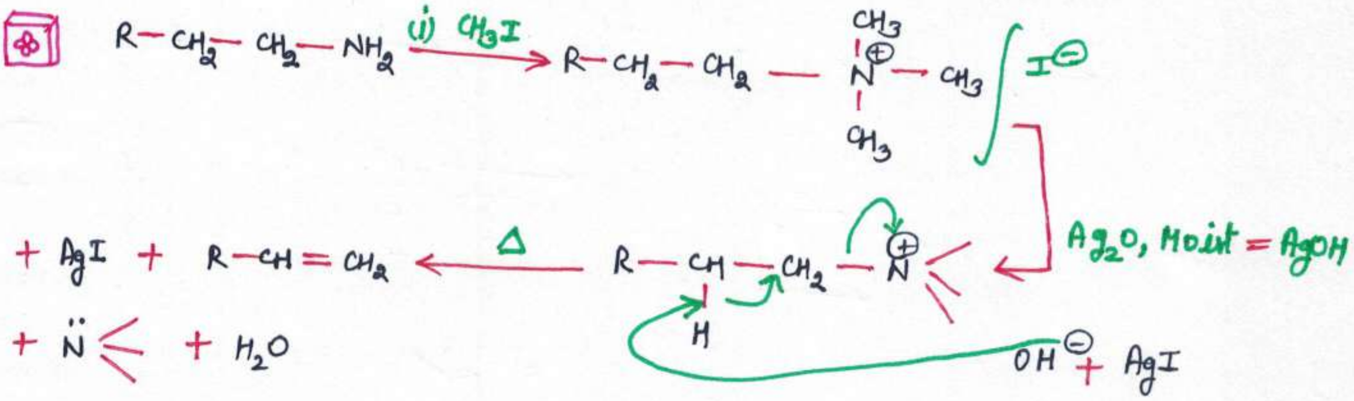
1.



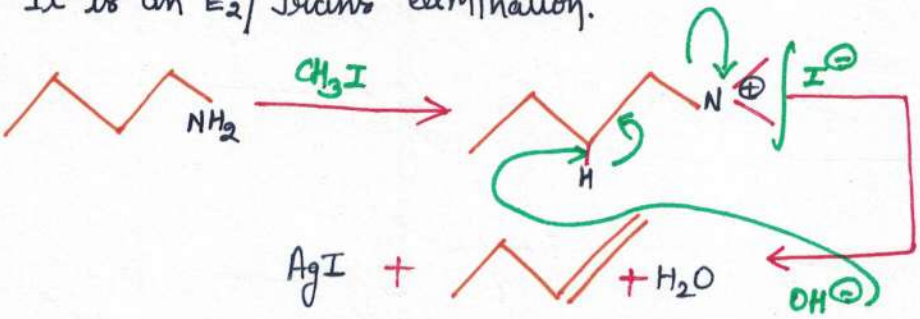




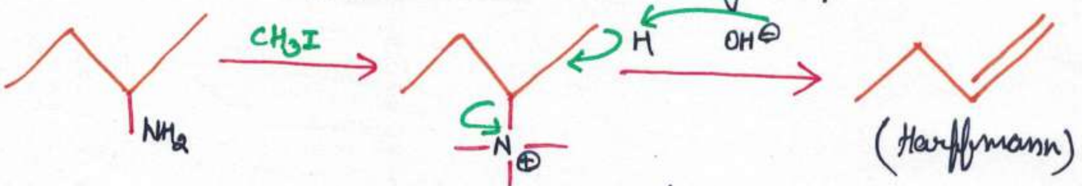
[F] PYROLYSIS OF QUATERNERY ANMONIUM HYDROXIDES



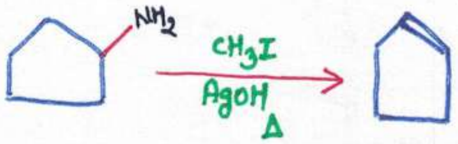
- It is an E2/ Trans elimination.



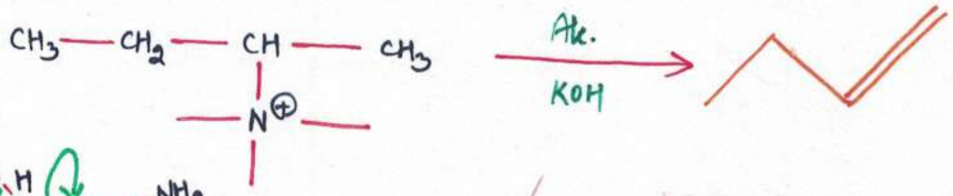
- Also called as Hoffman exhaustive methylation.

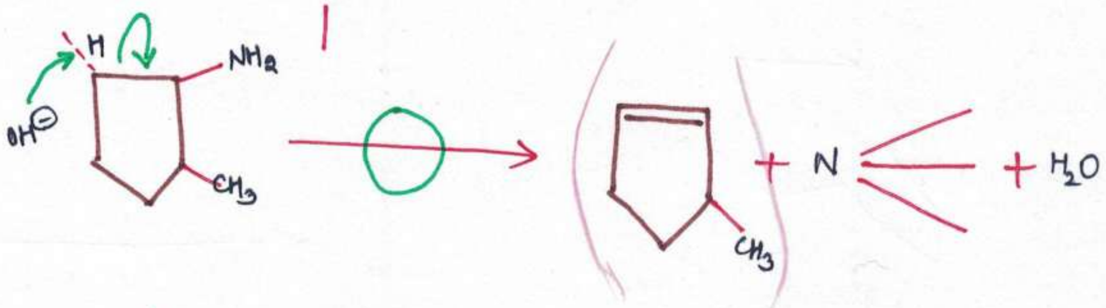


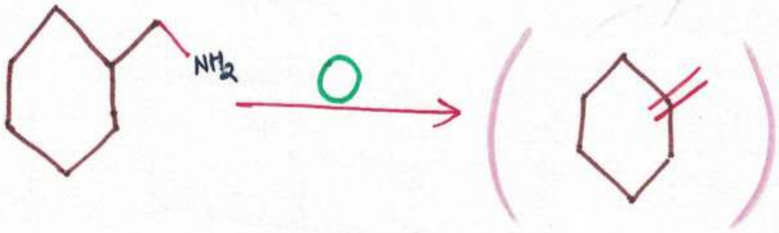
- It is a Hoffmann elimination. (Primary amine Sec. alkyl amine)
  E2/Trans.

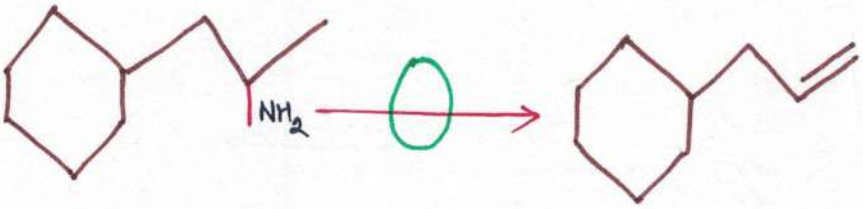


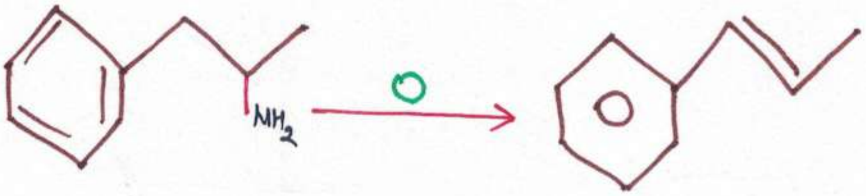
As the branching of leaving group↑, saytzeff ↓, Hoffman↑

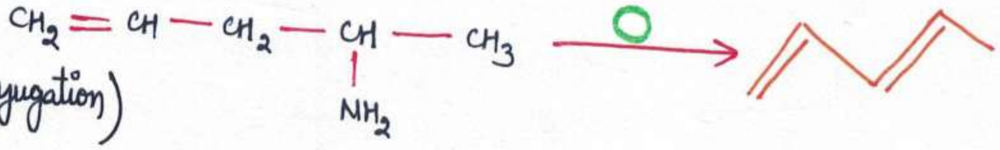




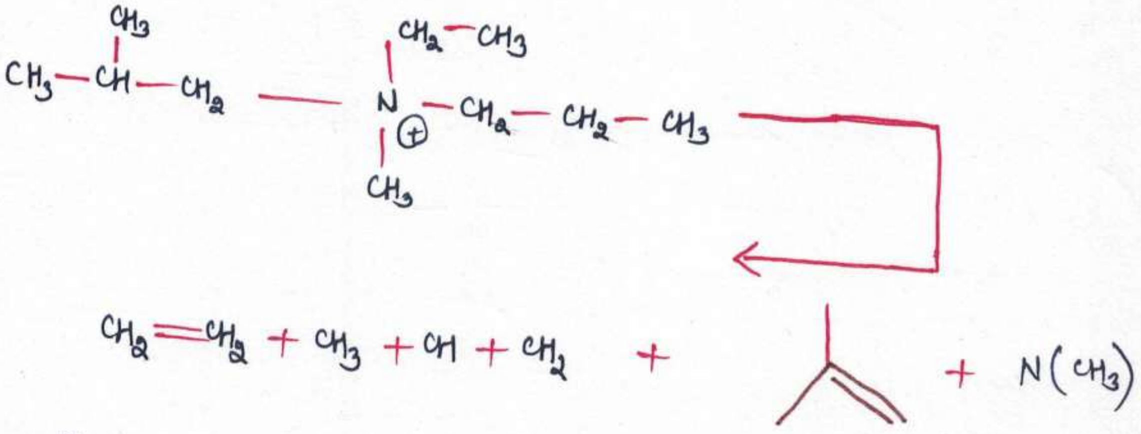






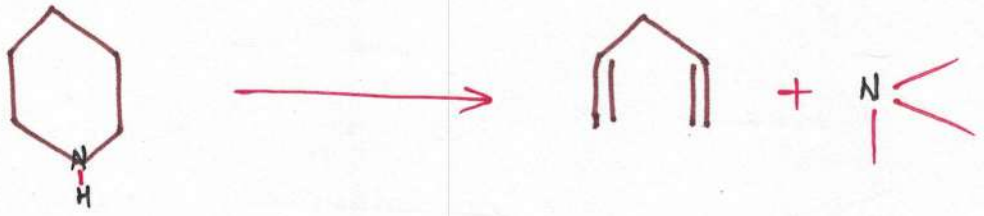


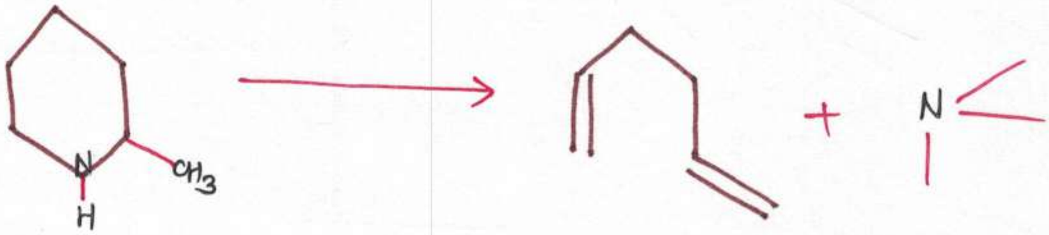
(Conjugation)

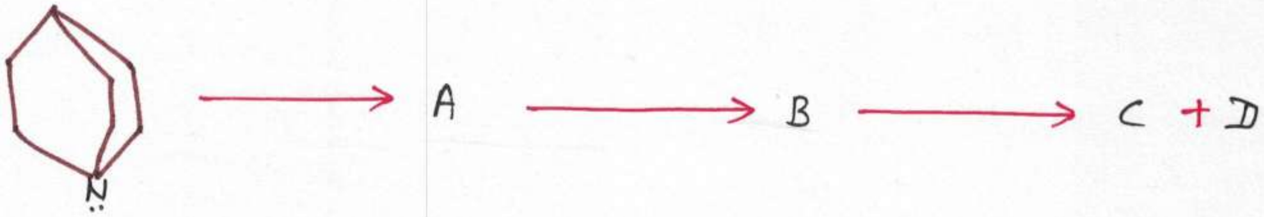


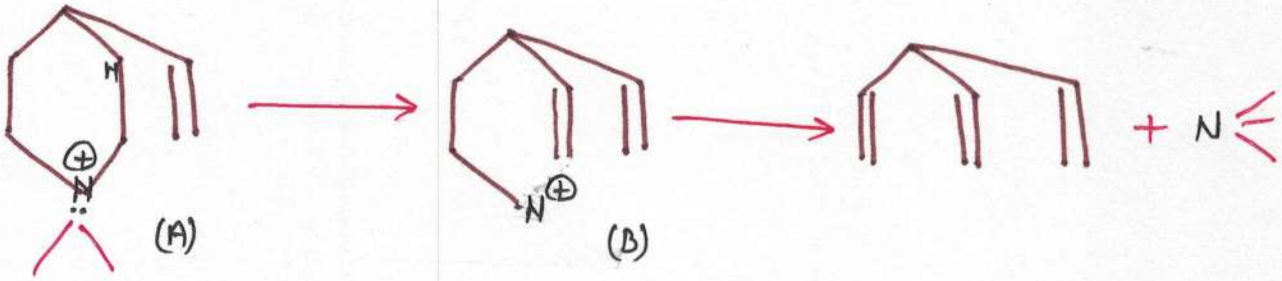
3 times we can do.

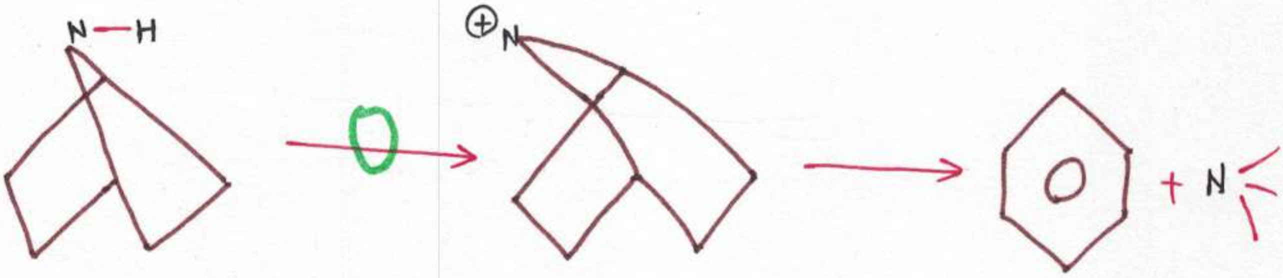
If O given once, then do process only once ;

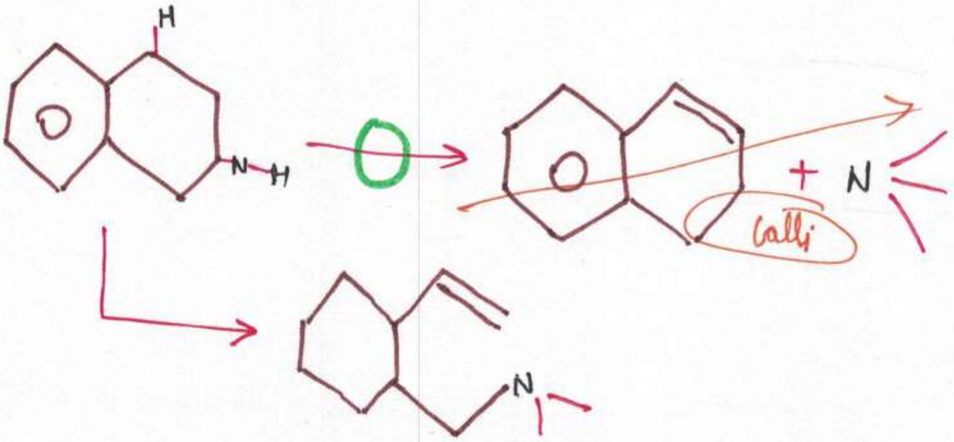


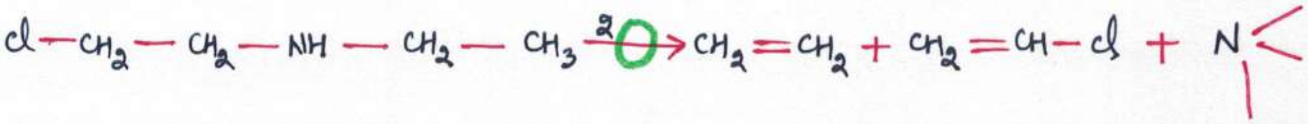


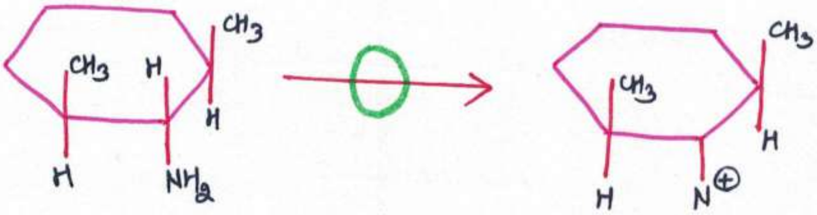










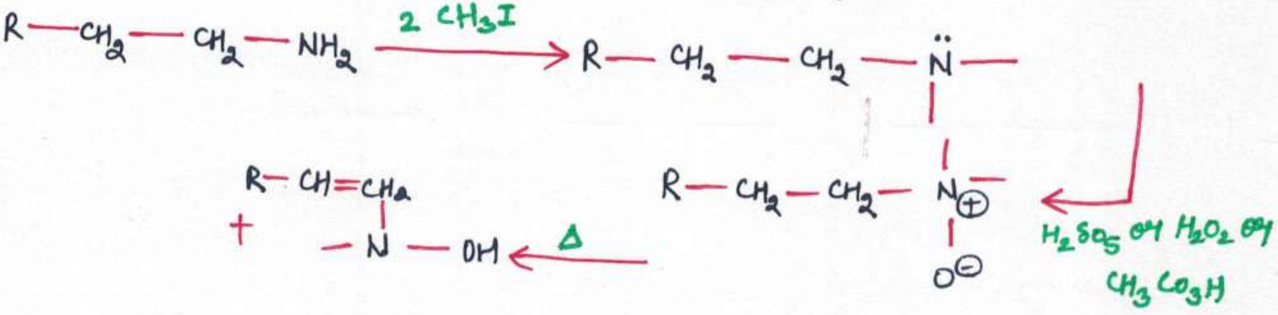


(N.R.)

(Trans elimination)

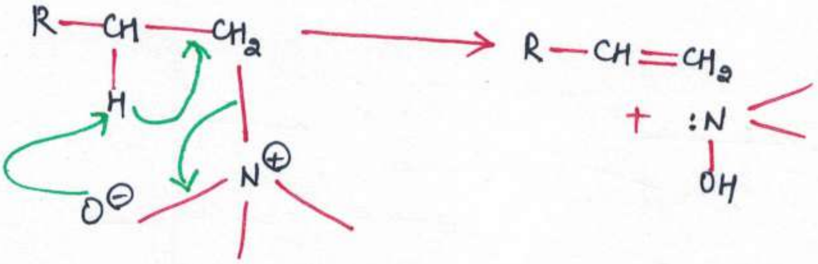
5 COPE'S REACTION

(Cyclic | Cis)

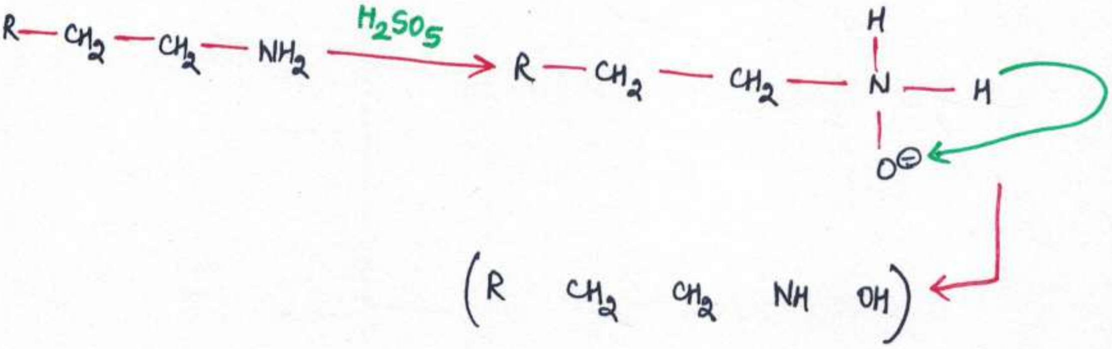


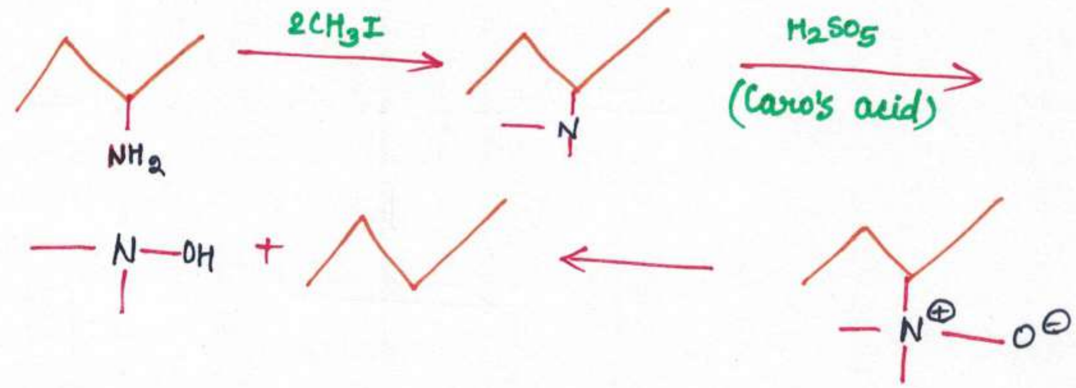
Amine oxides are formed only by secondary amines. Primary and tertiary don't form it.

MECHANISM

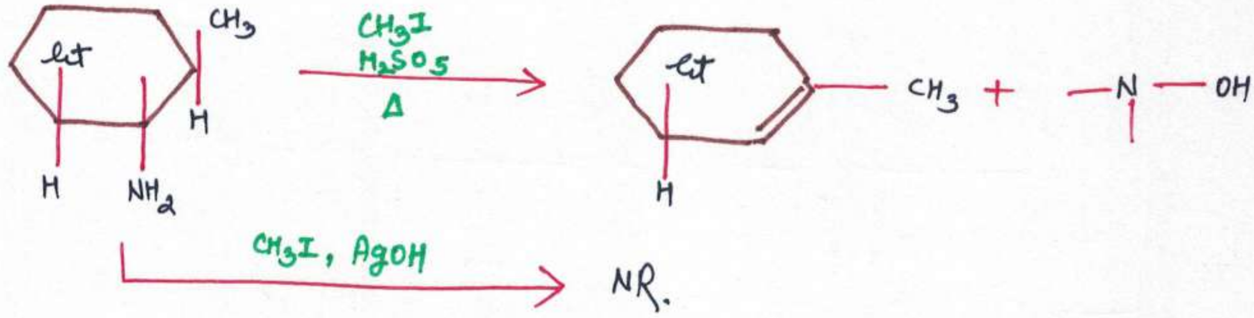


If primary is taken ;



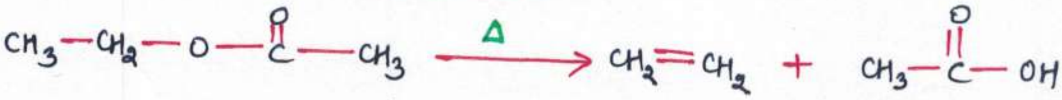


All cyclic elimination are (cis/ Harffmann elimination).
(stereoselective, regioselective).



The most acidic hydrogen has to be removed.

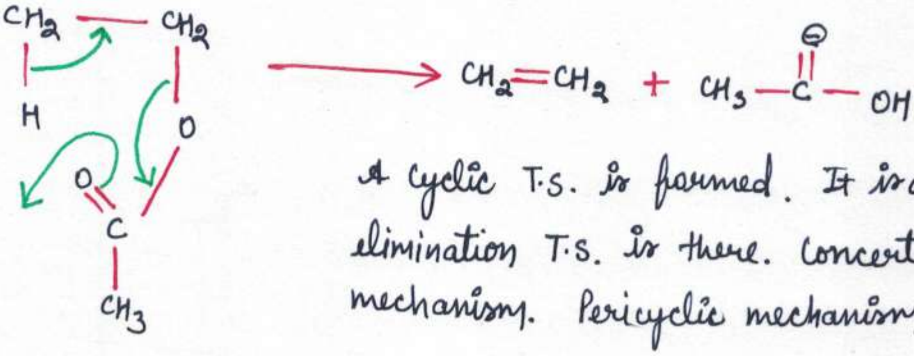
[H] PYRDYSIS OF ESTERS



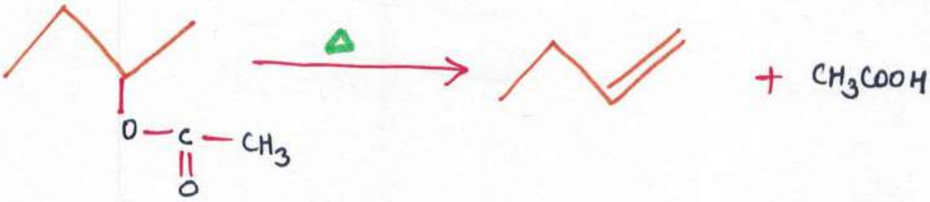
$$CH_3-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{\Delta} CH_2{=}CH_2 + CH_3-\overset{O}{\overset{\|}{C}}-OH$$

(Harffmann elimination)

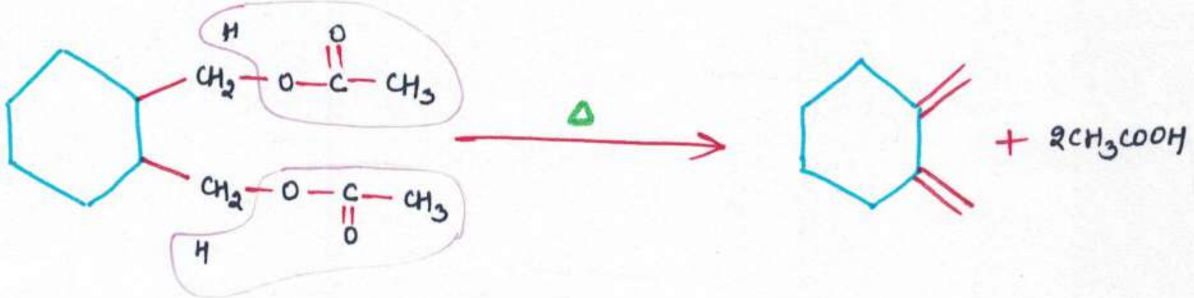
MECHANISM



A cyclic T.S. is formed. It is a Cis elimination T.S. is there. Concerted mechanism. Pericyclic mechanism.



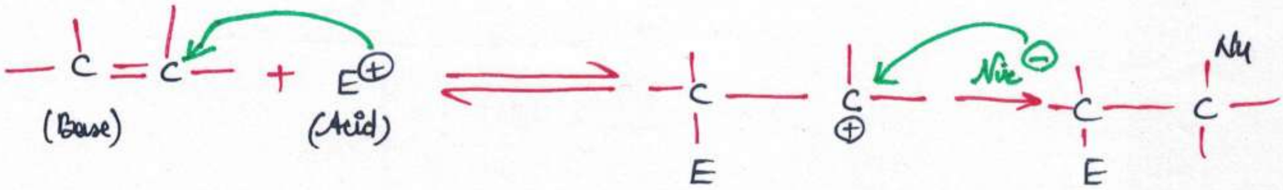
All cyclic elimination are Harffmann elimination. It is stereoselective / regioselective reaction.



PROPERTIES

Ⓐ ELECTROPHILIC ADDITION

It is a trans addition.



(i) As the reaction by an electrophile, thus, electrophilic addition.

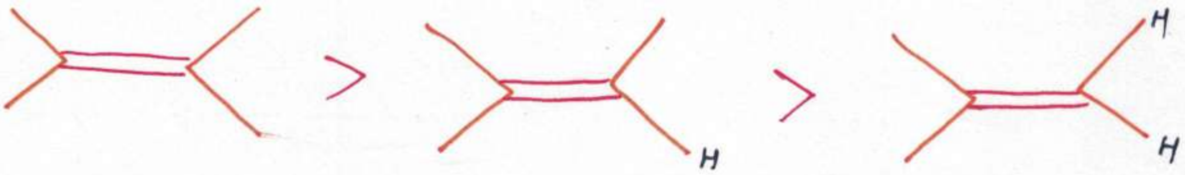
Rate $\propto$ [alkene][$E^{\oplus}$] ⟶ Bimolecular addition

(ii) R^+ is the intermediate. Rearrangement occurs. Trans addition "Trans addition".

(iii) Rate depends on :-

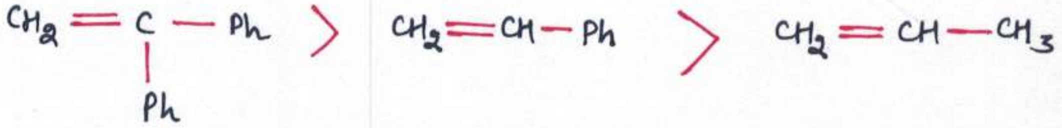
a. Basic nature of alkenes (π-bond)

b. Stability of R^+ formed as an intermediate.



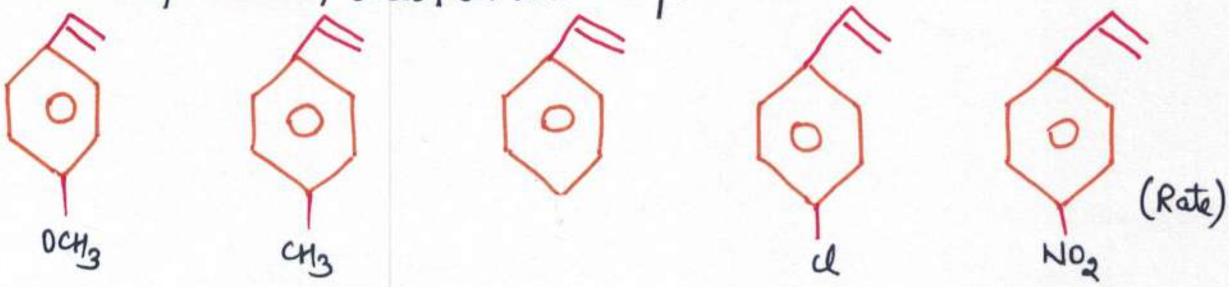
(Rate of electrophilic addition)

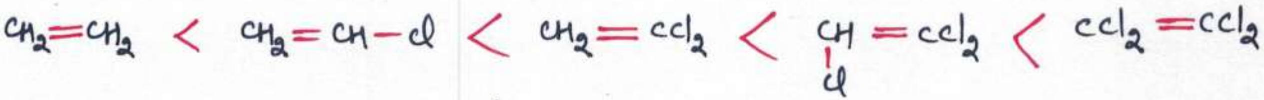
RATE :- 

RATE :- 

$$\underset{Ph}{CH_2=\overset{|}{C}-Ph} > CH_2=CH-Ph > CH_2=CH-CH_3$$

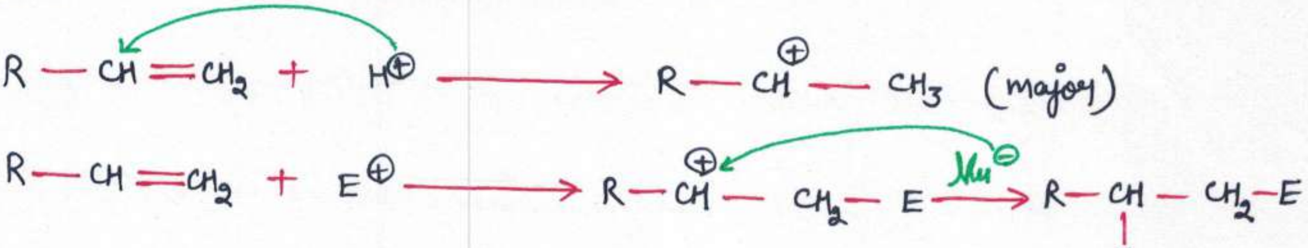
Addition reaction occur at low temp.





$$CH_2=CH_2 < CH_2=CH-Cl < CH_2=CCl_2 < \underset{Cl}{CH}=CCl_2 < CCl_2=CCl_2$$

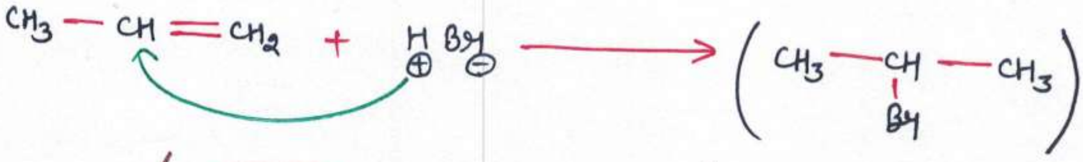
orientation



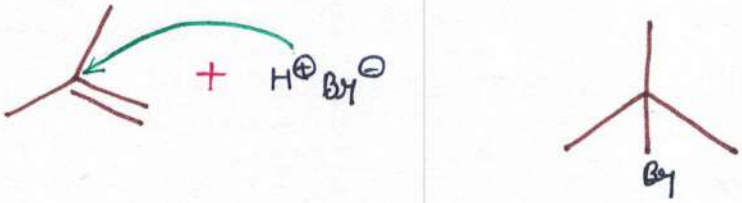
$$R-CH=CH_2 + H^{\oplus} \longrightarrow R-\overset{\oplus}{C}H-CH_3 \text{ (major)}$$

$$R-CH=CH_2 + E^{\oplus} \longrightarrow R-\overset{\oplus}{C}H-CH_2-E \xrightarrow{Nu^{\ominus}} R-\underset{Z}{CH}-CH_2-E$$

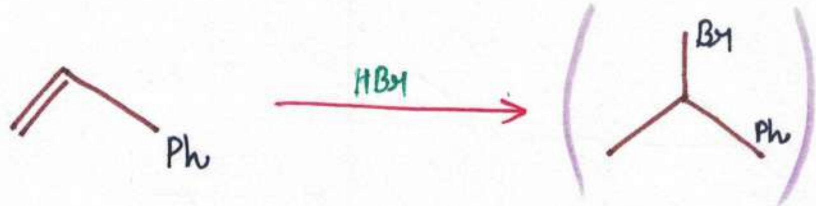
Regioselective, stereoselective

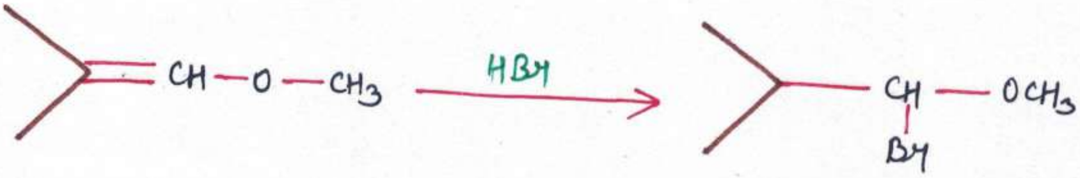


$$CH_3-CH=CH_2 + \overset{}{\underset{\oplus}{H}}\underset{\ominus}{Br} \longrightarrow \left(CH_3-\underset{Br}{CH}-CH_3\right)$$

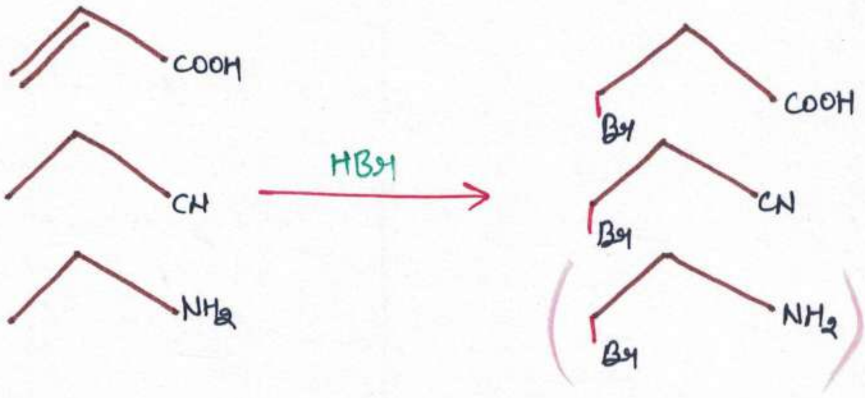


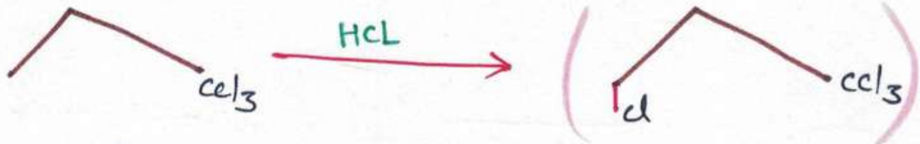
Markownikoff's rule — The $E^{\oplus}$ attacks carbon with more hydrogens so that $C^{\oplus}$ is stable.

