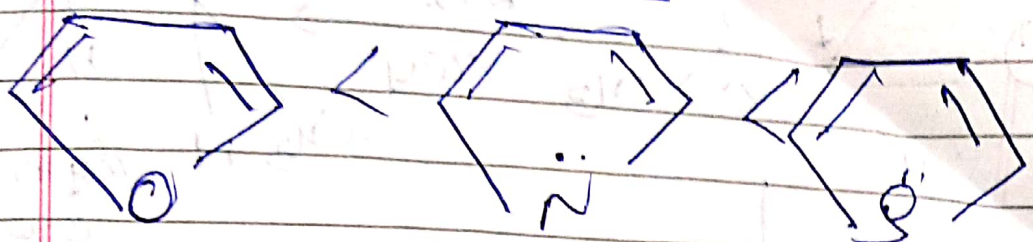
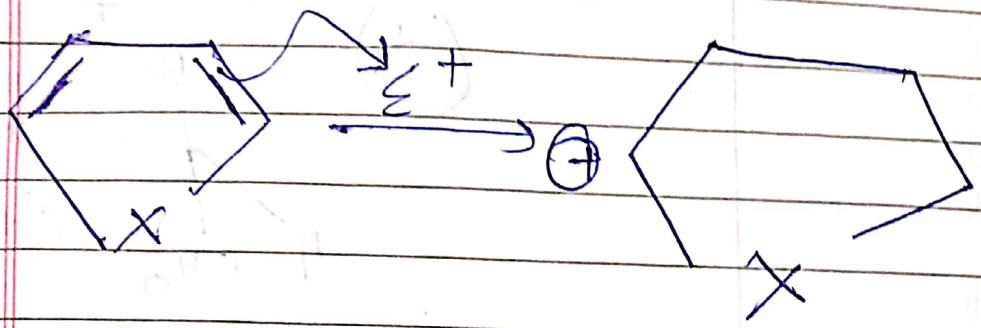
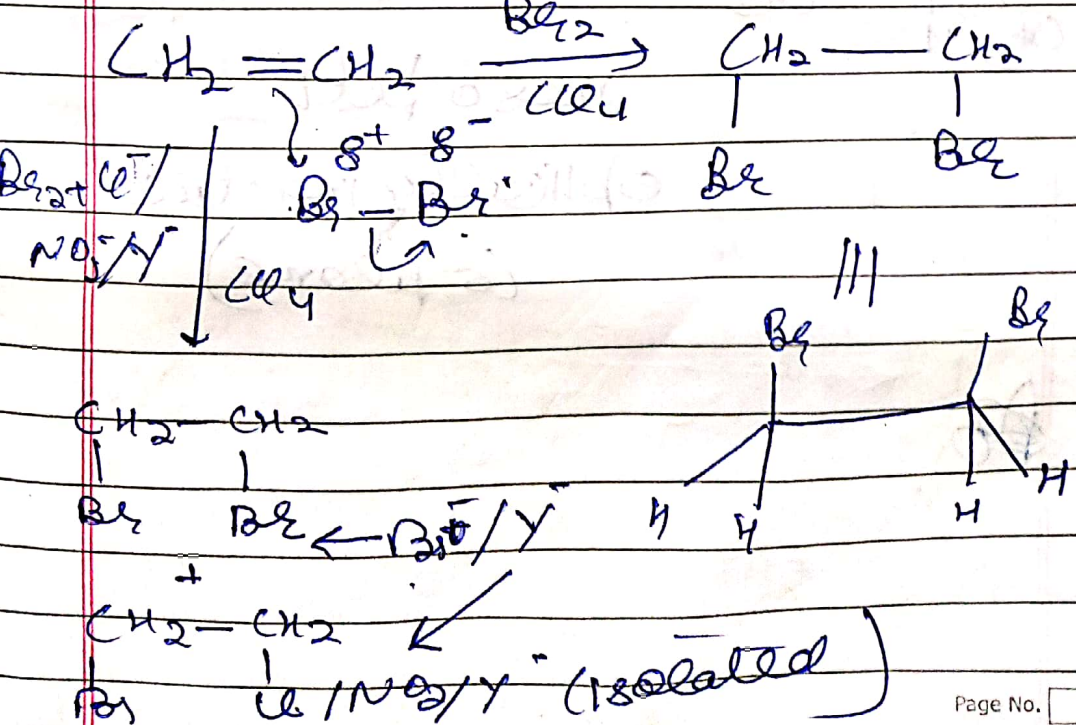
Aromaticity order



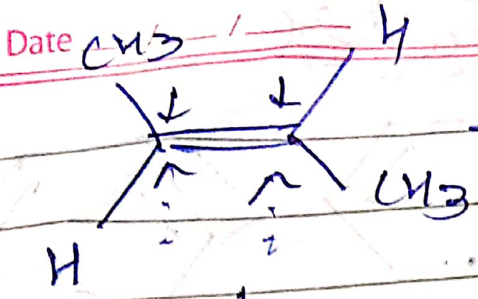


Electrophillic Addition to >C=C< via Halonium ion intermediate

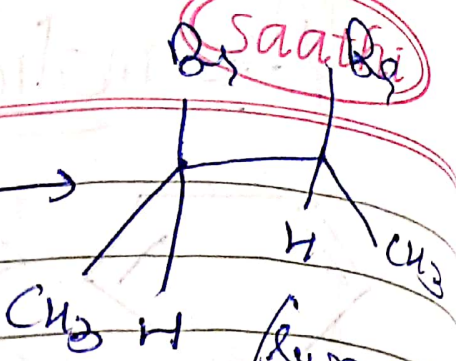


Date

(2)



Br_2
CCl_4



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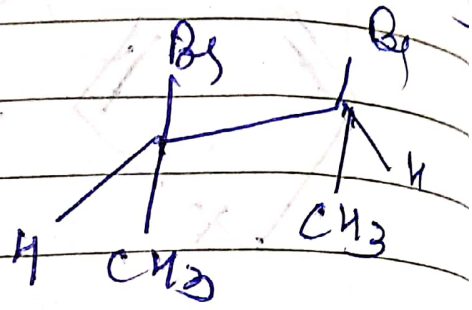
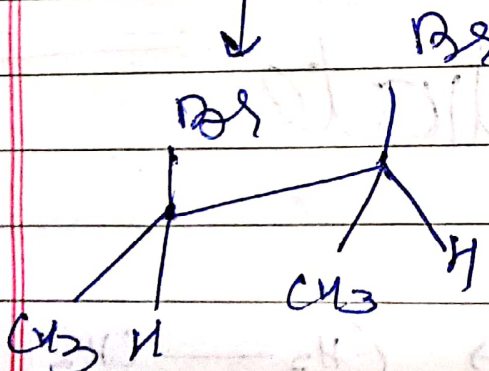
syn addn
one step
reaction

$50:50$
$(\pm)$



Racemic mixture
optically inactive
(not resolved)

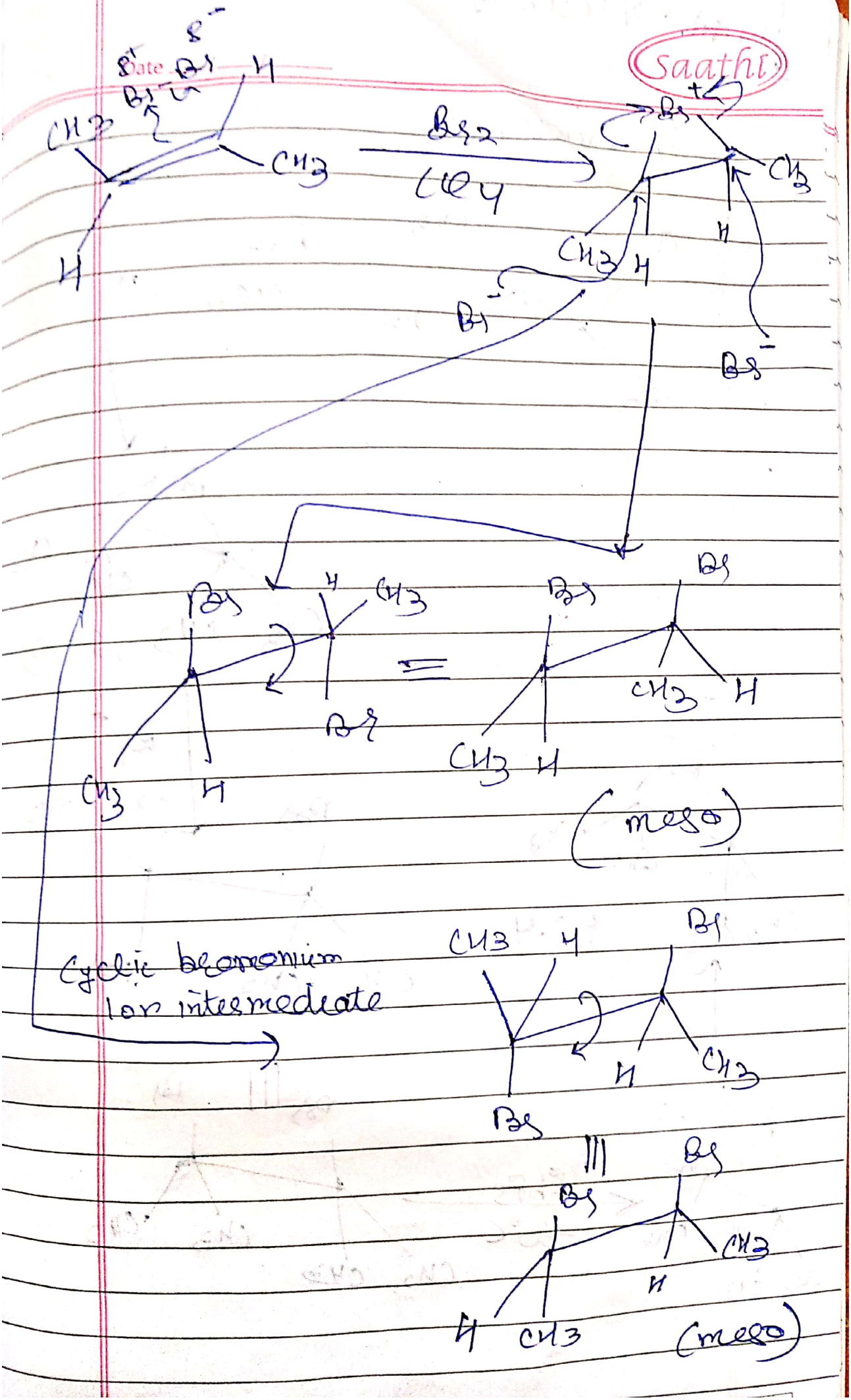
anti
addn
(stereo)



(resolved)
100%

meso pdt.
optically inactive
(c-plane)

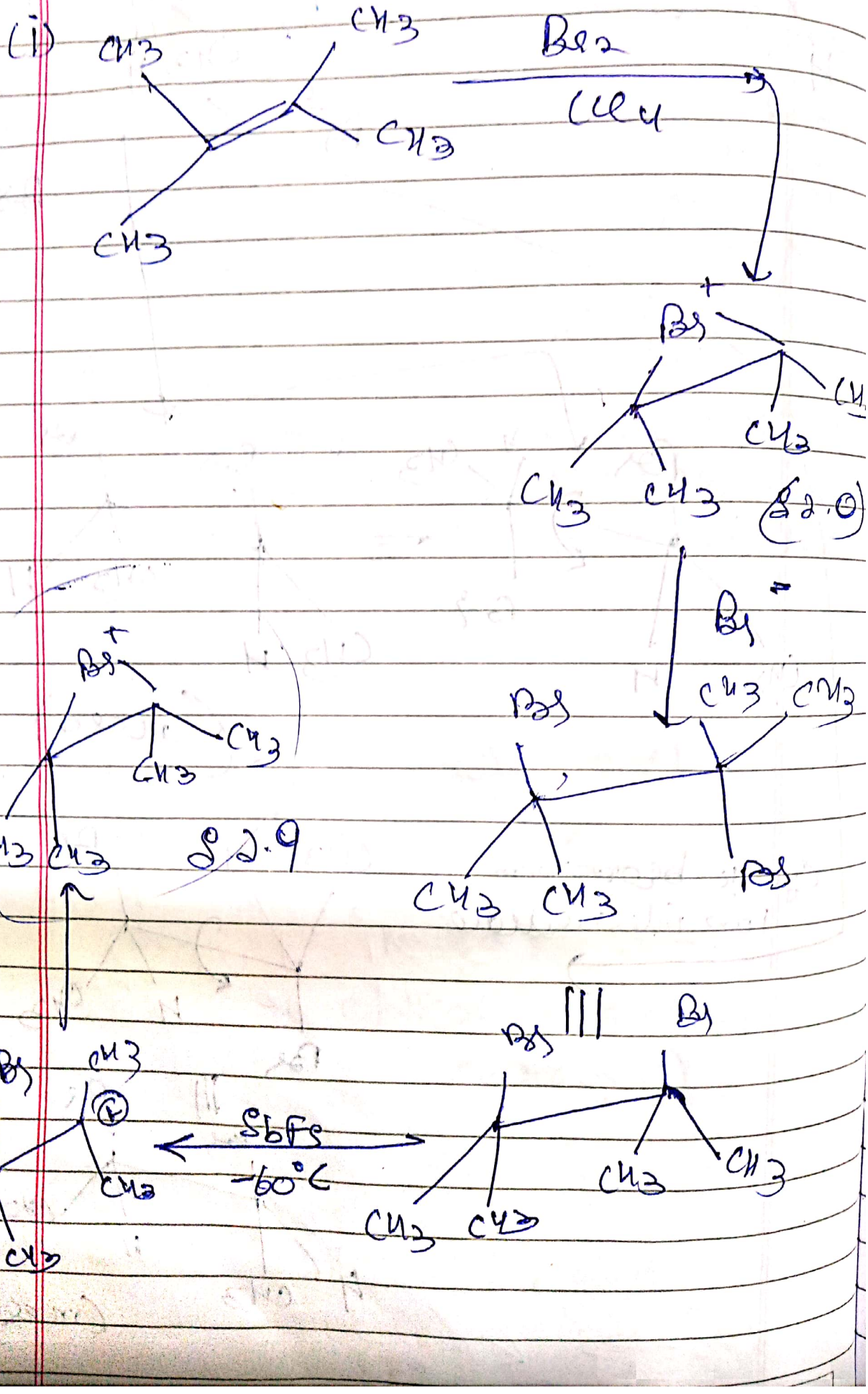
Scanned by CamScanner

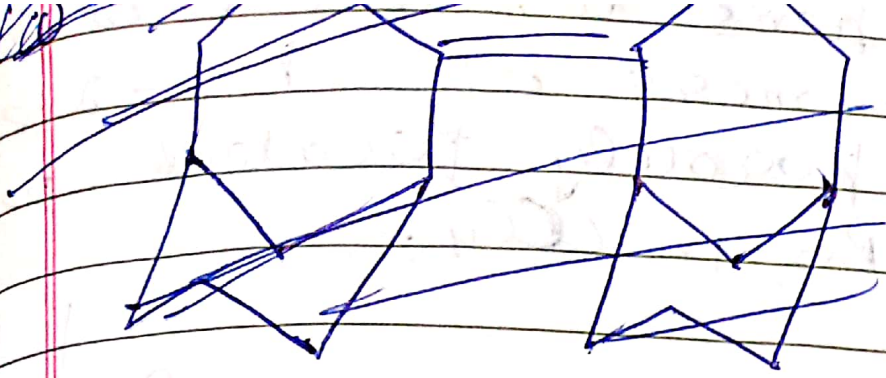


Date ___ / ___ / ___

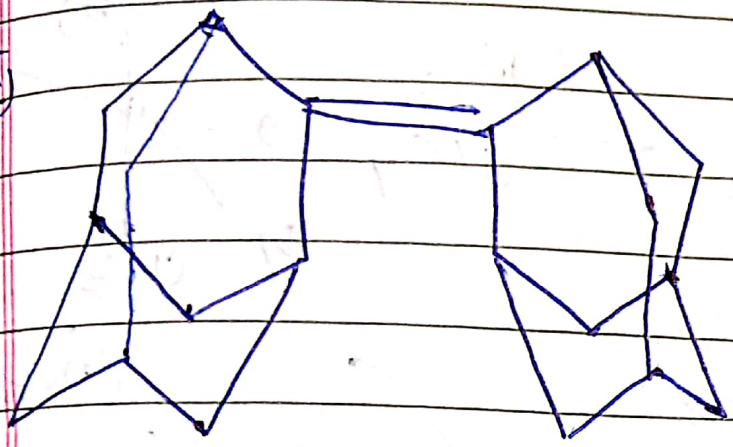
Exp. evidence

(i)

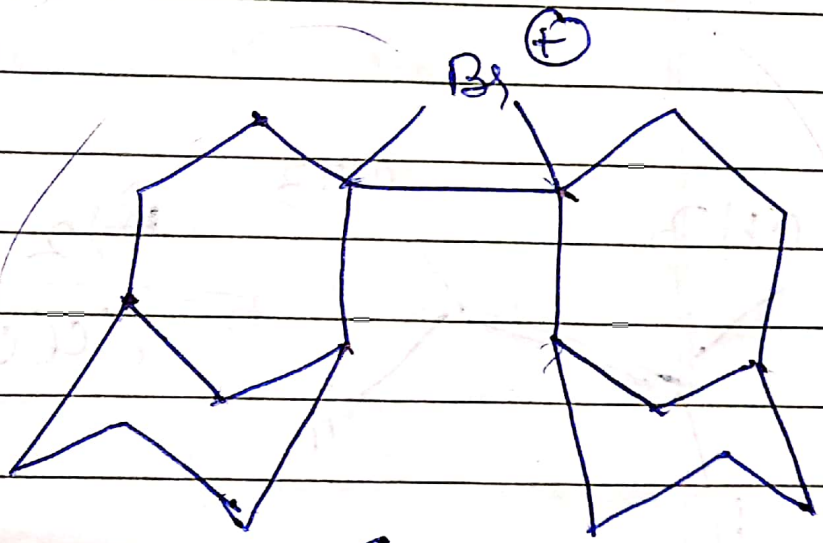




(ii)



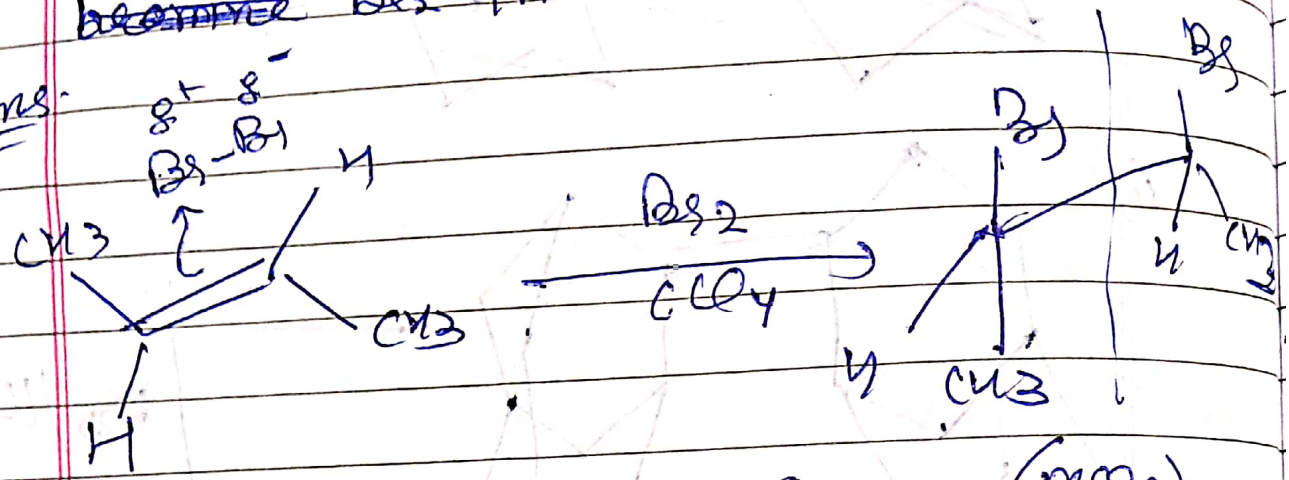
Br_2/CCl_4



(Isolated)

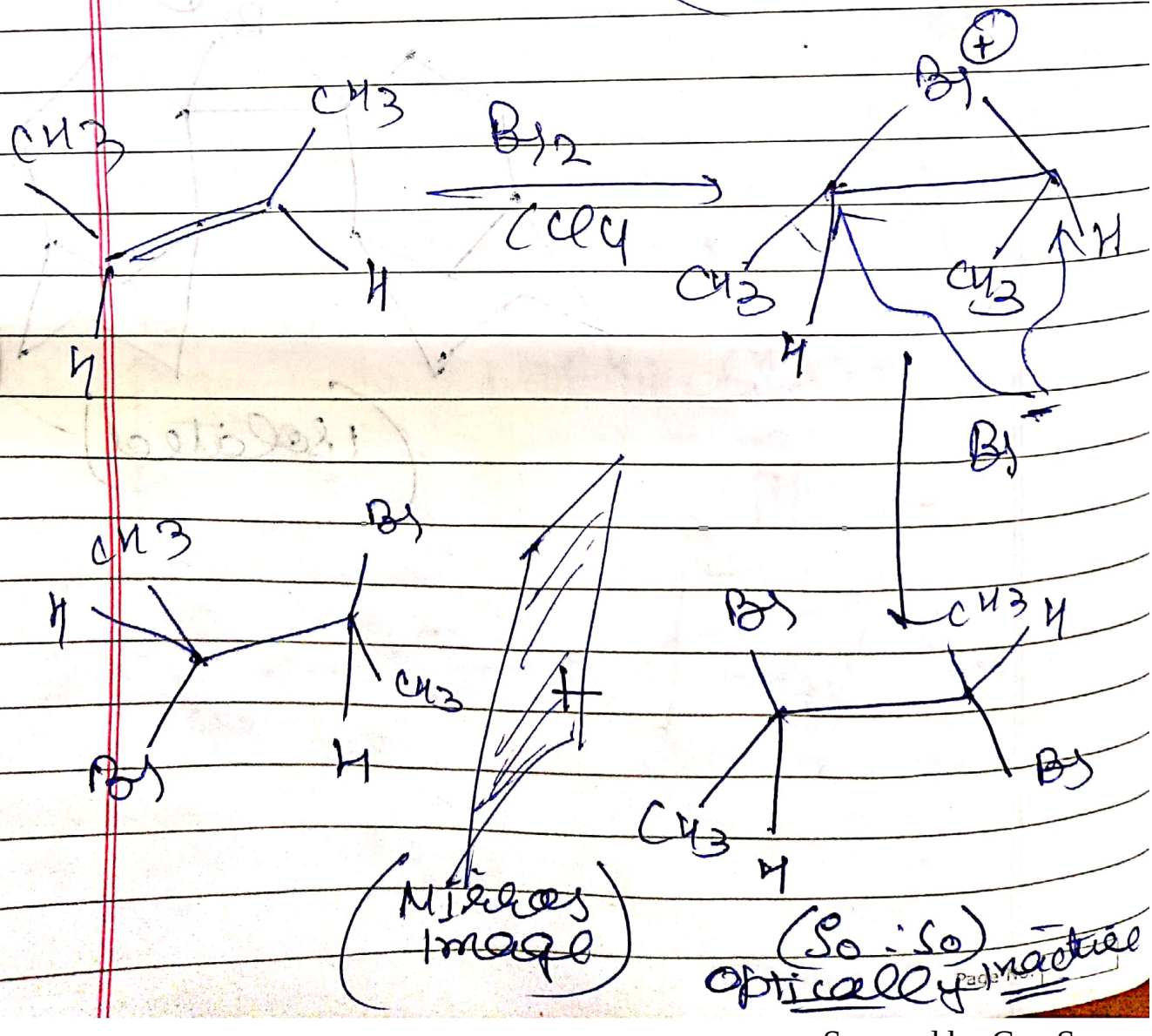
Q. What happens when cis and trans isomers of but-2-ene are separately treated with ~~bromine~~ Br_2 in CCl_4.

Ans:



trans -2-butene

(meso)
optically inactive due to plane



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(±) 2,3 dibromo butane

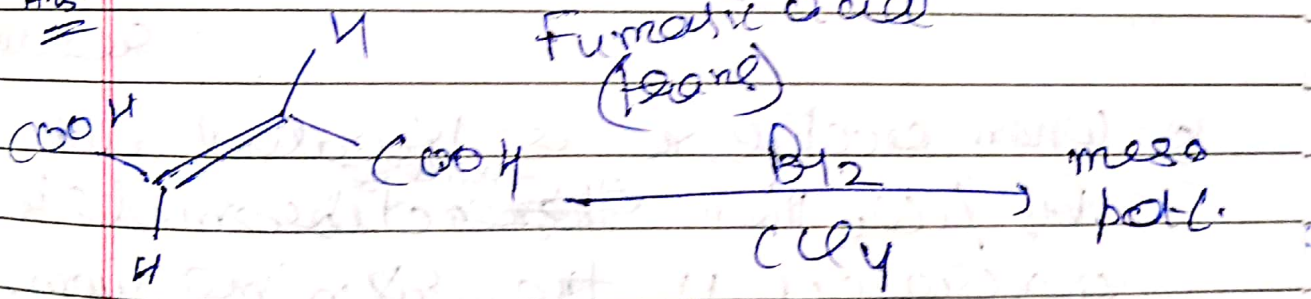
Enantiomers

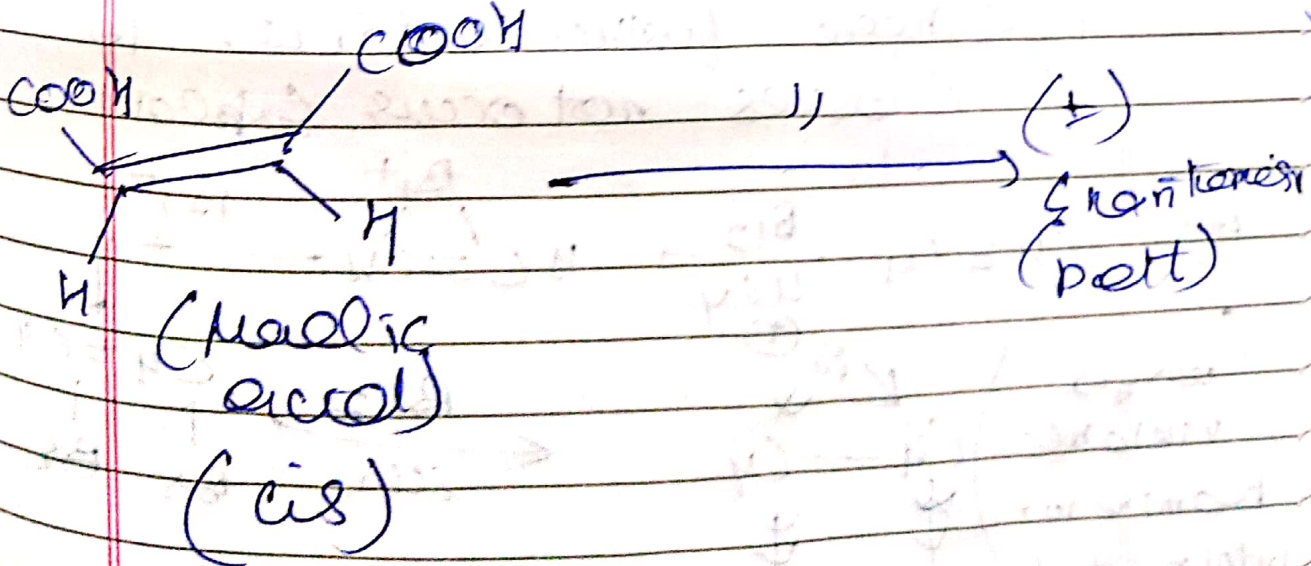
optically inactive due to external compensation.

trans - 2 - butene is more reactive than cis compound as the bromonium ion intermediate is more stable due to less steric hindrance

Q. What happens when maleic acid and fumaric acid are separately treated with Br_2 in CCl_4?

Ans.





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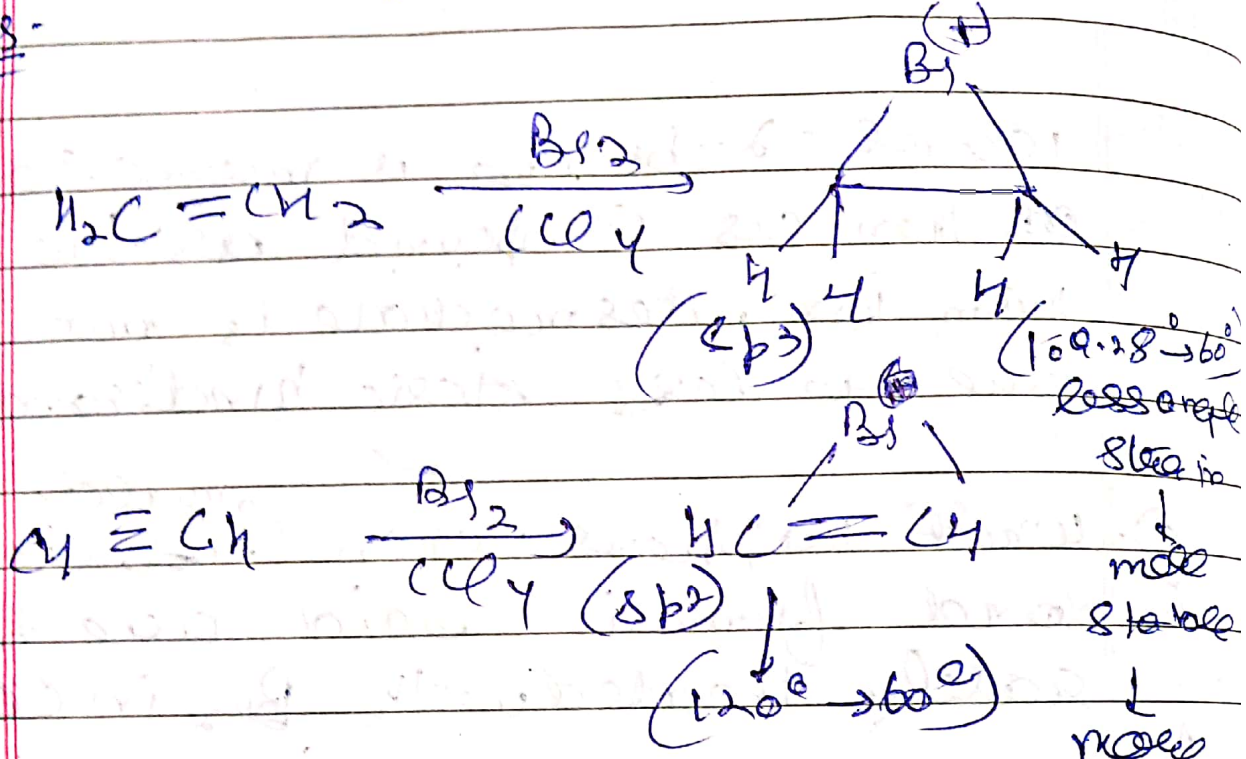
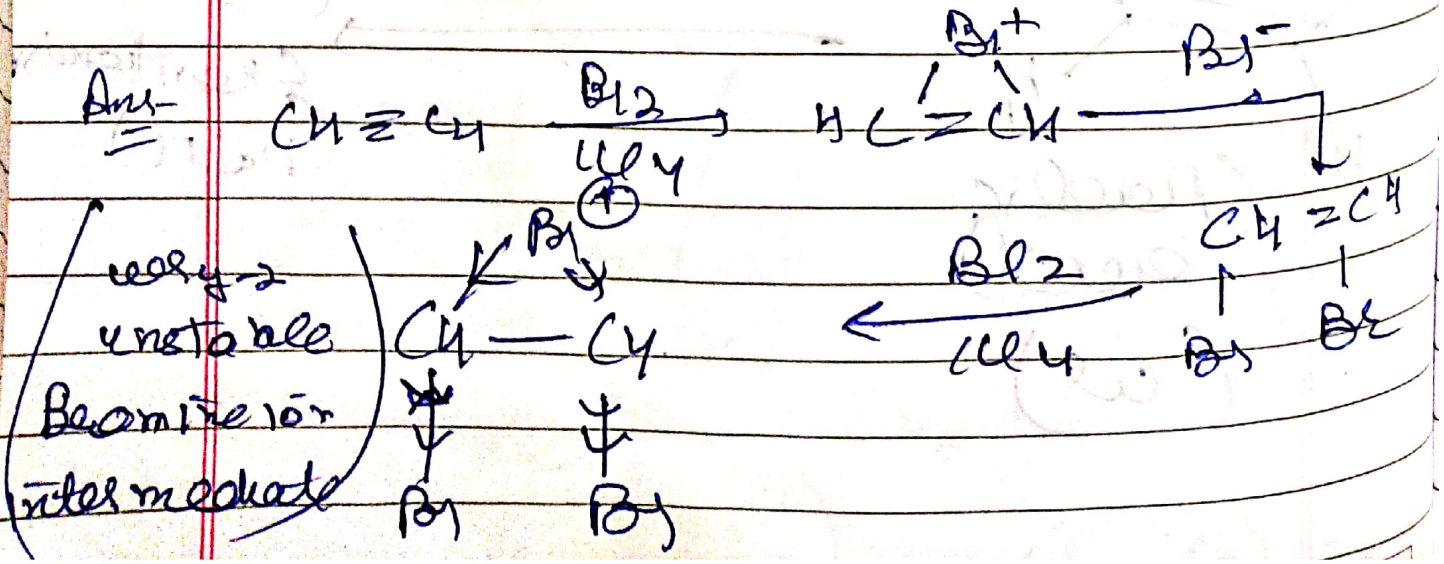
Q. B/w ethelene and acetylene, which one is more reactive towards Br_2 addition reaction?