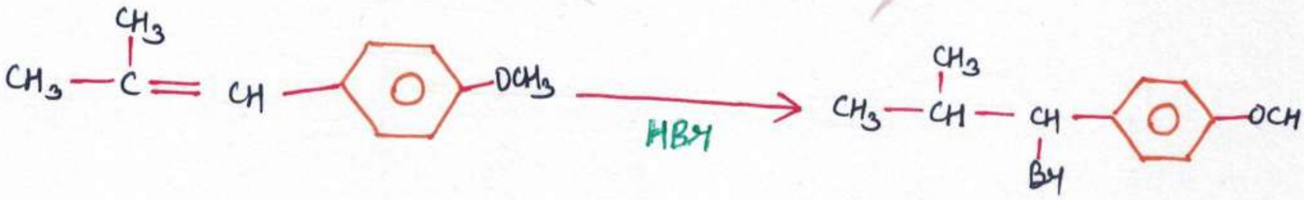




Markowikoff's fails here.

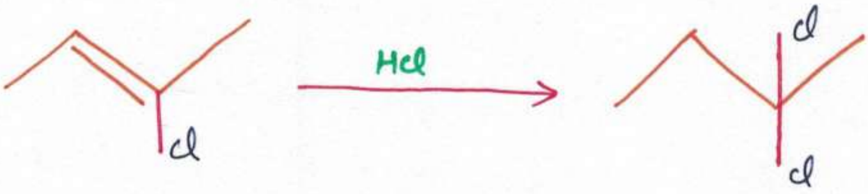






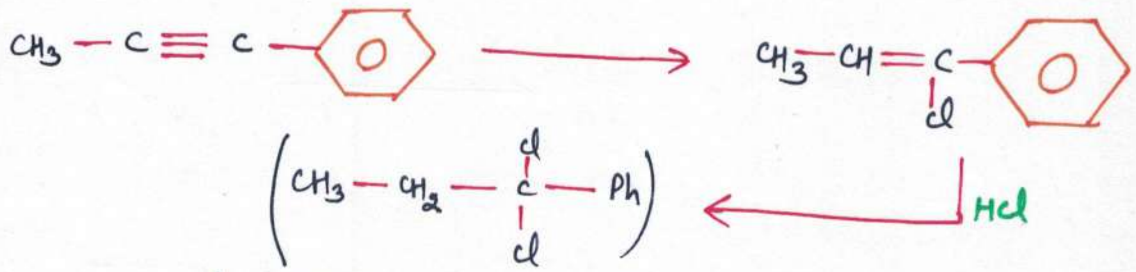
$$CH_2=CH-Cl \xrightarrow{HCL} \left(CH_3-\underset{Cl}{\underset{|}{CH}}-Cl\right)$$

when a carbon has hallogen on it, then on addition the hallogen goes on it always.



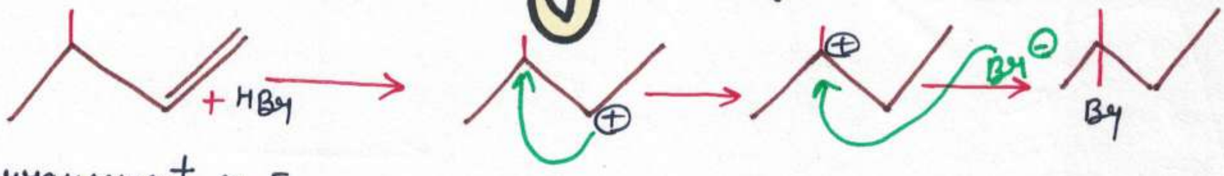
(gemdi hallides)

$$CH \equiv CH \xrightarrow{HCL} CH_2=CH-Cl \xrightarrow{HCl} (CH_3-CHCl_2)$$

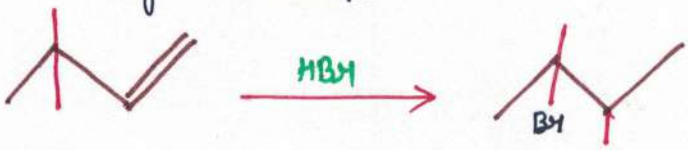


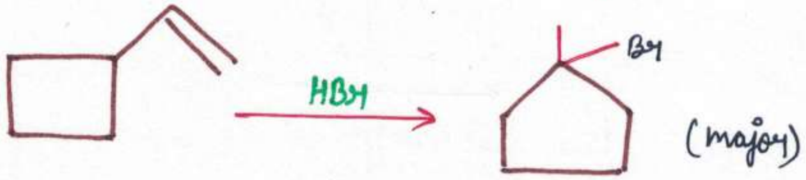
Gemdihalide are formed, not viscinal.

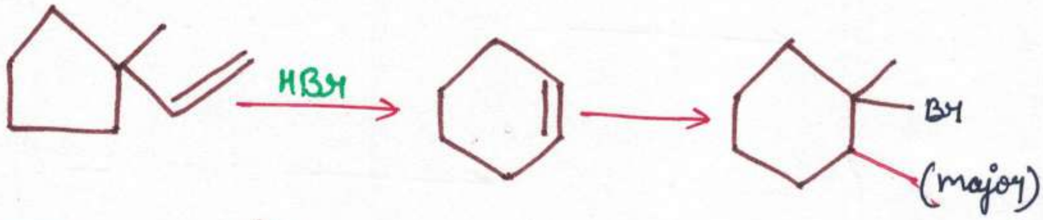
Rearrangement

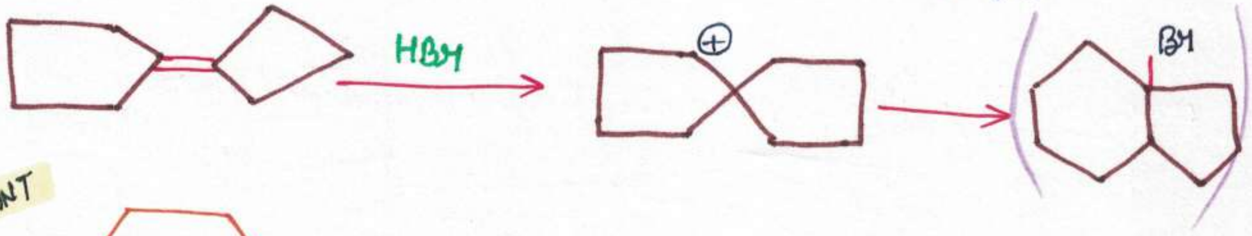


Rearrangement as E1.

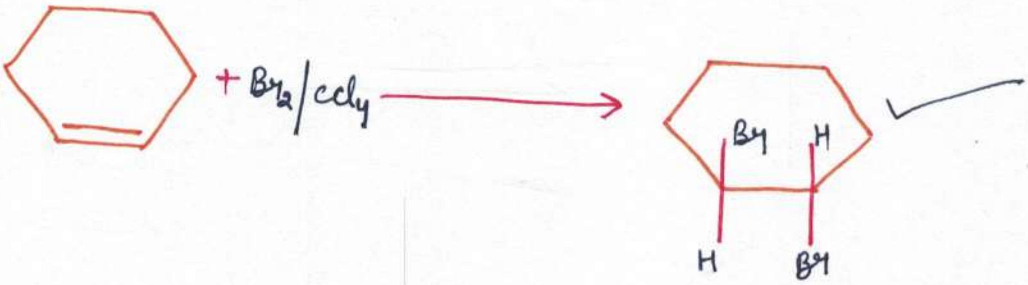




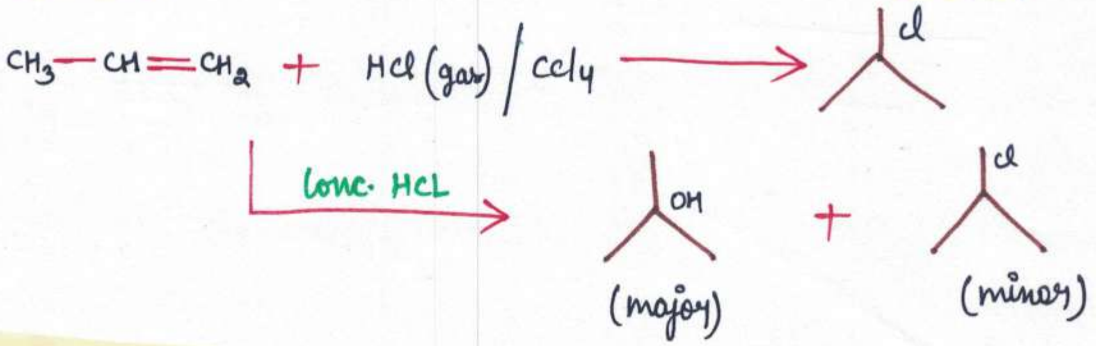




IMPORTANT

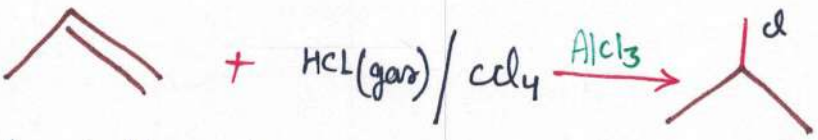


HYDROHALLOGENATION OF ALKENE



Conc. HCL → 40% HCL + 60% H_2O

when we do hydrohallogation we must take the catalyst free of moisture, otherwise alcohals are formed as major instead of alkyl hallides.



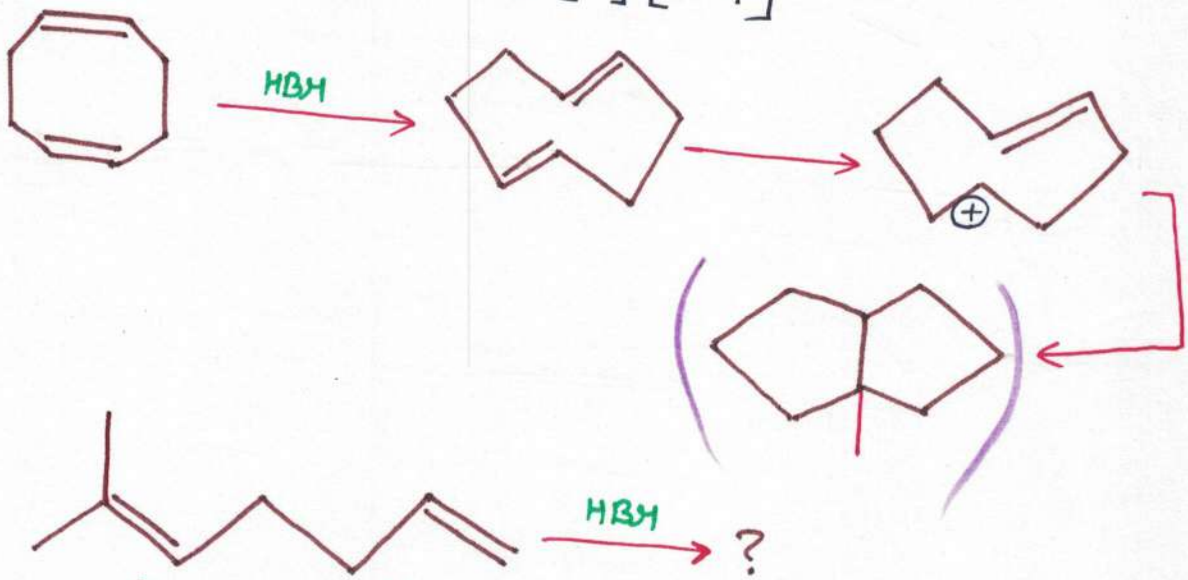
Rate of hallogenation is enhanced by Lewis acid.

E.g

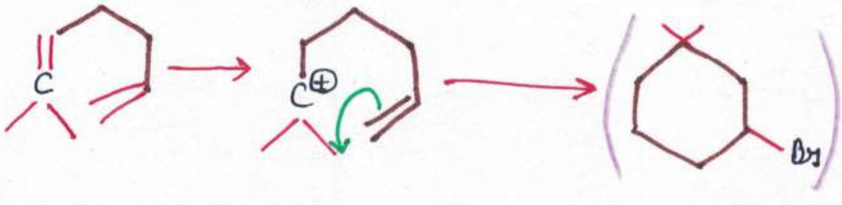
$FeCl_3$, $AlCl_3$

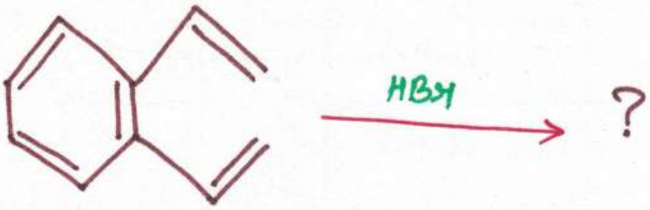
Presence of Lewis acid enhances the rate.

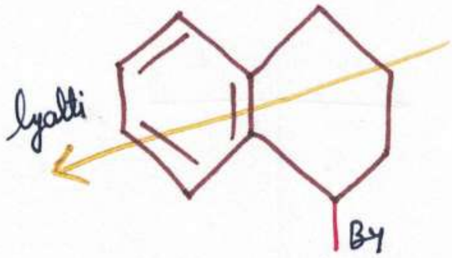
$HCl + AlCl_3 \longrightarrow [H^+]\,[AlCl_4^{-1}]$

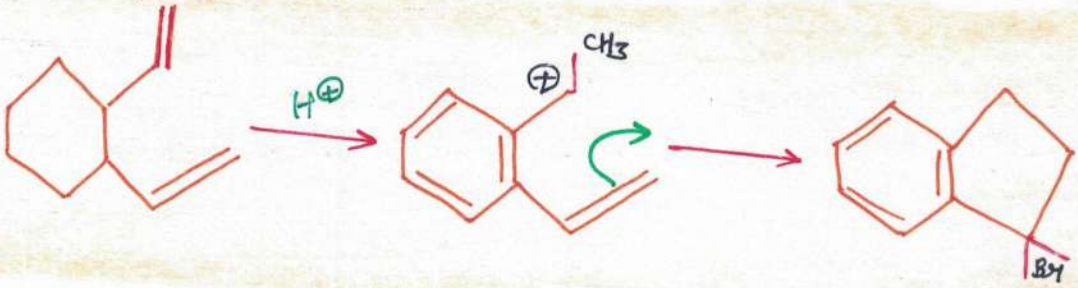


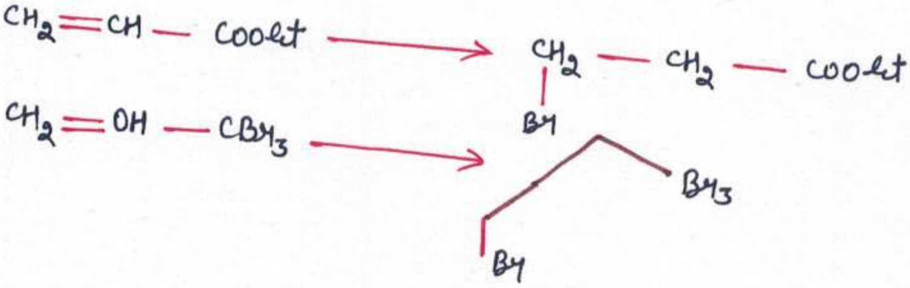
$\xrightarrow{HBr}$?



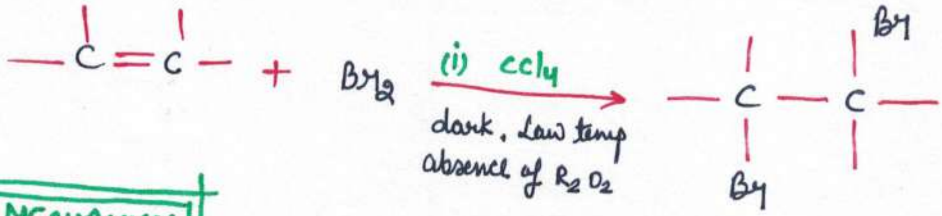




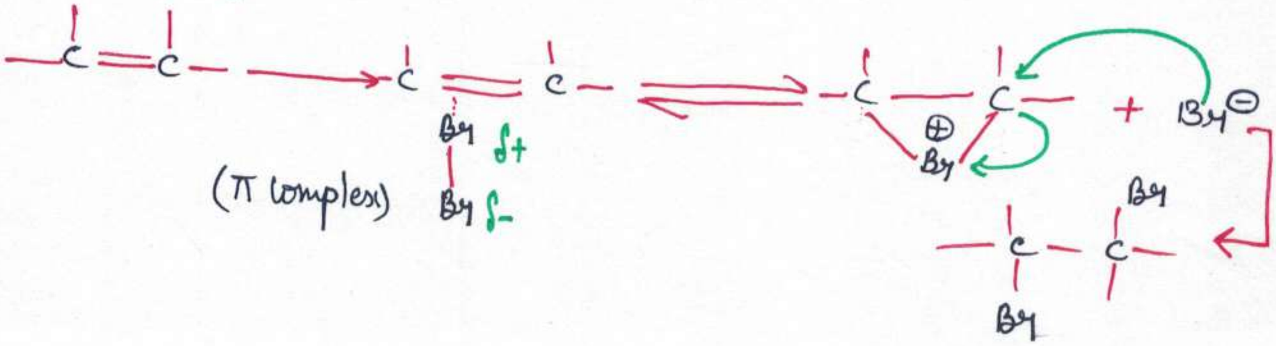




HALLOGENATION OF ALKENES



MECHANISM

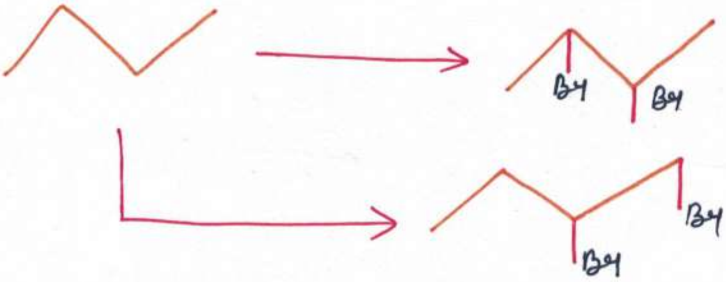


Rate $\longrightarrow Br_2 > Cl_2$

only chlorination and bromination are possible.