Ans.



Q. When acetylene is treated with Br_2/CCl_4 then ~~ethylene~~ dibromide is generated in the Rxn medium. i.e. more further addition to C=C does not occur. Explain.

Ans.



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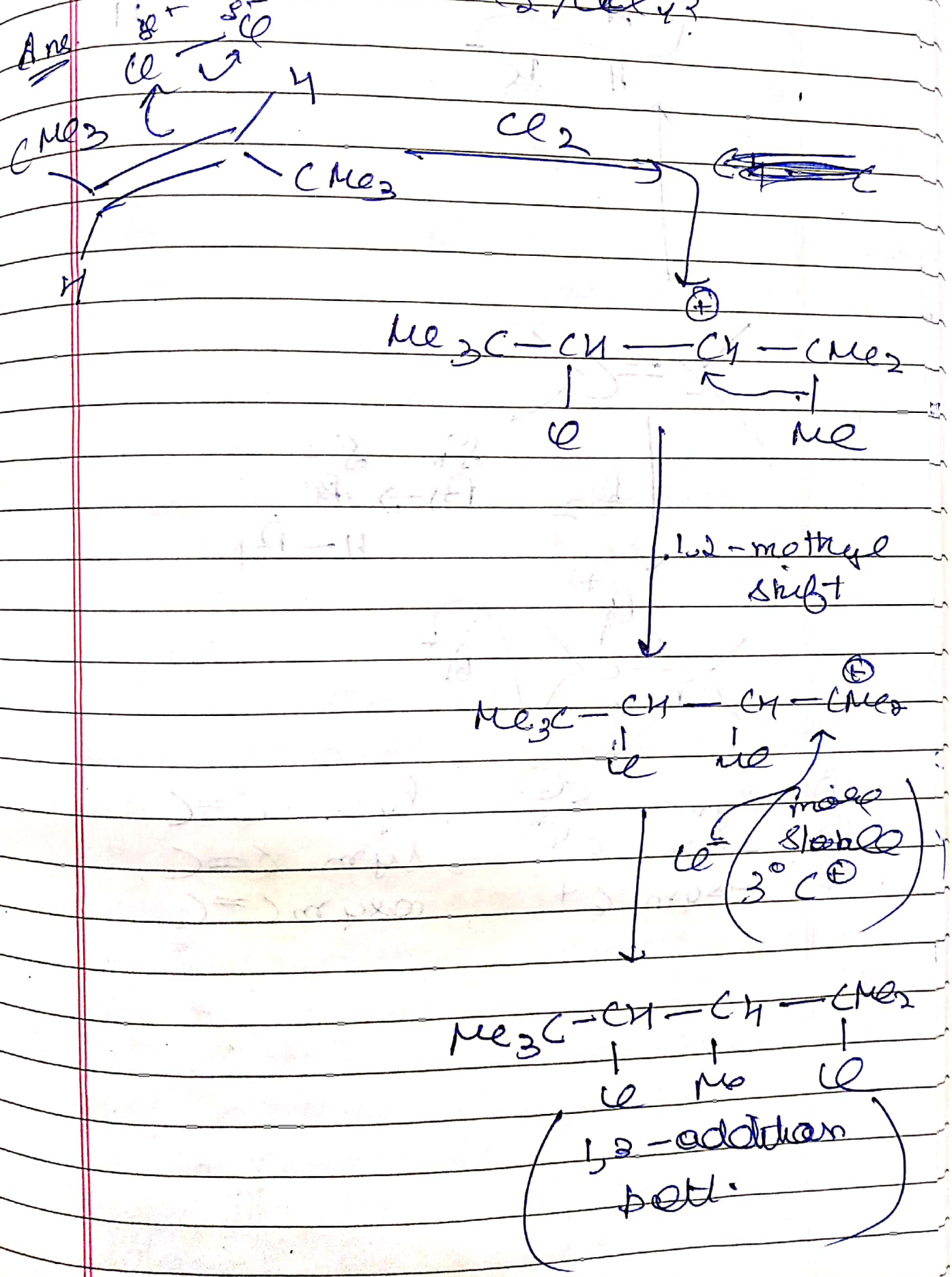
Q. What happens when trans 1,2 ditertiary butene is treated with chlorine Cl_2/CCl_4?

Ans.



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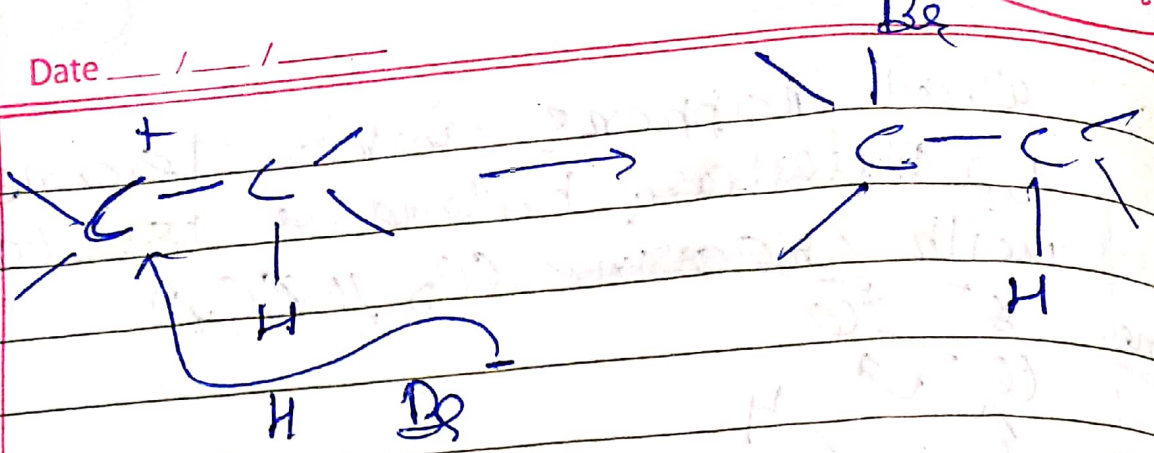
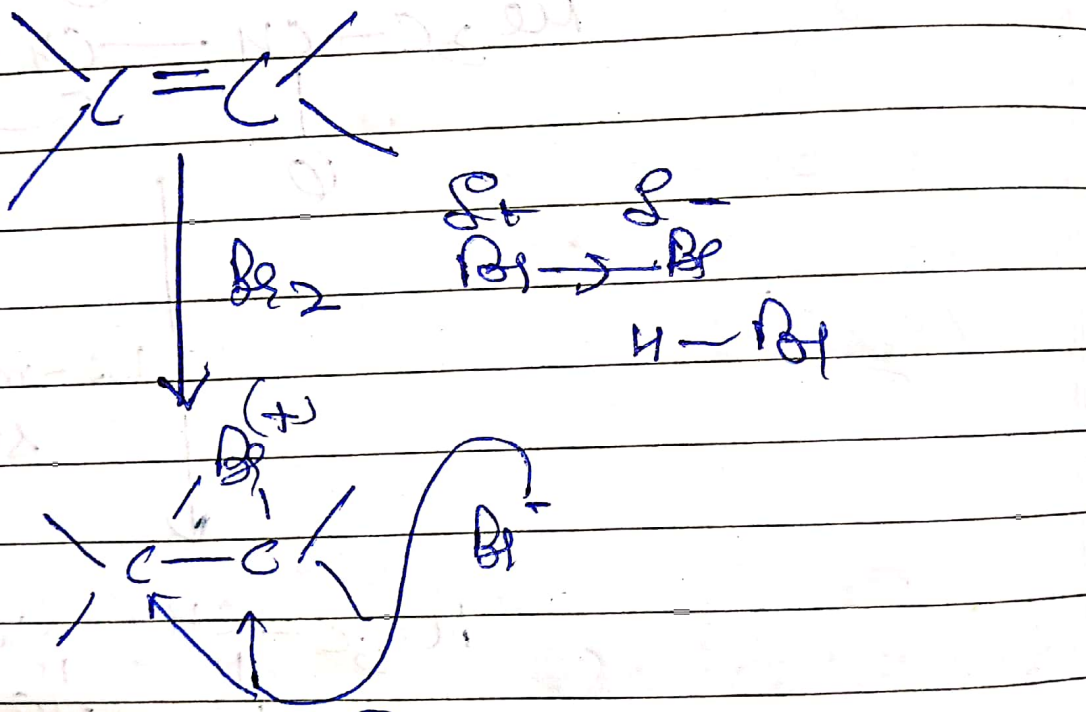
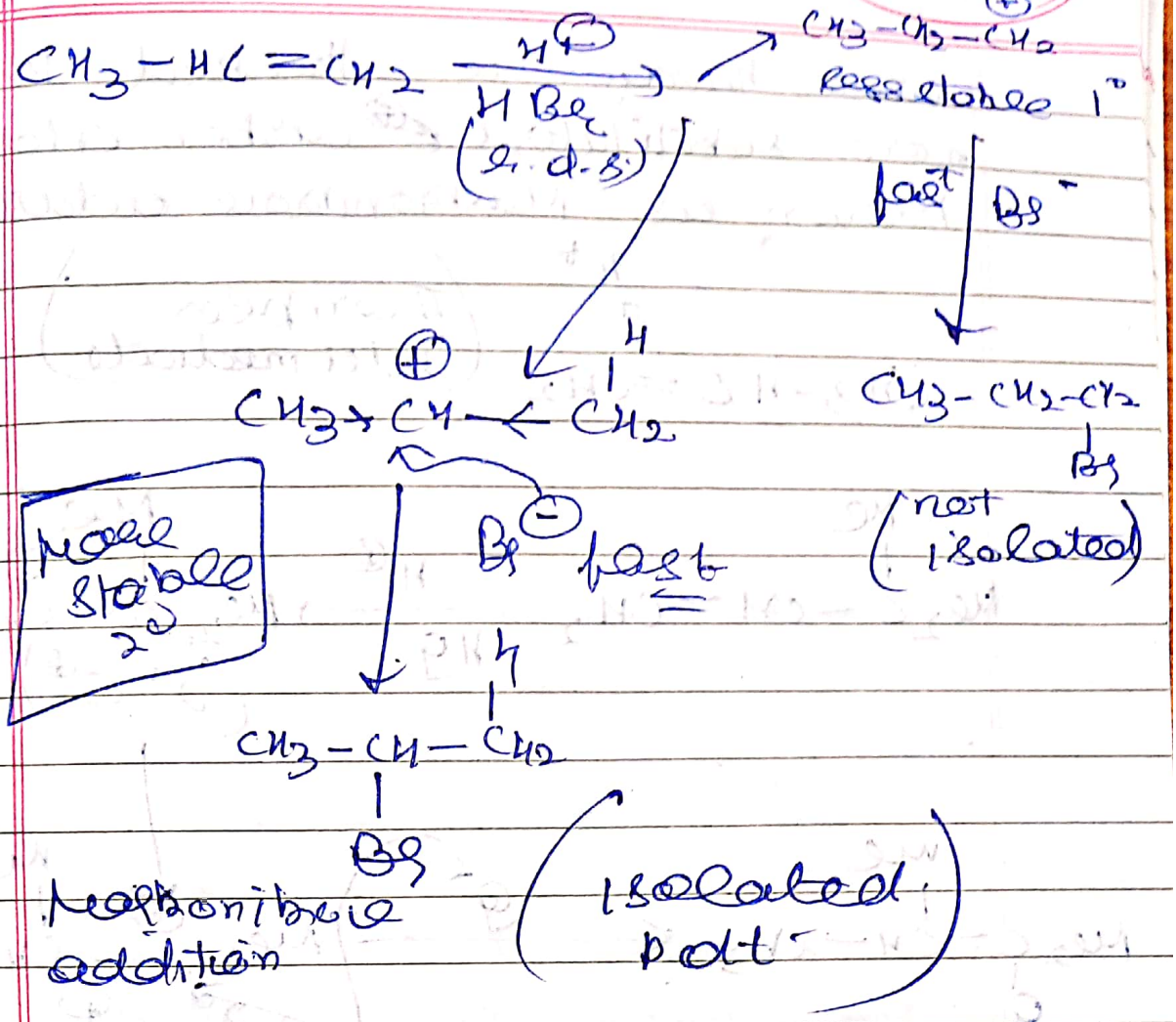




(1) Sym. ε^{+} , sym. C=C

(2) asym. ε^{+} , sym C=C

(3) asym ε^{+} , asym C=C



Here the first step is the r.d.s, therefore the rate of rxn depends on the acid strength HI > HBr > HCl > HF, with higher acid strength, the rate also increases.

Here bridged intermediate similar to Bromonium ion intermediate can not be formed as hydrogen has no electron pair available, however a π complex in the intermediate in some cases.

Here the stability of carbocations determine the overall orientation of addition. This type of addition

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where halogen is attached to the more substituted carbon atom is known as Markonikove addition.

$CH_3-HC=CH_2$ (H^+) (π complex intermediate)

$Me_2C-CH=CH_2 \xrightarrow[HBr]{H^+} Me_2\overset{\oplus}{C}-CH-CH_3$ ($2^\circ C^\oplus$)

$Me_2C(Br)-CH(Me)-CH_3 \xleftarrow{Br^-} Me_2\overset{\oplus}{C}-CH(Me)-CH_3$

Chloro also

$CH_2=CH-Br \xrightarrow{H^+} CH_2-\overset{\oplus}{C}H-Br \leftrightarrow CH_3-CH=\overset{\oplus}{Br}$

Resonance stabilized

$CH_2-CH(H)-Br \xrightarrow{Br^-} CH_2(Br)-CH_2-Br$

$CH_3-CH(Br)-Br$

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$CH_2=CH_2 \xrightarrow[H-Br]{H^+} CH_2-\overset{\oplus}{C}H_2$

$CH_2-CH_2-H \cdots Br^-$

CH_2-CH_3
|
Br

more faster than $CH_2=CH-Br$

In case of halogen +R effect controls the orientation and -I effect controls the rate.
In case of rate near -I effect of Br is destabilizes the corresponding $C^{\oplus}$ thus ethelene has better reactivity than vinyl group towards H-Br addition rxn.