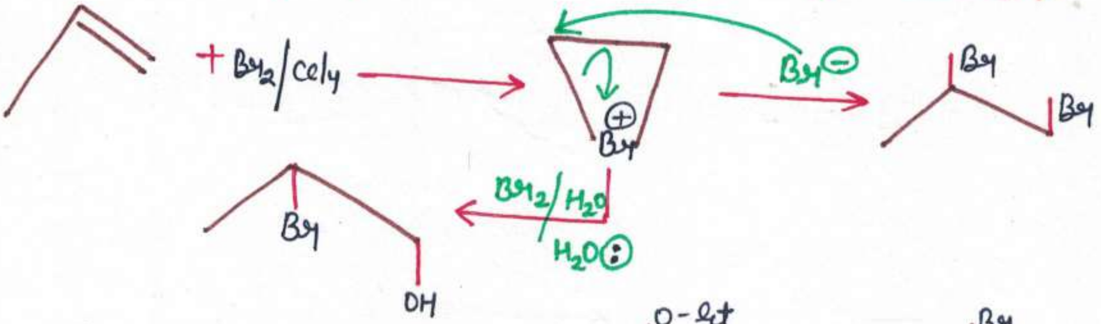
a

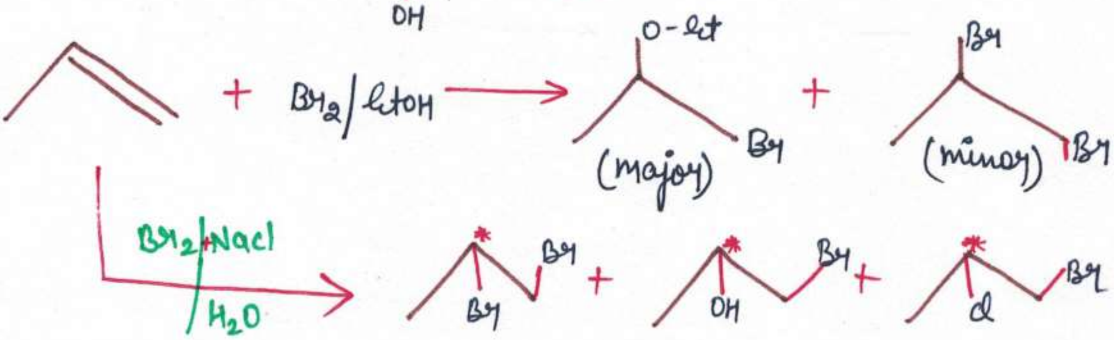
b



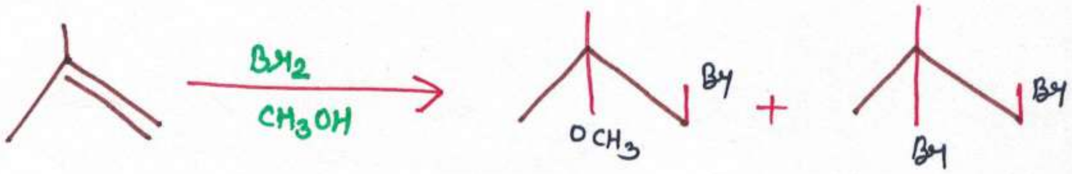
a

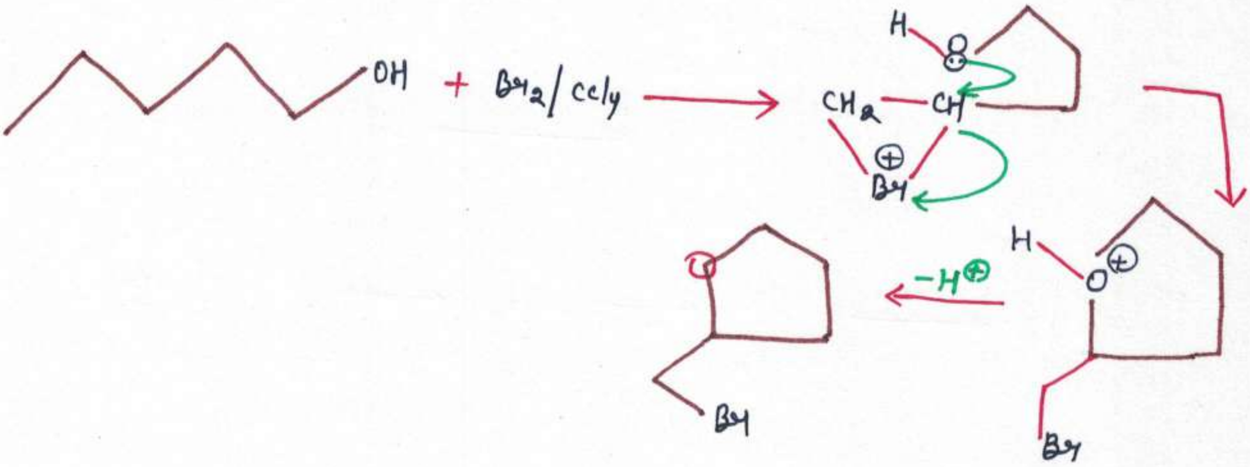
b

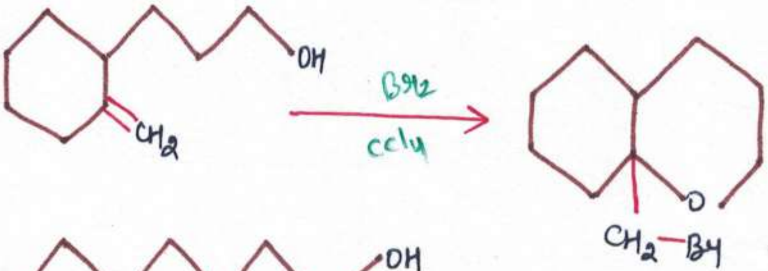


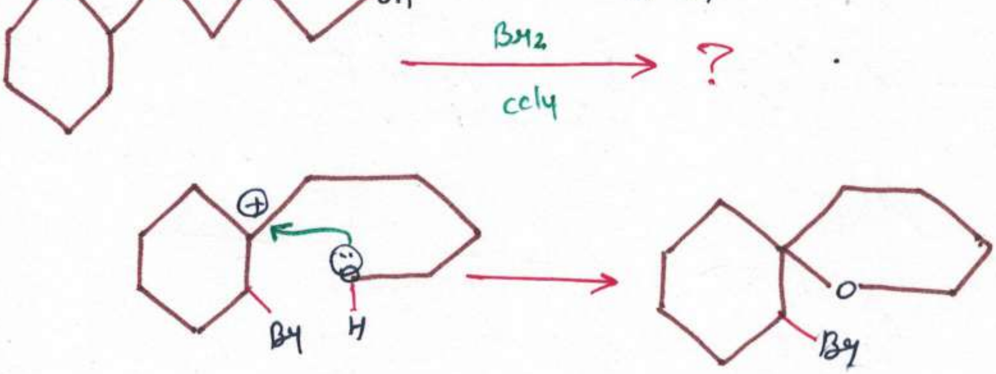


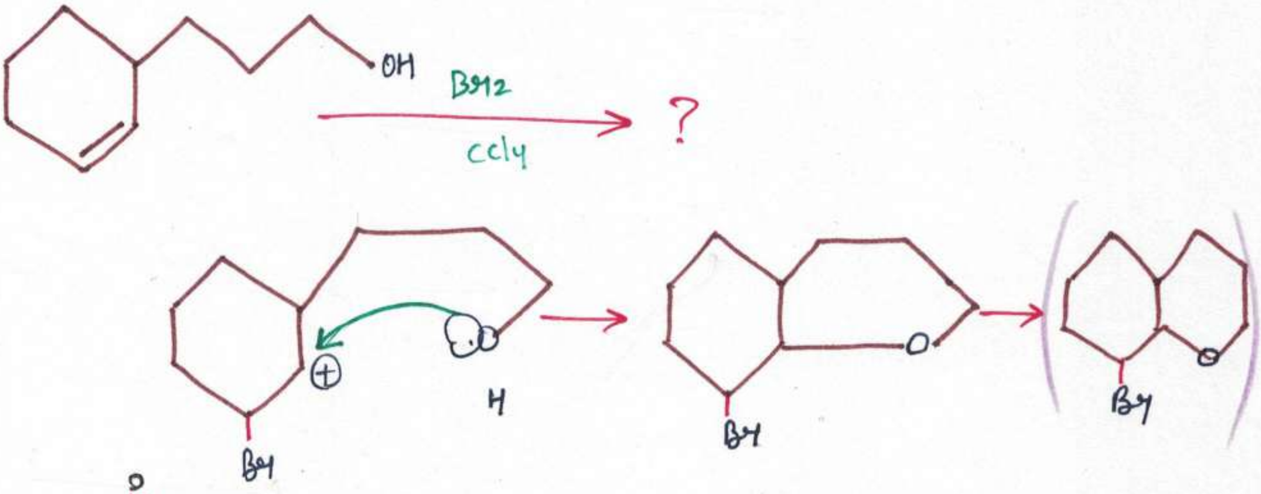
6 products

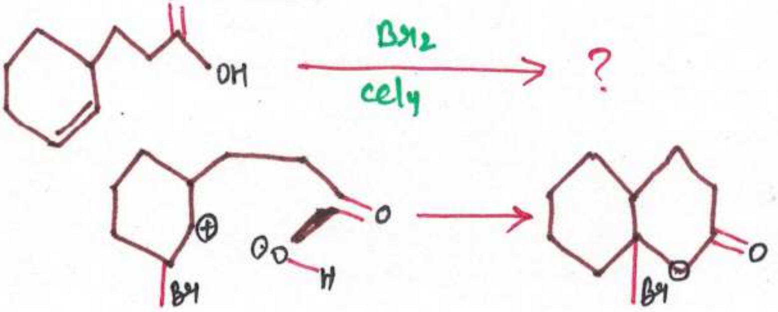

Br2
CH3OH
OCH3
Br
+
Br
Br

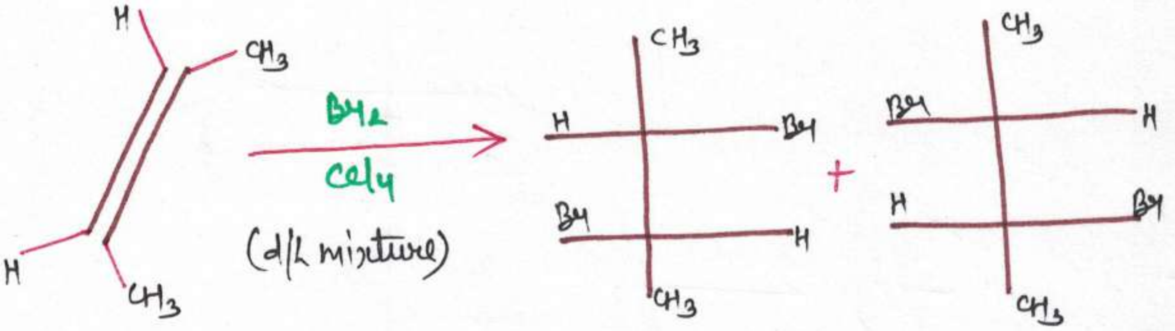

OH
+ Br2/CCl4
H
CH2
CH
Br
H
−H⊕
Br
Br

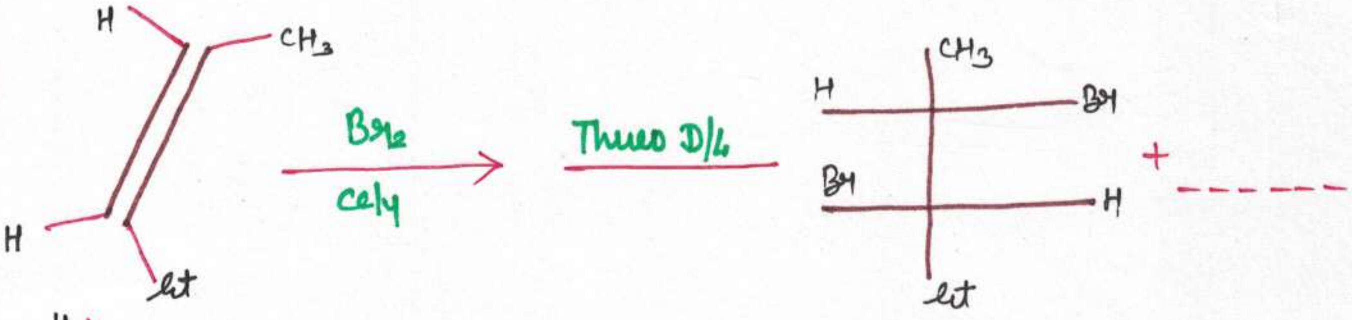

OH
CH2
Br2
CCl4
O
CH2−Br

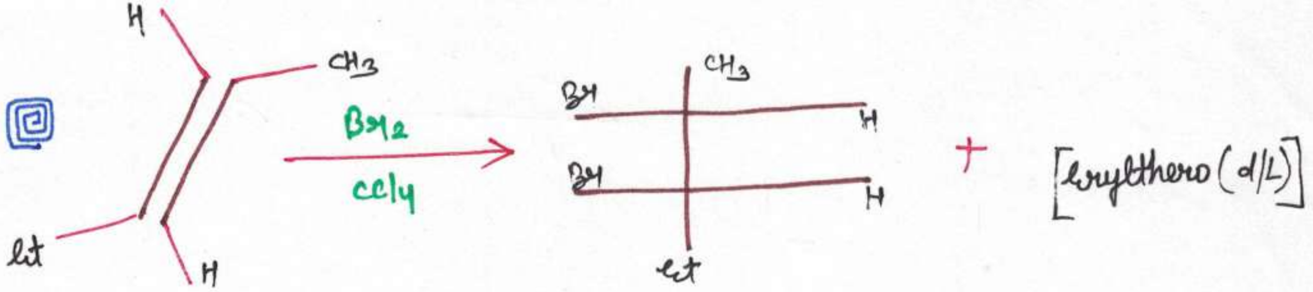

OH
Br2
CCl4
?
Br
H
O
Br

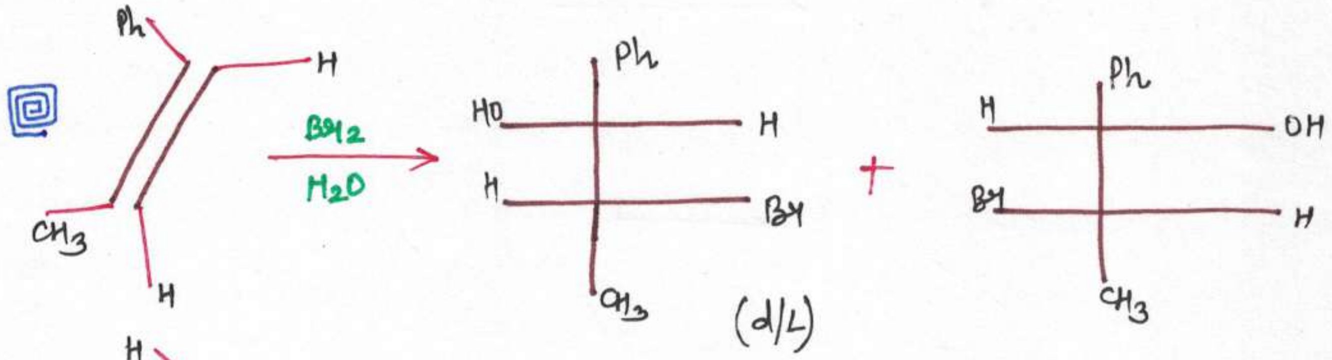

OH
Br2
CCl4
?
H
Br
O
Br
O
Br

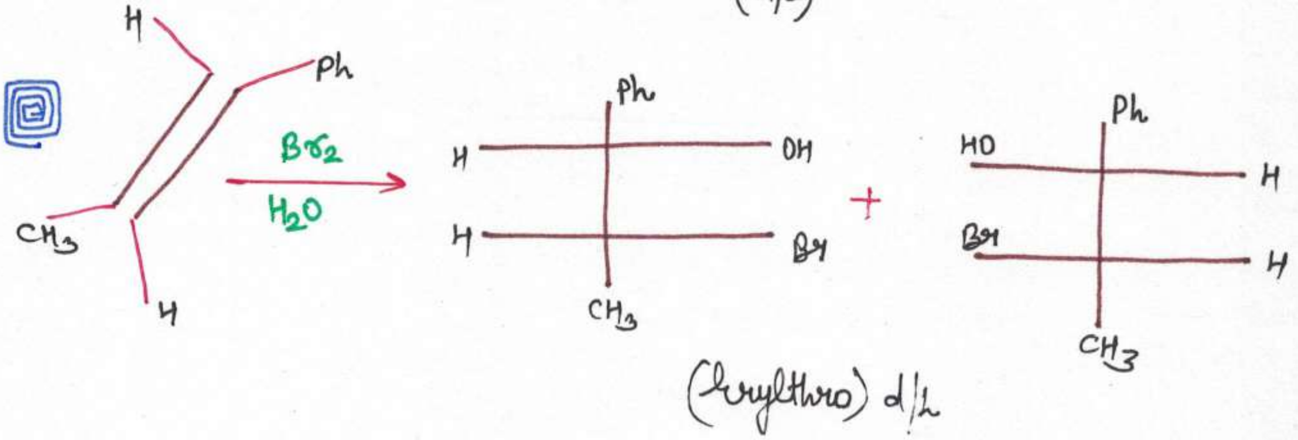

O
OH
Br2
CCl4
?
O
O
H
Br
O
Br





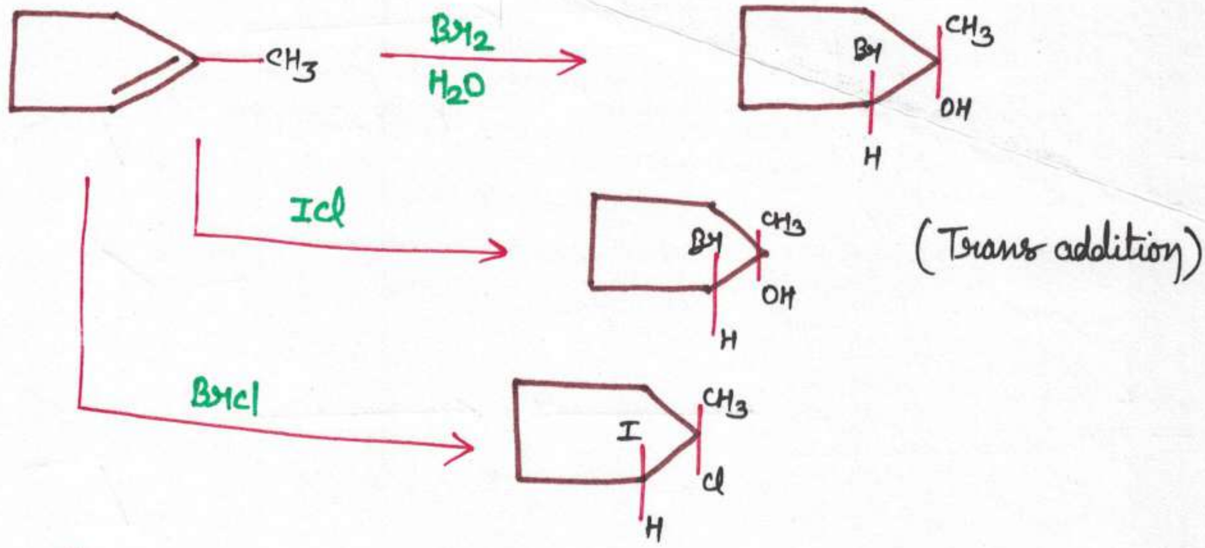


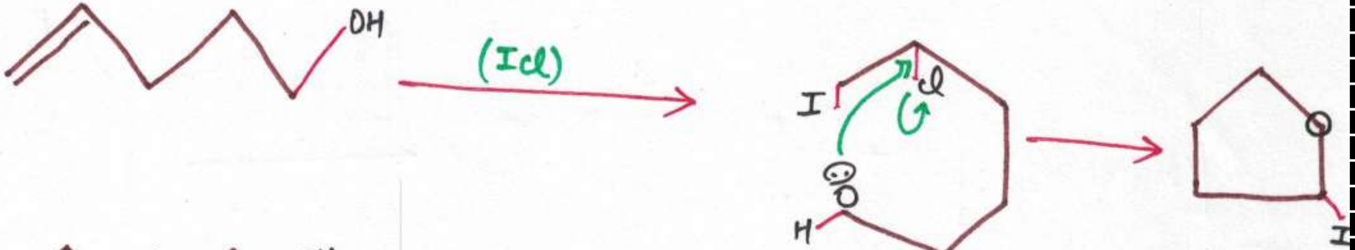


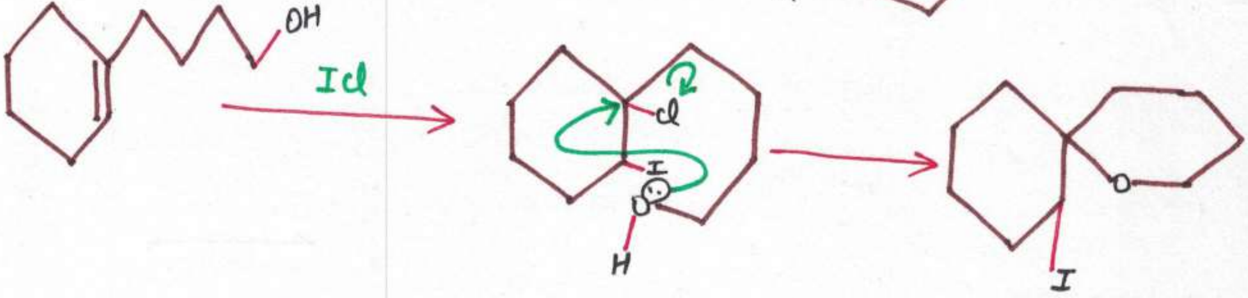


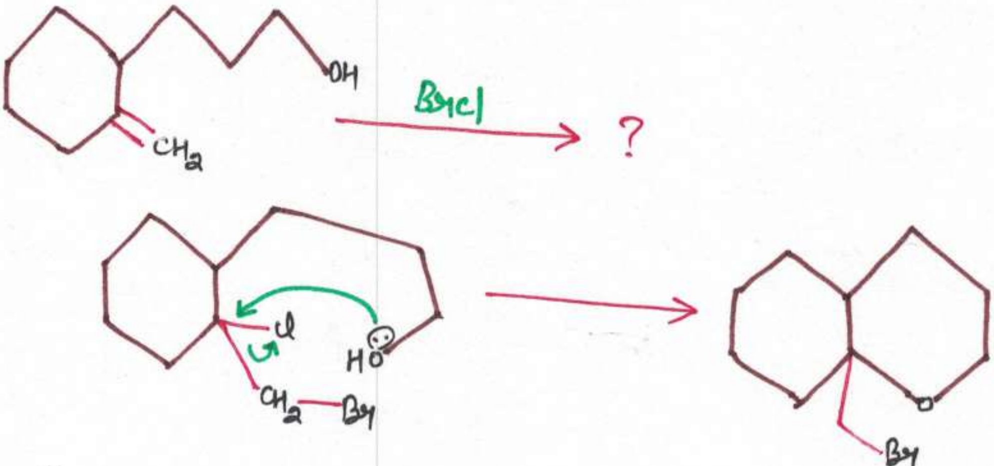
INTERHALLOGENATION OF ALKENES

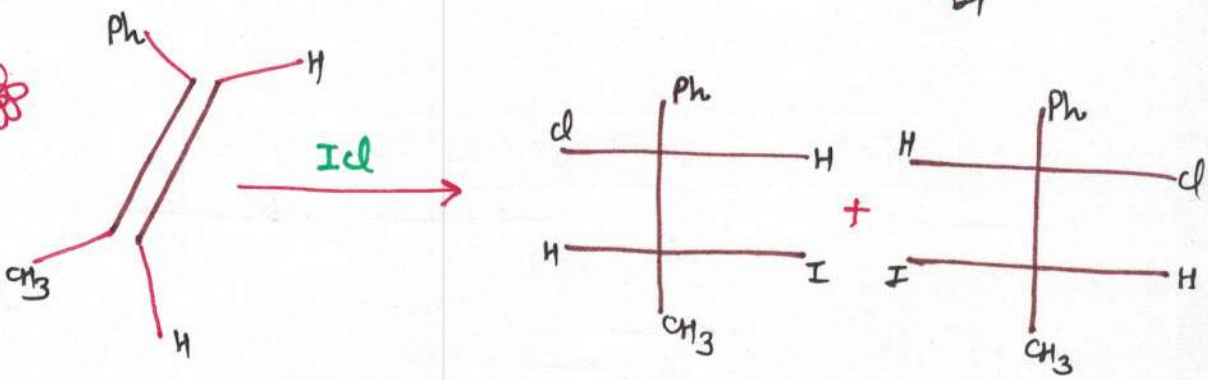
Higher hallogen is an electrophile.





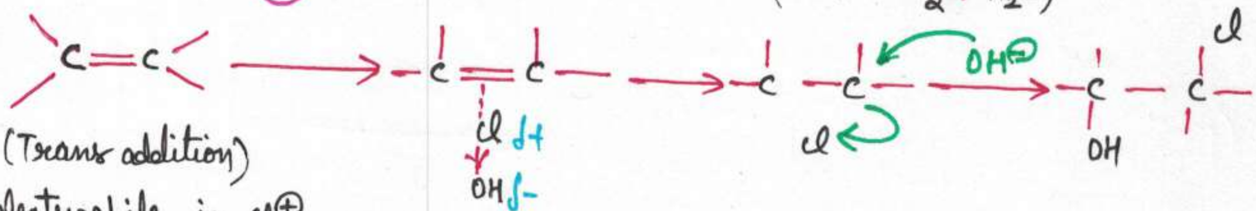






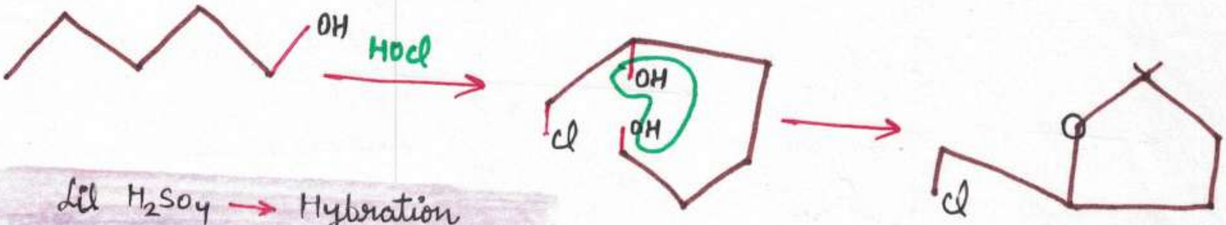
REACTION WITH HOCL

(It's $Cl_2 + H_2O$)



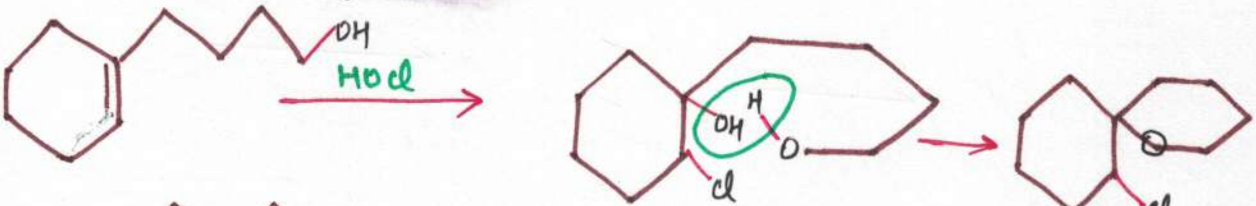
(Trans addition)

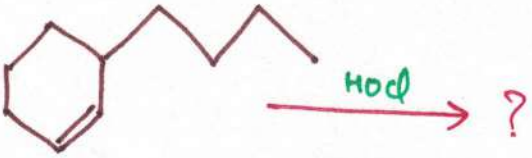
electrophile is $Cl^{\oplus}$

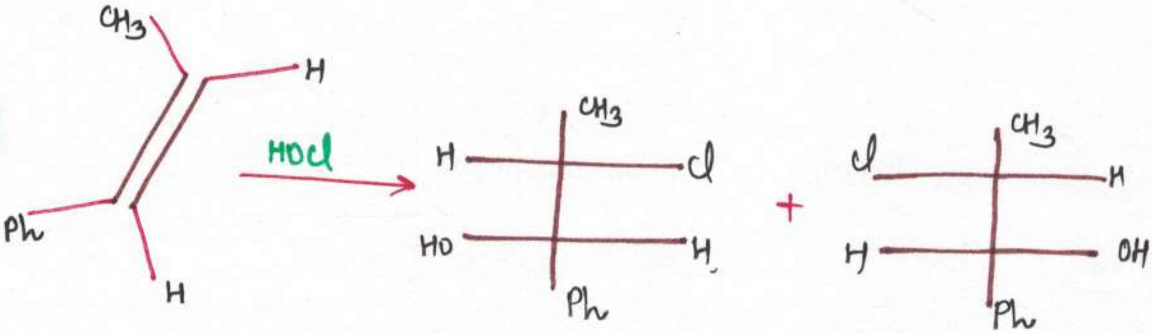


Dil H_2SO_4 → Hydration

Conc. H_2SO_4 → Dehydration

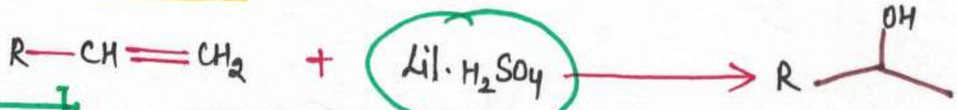




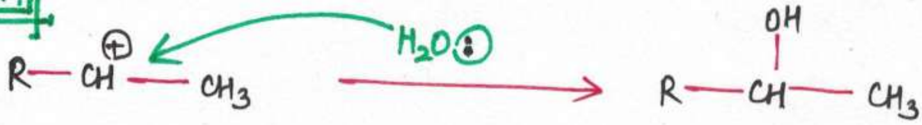


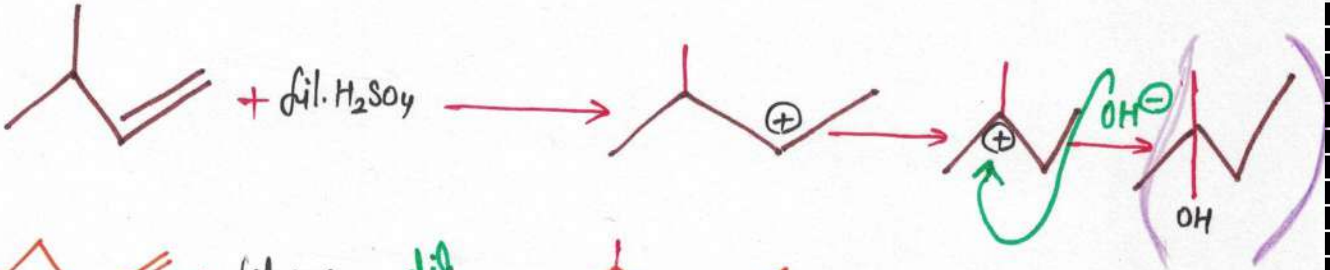
Regioselective, stereoselective, stereospecific (D/L)

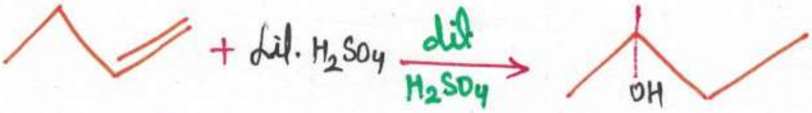
HYDRATION OF ALKENE

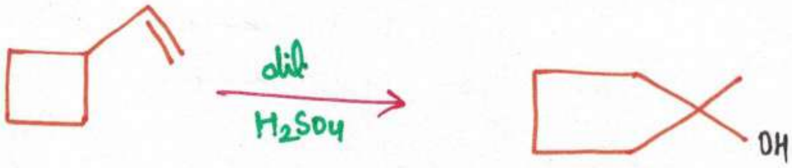


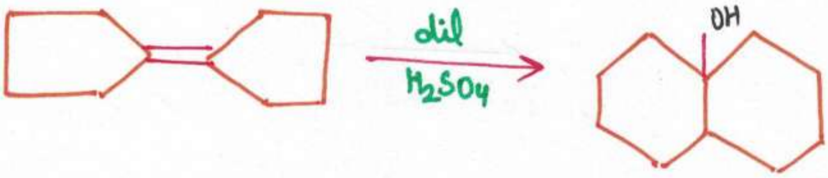
MECHANISM

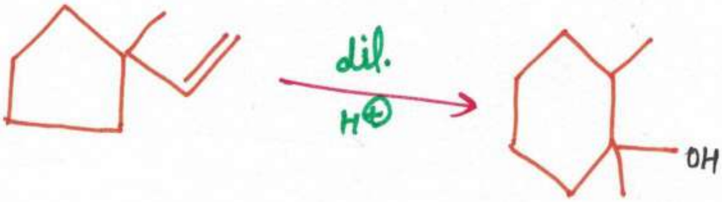


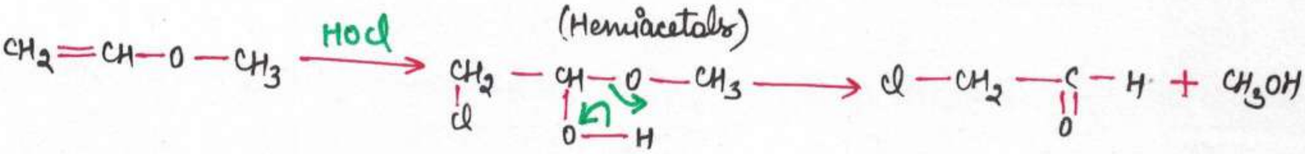




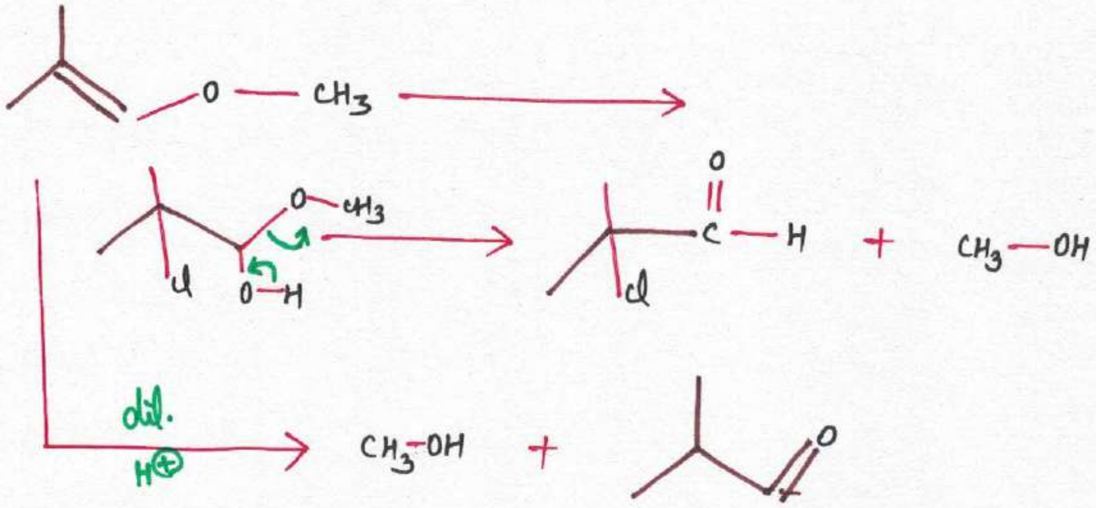


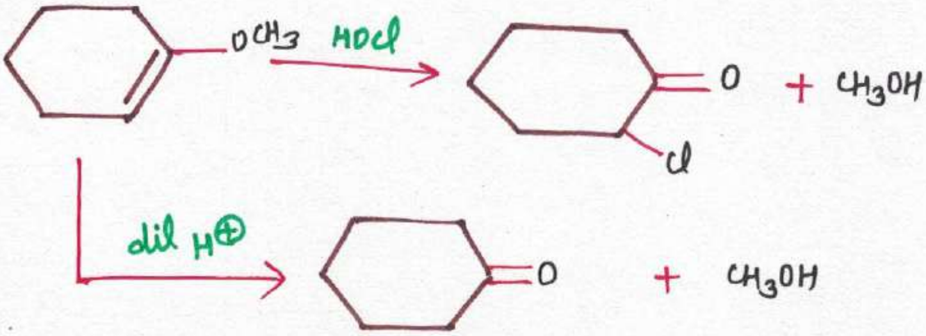




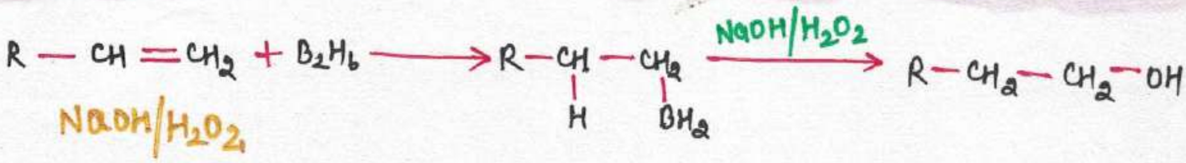


$$CH_2{=}CH{-}O{-}CH_3 \xrightarrow{HOCl} \underset{Cl}{CH_2}{-}\underset{OH}{CH}{-}O{-}CH_3 \longrightarrow Cl{-}CH_2{-}\underset{O}{\overset{}{C}}{-}H + CH_3OH$$



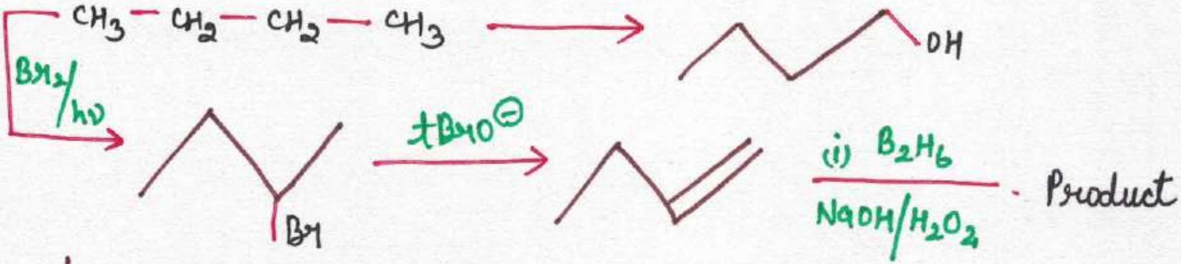


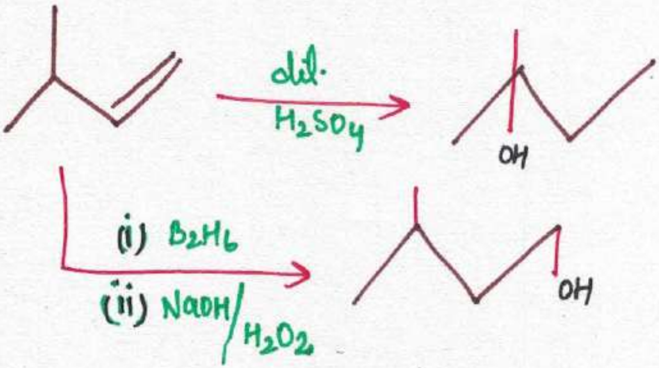
HYDRATION AND OXIDATION

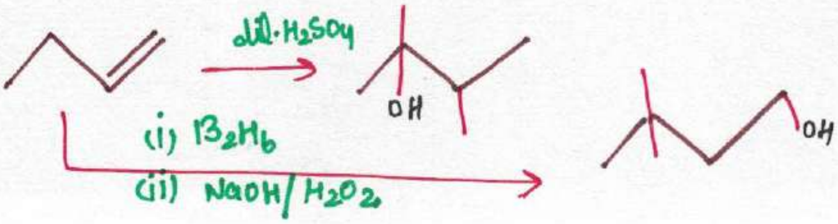


$R-CH=CH_2 + B_2H_6 \longrightarrow R-\underset{H}{CH}-\underset{BH_2}{CH_2} \xrightarrow{NaOH/H_2O_2} R-CH_2-CH_2-OH$

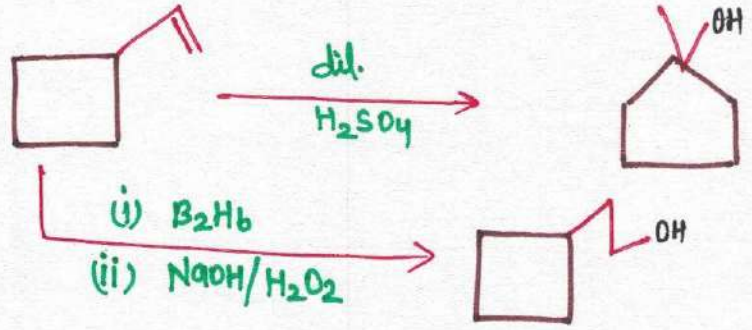
$NaOH/H_2O_2$

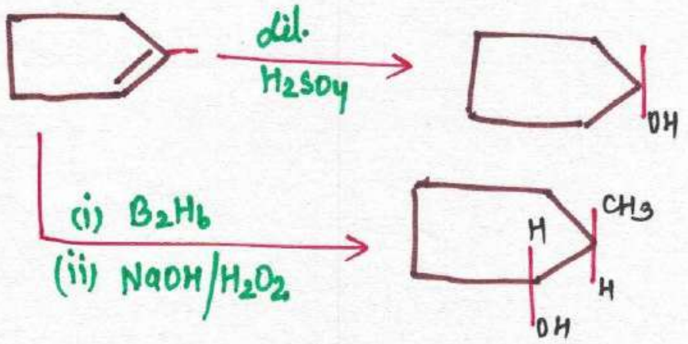






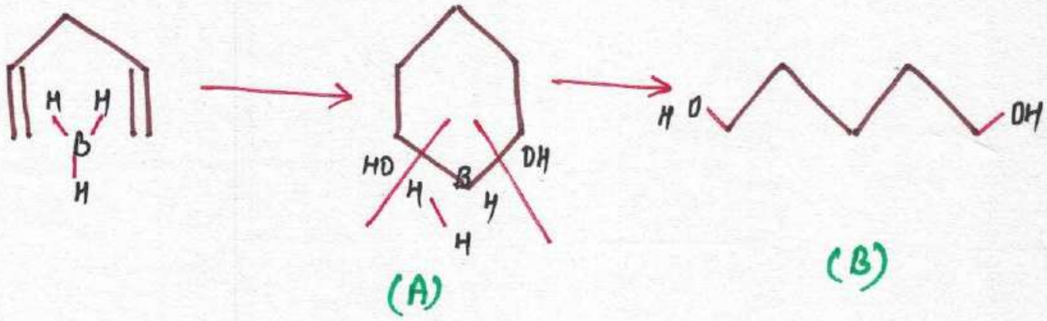
(Anti Markownikoff)



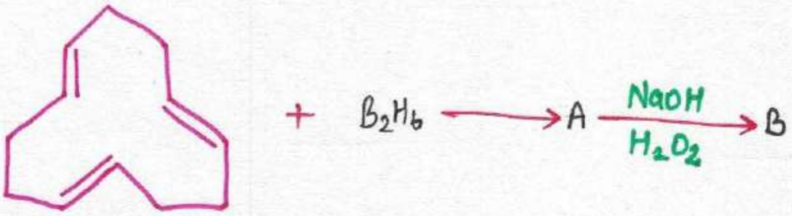


QUE

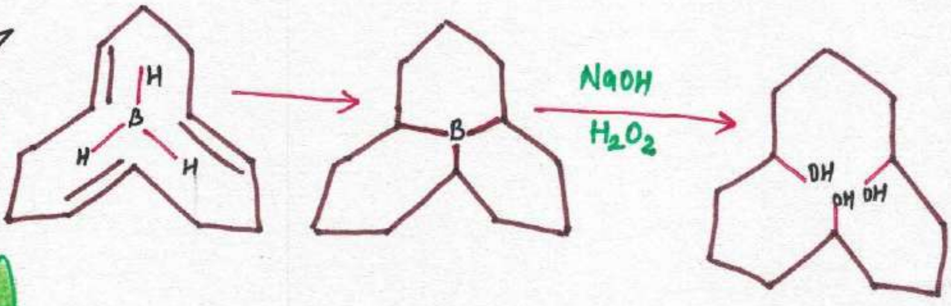
ANS



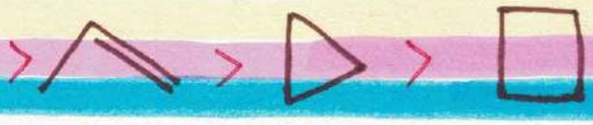
QUE



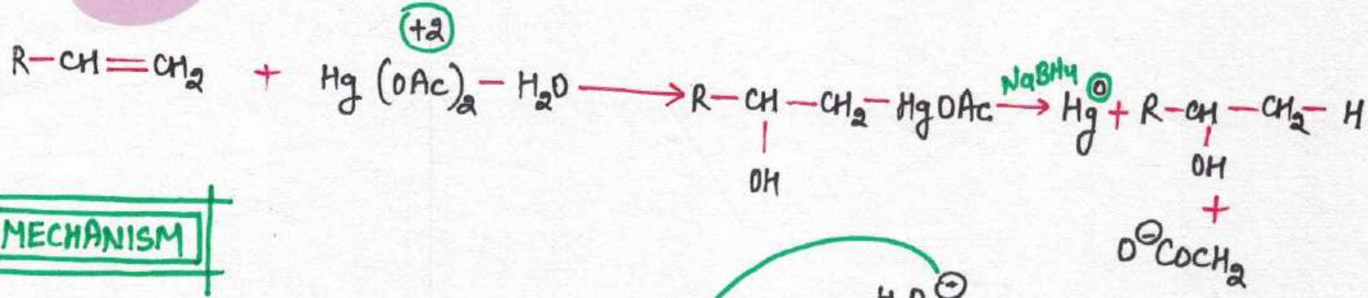
ANS



Rate of catalytic hydrogenation ⟶ CH≡CH >

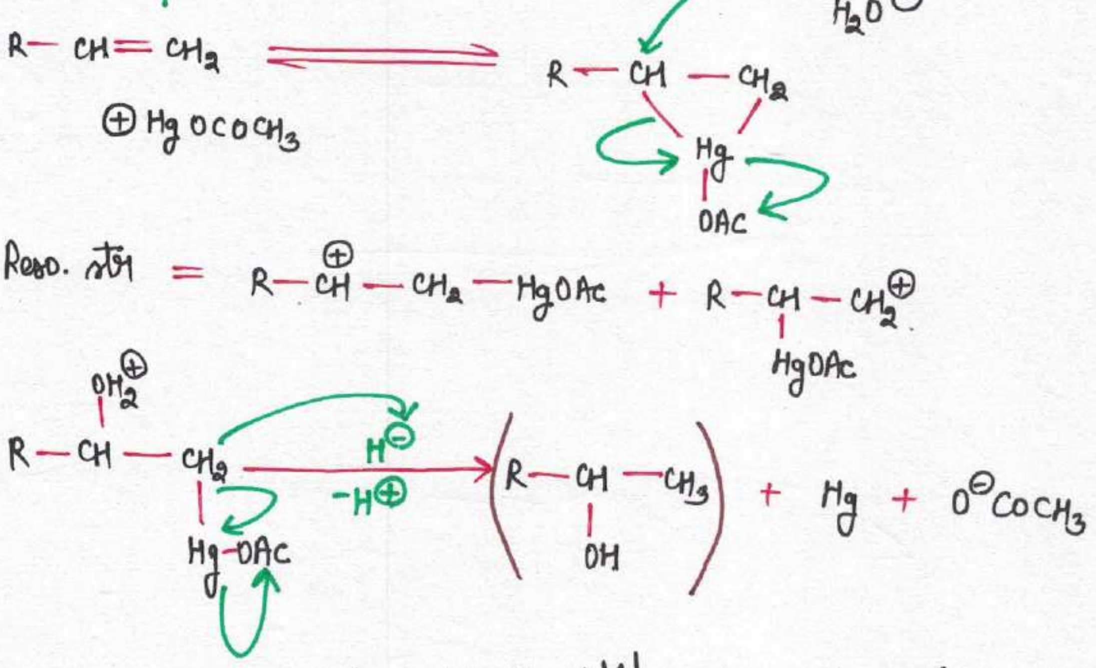


Oxymercuration Demercuration Of alkens



$$R{-}CH{=}CH_2 + \overset{+2}{Hg}(OAc)_2 - H_2O \longrightarrow R{-}\underset{OH}{CH}{-}CH_2{-}HgOAc \xrightarrow{NaBH_4} \overset{0}{Hg} + R{-}\underset{OH}{CH}{-}CH_2{-}H + O^{\ominus}COCH_2$$

MECHANISM



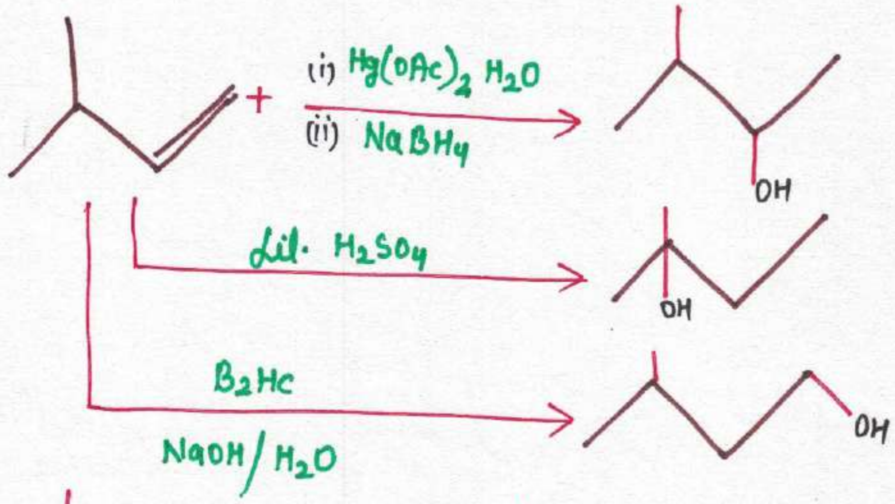
$$R{-}CH{=}CH_2 \;\; \oplus HgOCOCH_3 \rightleftharpoons R{-}CH{-}CH_2 \text{ (Hg–OAc bridged) } \quad H_2O^{\ominus}$$

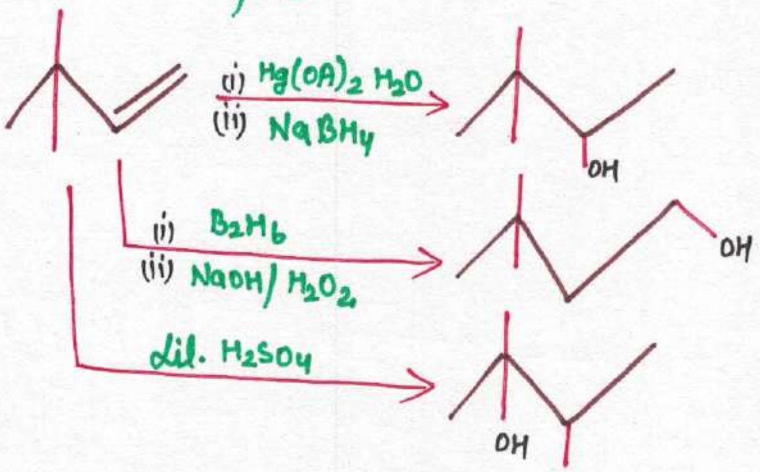
$$\text{Reso. str} = R{-}\overset{\oplus}{CH}{-}CH_2{-}HgOAc + R{-}\underset{HgOAc}{CH}{-}CH_2^{\oplus}$$

$$R{-}\overset{OH_2^{\oplus}}{CH}{-}\underset{Hg-OAc}{CH_2} \xrightarrow[-H^{\oplus}]{H^{\ominus}} \left(R{-}\underset{OH}{CH}{-}CH_3\right) + Hg + O^{\ominus}COCH_3$$

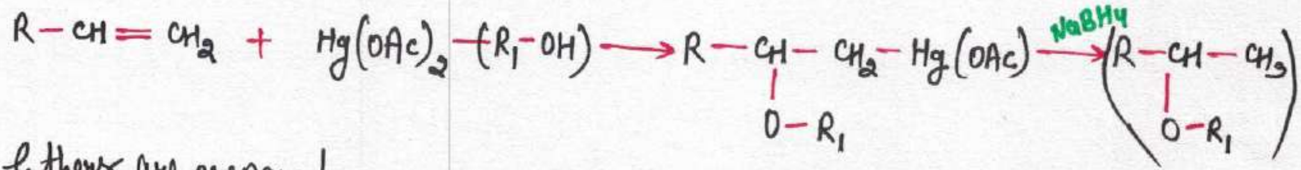
- It involves the Markownikoff addition, thus, there is no rearrangement as mercuronium ion is itself very stable.

- In reactant, Hg is +2 O.S while in product, it is '0' O.S, thus $\Delta O.S = 2$.

- 

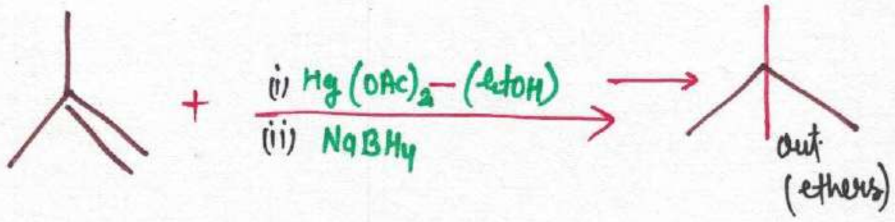
- 

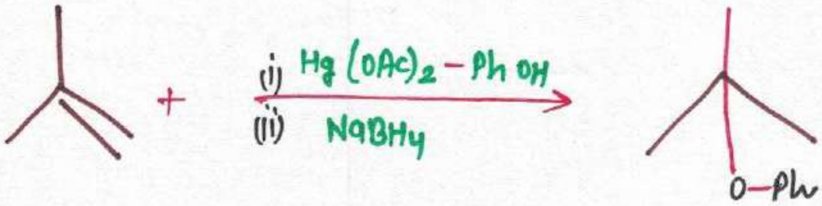
Alkoxy mercuration – demercuration

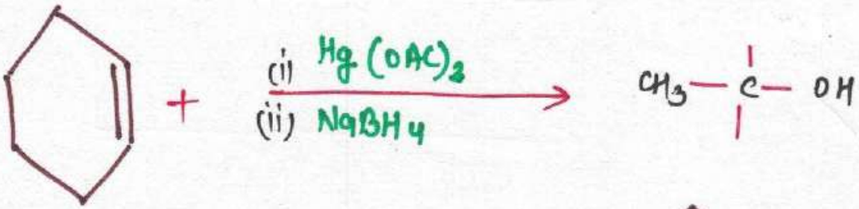


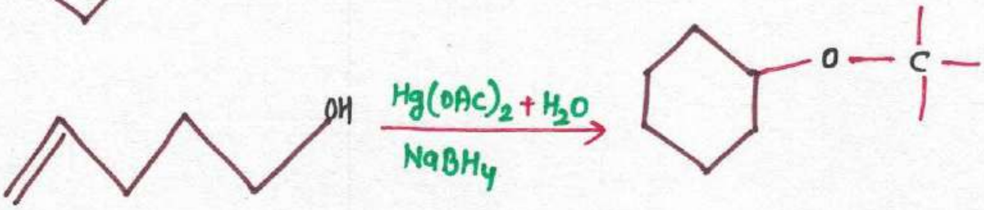
$$R-CH=CH_2 + Hg(OAc)_2 + (R_1-OH) \longrightarrow R-\underset{\underset{O-R_1}{|}}{CH}-CH_2-Hg(OAc) \xrightarrow{NaBH_4} \left(R-\underset{\underset{O-R_1}{|}}{CH}-CH_3\right)$$

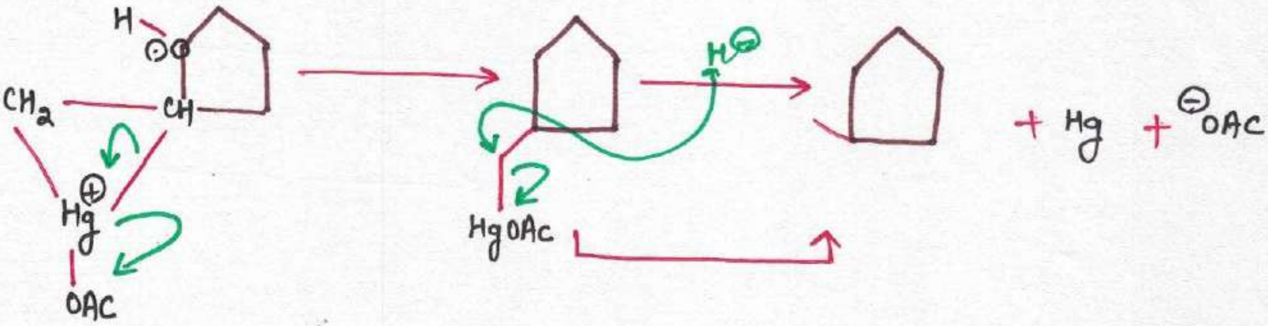
Ethers are prepared.

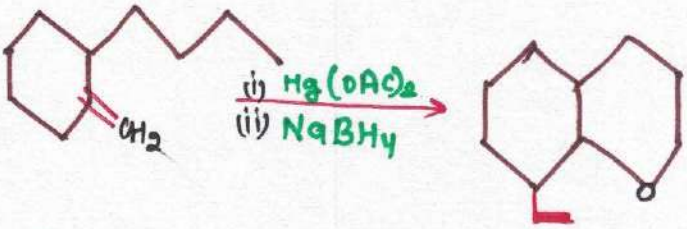

(i) Hg(OAc)2 – (EtOH)
(ii) NaBH4
OEt
(ethers)

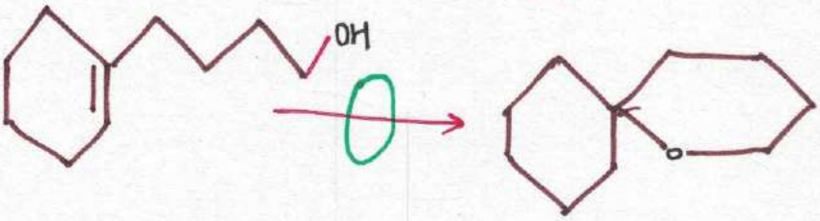

(i) Hg(OAc)2 – Ph OH
(ii) NaBH4
O–Ph

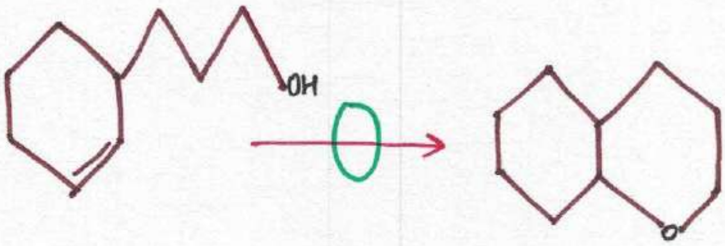

(i) Hg(OAc)2
(ii) NaBH4
CH3 – C – OH


OH
Hg(OAc)2 + H2O
NaBH4
O
C

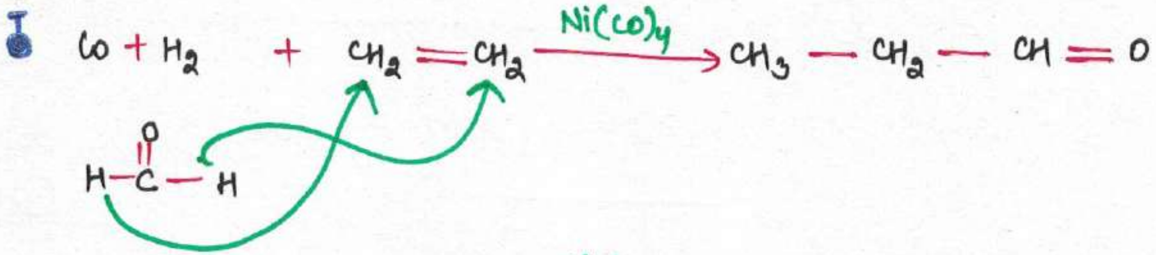

H
⊖O
CH2
CH
⊕
Hg
OAC
H⊖
HgOAc
+ Hg + ⊖OAC


CH2
(i) Hg(OAc)2
(ii) NaBH4
O


OH
O
O

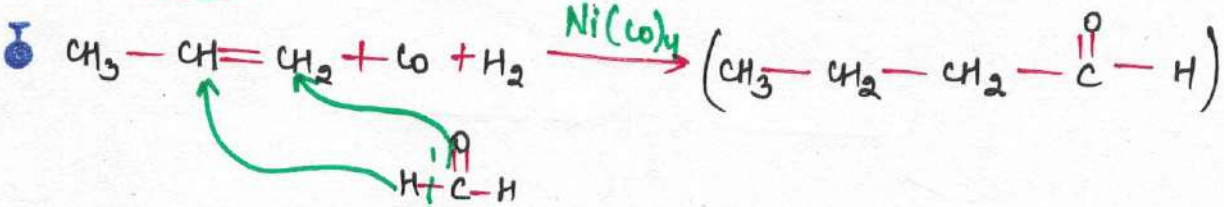

OH
O
O

Hydroformylation of alkens (oxo reaction)



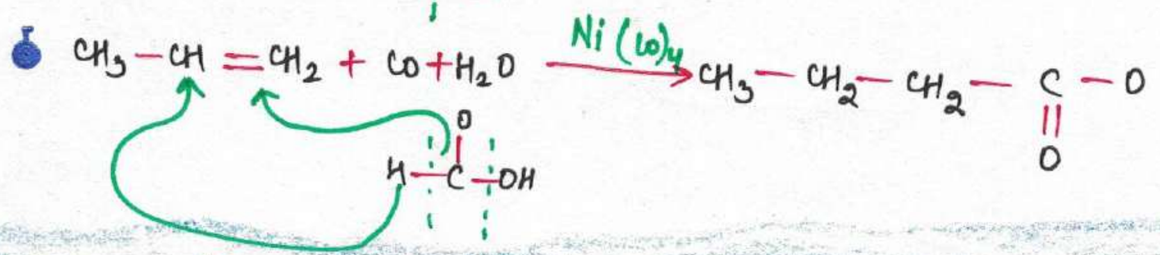
$$CO + H_2 + CH_2{=}CH_2 \xrightarrow{Ni(CO)_4} CH_3-CH_2-CH{=}O$$

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



$$CH_3-CH{=}CH_2 + CO + H_2 \xrightarrow{Ni(CO)_4} \left(CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-H\right)$$

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

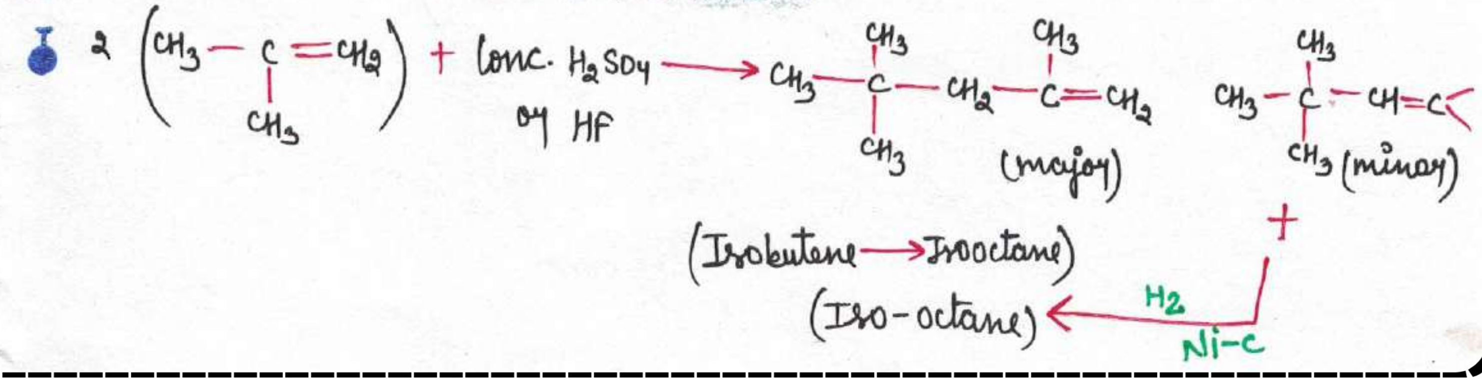


$$CH_3-CH{=}CH_2 + CO + H_2O \xrightarrow{Ni(CO)_4} CH_3-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-O$$

$$H-\overset{\overset{O}{\|}}{C}-OH$$

Diamerisation of alkenes

Harffman is major

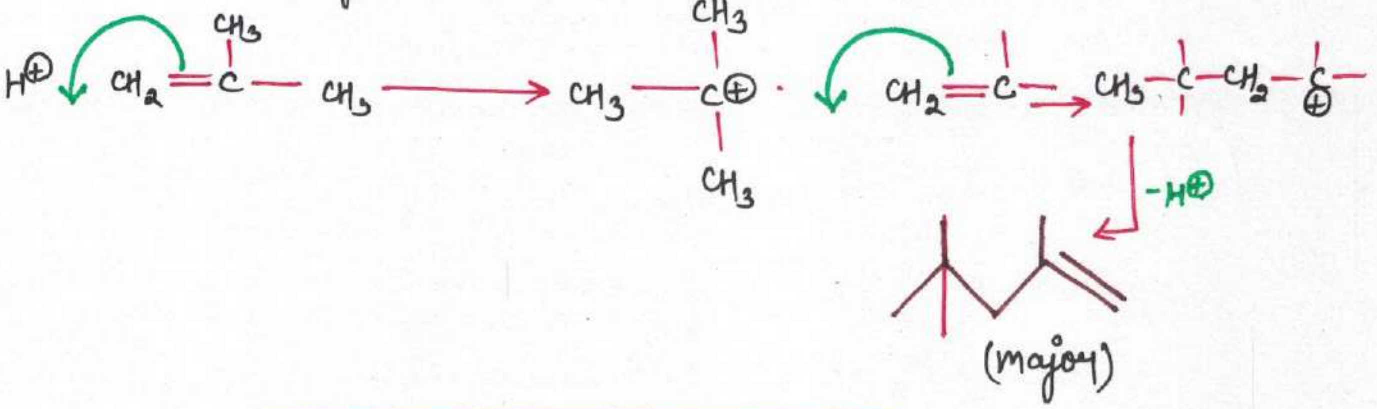


$$2\left(CH_3-\underset{\underset{CH_3}{|}}{C}{=}CH_2\right) + \text{conc. } H_2SO_4 \text{ or } HF \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{C}{=}CH_2 \ (\text{major}) \quad CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH{=}C< \ (\text{minor})$$

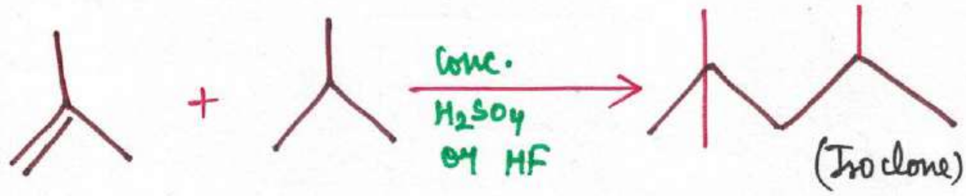
$$+ \xrightarrow[Ni-C]{H_2} (\text{Iso-octane})$$

(Isobutene → Isooctane)

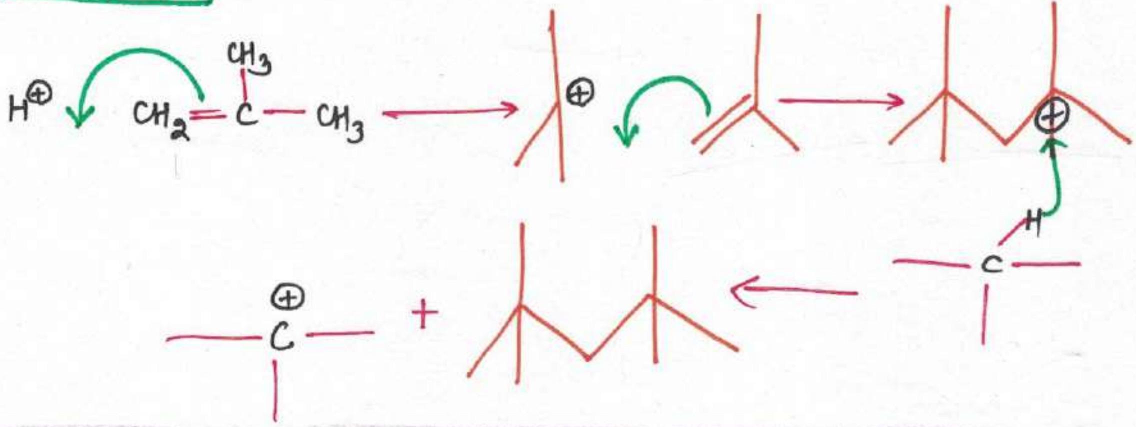
MECHANISM Tertiary group shows no. hyper conjugation, thus, the hoffman is major.



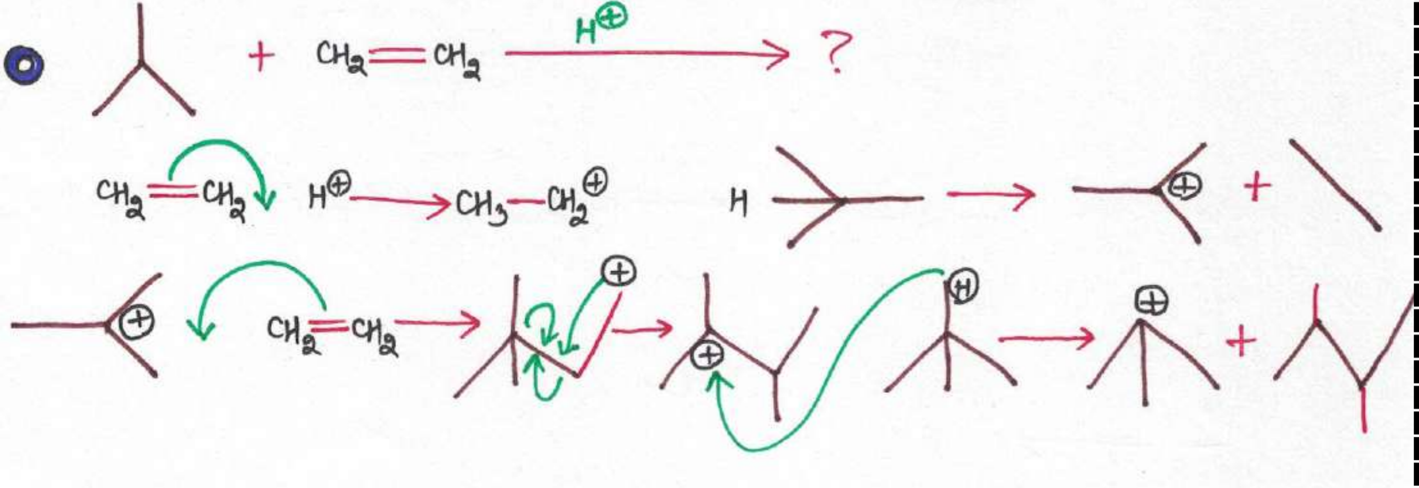
ALKYLATION OF ALKENES



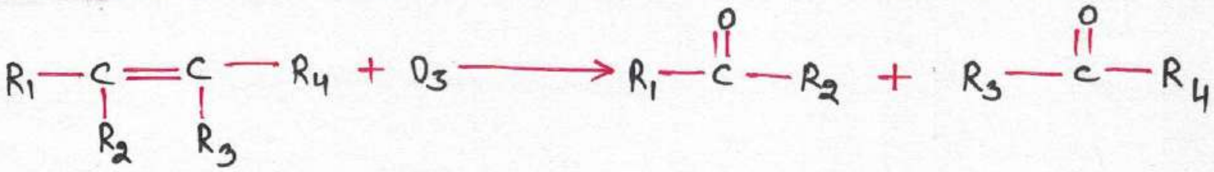
MECHANISM



Chain Reaction :- In Intermolecular hydride shift occurs.

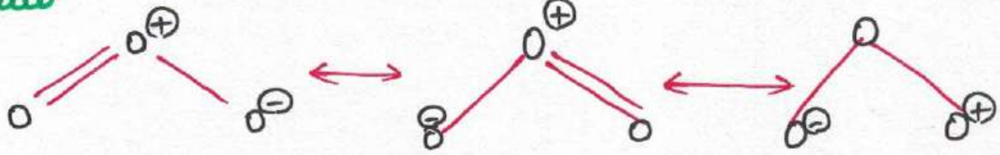


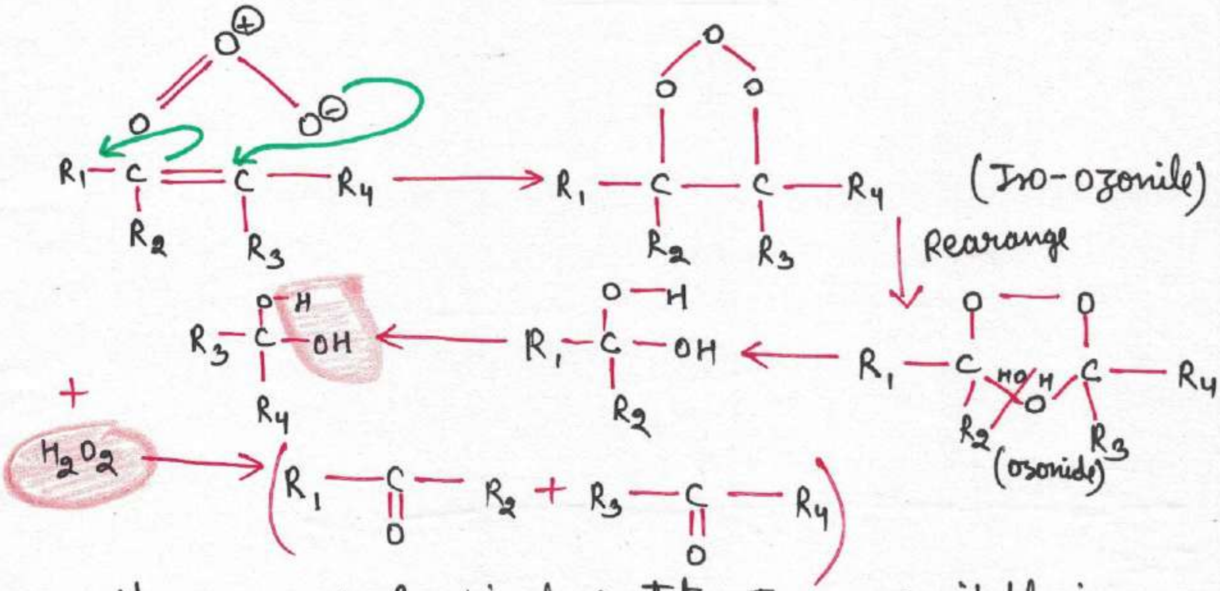
OZONOLYSIS



$$R_1-\underset{R_2}{C}=\underset{R_3}{C}-R_4 + O_3 \longrightarrow R_1-\overset{O}{\overset{\|}{C}}-R_2 + R_3-\overset{O}{\overset{\|}{C}}-R_4$$

MECHANISM

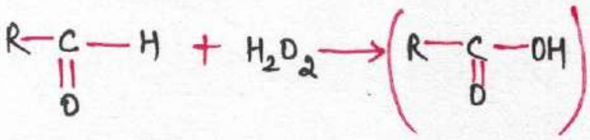




Ozonides are explosives in free state. Theyare available in aqueous medium only.

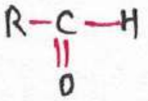
- $CH_3-CH_3 \xrightarrow[\text{(chlorinolysis)}]{} 2(CH_3-Cl)$

- If product formed is an aldehyde, then



$$R-\underset{O}{\underset{\|}{C}}-H + H_2O_2 \longrightarrow \left(R-\underset{O}{\underset{\|}{C}}-OH\right)$$

But when Zn is used.



$R-\underset{O}{\underset{\|}{C}}-H$ is only formed, because;

$$Zn + H_2O_2 \longrightarrow ZnO + H_2O$$

OXIDATIVE OZONOLYSIS

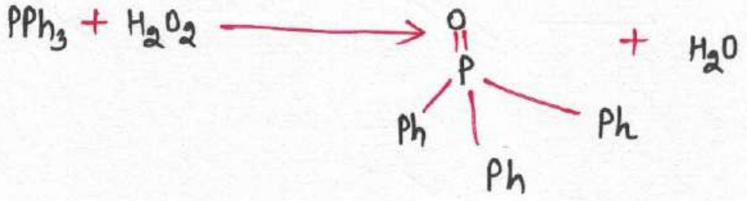
– The ozonolysis is there without Zn, thus, product of aldehydes gives acids.

REDUCTIVE OZONOLYSIS

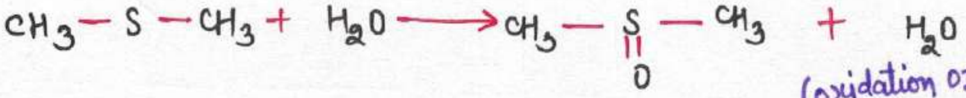
– Ozonolysis in presence of Zn or PPh_3 or CH_3 S CH_3 so that oxidation of aldehyde don't occur.