1) $CH_2=CH-OMe \xrightarrow[HBr]{H^{\oplus}} CH_2-\overset{\oplus}{C}H-OMe$
|
H

Resonance stabilization by l.p. of OMe
+R effect of OMe

$CH_3-CH-OMe$
|
Br^-

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Hydration

acid catalysed

1. $CH_3-CH=CH_2 \xrightarrow{H^+} CH_3-\overset{\oplus}{C}H-CH_3$

[Conc. H_2SO_4]

$CH_3-\overset{\oplus}{C}H-CH_3 \xrightarrow{H_2O} CH_3-CH(OH)-CH_3$

$CH_3-CH(OH)-CH_3 \xrightleftharpoons{-H^+} CH_3-CH(\overset{\oplus}{O}H_2)-CH_3$

(Markovnikov's addition)

2. $CMe_3-CH=CH_2 \xrightarrow{H^+} Me_2\overset{\oplus}{C}-CH-CH_3$

(2°) ⊕

(2-Me shift)

$Me_2\overset{\oplus}{C}-CH(Me)-CH_3 \xrightleftharpoons{H_2O/-H^+} Me_2-C(OH)-CH(Me)-CH_3$

$Me_2-C(OH)-CHMe_2$

(3°⊕)

→ More stable

3. $Me_2C=CH_2 \xrightarrow{H^+} Me_2\overset{\oplus}{C}-CH_3$

$Me_2\overset{\oplus}{C}-CH_3 \xrightarrow{H_2O/-H^+} Me_2C(OH)-CH_3$

4. $CH_2=CH-CH_2-Cl \xrightarrow{dil.H_2SO_4} [A]$

$CH_2=CH-CH_2-Br \xrightarrow{dil.H_2SO_4} [B]+[C]$

$CH_2=CH-CH_2-Cl \xrightarrow{H^+}$ ie $CH_3-\overset{\oplus}{C}H-CH_2$ (2°)

$CH_3-CH(OH)-CH_2Cl \xleftarrow[\text{n.g.p.}]{H_2O/-H^+} CH_3-\overset{\oplus}{C}H-CH_2$

[A] is not feasible because Cl is more EN

$CH_2=CH-CH_2-Br \xrightarrow{H^+} CH_3-\overset{\oplus}{C}H-CH_2(:Br:)$

Bromonium ion intermediate formation

$CH_3-CH(\overset{\oplus}{Br})-CH_2 \xrightarrow{\text{n.g.p. takes place}} CH_3-CH(OH)-CH_2Br + CH_3-CH(OH)-CH_2OH$

[B] [A]

Date ___/___/___

Hydroboration Oxidation Rxn

Anti Markonikov Addn to C=C

$CH_3-CH=CH_2 \xrightarrow{B_2H_6} (CH_3CH_2CH_2-)_3B$

Trialkyl Borane

$\xrightarrow{H_2O_2 \text{ in alkaline } pH}$

$CH_3CH_2CH_2-OH$

1° alcohol instead of 2° for Markonikov addn

+

$B(OH)_3$

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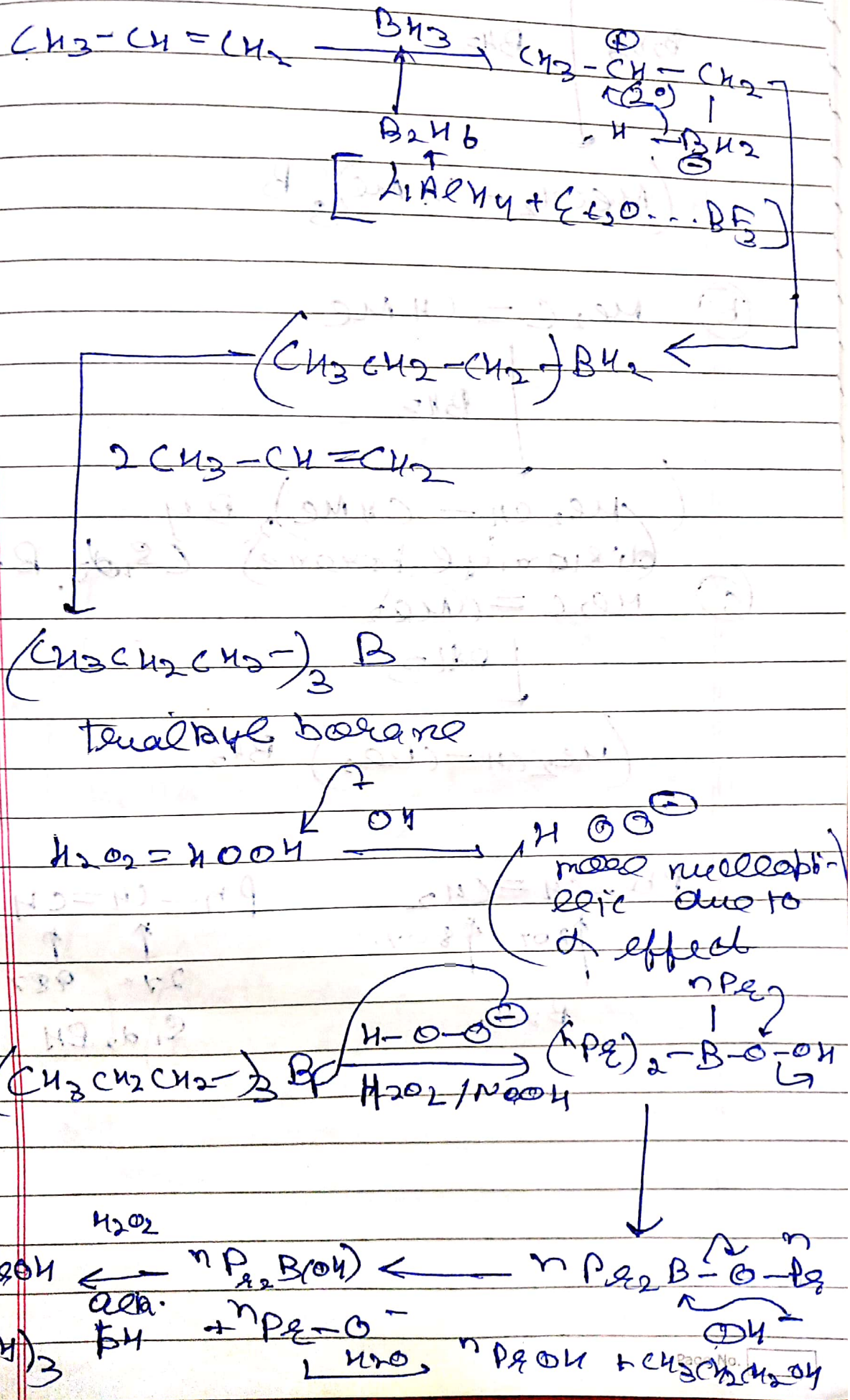
Mechanism



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Date ___/___/_____

(a) $MeCH=CHMe$

B_2H_6 | BH_3

$(MeCH_2-CHMe)_3B$

(b) $Me_2C=CHMe$

BH_3

$(Me_2CH-CHMe)_2BH$

(disiamyl borane) (Sia$_2$BH)

(c) $Me_2C=CH_2$

BH_3

$(Me_2CH-CH_2)BH_2$

$Ph-CH=CH_2$

20% 80%

B_2H_6

$Ph-CH=CH$

27% 98%

Sia$_2$BH

Date ___/___/_____

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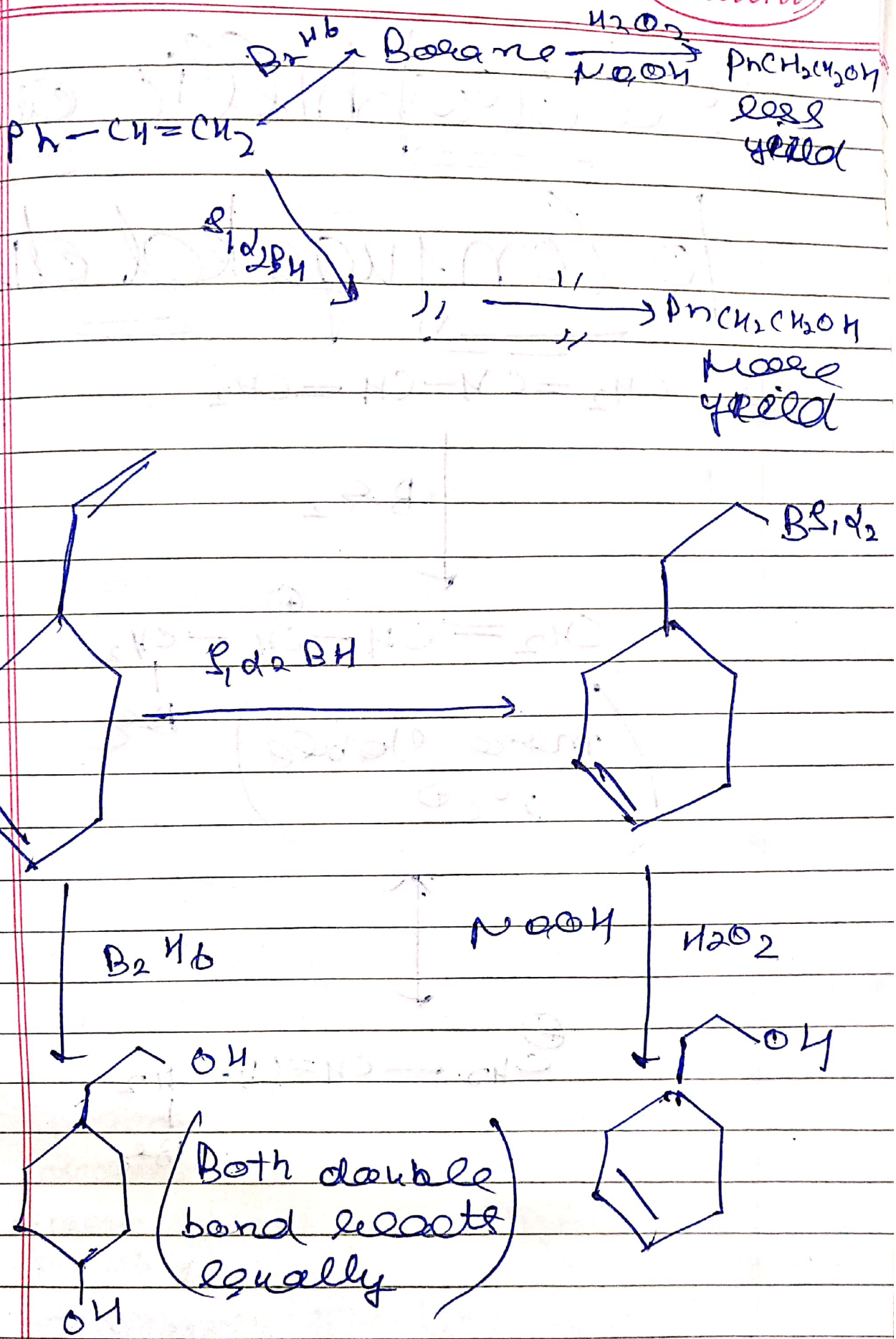

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Date __/__/____

Electrophillic addn to Conjugated dienes

1. $CH_2=CH-CH=CH_2$

$\downarrow Br_2$

$CH_2=CH-\overset{\oplus}{C}H-CH_2$

$|$

Br

(more stable $2^\circ C^\oplus$)

$\updownarrow$

$\overset{\oplus}{C}H_2-CH=CH-CH_2$

$|$

Br

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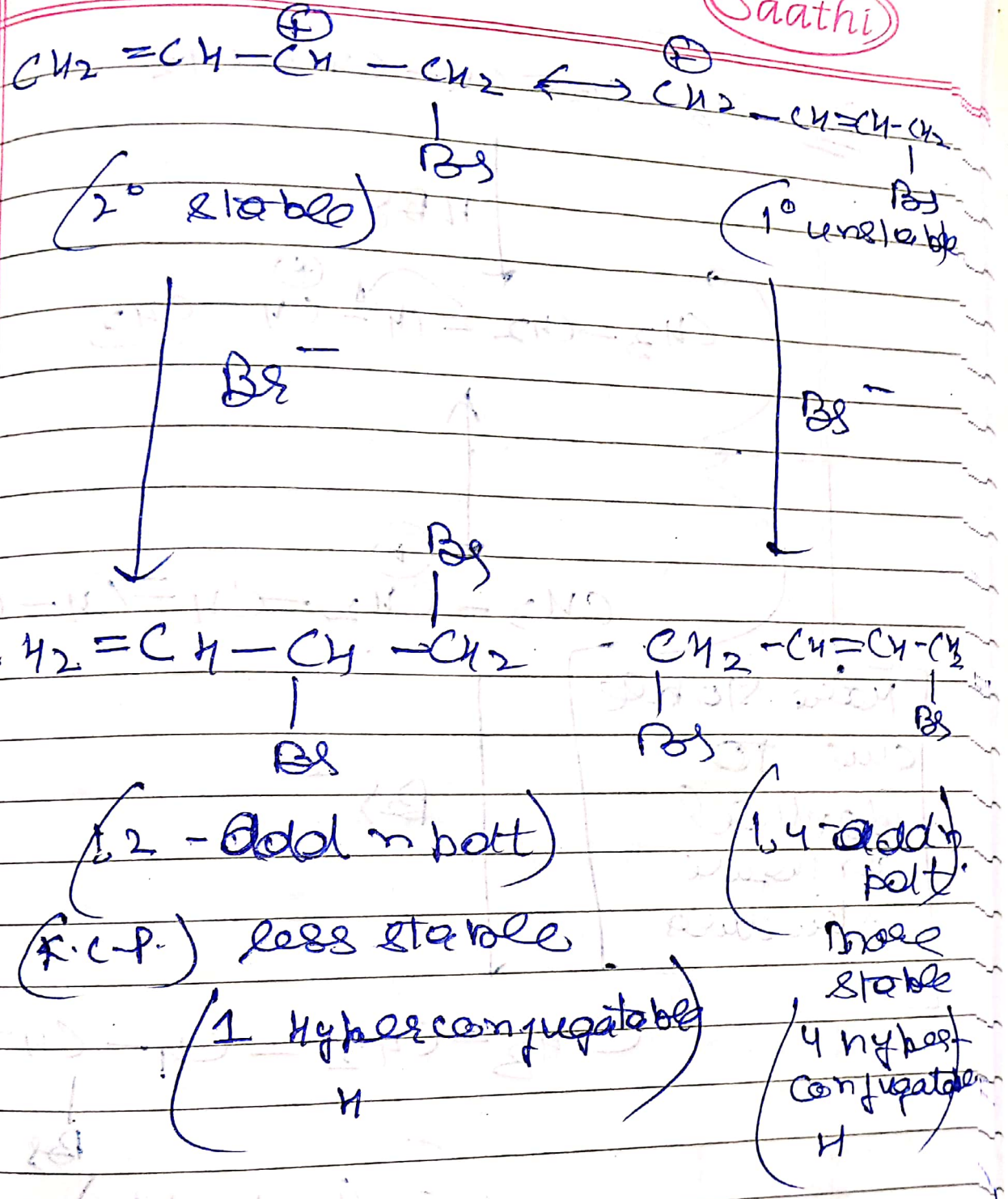
Saathi



increase temp → TCP ↑, KCP ↓

decrease " → TCP ↓ KCP ↑

increase solvent polarity → 1,4 patt ↑, 1,2-patt ↓ (pol + contribution)

decrease " → 1,4 patt ↓, 1,2 patt ↑

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2. $CH_3-CH_2=CH-CH=CH_2$

$\downarrow HBr$

$CH_3-CH_2=\overset{\oplus}{CH}-CH-CH_3$ ⟷ $CH_3-CH_2-CH=CH-CH_3$ (⊕)