Zn / PPh_3 / CH_3 S CH_3

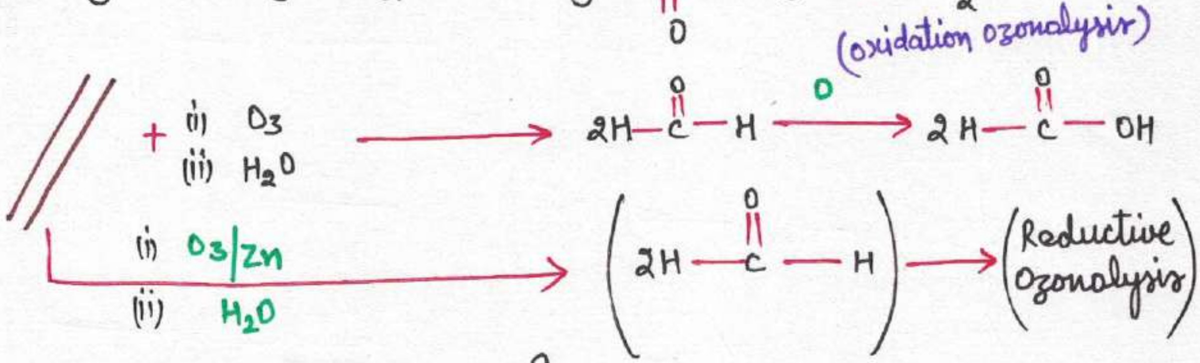
$$Zn + H_2O_2 \longrightarrow ZnO + H_2O$$

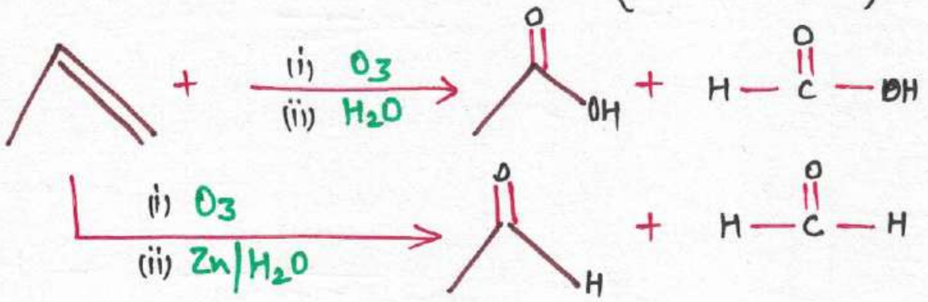


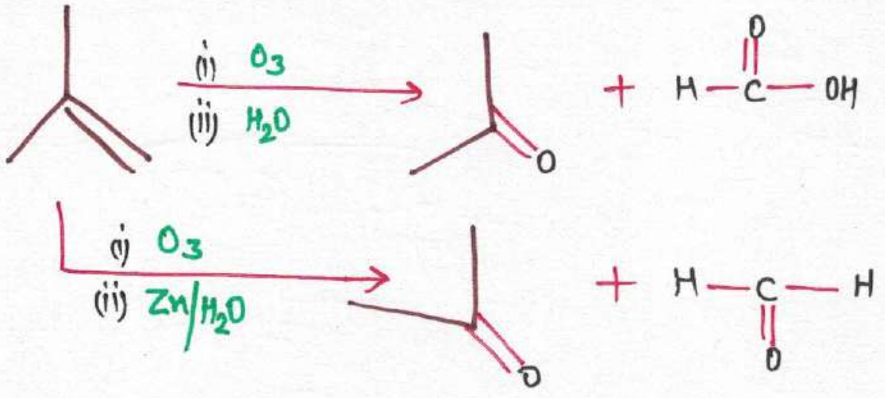
$$PPh_3 + H_2O_2 \longrightarrow Ph_3P{=}O + H_2O$$



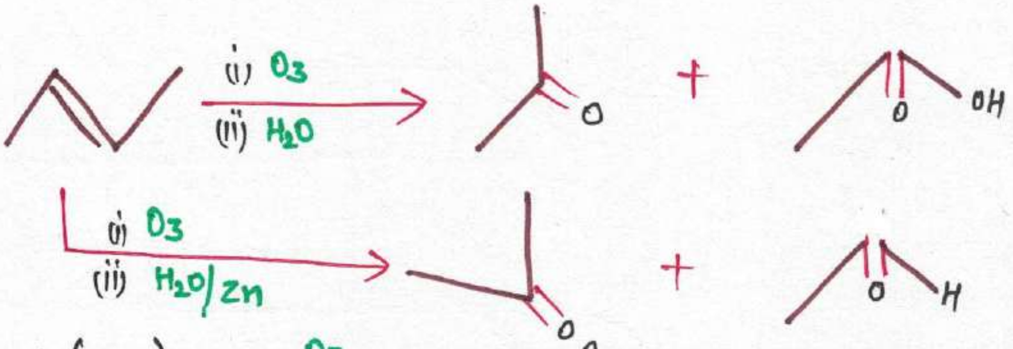
$$CH_3-S-CH_3 + H_2O \longrightarrow CH_3-\underset{O}{\overset{\|}{S}}-CH_3 + H_2O$$





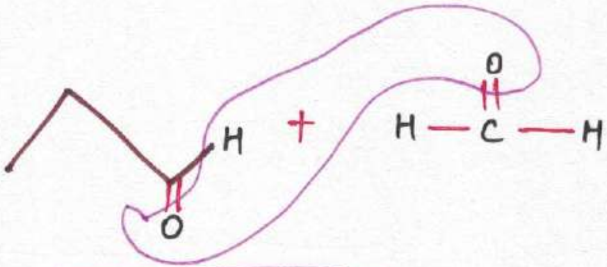


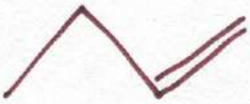
☐



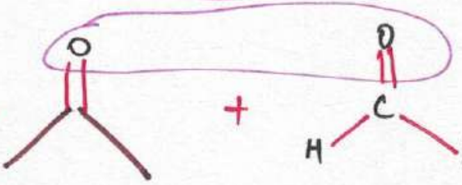
☐ A (C_4H_8) $\xrightarrow{O_3}$ $2CH_3-\overset{O}{\overset{\|}{C}}-H$

☐ B (C_4H_8) $\xrightarrow{O_3}$



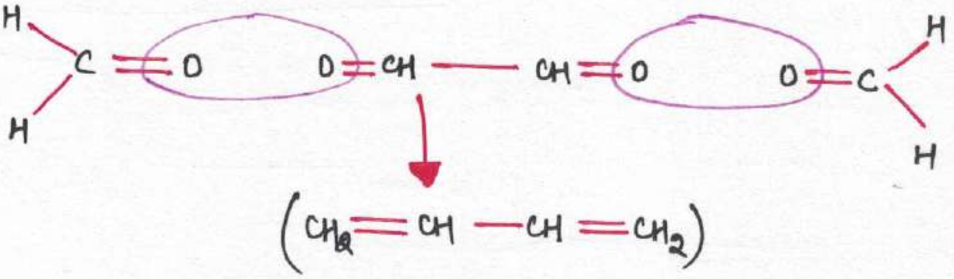


☐ C (C_4H_8) $\xrightarrow{O_3}$



☐ A (C_4H_6) $\xrightarrow{O_3}$ $H-\overset{O}{\overset{\|}{C}}-H$ + glyoxal

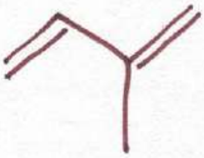
DV=2



☐ A(C_5H_8) $\xrightarrow{O_3}$ HCHO + Pyrune aldehyde $CH_3\ \overset{O}{C}\ CH\ O$

DV=2 (2 oxo- propanal)

A

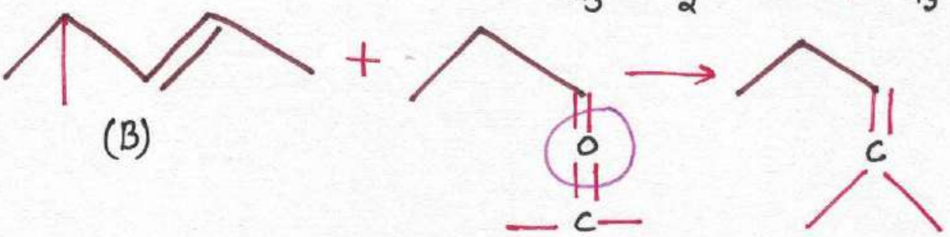


(Isoprene)

(2 methyl- 1,3 - butadiene)

When not mentioned ⟶ Reductive Ozonolysis

$$A\,(C_6H_{13}Cl) \xrightarrow[KOH]{Alc.} (B+C) \xrightarrow{O_3} CH_3-\overset{\overset{O}{\|}}{C}-H + CH_3-\underset{\underset{O}{\|}}{C}-CH_2 + CH_3-CH_2-CH{=}O + CH_3-\underset{\underset{CH_3}{|}}{CH}-CH{=}O$$



(B)

(C)

$$\text{Allene}\ (CH_2{=}C{=}CH_2) \xrightarrow[Zn]{O_3} CO_2 + 2HCHO$$

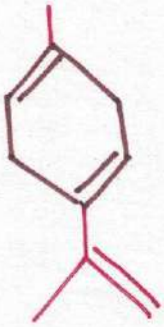
$$A\,(C_6H_8) \xrightarrow{O_3} H-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-H$$

DV = 7 − 4 = 3

$$A\,(C_{10}H_{14}) \xrightarrow[Ni-C]{H_2}$$

$$\xrightarrow{O_3} H-\overset{\overset{O}{\|}}{C}-H + CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH{=}O + CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-H$$

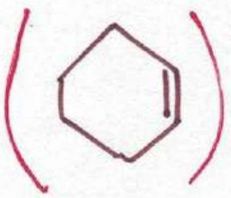
DV = 11 − 7 = 4 → 3 double

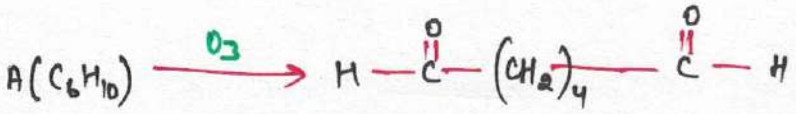


(A)

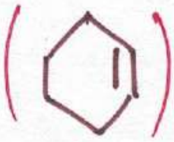
$$A\,(C_6H_{10}) \xrightarrow{O_3} H-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-H$$

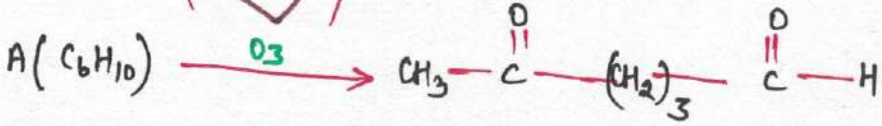
D.V = 2



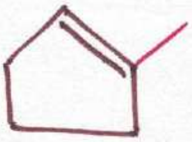


$A(C_6H_{10}) \xrightarrow{O_3} H-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-H$





$A(C_6H_{10}) \xrightarrow{O_3} CH_3-\overset{O}{\overset{\|}{C}}-(CH_2)_3-\overset{O}{\overset{\|}{C}}-H$



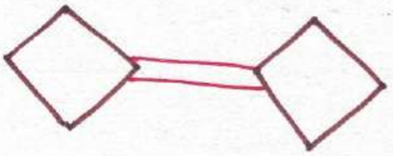
$A(C_8H_{12}) \xrightarrow[Ni-C]{1\ H_2} B(C_8H_{14})$

$\xrightarrow{O_3} C(C_8H_{12}O_2)$ (symmetric alkalones)

$C_8H_{12} \rightarrow DV = 3 \rightarrow$ Double $= 1$, 2 rings

$A(C_8H_{12}) \xrightarrow[Ni/C]{1\ H_2} B(C_8H_{14})$

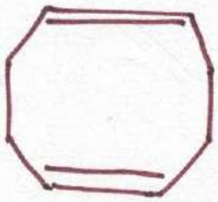
$\xrightarrow{O_3} C(C_4H_6O_2) \rightarrow$ (Single ketone)



$A(C_8H_{12}) \xrightarrow[Ni-C]{1\ H_2} B(C_8H_{14})$

$\xrightarrow{O_3} C(C_4H_6O_2)$

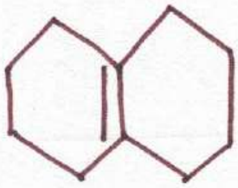
$DV = 9 - 6 = 3$, Ring $= 1$, Double bond $= 2$



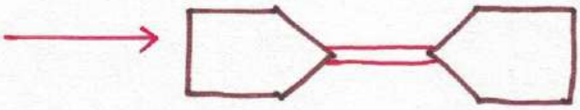
$A(C_{10}H_{16}) \xrightarrow[Ni-C]{1H_2} B(C_{10}H_{18})$

$A(C_{10}H_{16}) \xrightarrow{O_3} C(C_{10}H_{16}O_2)$ Symmetrical

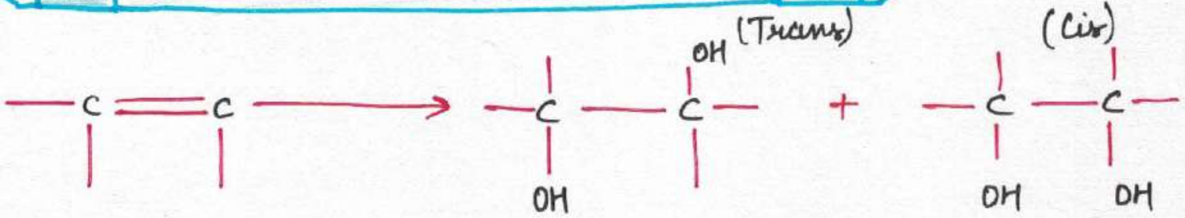
D.V = 11 − 8 = 3 , Ring = 2 D.B = 1



If C is (C_5H_8O)



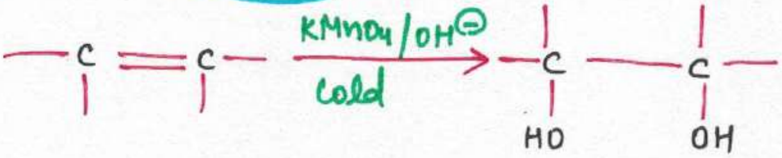
HYDROXYLATION OF ALKENES



(RCO_3H / H^+)
(Ag_2O / H^+)

(Cold alkaline
$KMnO_4$)
(OsO_4)

Q. Cold alkaline $KMnO_4$

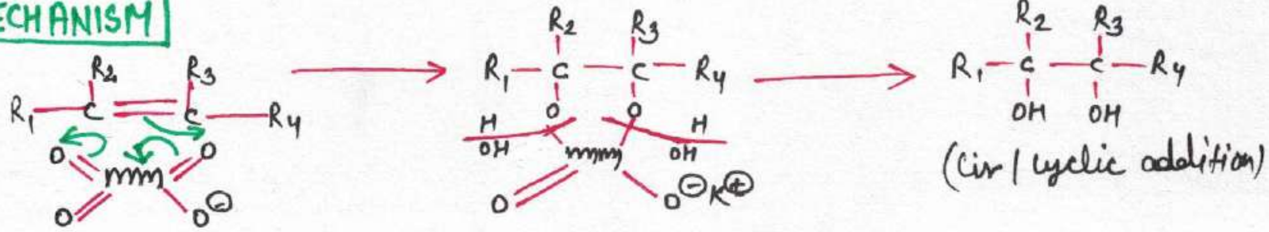


$2MnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5(O)$
(strong OA)

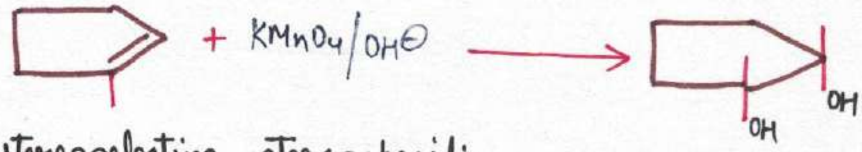
$2KMnO_4 + H_2O \longrightarrow 2MnO_2 + 2KOH + 3(O)$

$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + (O)$
(weak OA)

MECHANISM

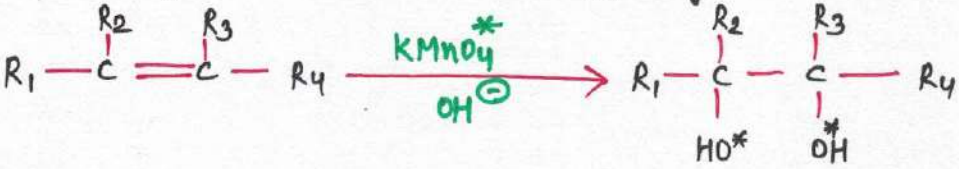


(Cis / cyclic addition)

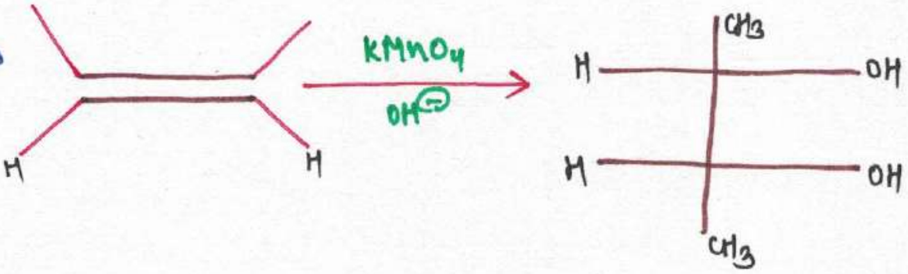


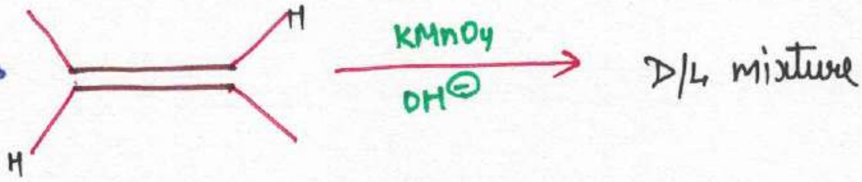
stereoselective, stereospecific

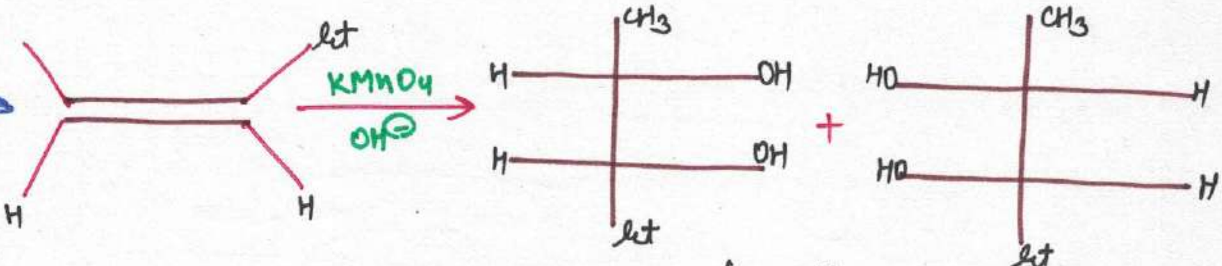
The -OH groups are from the oxygen of the $KMnO_4$, not H_2O.



$$R_1-\overset{R_2}{\overset{|}{C}}=\overset{R_3}{\overset{|}{C}}-R_4 \xrightarrow[OH^\ominus]{KMnO_4^*} R_1-\underset{HO^*}{\underset{|}{\overset{R_2}{\overset{|}{C}}}}-\underset{OH^*}{\underset{|}{\overset{R_3}{\overset{|}{C}}}}-R_4$$

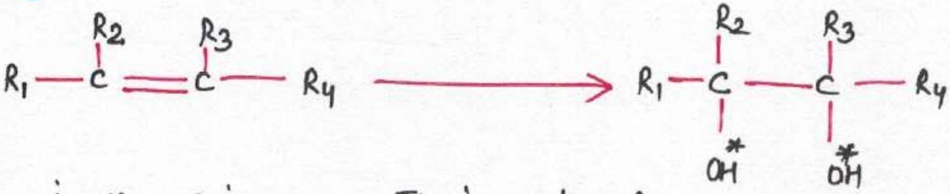






(erythro d/L)

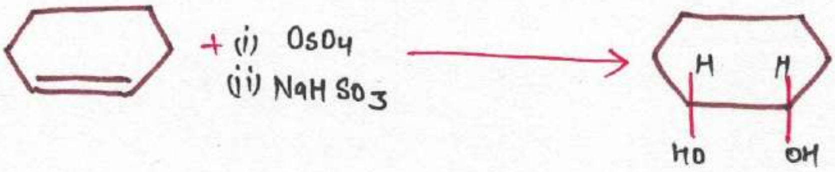
b By OsO_4



$$R_1-\overset{R_2}{\overset{|}{C}}=\overset{R_3}{\overset{|}{C}}-R_4 \longrightarrow R_1-\underset{OH^*}{\underset{|}{\overset{R_2}{\overset{|}{C}}}}-\underset{OH^*}{\underset{|}{\overset{R_3}{\overset{|}{C}}}}-R_4$$

OsO_4 is very poisonous. It imparts blindness. Thus, we use catalytic amount of H_2O_2 so that the product is oxidised to further product.

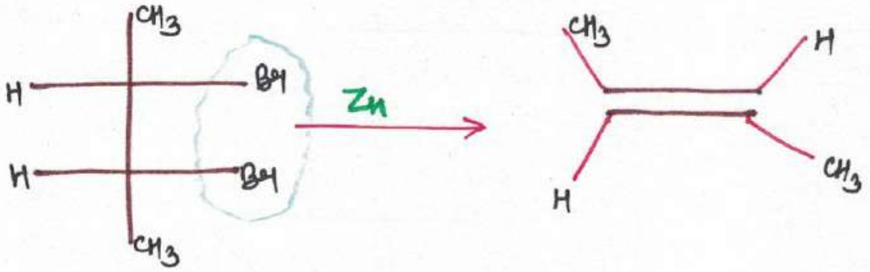
The hydrolysis can also be done by Na_2SO_3/ $NaHSO_3$.

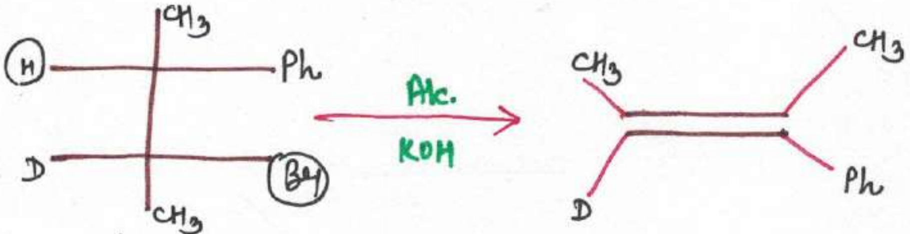


Kharash effect is only shown by HBr.
HCL/HF/HI don't show the kharash effect.

If the regent does trans elimination then the removal of the elements from same side gives a trans product.

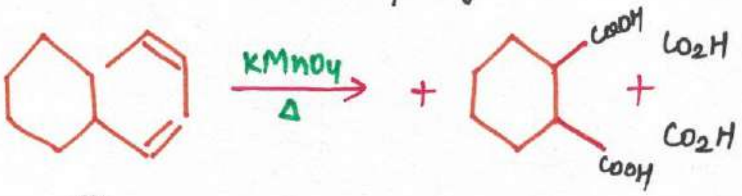
E.g.

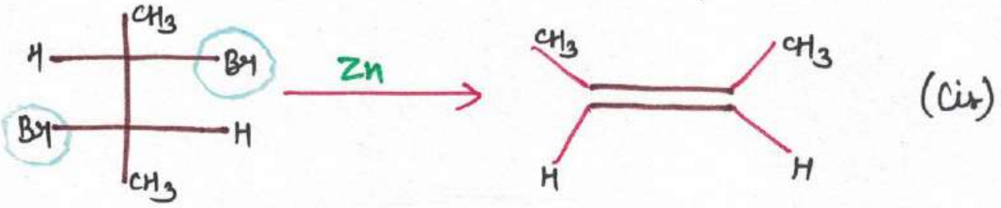




Diff. side.

Conjugated dienes on $KMnO_4/\Delta$ gives oxalic acid



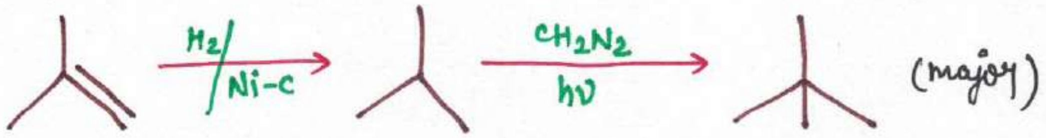


▲ In $Br_2 | ccl_4$, there is formation of π complex. (Trans addn)

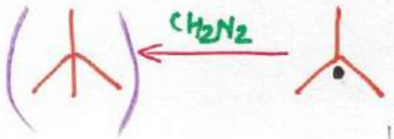
$$R-CH=CH_2 \longrightarrow R-CH\underset{Br}{\overset{}{=}}CH_2$$

▲ In hydroxylation by $R-\overset{O}{\overset{\|}{C}}-O-O-H$, epoxide is the intermediate.

▲



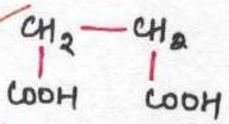
It will be a radical reaction and more stable radical is



QUE.

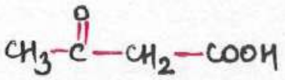
How many evolve CO_2 on heating?

(a) $HCOOH$ (b) $(COOH)_2$ (c) $CH_2(COOH)_2$ ✓ (d) ✓



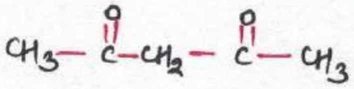
$HOOC-CH_2-CH_2-COOH$

(e)



$CH_3-CO-CH_2-COOH$

(f)



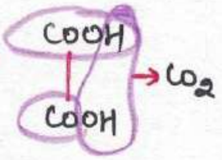
$CH_3-CO-CH_2-CO-CH_3$

(g) CH_3COOH

ANS.

(a) ✗

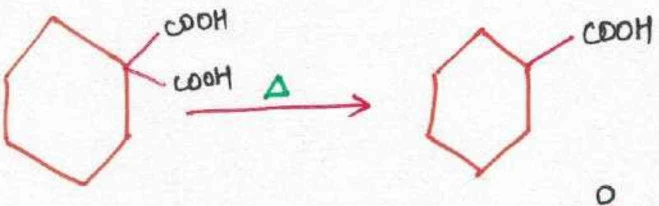
(b)

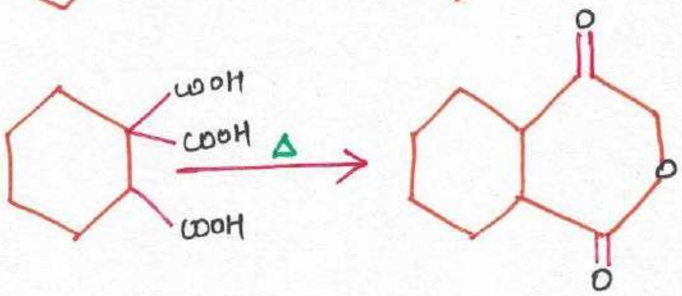


(c) CO_2 ✓

(d) CO_2 ✓

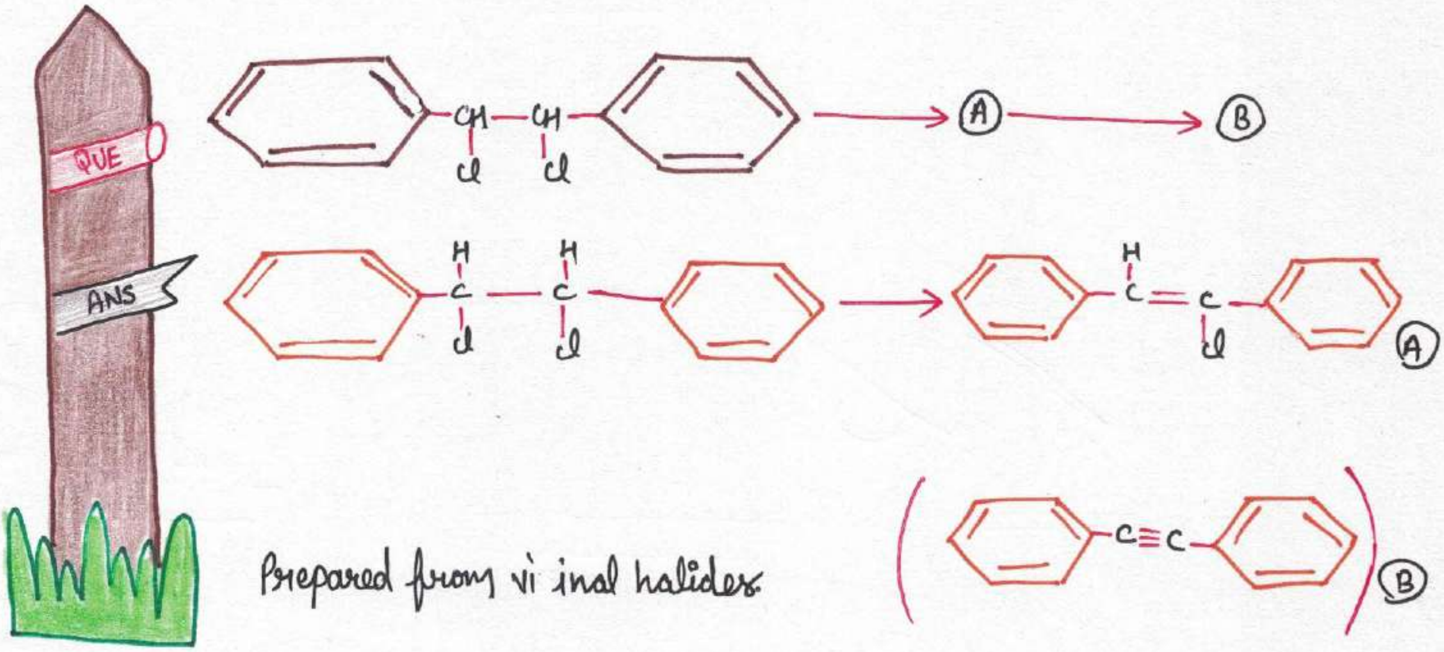
QUE



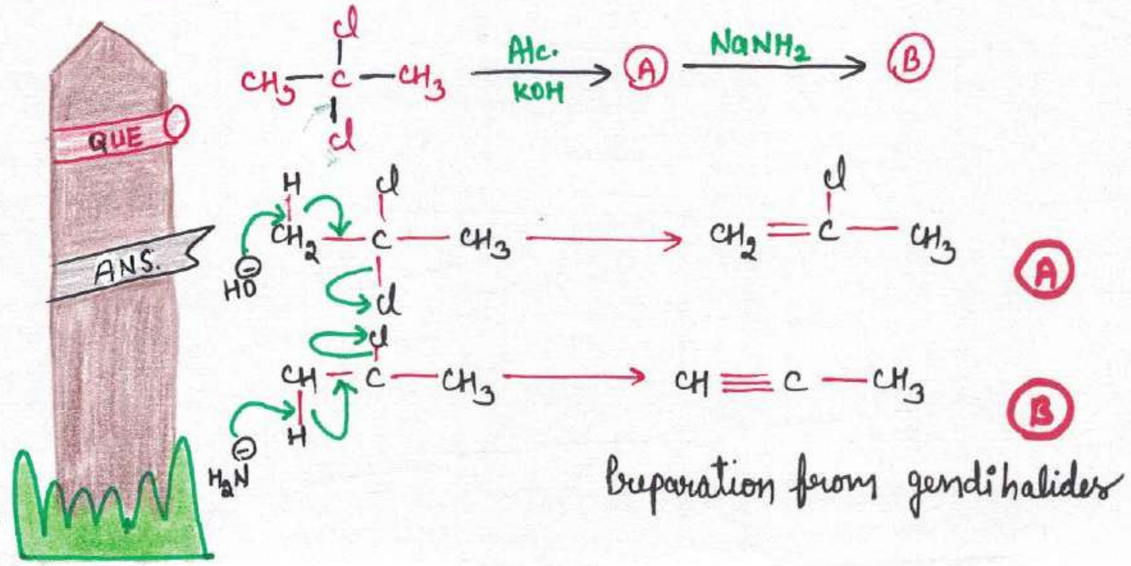


ALKYNES

- i. Dehydrohalogenation will occur.
- ii. The alkynes can be prepared by using both the vicinal halides or gemdihalides.
- iii. $NaNH_2$ is a better base than alc. KOH.
- iv. Always remember that non terminal alkyne is more stable as it's less reactive.



Prepared from vi inal halides



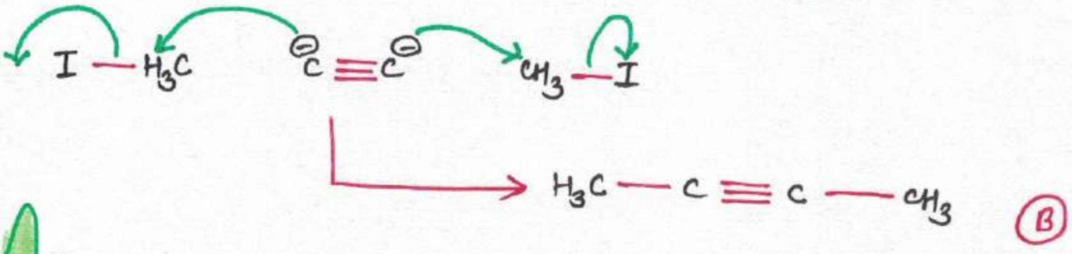
Preparation from gendihalides

Terminal alkynes forms a salt with $NaNH_2$.

E.g. $CH_3-C\equiv CH \longrightarrow CH_3-C\equiv C^{\ominus}Na^{\oplus} + NH_3$

$CH\equiv CH \longrightarrow$ Ⓐ $\longrightarrow$ Ⓑ

$CH\equiv CH \longrightarrow Na^{\oplus}\,{}^{\ominus}C\equiv C^{\ominus}\,Na^{\oplus}$ Ⓐ

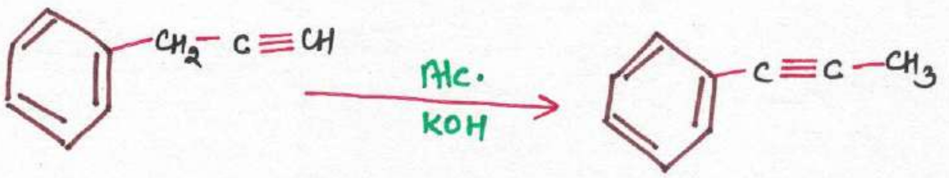


Thus, terminal can be converted to a non-terminal by using this method.

BOILING WITH alc. KOH

1. $CH_3-CH_2-C\equiv CH \xrightarrow[KOH]{Alc.} CH_3-C\equiv C-CH_3$

2.



It is used for the conversion of the less stable "terminal" alkynes to "non-terminal" alkynes.