More Stable due to identical conjugate structures

$\downarrow Br^-$

$CH_3-CH_2=CH-\underset{Br}{CH}-CH_3$

(only pdt)

Date ___/___/_____

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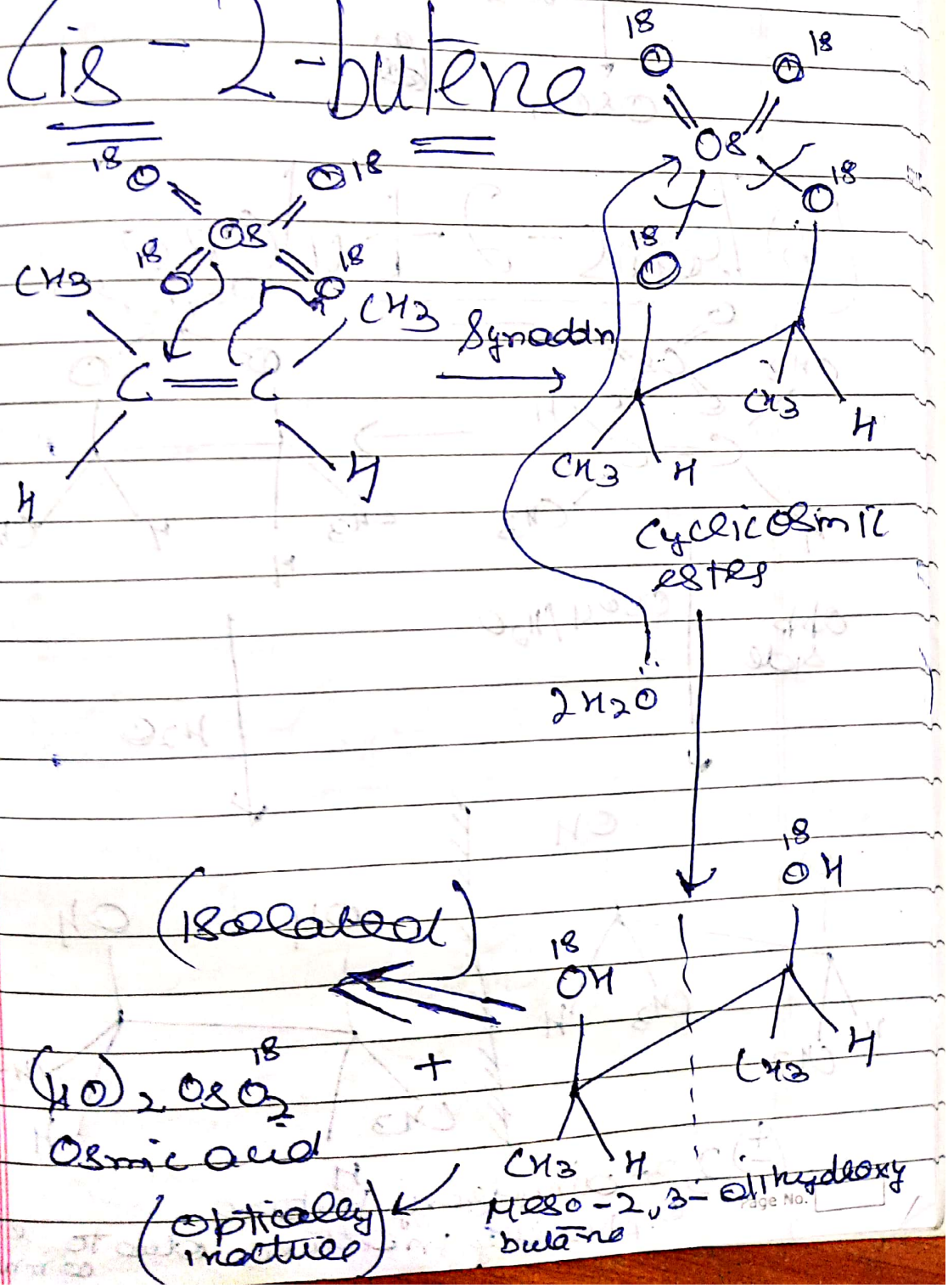
Hydroxylation Rxn

Syn / Cis :-

(a) Cis - 2 - butene



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Disadvantages of this Rxn.

(i) OsO_4 is highly toxic

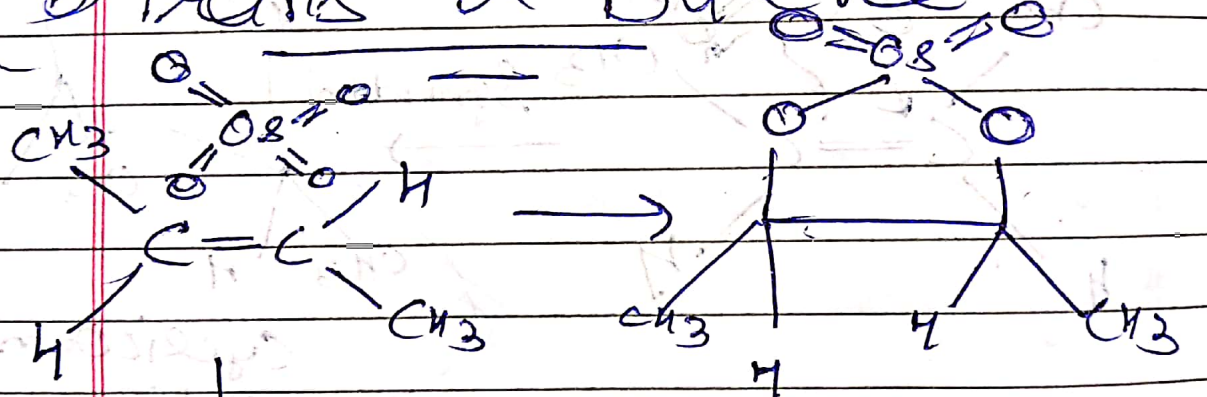
(ii) ~~highly~~ OsO_4 is highly expensive

$(HO)_2OsO_2$ — we need do this to remove the above two disadvantages

$\downarrow H_2O_2$

OsO_4

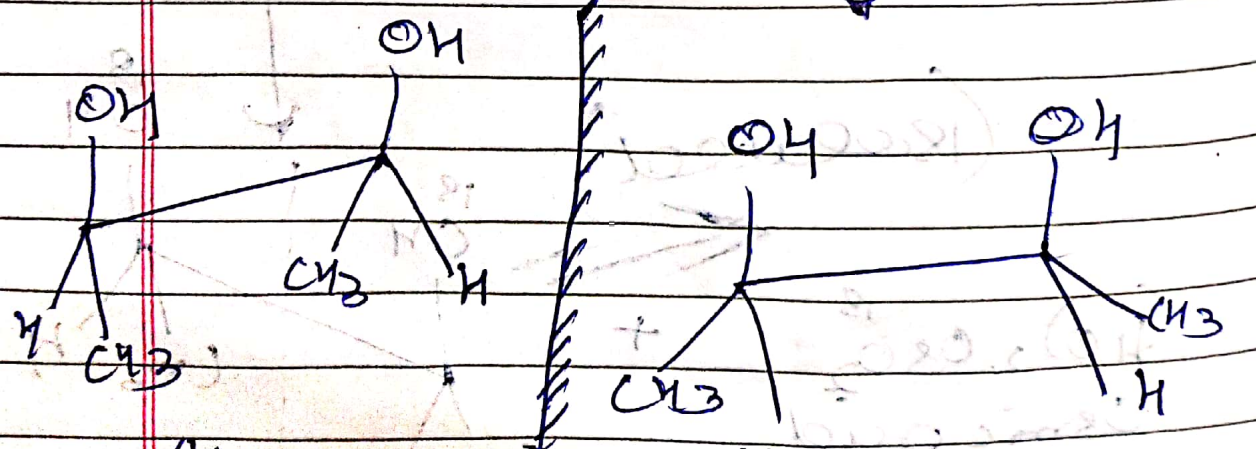
(b) Trans-2-butene



Opp side

OsO_4/H_2O

H_2O



(±) 2,3-dihydroxy butane

optically inactive due to external compensation

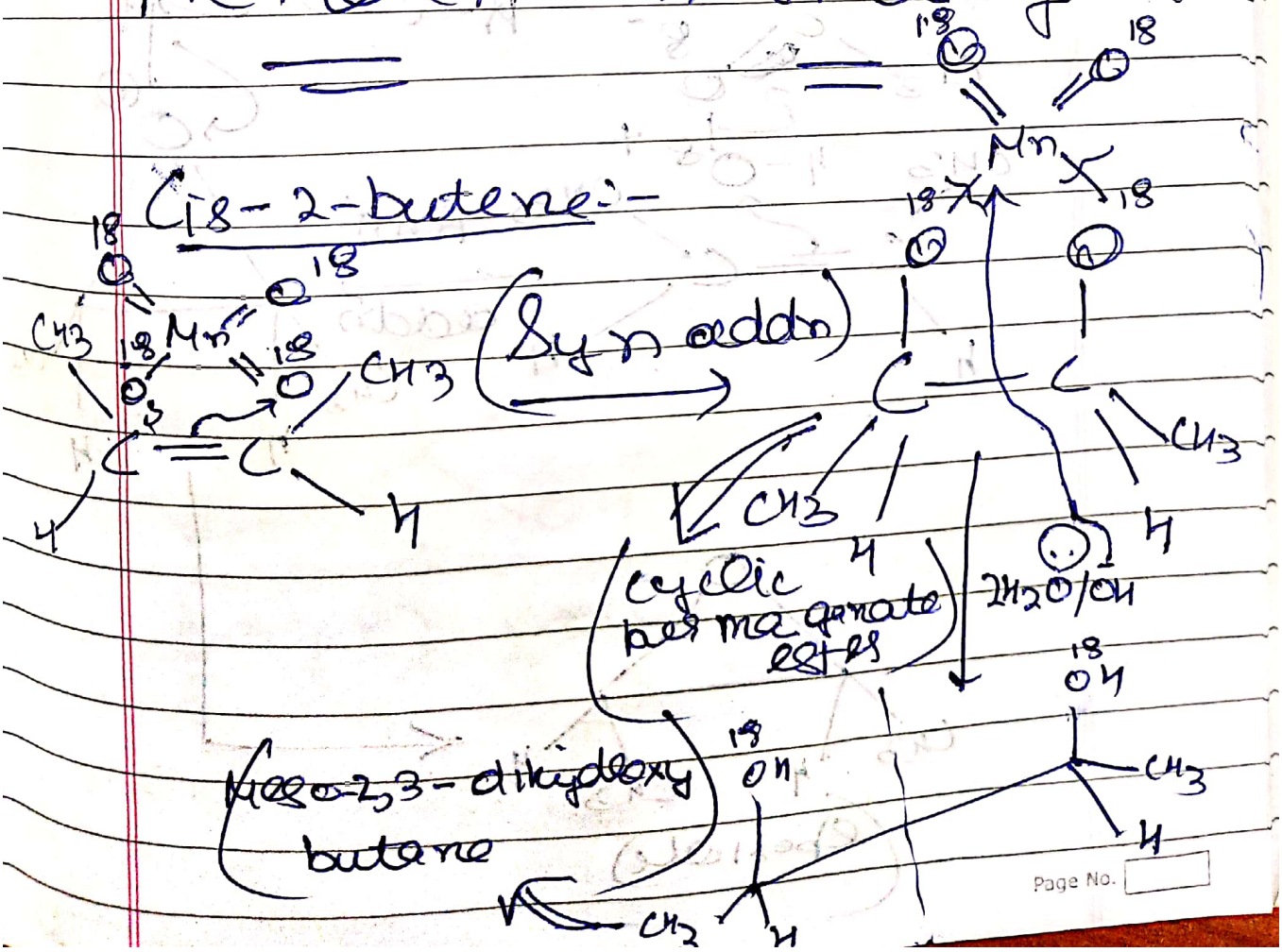
⑥ Maleic acid

Maleic acid (cis) $\xrightarrow{OsO_4/H_2O_2}$ meso

Fumaric acid $\xrightarrow{OsO_4/H_2O_2}$ threo

Cis-Hydroxylation Using Alkaline Permanganate

Cis-2-butene:-



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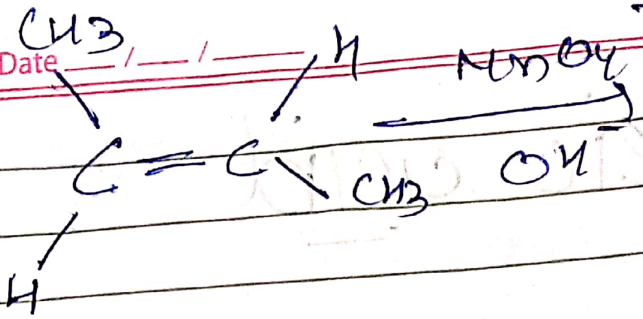
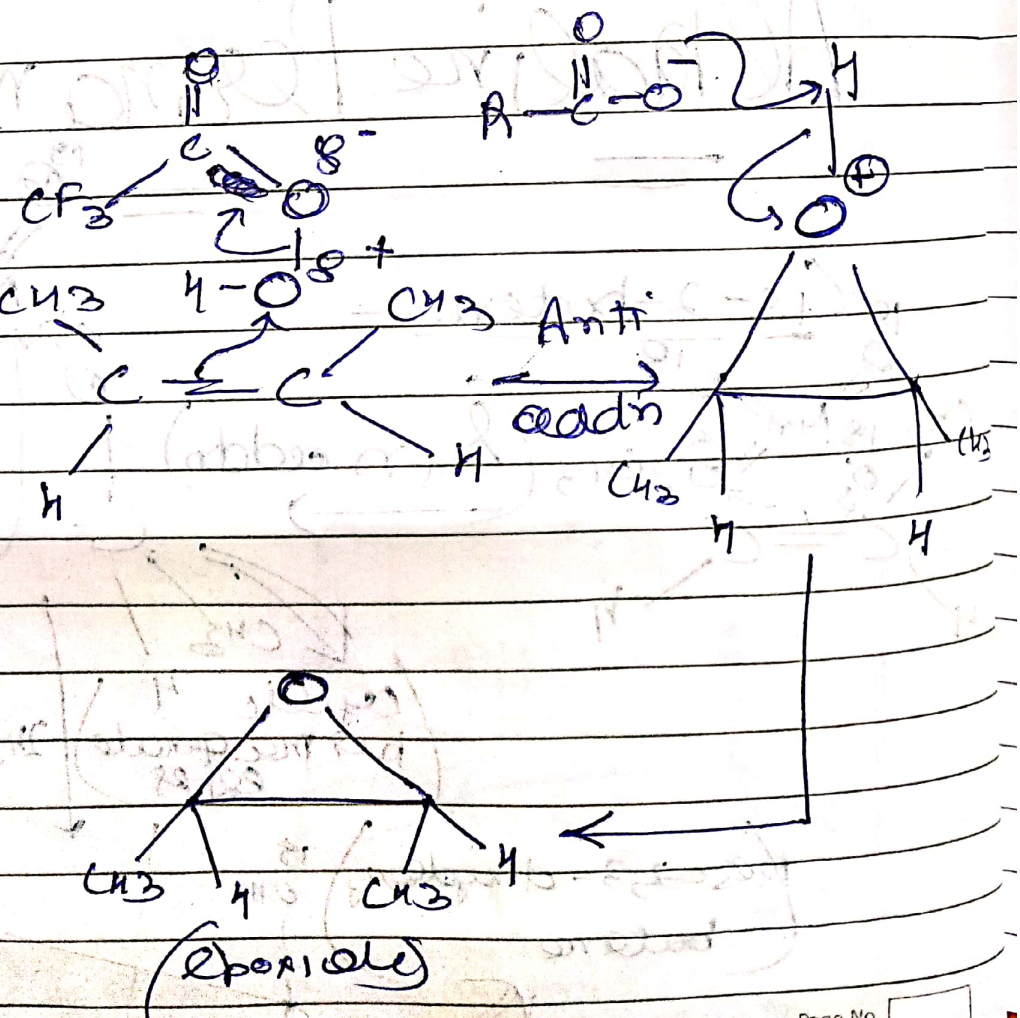


Disadvantage

(i) Highly oxidising in nature, hence there is chance of product getting oxidised

Trans Hydroxylation

Using Peroxy Acid



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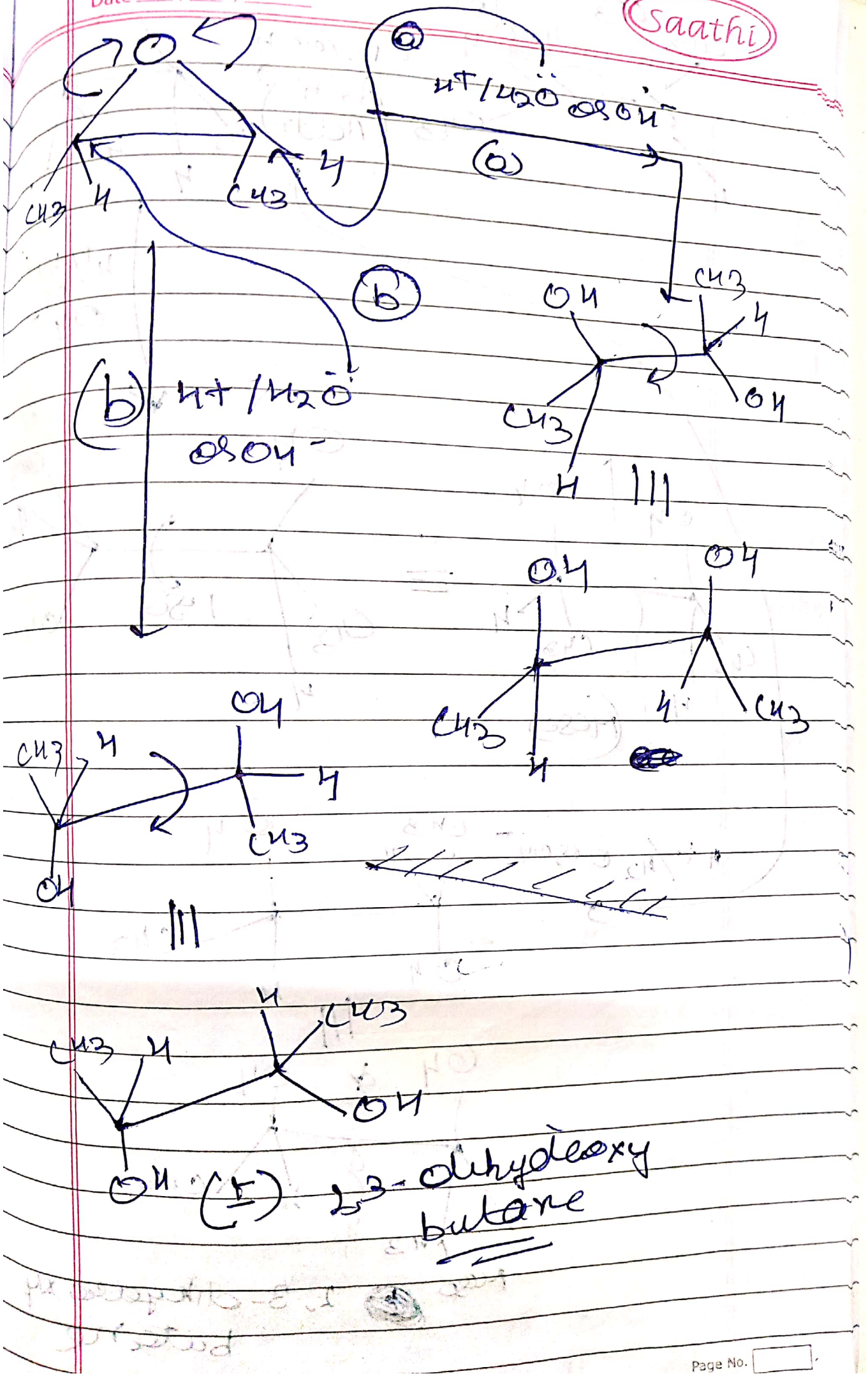
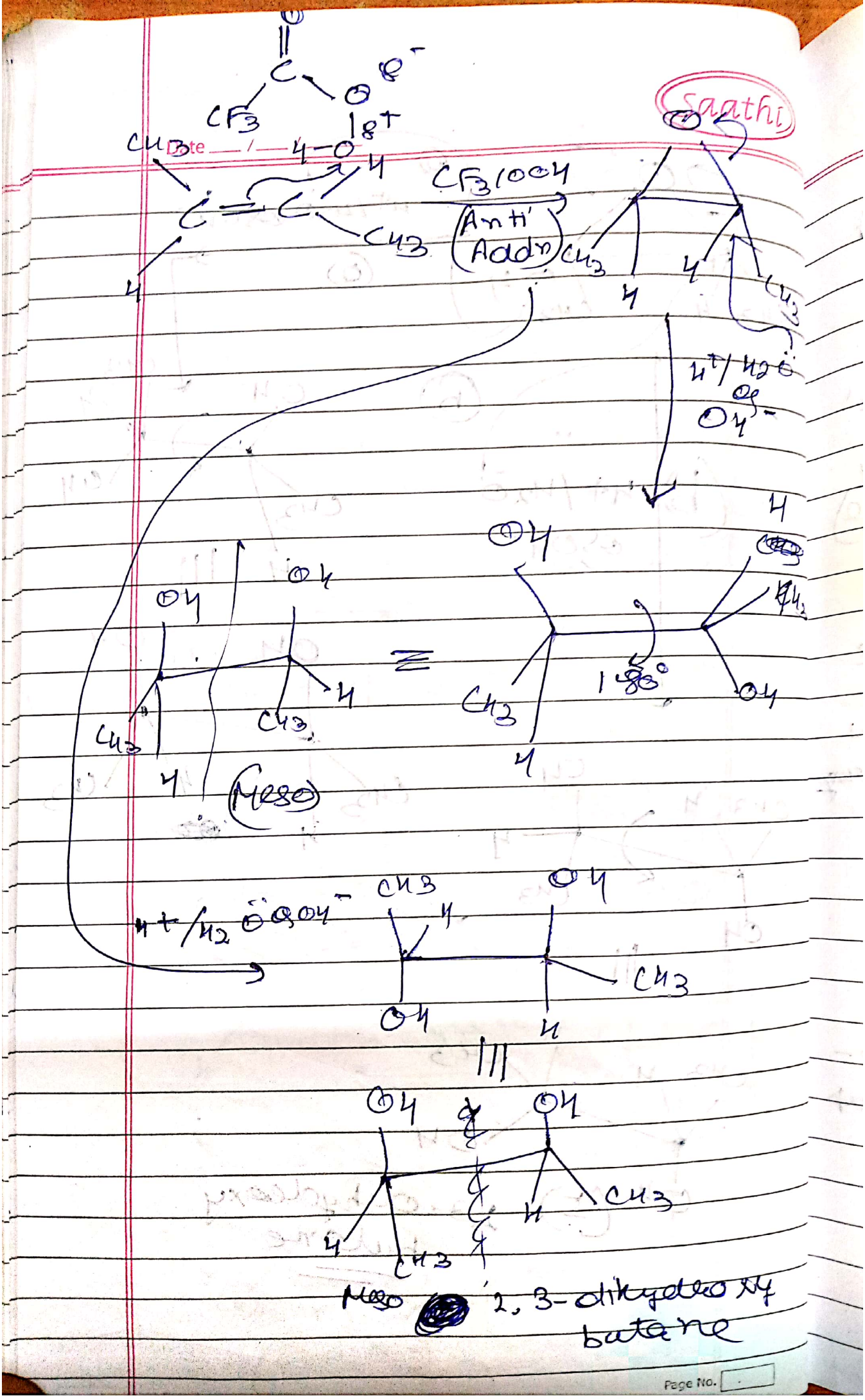
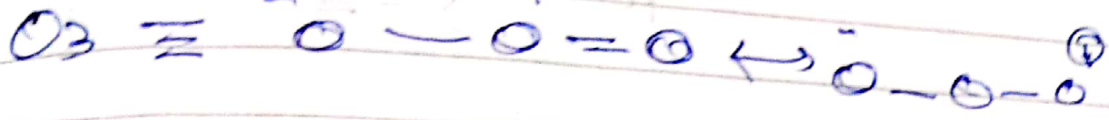
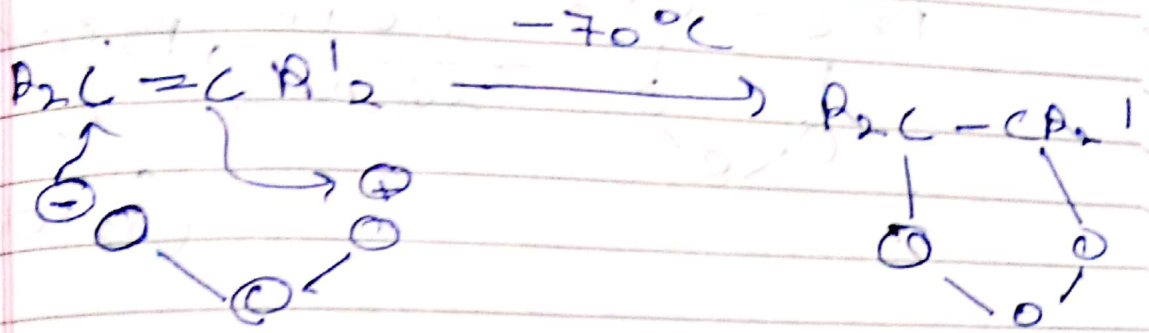
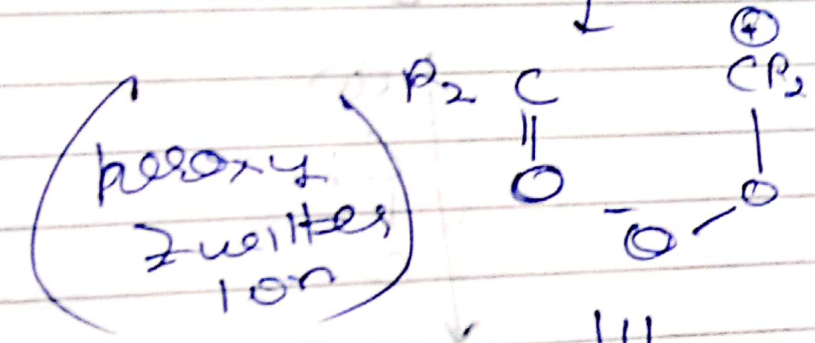