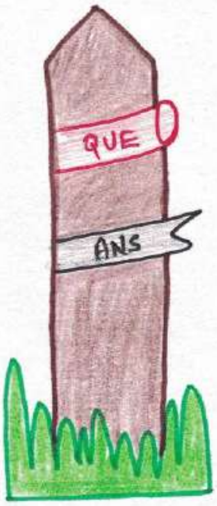
WITH NaNH₂/PARAFFIN

1. $CH_3-C\equiv C-CH_3 \xrightarrow[Paraffin]{NaNH_2} CH_3-CH_2-C\equiv CH$

Paraffin is a non-polar solvent.

It is used for the conversion of the more stable 'non terminal' alkynes to the less stable 'terminal' alkynes.

Hydrohalogenation
Halogenation of Alkyne

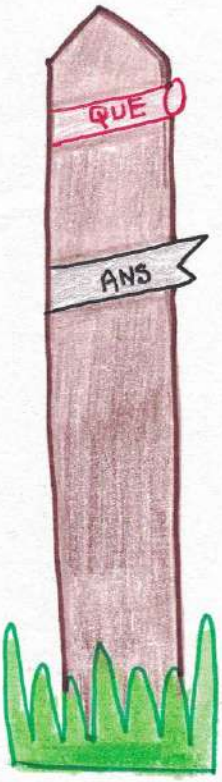


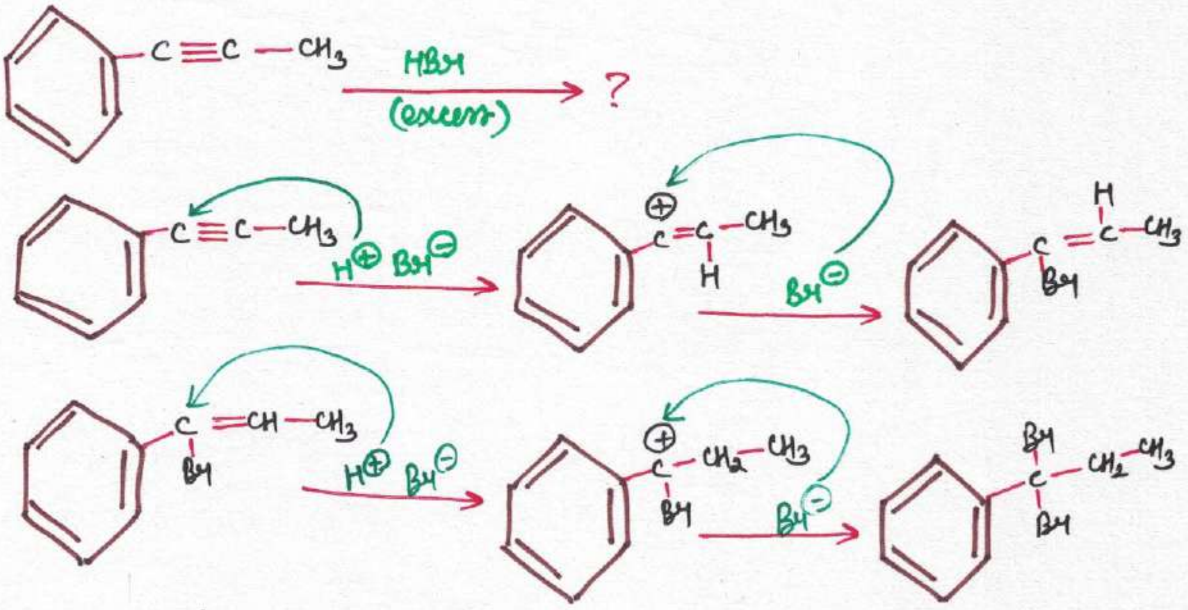
$CH \equiv CH \longrightarrow ?$

$CH \equiv CH \xrightarrow{H^{\oplus}\ Cl^{\ominus}} CH_2 = \overset{\oplus}{CH} \xrightarrow{Cl^{\ominus}} Cl^{\ominus}$ $(CH_2 = CH - Cl)$

$CH_2 = CH - Cl \xrightarrow{H^{\oplus} Cl^{\ominus}} CH_3 - \overset{\oplus}{CH} - Cl \xrightarrow{Cl^{\ominus}} CH_3 - \underset{\underset{Cl}{|}}{CH} - Cl$

Gemdihalide formation



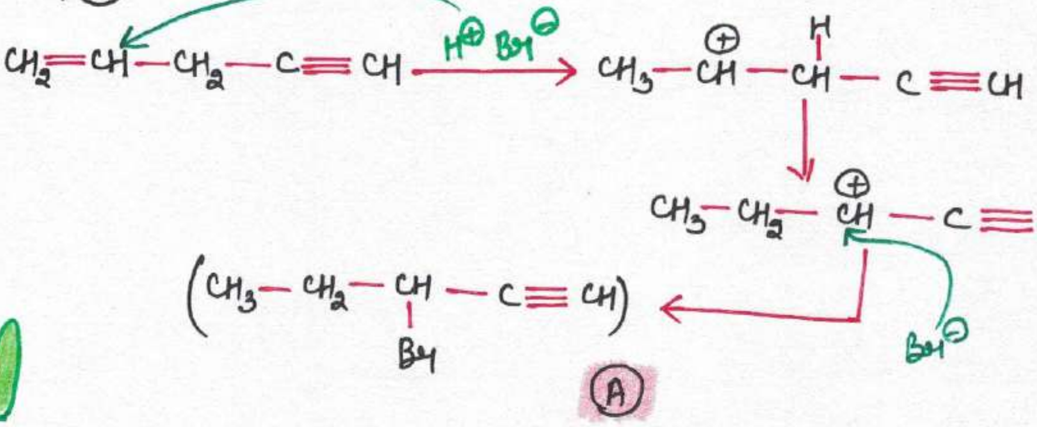


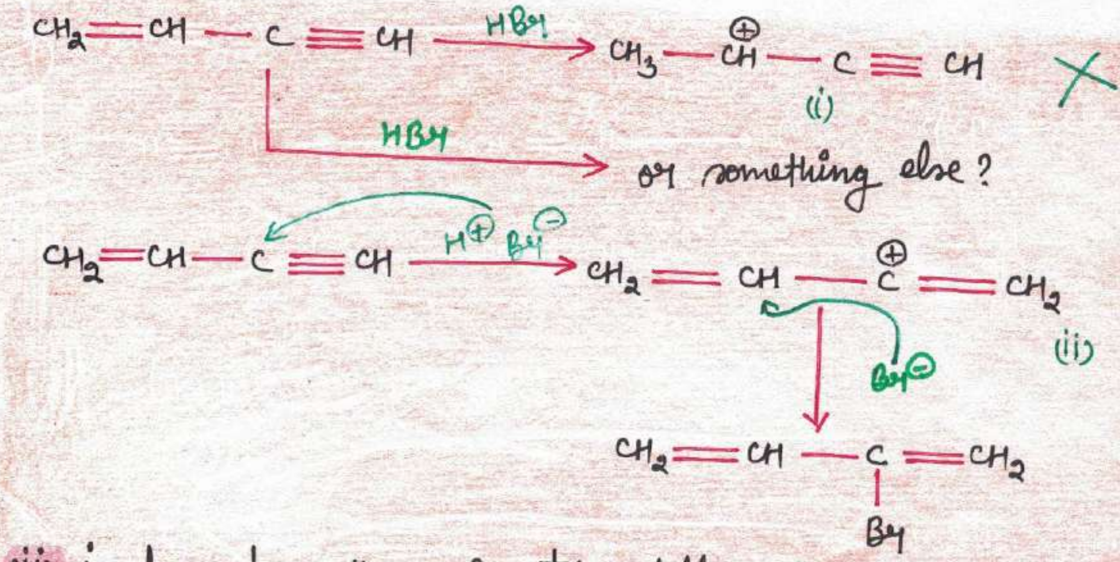
Gemdihalides prepared

$CH_2=CH-CH_2-C\equiv CH \longrightarrow$ Ⓐ

$CH_2=CH-C\equiv CH \longrightarrow$ Ⓑ

For Ⓐ

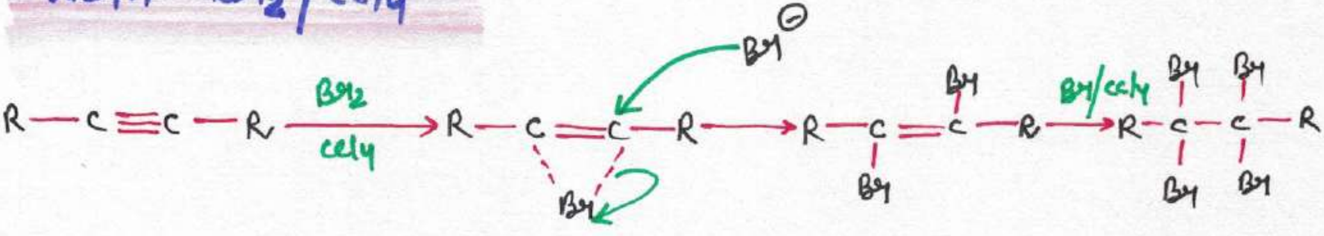




(ii) is formed as the conjugation still remains intact whereas in (i) the conjugation isn't intact.

- Double and triple bond not in conjugation, double bond's attacked.
  Double and triple bond are in conjugation, triple bond's attacked.

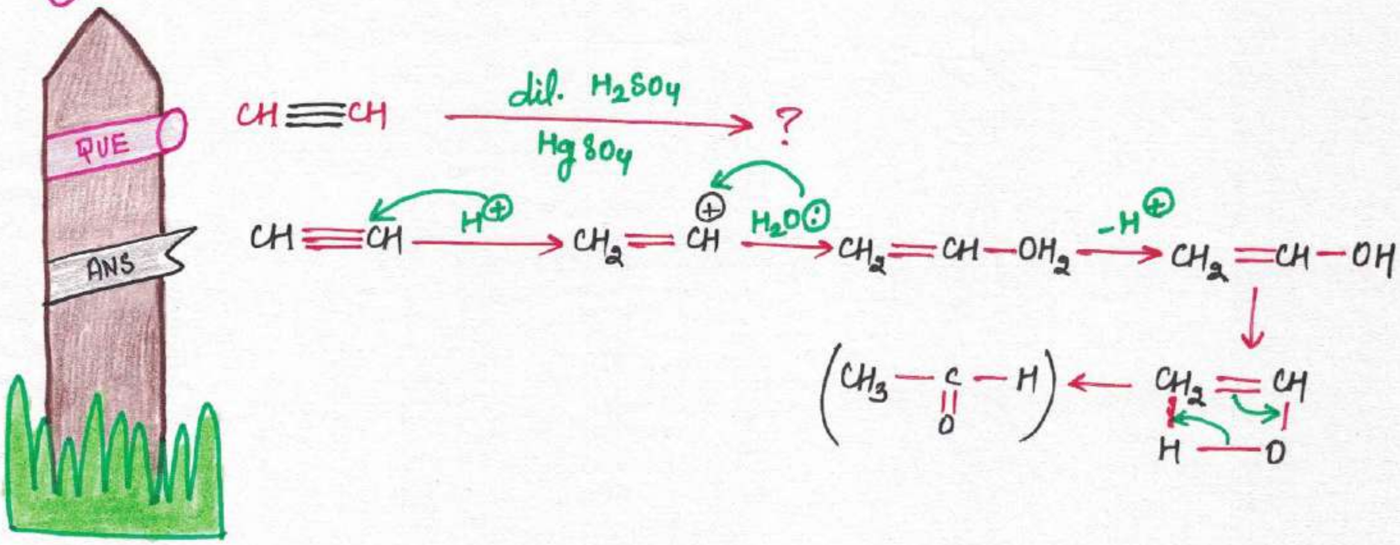
WITH Br_2/CCl_4

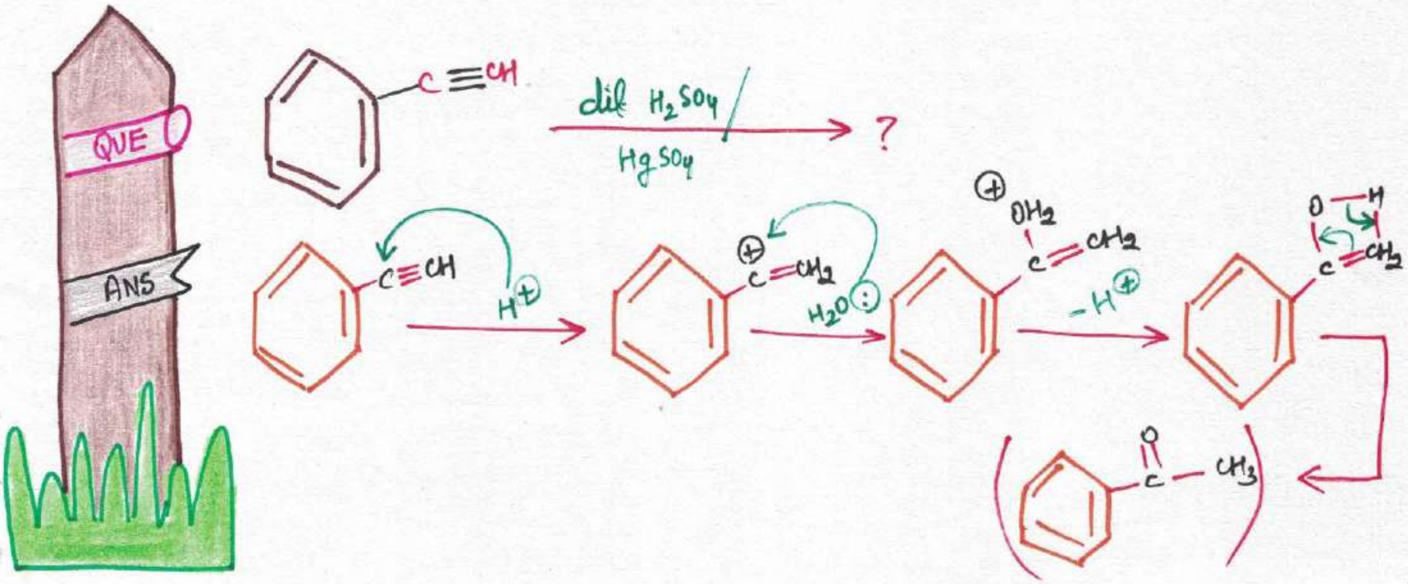


Hydration, Hydroboration of alkynes

Hydration of alkynes

we use (dil. H_2SO_4/$HgSO_4$) for hydration.

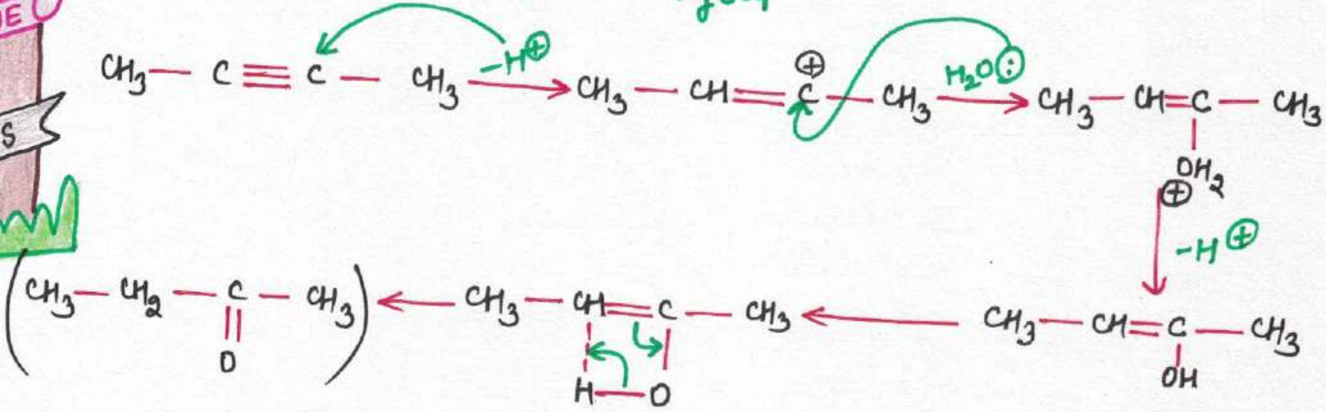




QUE

$CH_3-C\equiv C-CH_3 \xrightarrow[HgSO_4]{dil.\ H_2SO_4} ?$

ANS



$$CH_3-C\equiv C-CH_3 \xrightarrow{-H^{\oplus}} CH_3-CH=\overset{\oplus}{C}-CH_3 \xrightarrow{H_2\ddot{O}} CH_3-CH=\underset{\overset{\oplus}{O}H_2}{\underset{|}{C}}-CH_3$$

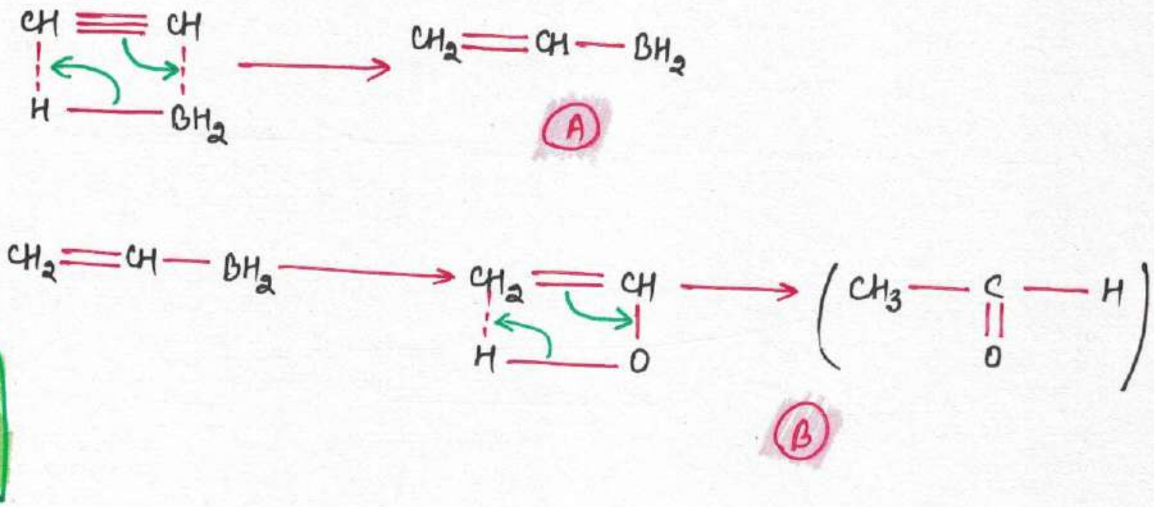
$$\xrightarrow{-H^{\oplus}} CH_3-CH=\underset{OH}{\underset{|}{C}}-CH_3 \longrightarrow CH_3-CH=C-CH_3 \longrightarrow \left(CH_3-CH_2-\underset{O}{\underset{\|}{C}}-CH_3\right)$$

HYDROBORATION AND OXIDATION

QUE

$CH\equiv CH \xrightarrow{B_2H_6} Ⓐ \xrightarrow{NaOH/H_2O_2} Ⓑ$

ANS



$$CH\equiv CH \longrightarrow CH_2=CH-BH_2 \quad Ⓐ$$

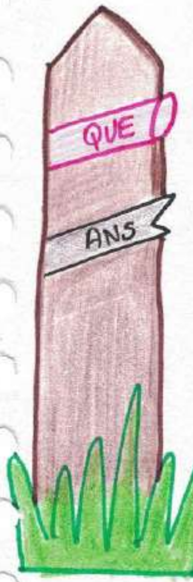
$$CH_2=CH-BH_2 \longrightarrow CH_2=CH \longrightarrow \left(CH_3-\underset{O}{\underset{\|}{C}}-H\right) \quad Ⓑ$$

QUE

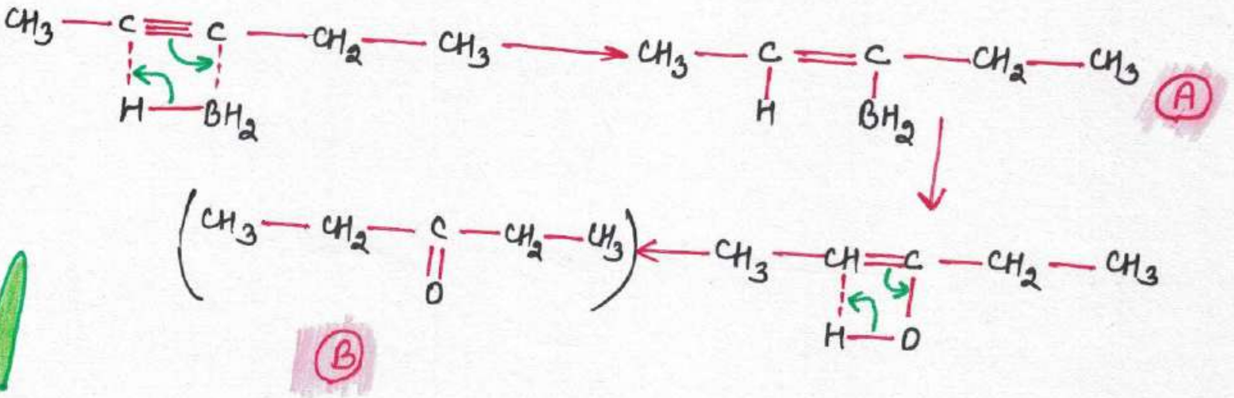
$\xrightarrow[KOH]{Alc.} Ⓐ \xrightarrow{NaNH_2} Ⓑ$

ANS

$\xrightarrow{HO^{\ominus}}$



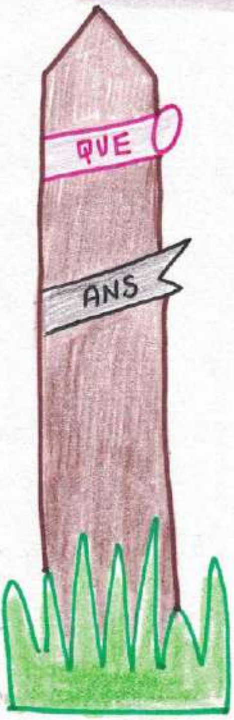
$CH_3-C\equiv C-CH_2-CH_3 \xrightarrow{B_2H_6}$ Ⓐ $\xrightarrow[H_2O_2]{NaOH}$ Ⓑ

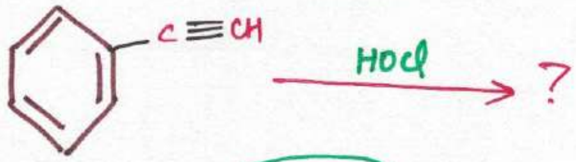


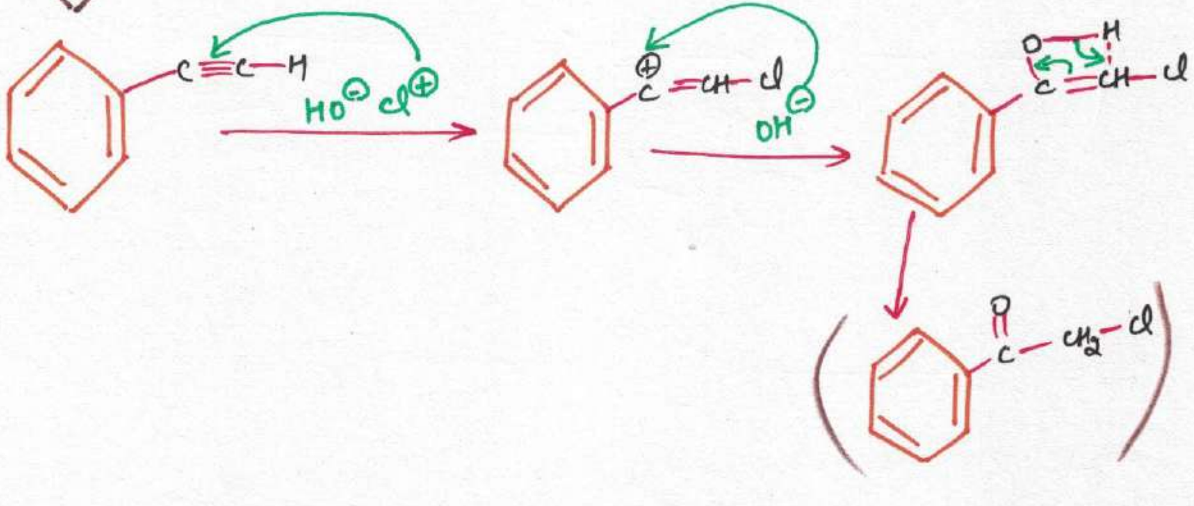
POLYMERISATION REACTIONS

REACTION WITH HOCL

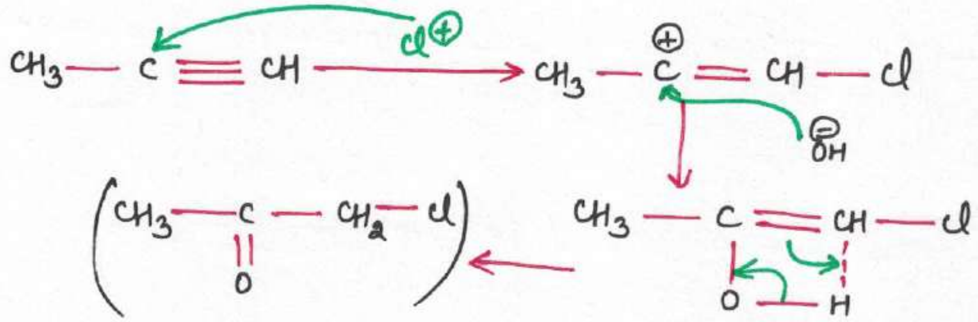
REACTION WITH HOCL







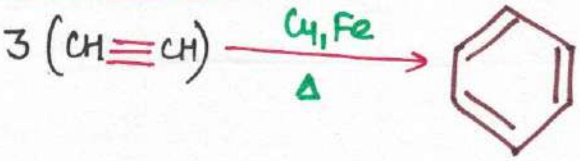
$CH_3-C\equiv CH \xrightarrow{HOCl} ?$



In many places, the answers are given in form of dichlorides; which is completely wrong.

POLYMERISATION REACTIONS

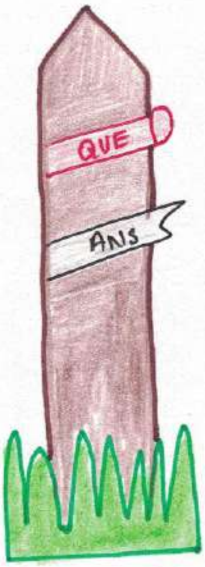
(a) TRIMERISATION



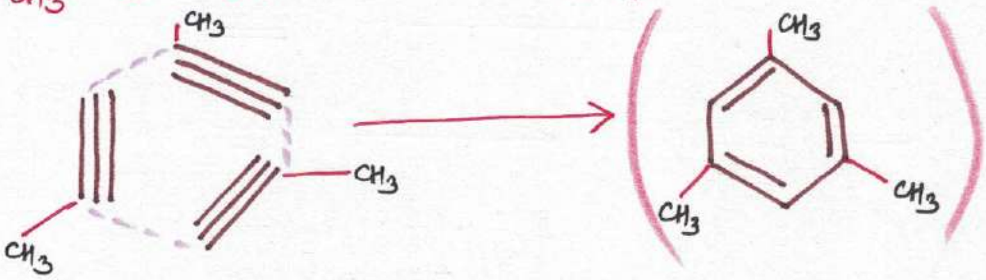
MECHANISM

Thus, it is a cyclic mechanism and benzene can be prepared by this mechanism.

(Cu, Fe/Δ) is also written as 'hot Cu/Fe tube'.



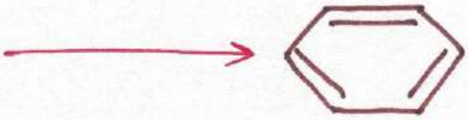
$CH_3-C\equiv OH \xrightarrow{Cu,\ \Delta} ?$



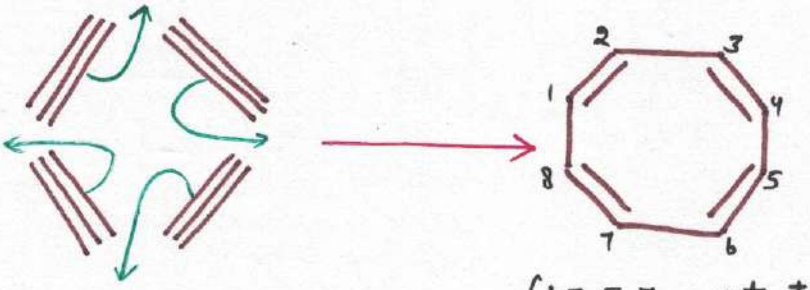
(Thus, mesitylene can also be formed by using this reaction.)

TETRAMERISATION

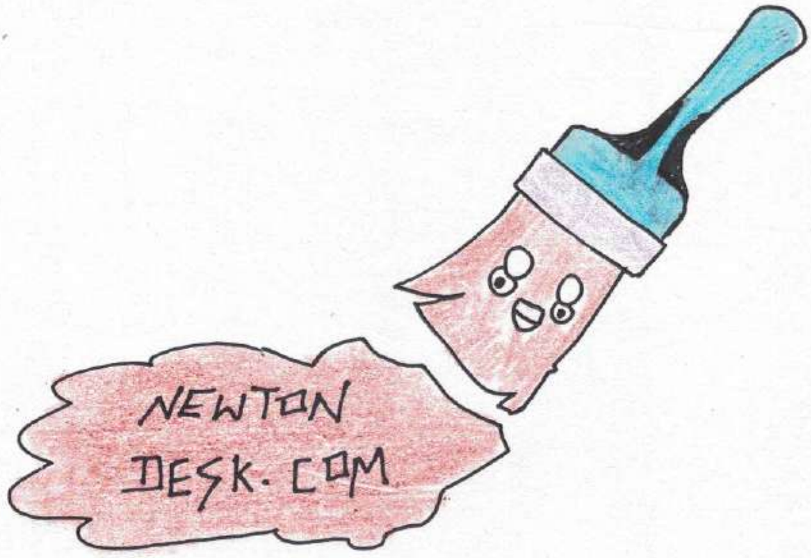
$4(CH\equiv CH) \longrightarrow$



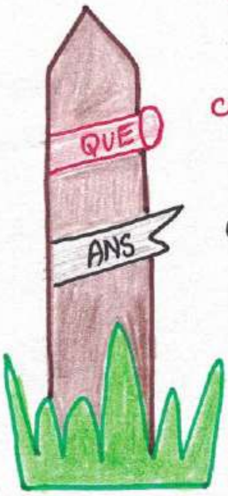
MECHANISM



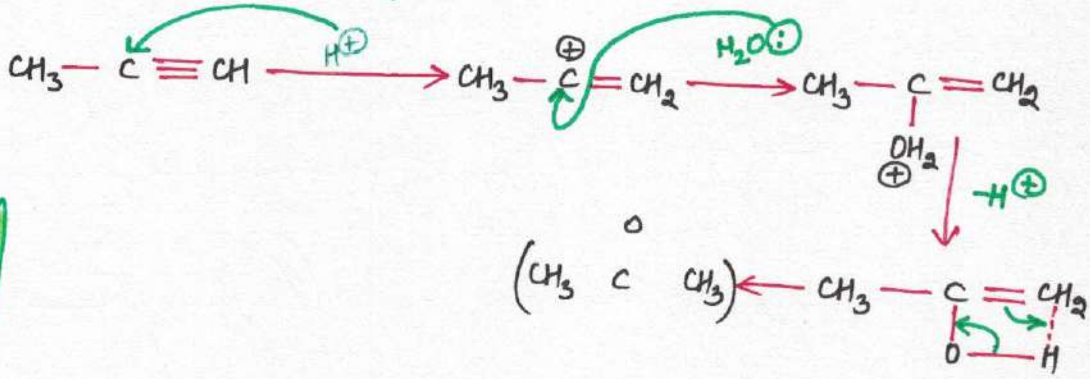
(1,3,5,7 - octa tetraene)

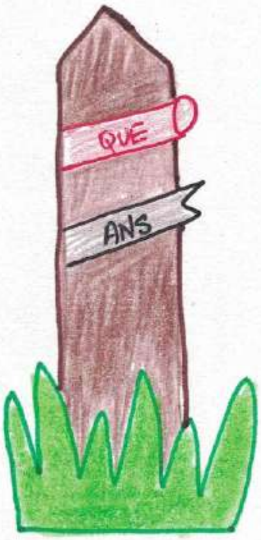


IMPORTANT QUESTION

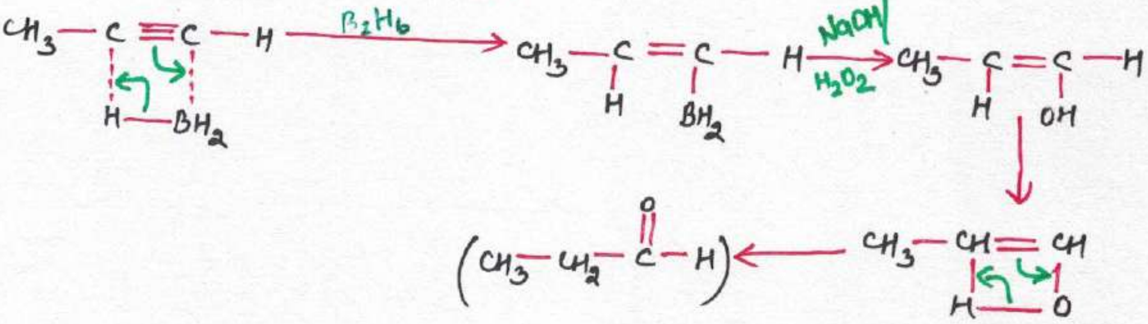


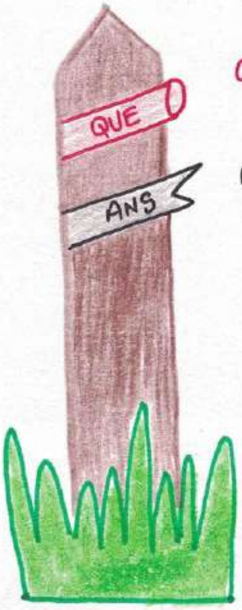
$CH_3-C\equiv CH \xrightarrow[HgSO_4]{dil\ H_2SO_4} (A)$



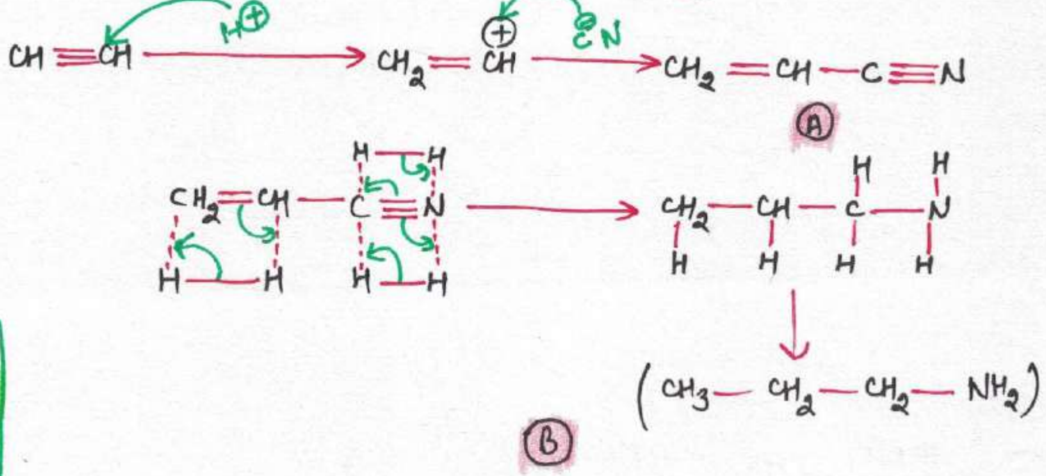


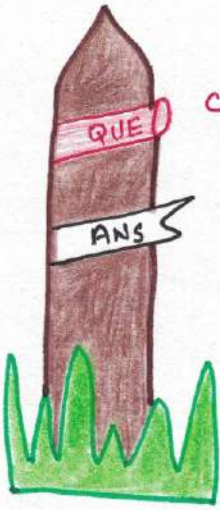
$CH_3-C\equiv CH \xrightarrow[(ii)\ H_2O_2,\ NaOH]{(i)\ B_2H_6} ?$



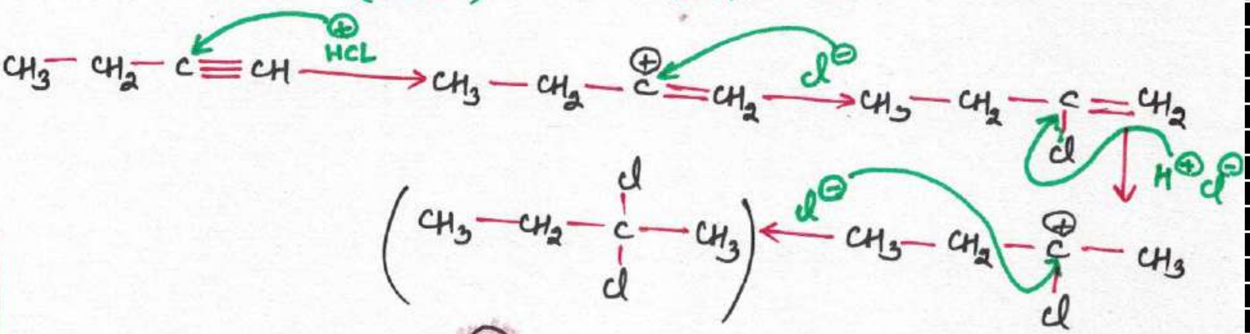


$CH\equiv CH \xrightarrow{HCN} (A) \xrightarrow[excess]{H_2/Pd-C} (B)$



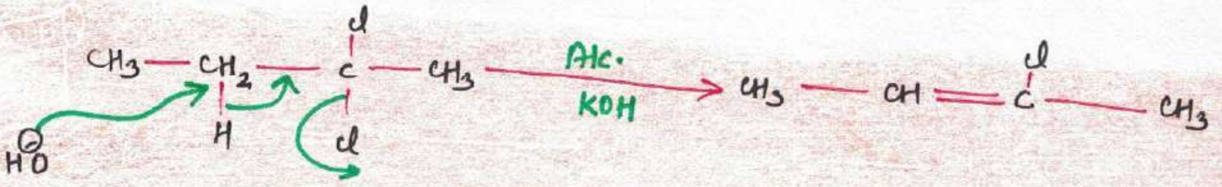


$CH_3-CH_2-C\equiv CH \xrightarrow[\text{(excess)}]{HCl} (A) \xrightarrow[KOH]{Alc.} (B) \xrightarrow{NaNH_2} (C)$



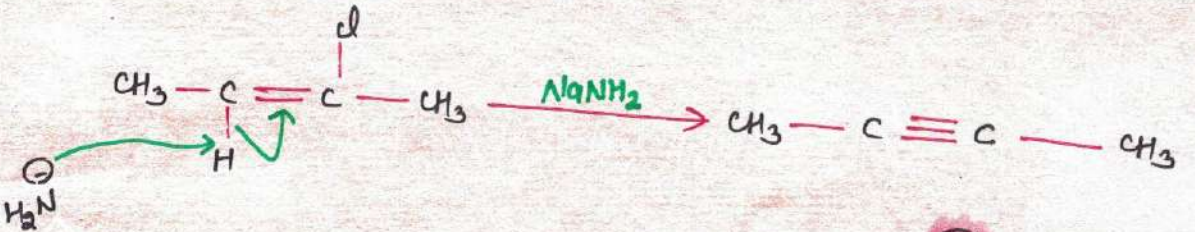
$CH_3-CH_2-C\equiv CH \xrightarrow{H^{\oplus}Cl} CH_3-CH_2-\overset{\oplus}{C}=CH_2 \xrightarrow{Cl^{\ominus}} CH_3-CH_2-\underset{Cl}{C}=CH_2 \xrightarrow{H^{\oplus}Cl^{\ominus}} CH_3-CH_2-\underset{Cl}{\overset{\oplus}{C}}-CH_3 \xrightarrow{Cl^{\ominus}} \left(CH_3-CH_2-\underset{Cl}{\overset{Cl}{C}}-CH_3\right)$

Ⓐ



$CH_3-\underset{H}{CH_2}-\underset{Cl}{\overset{Cl}{C}}-CH_3 \xrightarrow[KOH]{Alc.} CH_3-CH=\overset{Cl}{C}-CH_3$ (with $\overset{\ominus}{HO}$)

Ⓑ



$CH_3-\underset{H}{C}=\overset{Cl}{C}-CH_3 \xrightarrow{NaNH_2} CH_3-C\equiv C-CH_3$ (with $H_2\overset{\ominus}{N}$)

Ⓒ

(we've converted a terminal alkyne to a non-terminal alkyne by using this reactions)

$CH_3-CH_2-C\equiv CH \underset{B}{\overset{A}{\rightleftharpoons}} CH_3-C\equiv C-CH_3$

Ⓐ = Alc. KOH

Ⓑ = $NaNH_2$

ALKADIENES

Basics of Dienes, some reaction

Dienes are of three types :-

conjugated diene Alternate double bonds.

E.g. $(CH_2=CH-CH=CH_2)$

Isolated diene Separated by a sp^3 carbon.

E.g. $CH_2=CH-\underset{\underset{sp^3}{\uparrow}}{CH_2}-CH=CH_2$

cumulated diene Adjacent double bonds.

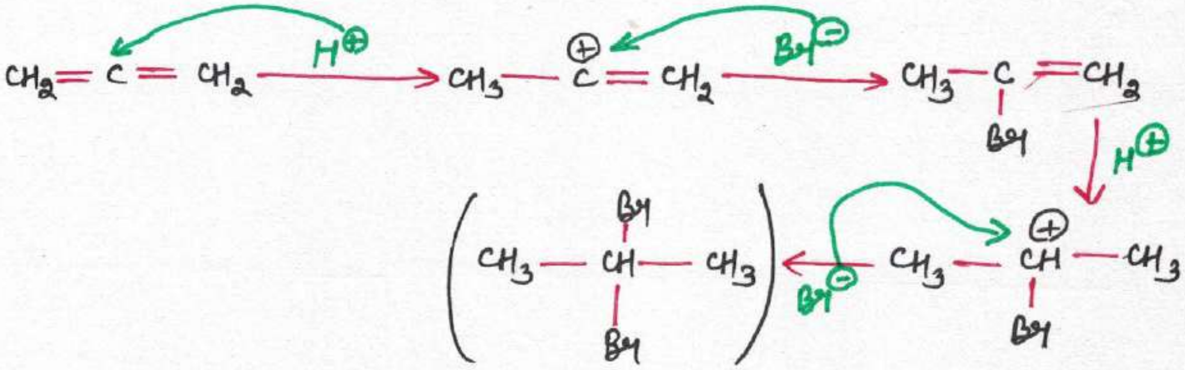
E.g. $CH_2=C=CH_2$

This are unstable.

Q

$$CH_2=C=CH_2 \xrightarrow[\text{(excess)}]{HBr} ?$$

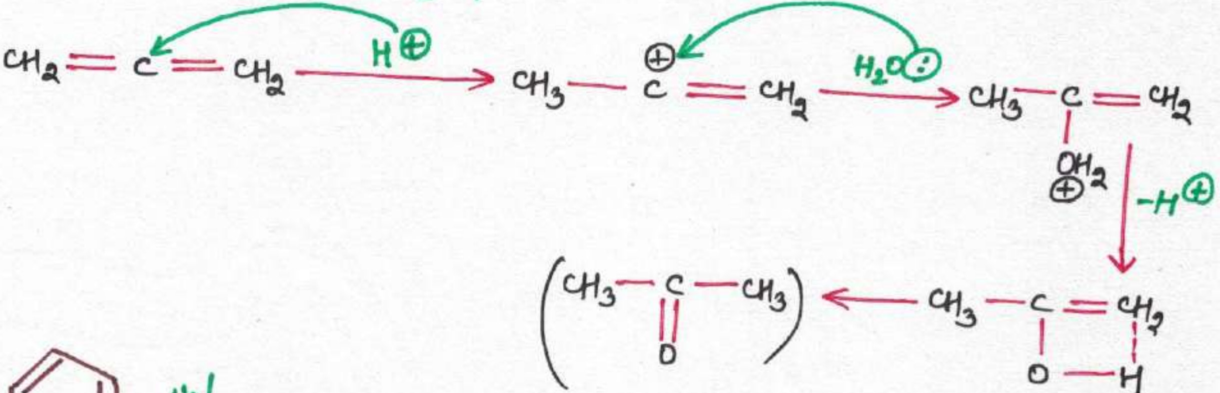
A



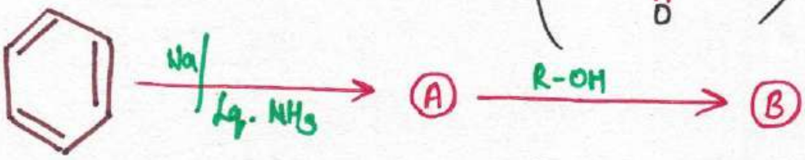
Q

$$CH_2 \quad C \quad CH_2 \xrightarrow[H_2SO_4]{\text{dil.}} ?$$

A

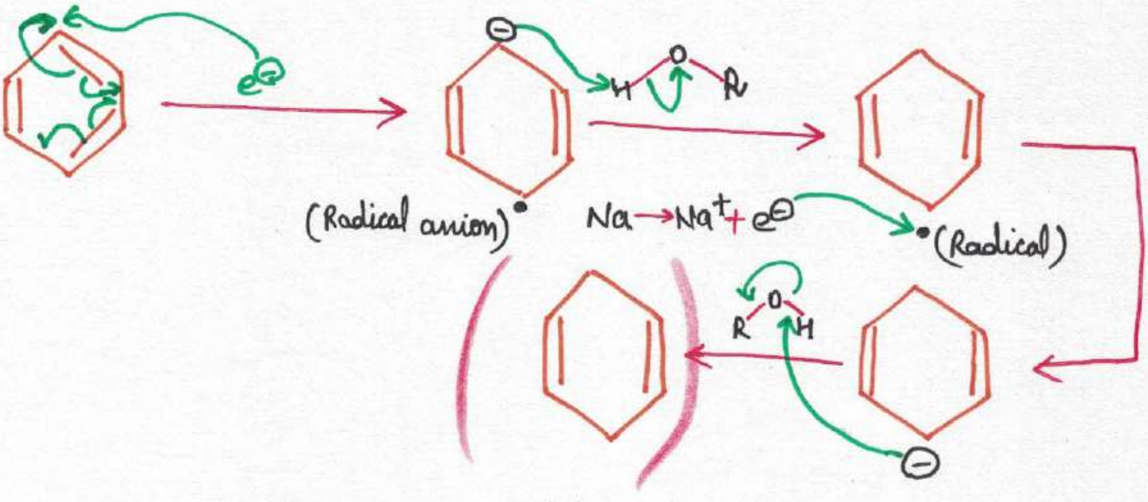


Q



A

$Na \rightarrow Na^{\oplus} + e^{\ominus}$



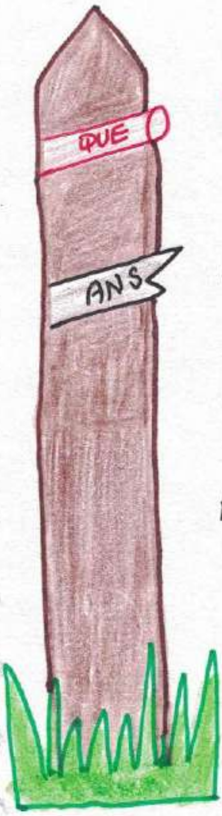
Isolated diene

TYPES OF ADDITION

(a) (1,2) Addition – Kinetically done. Less stable product.
(Lower temp.)

[b] (1,4) addition Thermodynamically done. More stable product. (Higher temp.)

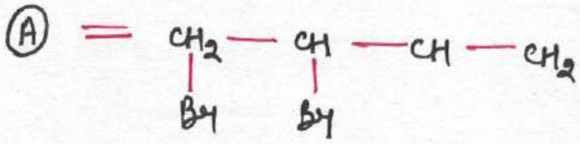
- In (1,2) addition, the (3,4) bond remains.
- In (1,4) addition, the (2,3) bond remains.



$CH_2=CH-CH=CH_2 \xrightarrow[-80^\circ C]{Br_2/CCl_4}$ Ⓐ

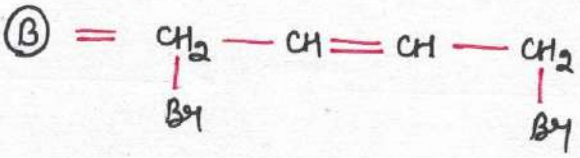
$\xrightarrow[40^\circ C]{Br_2/CCl_4}$ Ⓑ

At lower temp; (1,2) addition occurs

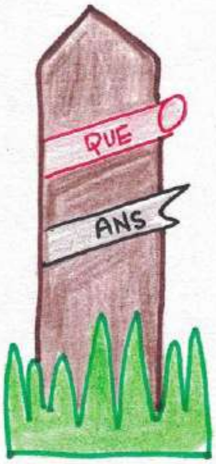


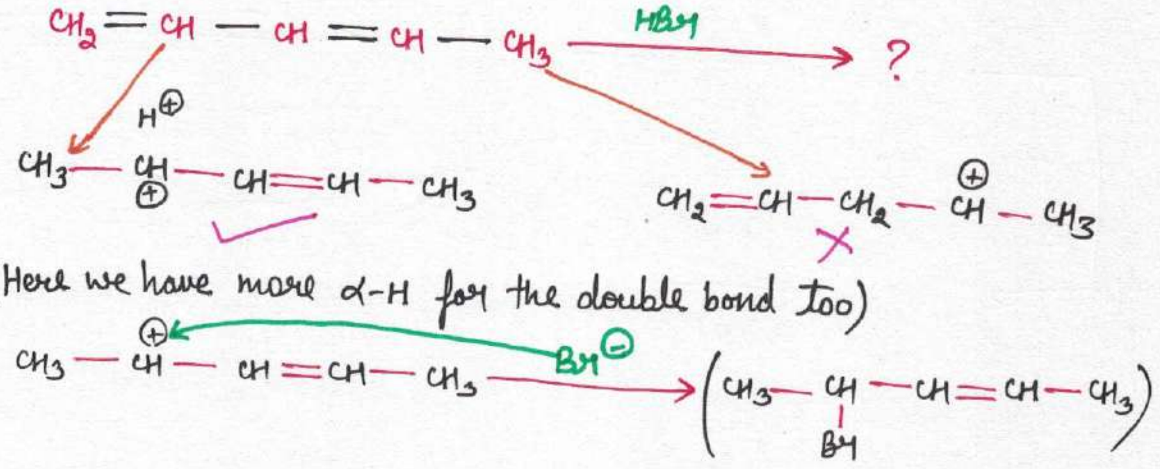
$$Ⓐ = \underset{Br}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{CH}}-CH=CH_2$$

At higher temp; (1,4) addition occurs



$$Ⓑ = \underset{Br}{\underset{|}{CH_2}}-CH=CH-\underset{Br}{\underset{|}{CH_2}}$$





$CH_2=CH-CH=CH-CH_3 \xrightarrow{HBr}$?

$CH_3-\overset{H^\oplus}{\underset{\oplus}{CH}}-CH=CH-CH_3$ ✓ $\qquad CH_2=CH-CH_2-\overset{\oplus}{CH}-CH_3$ ✗

(Here we have more α-H for the double bond too)

$CH_3-\overset{\oplus}{CH}-CH=CH-CH_3 \xrightarrow{Br^\ominus} \left(CH_3-\underset{Br}{\underset{|}{CH}}-CH=CH-CH_3\right)$

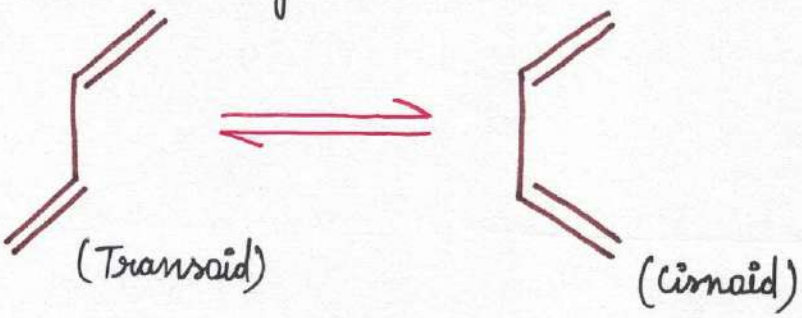
DIELS ALDER REACTION (Part-I)

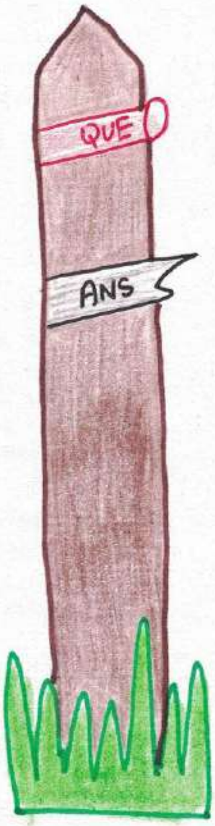
(i) Cyclic addition of dienes with alkenes to obtain a ring is called diel alder-reaction.

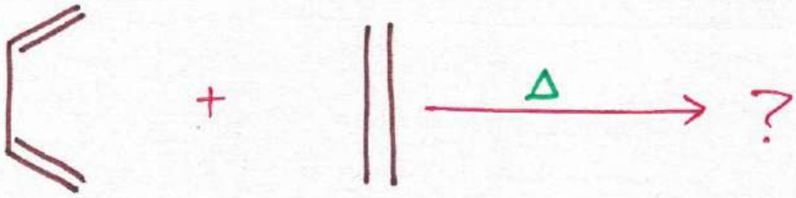
[ii] It is a (4+2) cyclic addition.

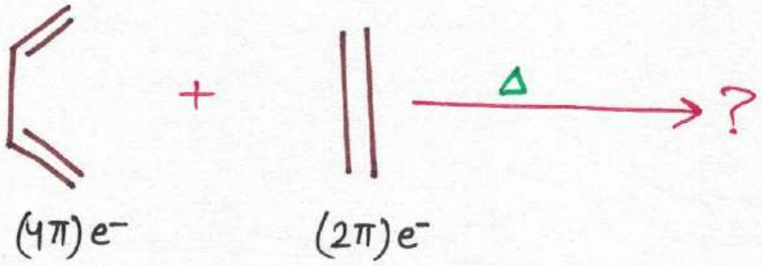
[iii] The 'dienes attracting' species are known as "dienophilic."

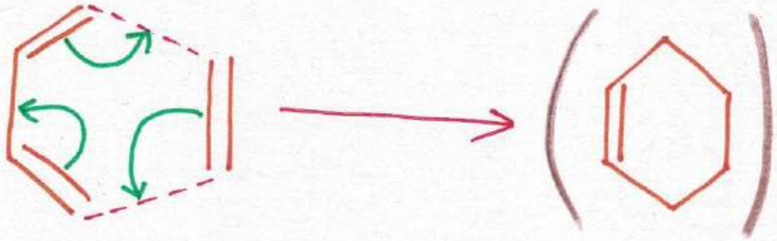
[iv] Only cisnoid undergoes diels alder reaction.

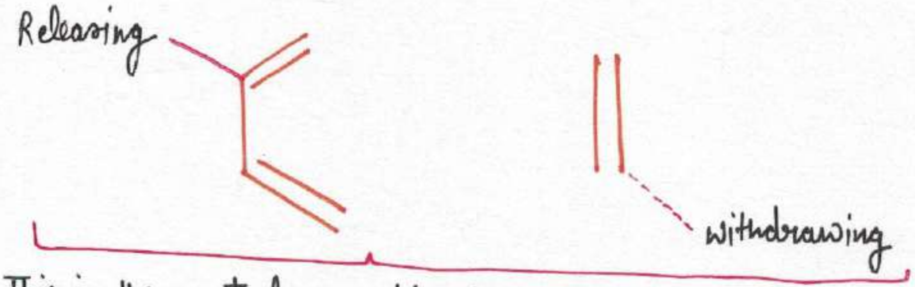








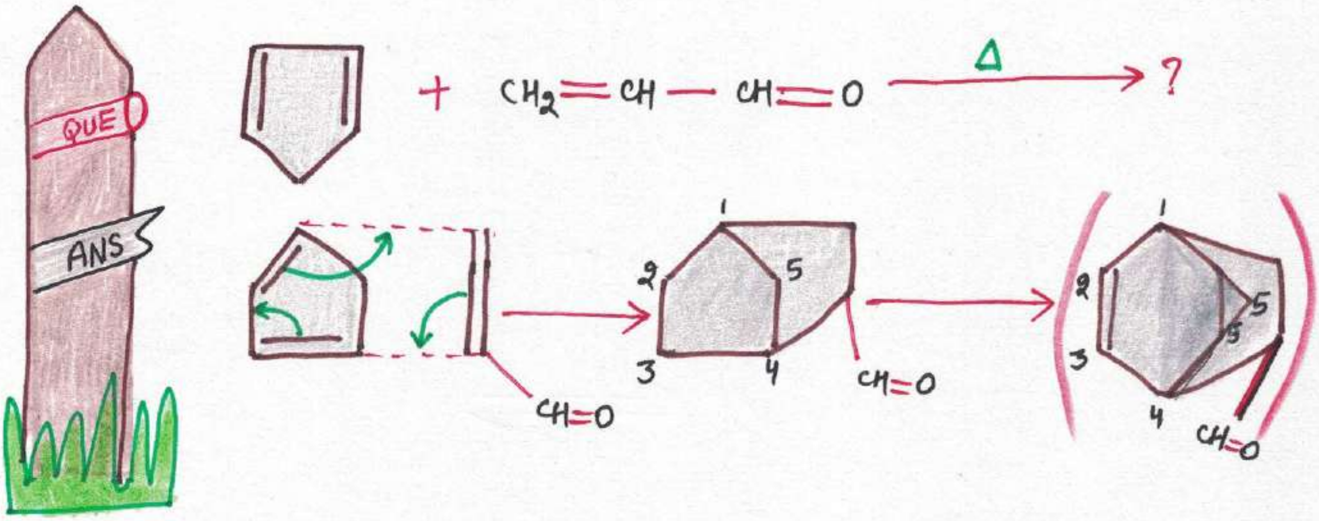


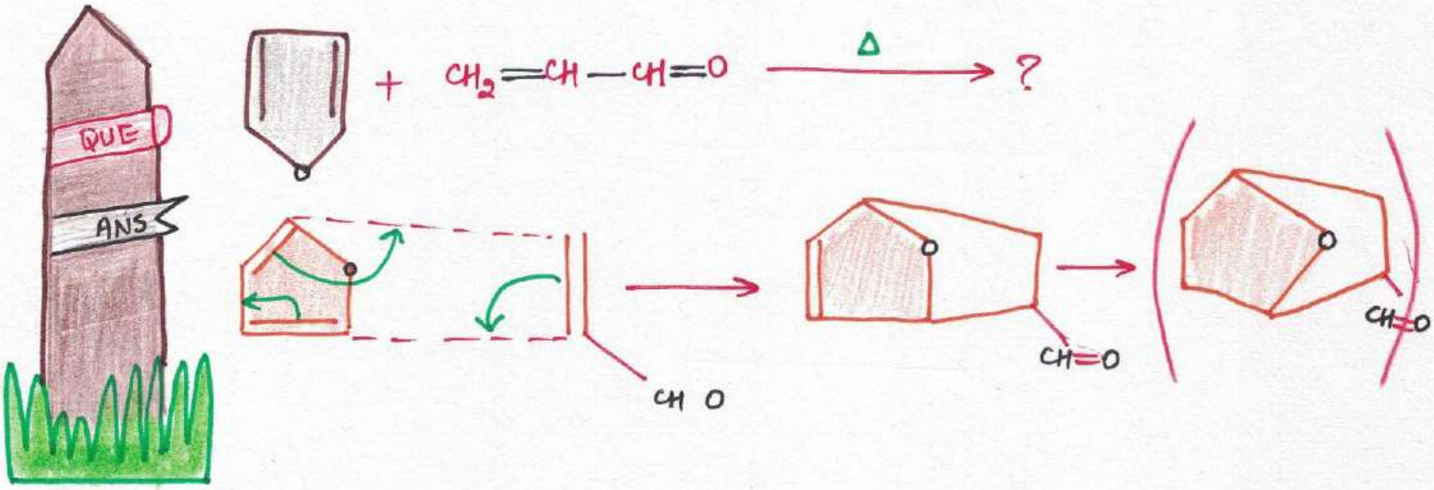


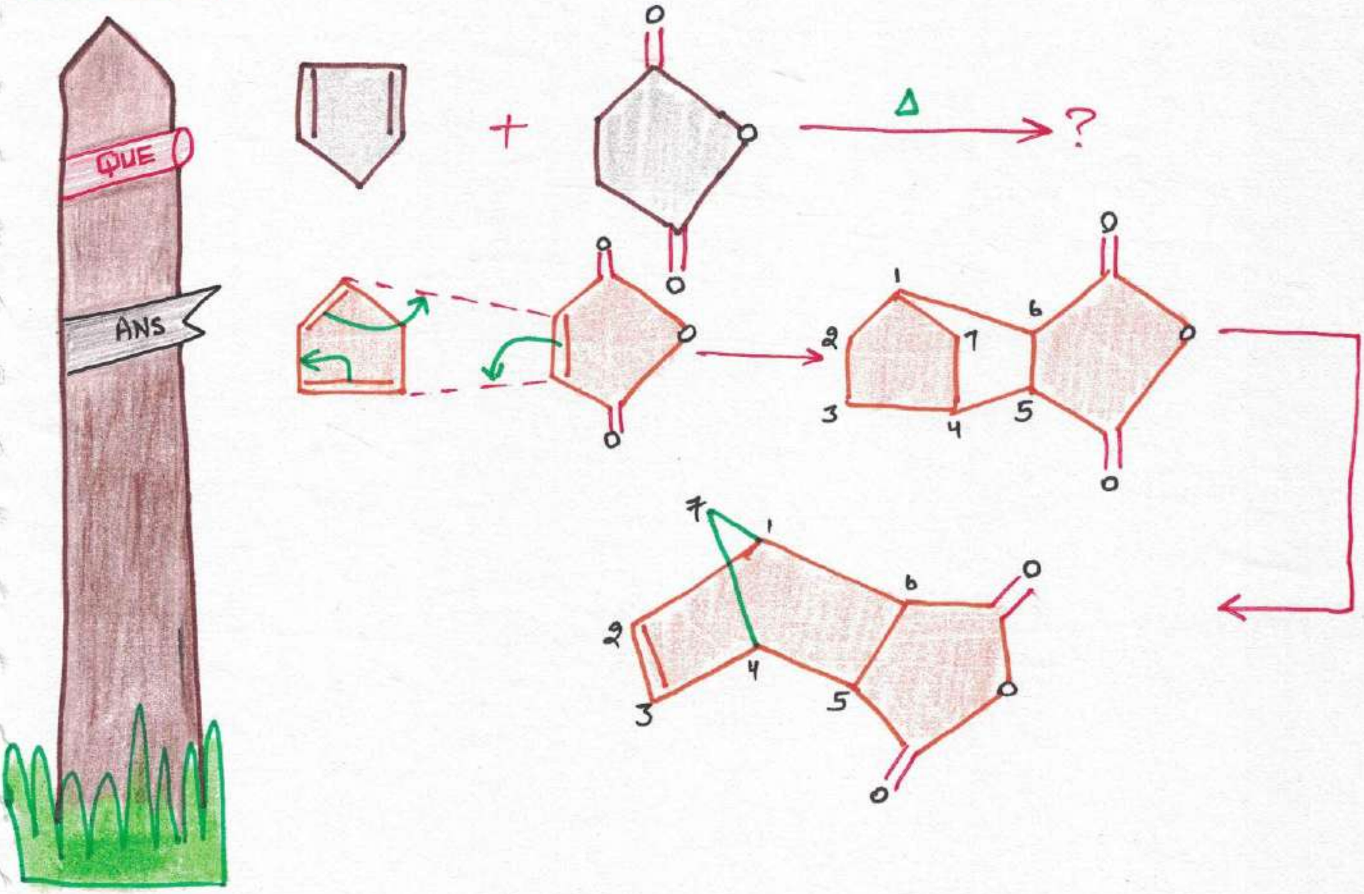
This is the most favourable situation for diels-alder to occurs:-

Releasing group(s) should be on (diene).

withdrawing group(s) should be on (alkene).

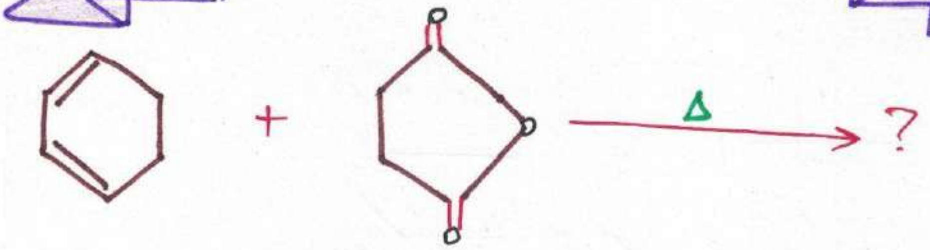

QUE
ANS
+
CH2=CH—CH=O
Δ
?
CH=O
1
2
3
4
5
CH=O
1
2
3
4
5
5
CH=O


QUE
ANS
+
CH2=CH—CH=O
Δ
?
CH O
CH=O
CH=O

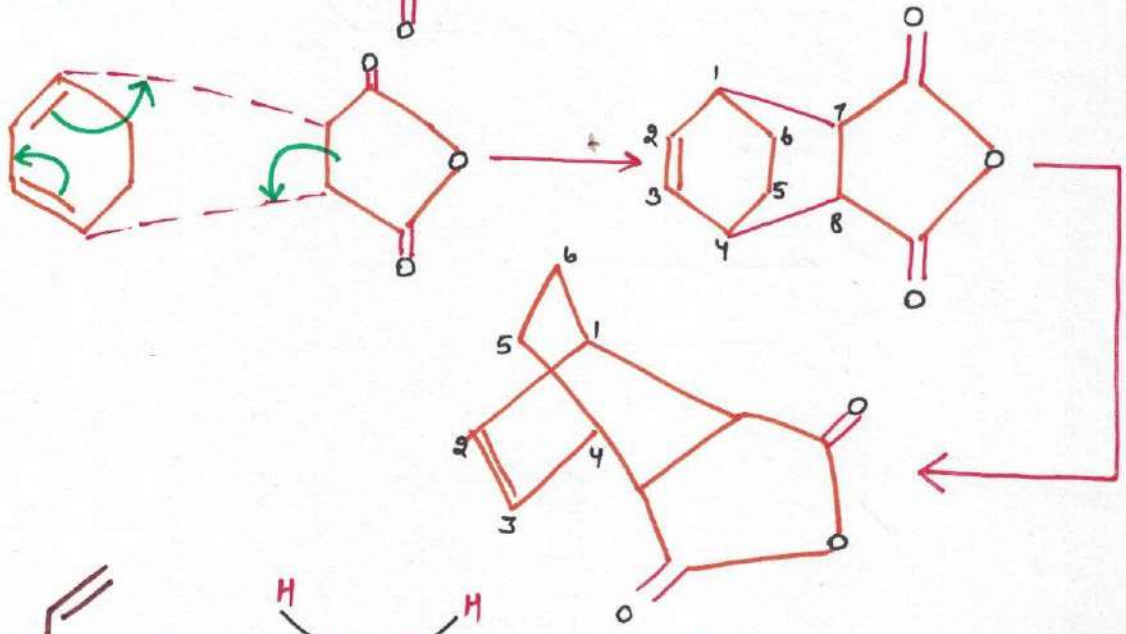

QUE
ANS
+
O
O
O
Δ
?
O
O
O
1
2
3
4
5
6
7
O
O
O
7
1
2
3
4
5
6
O
O
O

DIELS ALDER REACTION (Part-II)

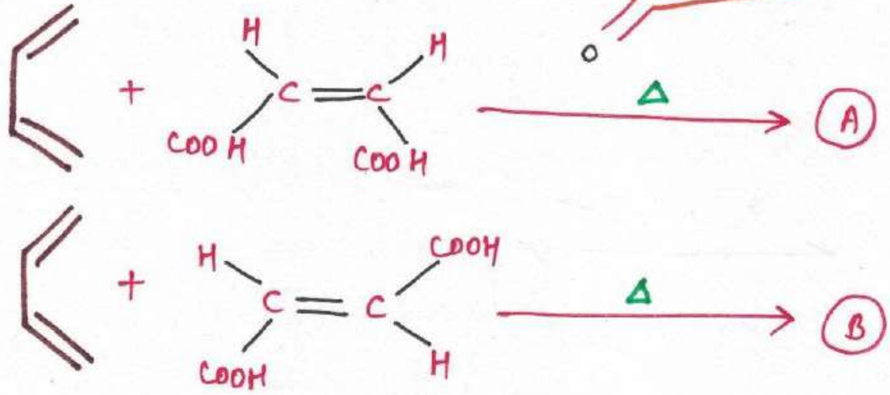
Q.