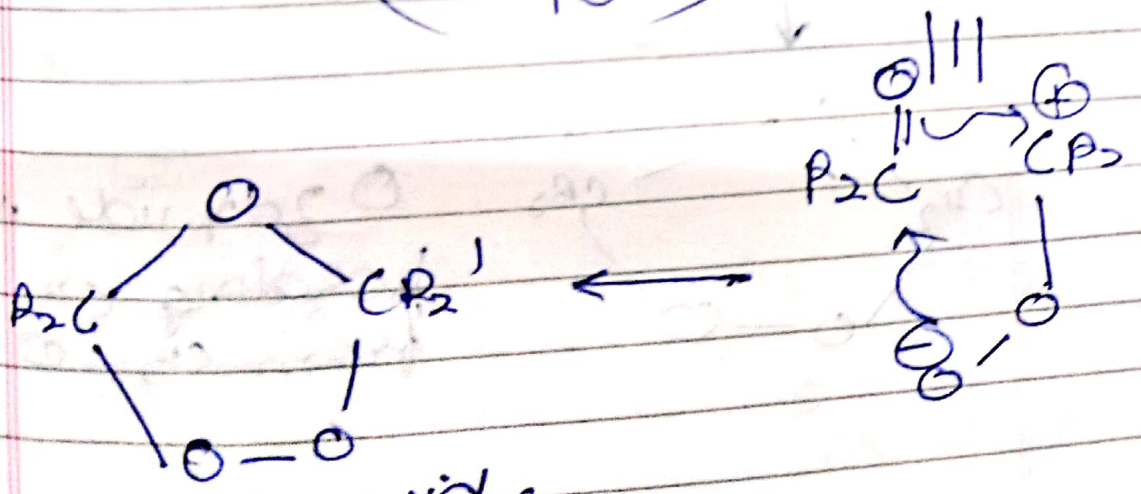

Saathi
Anti Addn
(Meso)
≡
Meso 2,3-dihydroxy butane

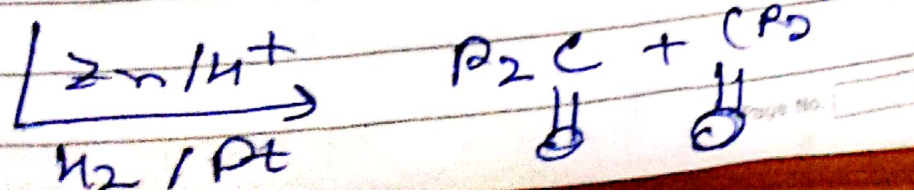
Ozonolysis Rxn











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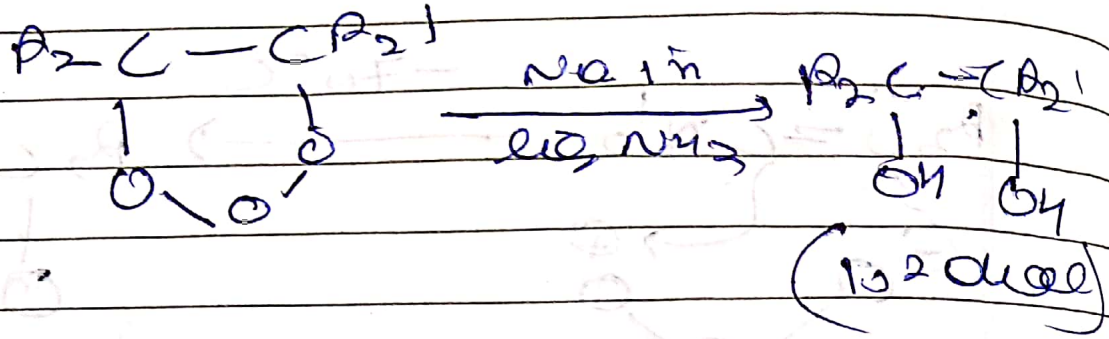
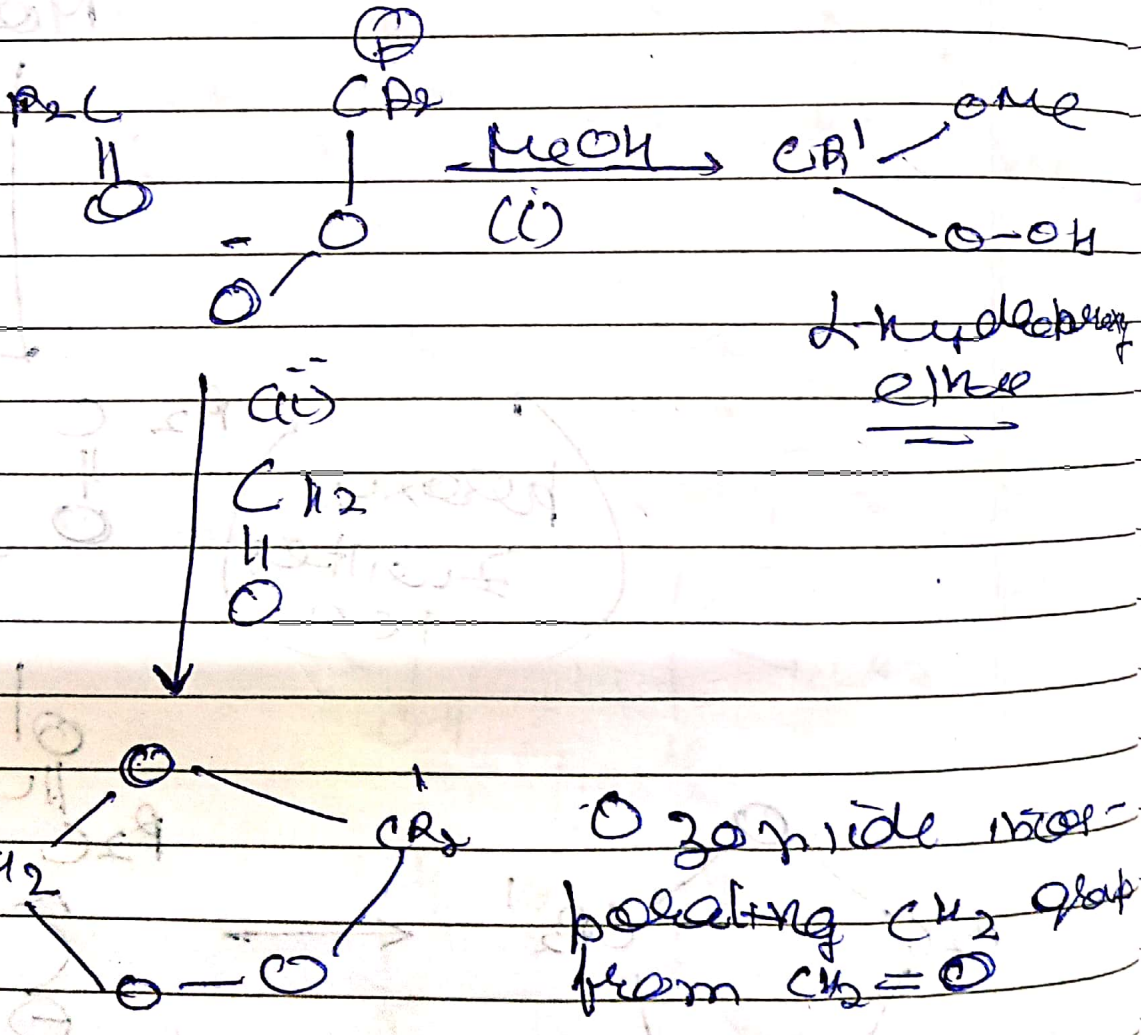
Date ___/___/_____

Experimental evidence behind molozonide & peroxy zwitter ion





Date ___/___/___

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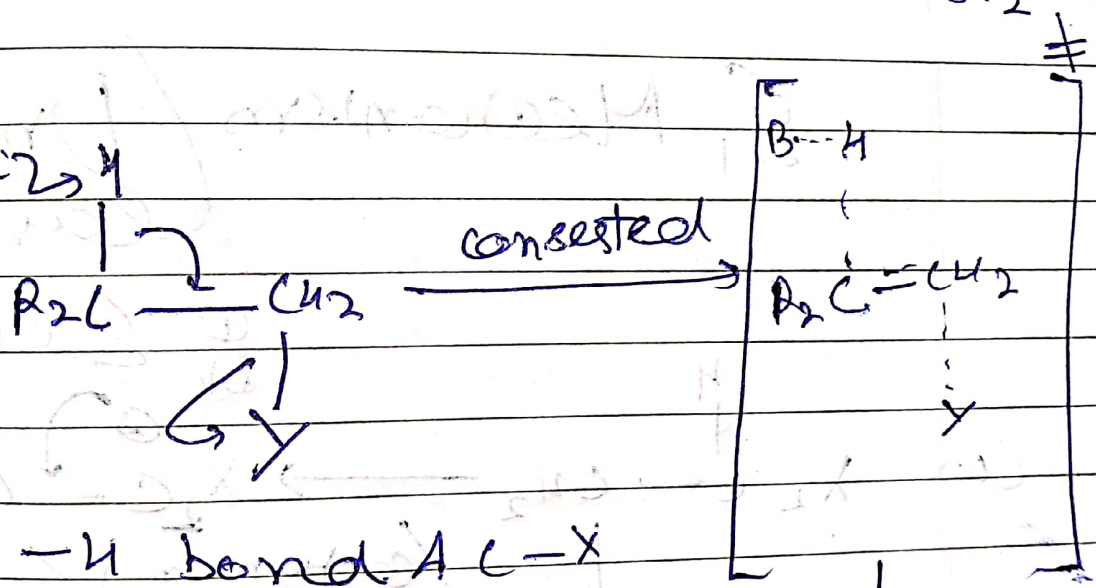
Elimination Rxns

(i) $R CH_2 CH_2 Br \xrightarrow[-OH]{Base} R CH = CH_2$

(ii) $R CH_2 CH_2 - OH \xrightarrow{H^+} R CH = CH_2$

(iii) $R CH_2 CH_2 \overset{\oplus}{N} Me_3 \; \bar{O}H \longrightarrow R CH = CH_2$

(iv) 

C–H bond & C–X bond breaking happens simultaneously

E2 mechanism
(Elimination Bimolecular)

$R_2C=CH_2 + \overset{\oplus}{B}H + Y^-$

(ii) CH_2-CR_2 (H, Y) $\longrightarrow$ CH_2-CR_2 ($B{:}\rightarrow H$, $\oplus$) + Y^-

$C^{\oplus}$ intermediate

$H_2C=CR_2$ + $\overset{\oplus}{B}H$ + Y^-

C-Y bond breaks before C-H bond

E_1 Mechanism (Unimolecular)

(iii) $X_2C(H)-CH_2Y$ $\longrightarrow$ $X_2C^{\oplus}-CH_2Y$ (carbanion intermediate)

$\overset{\oplus}{B}H$ Eliminate

$X_2C=CH_2$ + $\overset{\oplus}{B}H$ + Y^-

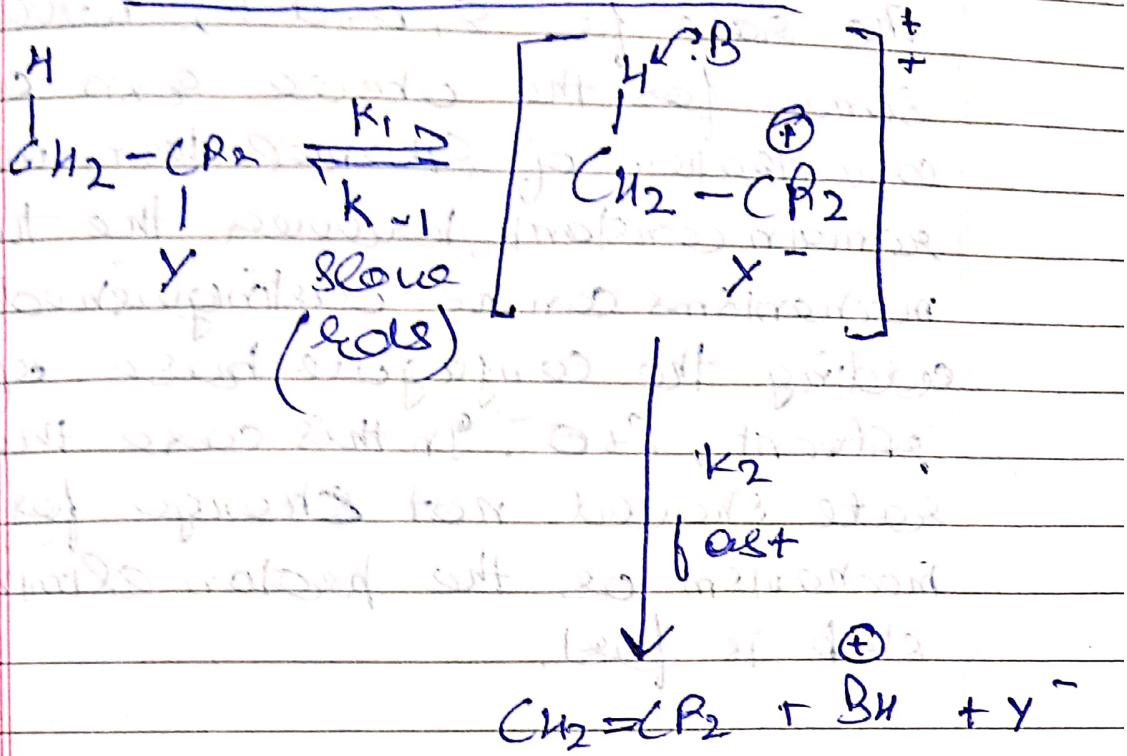
C-H bond breaks before C-Y bond

E1cb mechanism [elimination unimolecular conjugate base]

Date ___/___/___

Saathi

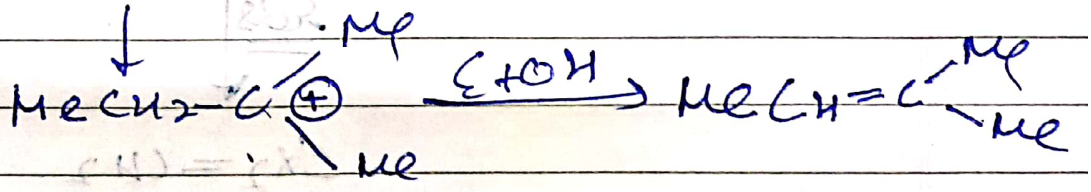
E1 Elimination



E1 : I^st step is slow/rds
2nd " " fast
k2 > k-1

Rate = K[CH3 – CR2X]
↳ I^st eqn

Me CH2 – CMe2Br



Rate = K[Me CH2 CMe2Br][EtOH]

E2 ↑ eq

Rate = K[Me CH2 CMe2Br]
↓ E1

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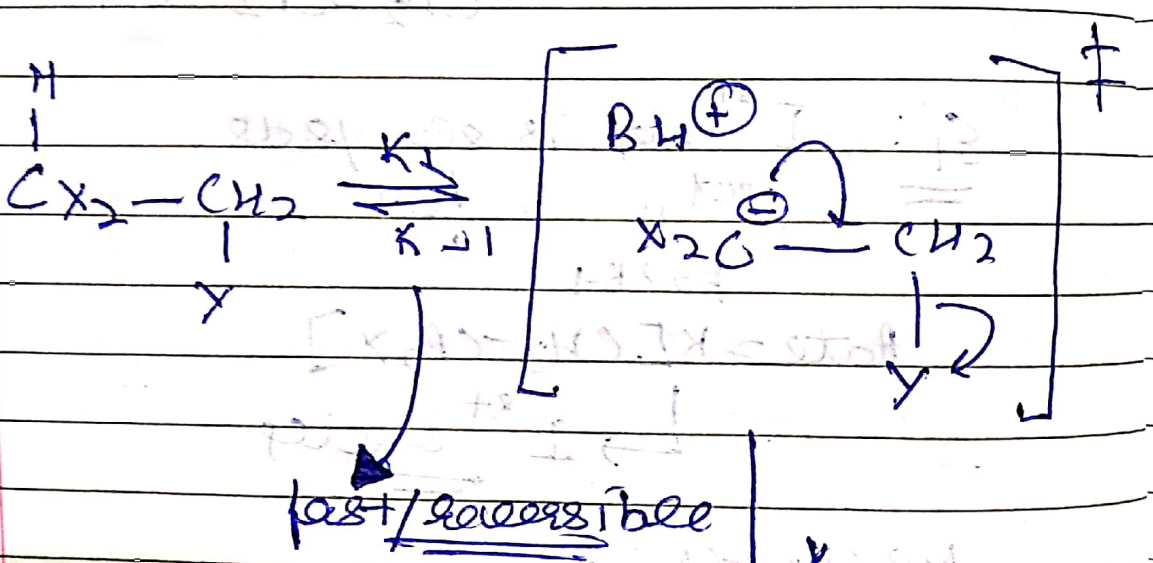
Discrimination b/w E_1 and E_2

The rate for E_1 and E_2 will be same for the above rxn as the concentration of Ethanol term will remain constant, however the two mechanisms can be distinguished by adding the conjugate base of the solvent, EtO^-. In this case the rate should not change for E_1 mechanism as the proton elimination step is fast.



E1cB: 1st step is fast/reversible
2nd step is slow/rds

Rate = $K[CHX_2-CH_2Y][B]$

Differentiated from E_2 by primary proton is absent

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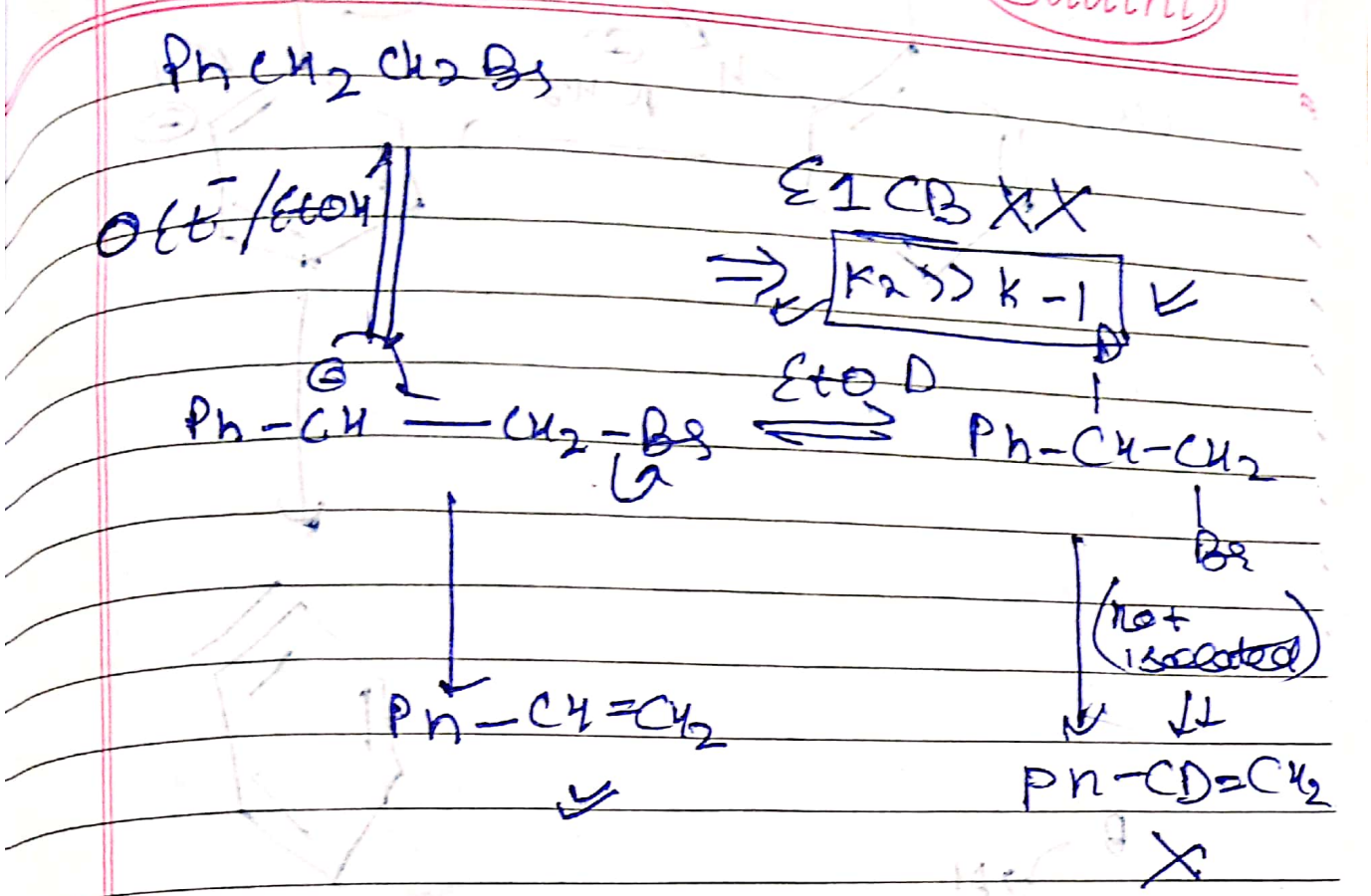