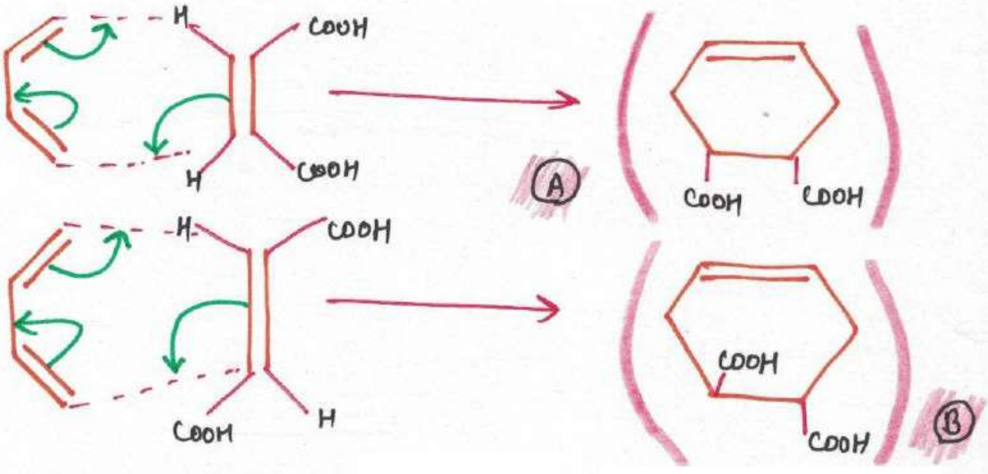
A.



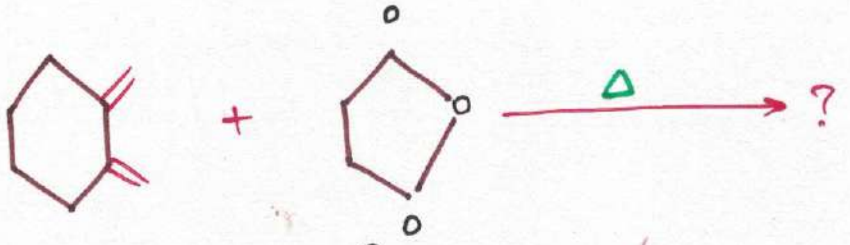
Q.



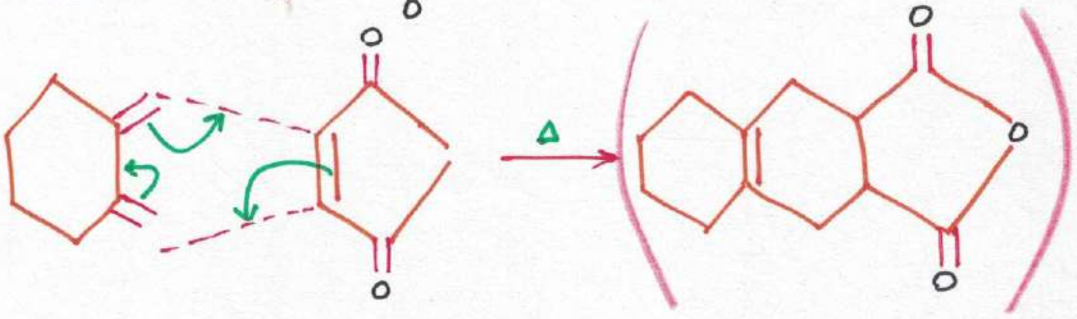
A.



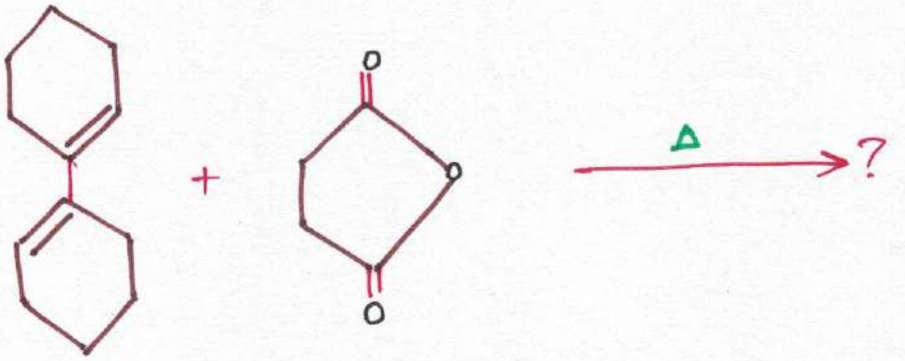
Q.



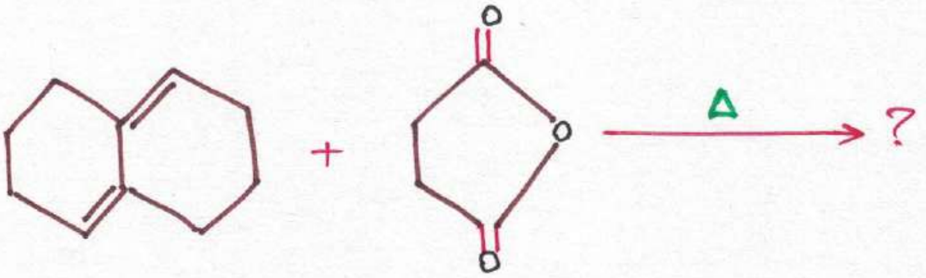
A.



Q.



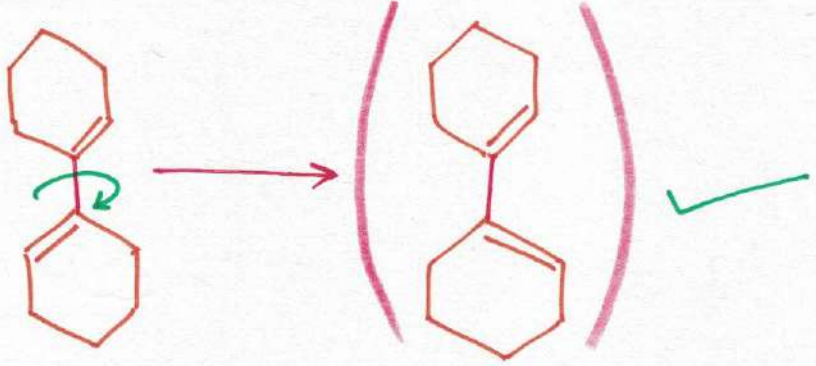
Ⓐ

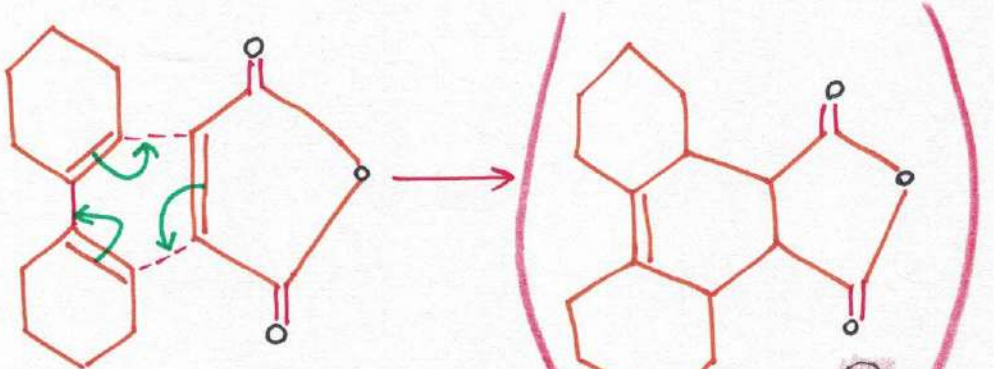


Ⓑ

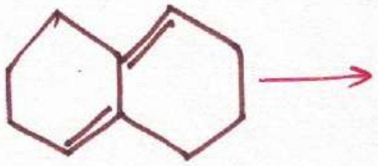
A.

(only cisnoids give diels alder)

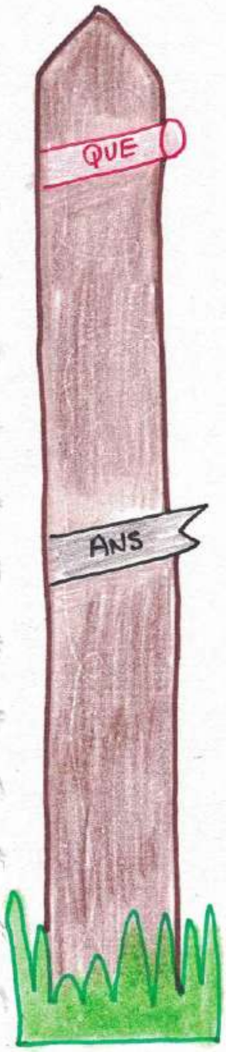


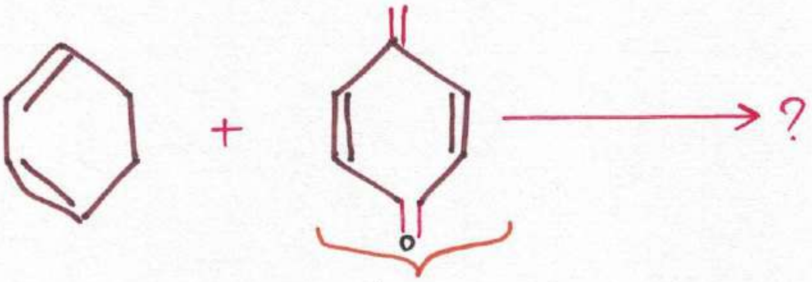


Ⓐ



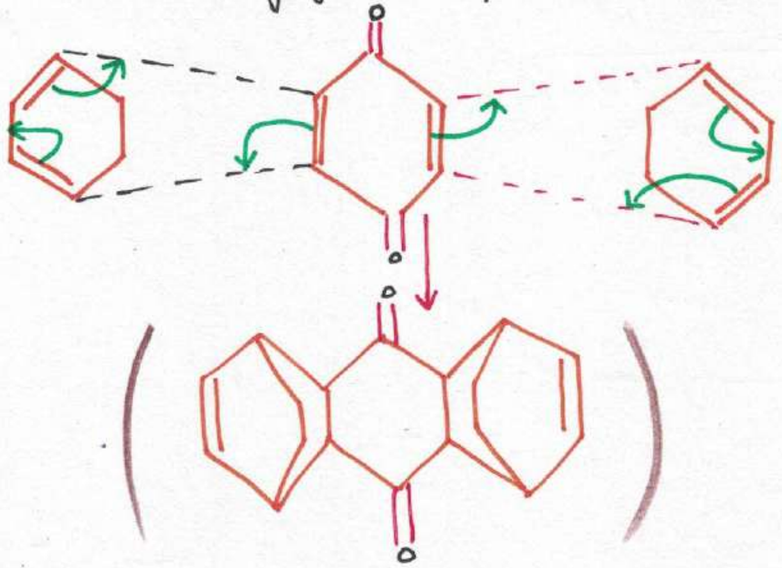
This is a fused ring. Here transoid can't be converted to cisoid.



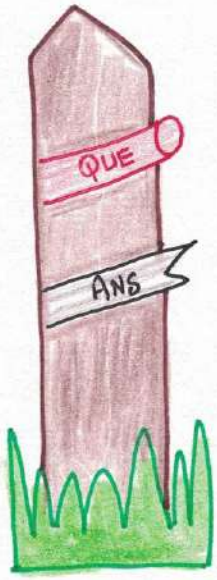


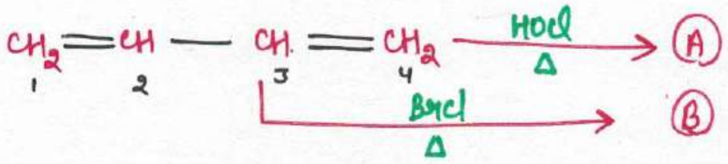
(Quinone)

Quinone is a very good dienophile and can react with multiple



REACTION WITH HOCl, BrCl etc.

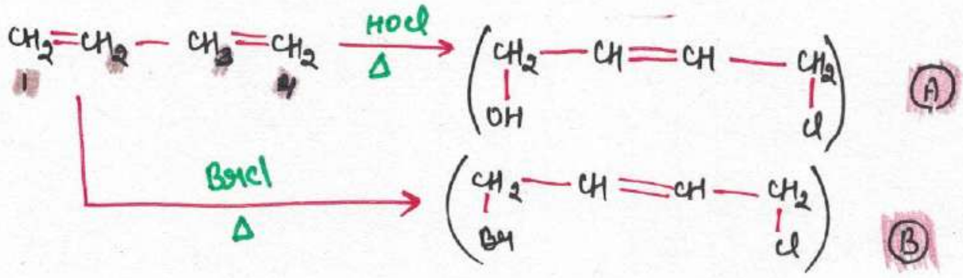




$$\underset{1}{CH_2}{=}\underset{2}{CH} - \underset{3}{CH}{=}\underset{4}{CH_2} \xrightarrow[\Delta]{HOCl} Ⓐ$$

$$\xrightarrow[\Delta]{BrCl} Ⓑ$$

At higher temp. (1,4) addition is more preferred.

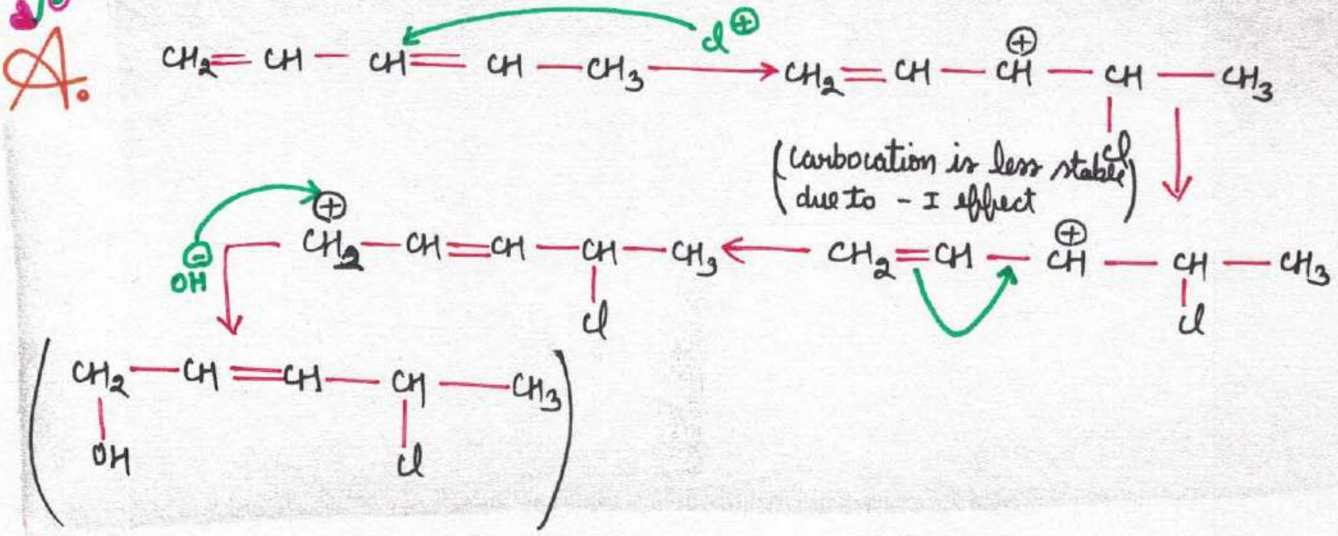


$$\underset{1}{CH_2}{=}\underset{2}{CH_2} - \underset{3}{CH_3}{=}\underset{4}{CH_2} \xrightarrow[\Delta]{HOCl} \left(\underset{OH}{\underset{|}{CH_2}} - CH{=}CH - \underset{Cl}{\underset{|}{CH_2}}\right) Ⓐ$$

$$\xrightarrow[\Delta]{BrCl} \left(\underset{Br}{\underset{|}{CH_2}} - CH{=}CH - \underset{Cl}{\underset{|}{CH_2}}\right) Ⓑ$$

Q. $CH_2=CH-CH=CH-CH_3 \xrightarrow{HOCl} ?$

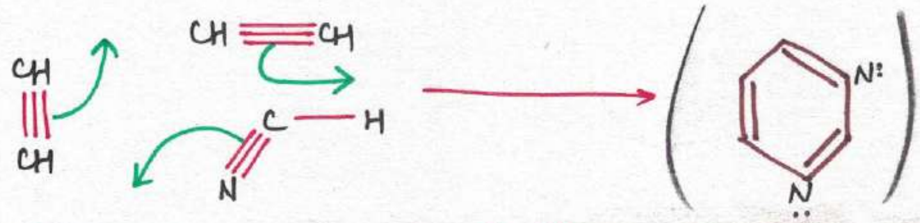
A.



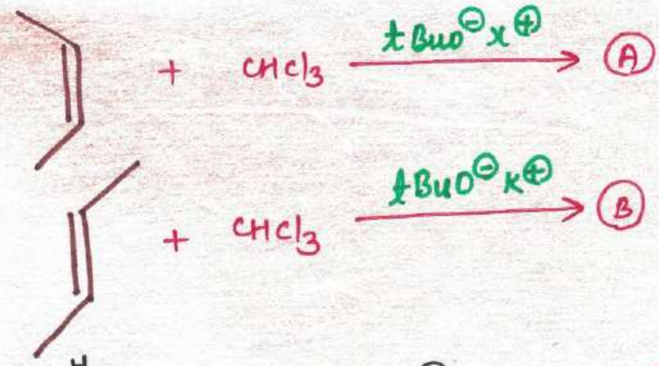
(carbocation is less stable due to - I effect)

Q. $2(CH\equiv CH) \xrightarrow{HCN} ?$

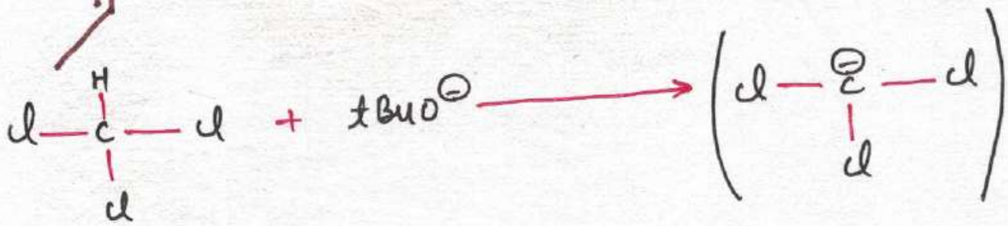
A.



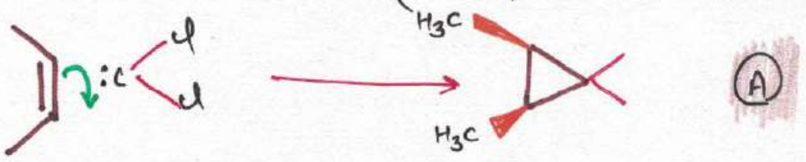
Q.

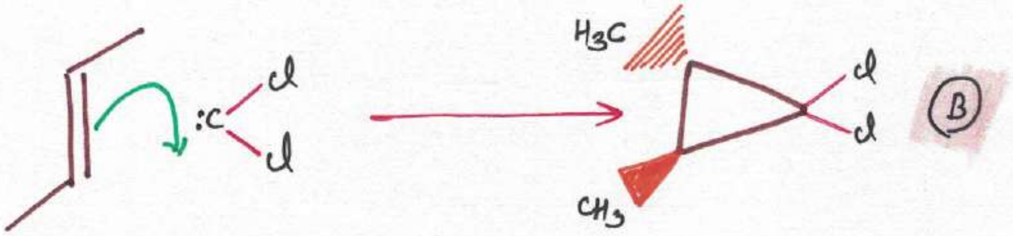


A.

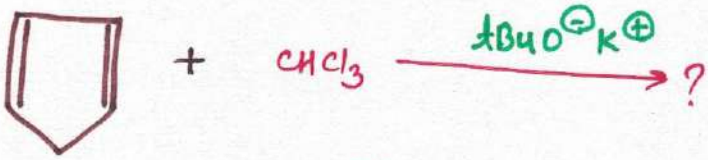


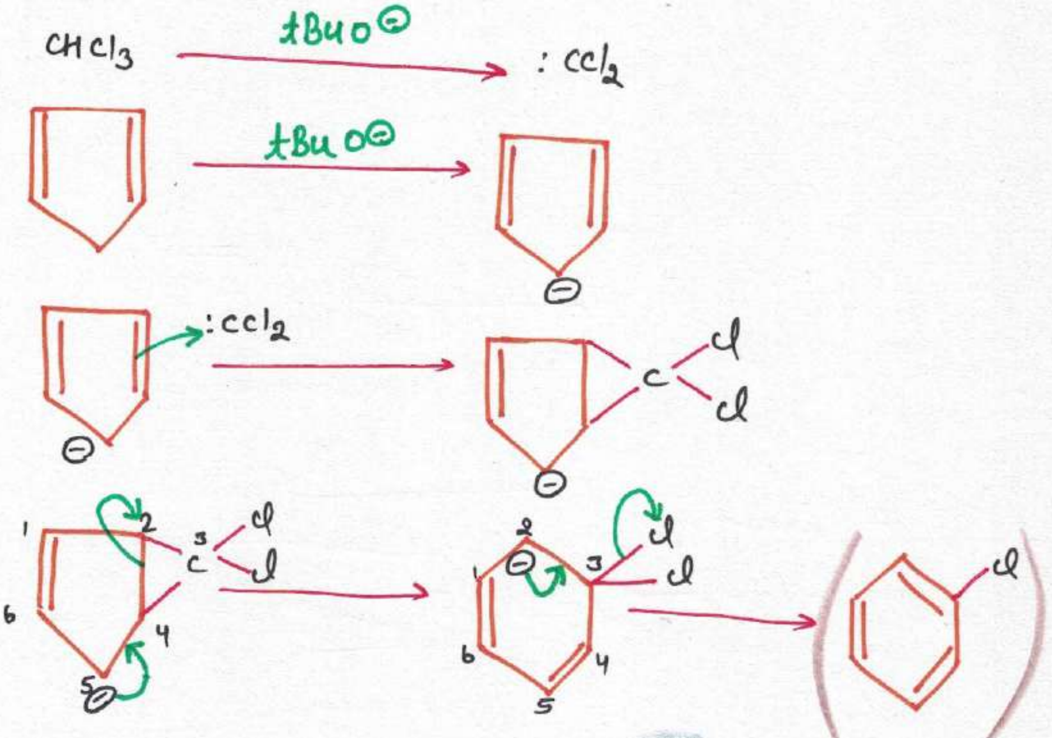
(carbon is an intermediate)



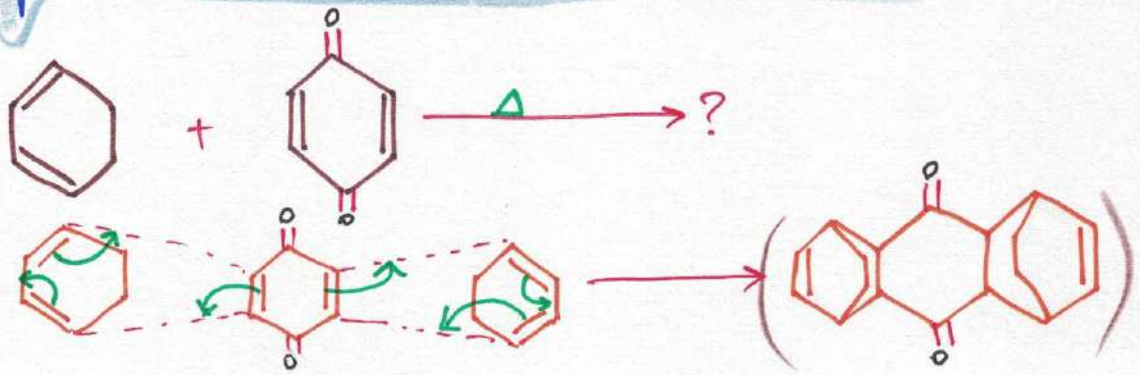


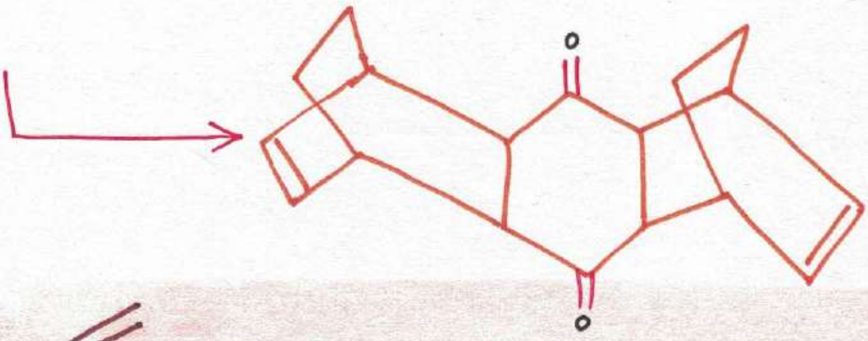
The question was used to teach the formation of carbene (one of the ways); we'll use it in the question further.





IMPORTANT QUESTION

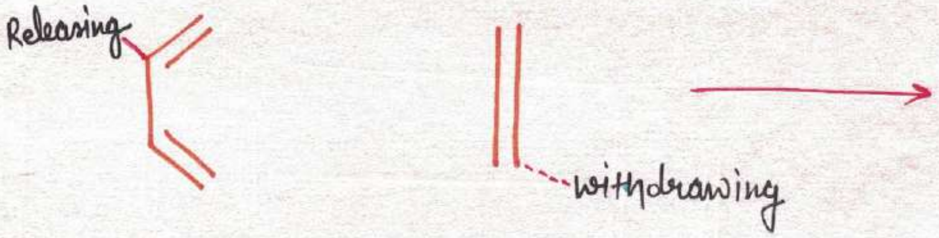




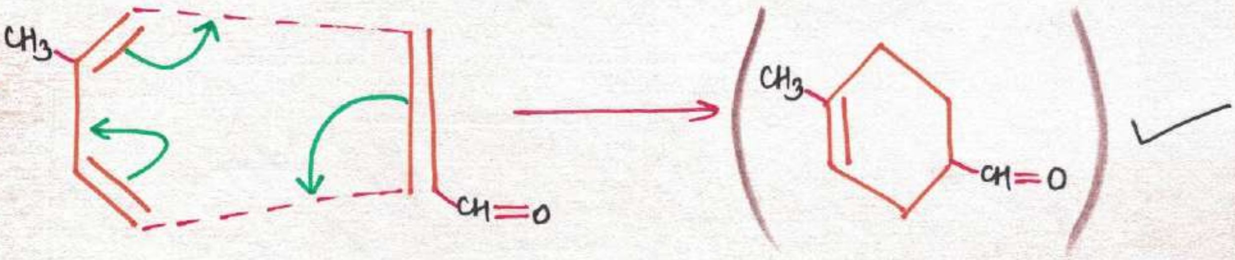
Q.

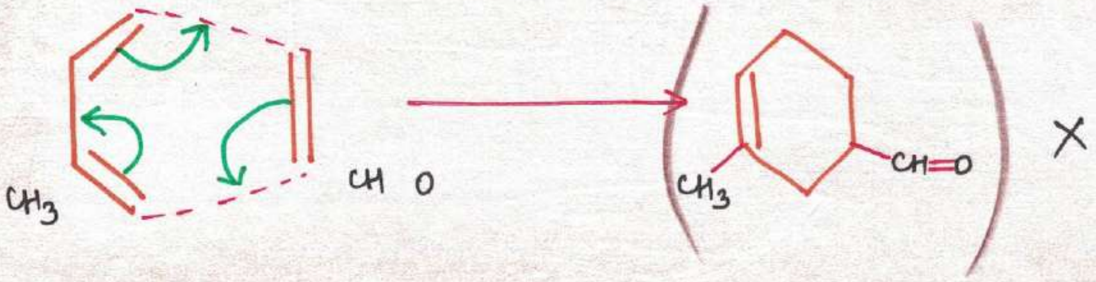
+ $CH_2=CH-CH=O \xrightarrow{\Delta}$?

A. As already discussed

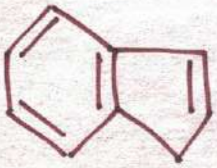


(Best Deals Alder)





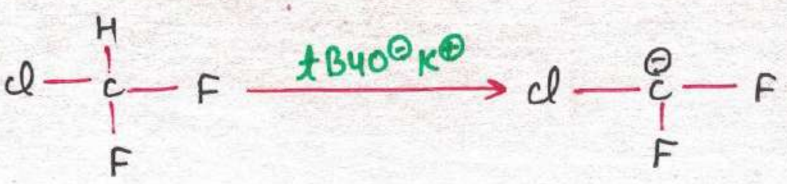
Q.



$\xrightarrow[tBuO^{\ominus}K^{\oplus}]{CHClF_2}$?

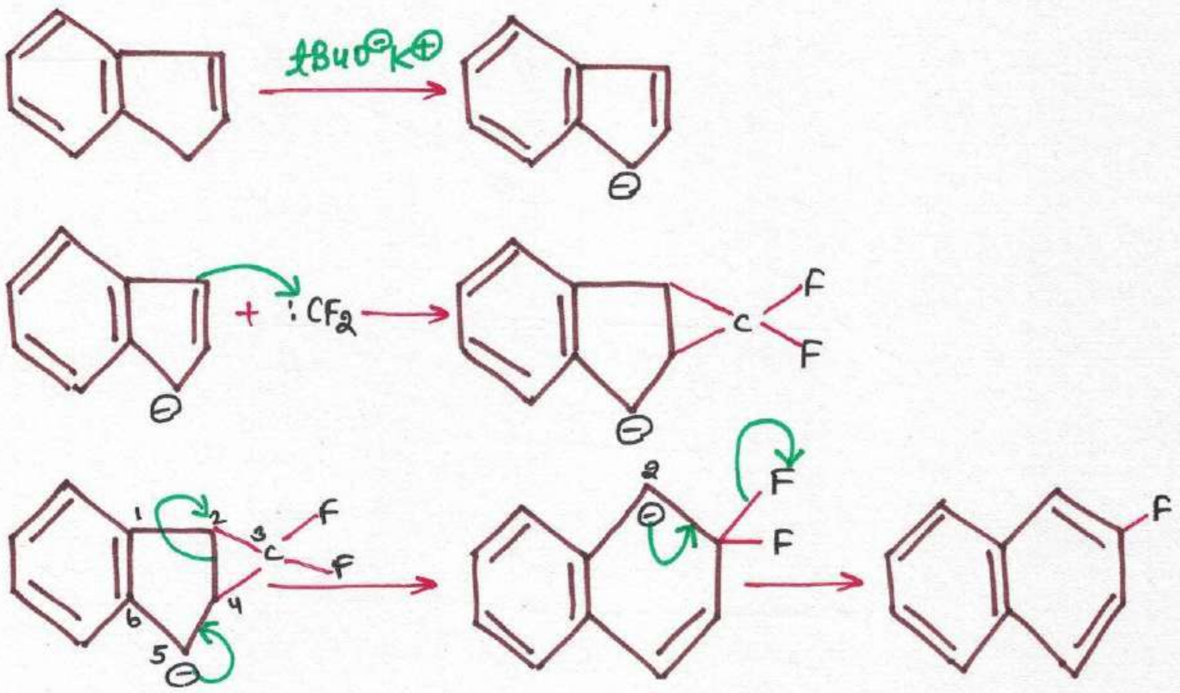
$CHClF_2 \xrightarrow{tBuO^{\ominus}K^{\oplus}}$?

A.



$$Cl-\overset{H}{\underset{F}{C}}-F \xrightarrow{tBuO^{\ominus}K^{\oplus}} Cl-\overset{\ominus}{\underset{F}{C}}-F$$

$$F-\overset{\ominus}{\underset{F}{C}}-F \longrightarrow (:CF_2)$$


tBuO⊖K⊕
+ :CF₂
C
F
F
1
2
3
4
5
6
2
F