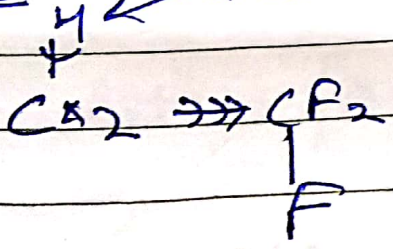
E1cb

(i) presence of EW groups at β-carbon makes the β-H acidic

(ii) stabilization of the -ve charge

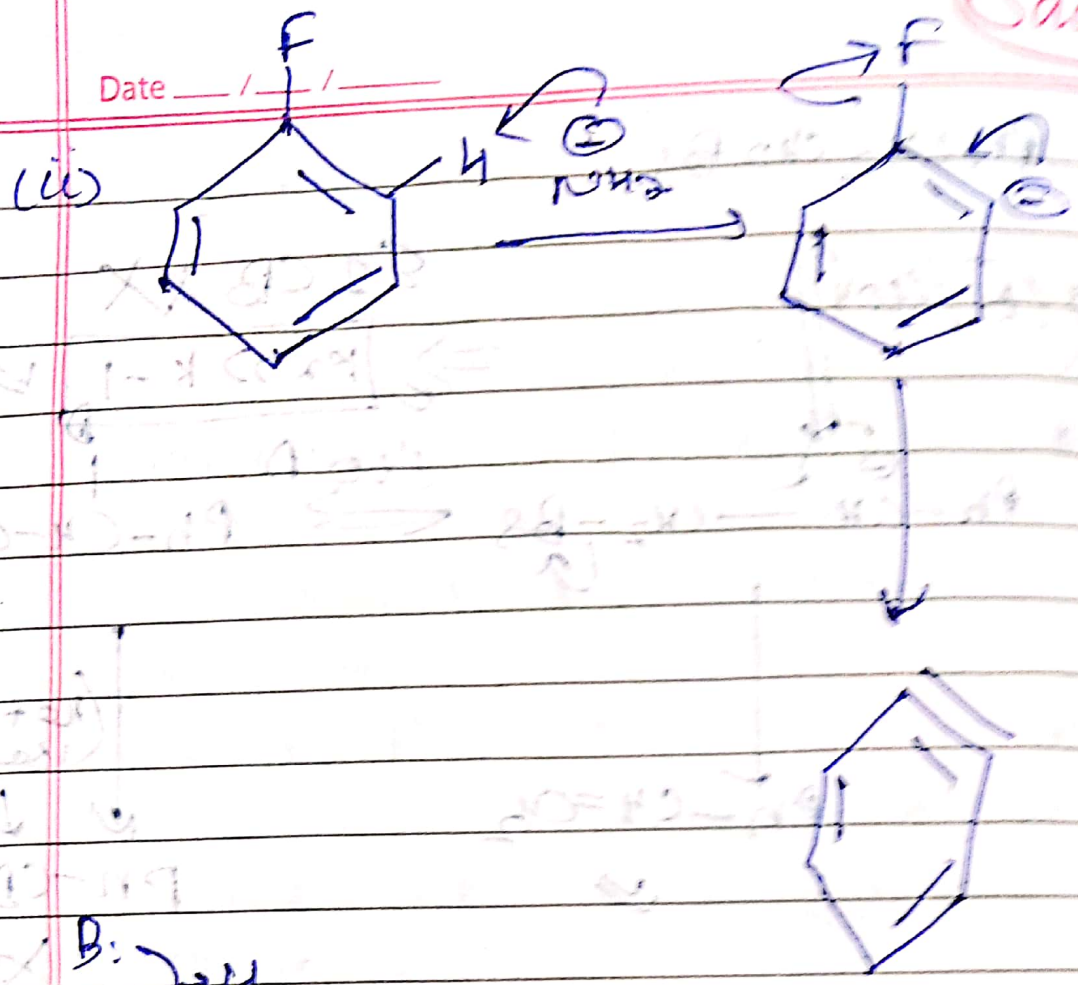
(iii) L.G. Ability of Y should be less.

Examples



X = halogens

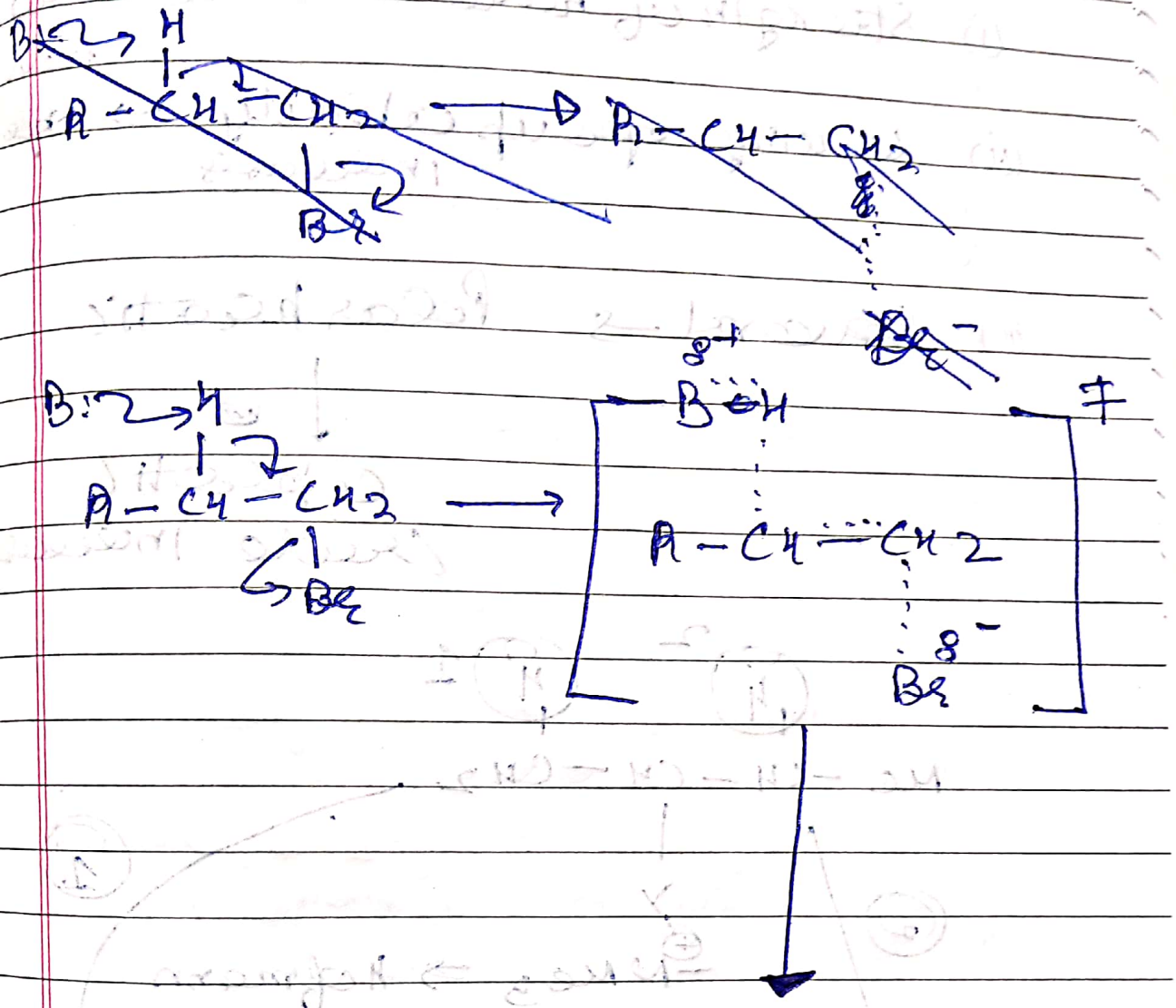
Date ___ / ___ / ___



Date ___/___/_____

Saathi

E2 Elimination



$$R-CH=CH_2 + BH + Y^{\ominus}$$

$$\text{Rate} = [RCH_2CH_2Br][B^-]$$

Exp. evidence: Primary Kinetic isotopic effect.

Date __/__/____

Factors:-

(i) Strength of base increase → rate increase

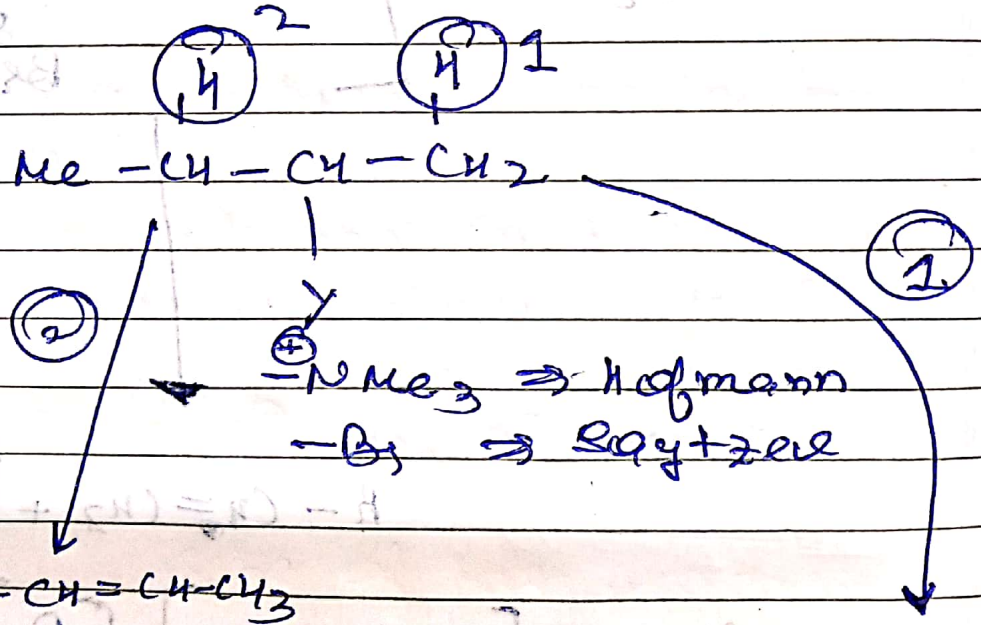
(ii) leaving group ability → increases

(iii) Solvent → Polar protic

↓

Aprotic

(rate increases)



(i) Alkene with more substitution

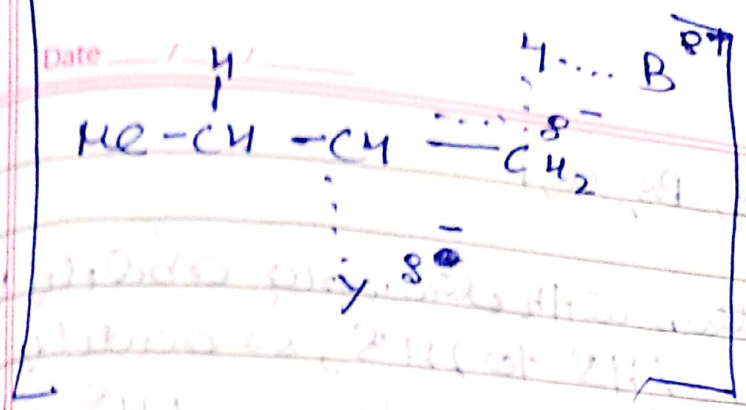
(ii) Br is a good L.G.

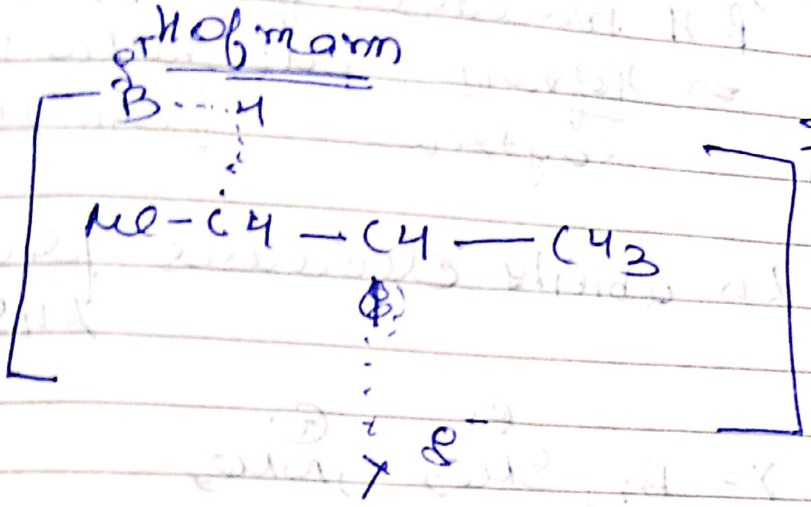
(iii) Syn mech. can go via alkene like transition state

(i) Alkene with less

(ii) Carbanion like transition state

(iii) leaving group is highly Ek in nature.



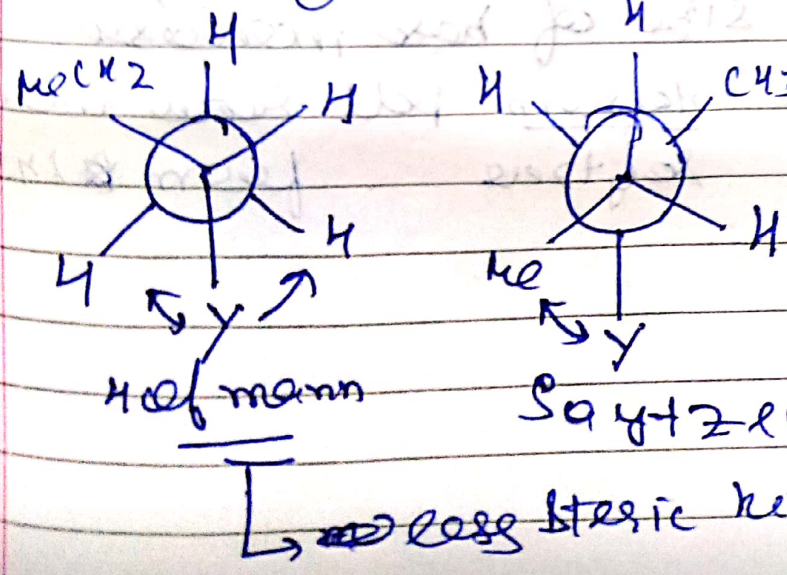


Saytzeve

(i) Increase size of base :→

Hofmann/Saytzeve pdt ratio increases

(ii) If size of L.G. ↑ H/S pdt. ratio increases



Hofmann

Saytzeve

↳ less steric hindrance

Date ___/___/___

(iii) $Y = I, Br, Cl, F$

(i) Electron withdrawing ability increases from 1° to 3°, so acidity of β-H increases from $1^\circ \rightarrow 2^\circ \rightarrow 3^\circ$

$\Rightarrow$ Hofmann pdt. ratio increases from $1^\circ \rightarrow 2^\circ \rightarrow 3^\circ$
Saytzeff

L.G. ability decreases from 1° to 2° to 3°

(iv) $Y = Br, \overset{\oplus}{S}Me_2, \overset{+}{N}Me_3$

E.W. ability increases from 1° to 3°

So, Hofmann / Saytzeff pdt. ratio increases from 1° to 3°.

(v) $B = Et\overset{\ominus}{O}$, $Me_3C\overset{-}{O}$, $Me_2CEt\overset{-}{O}$, $Et_3C\overset{-}{O}$

Size of base, increases

So, Hofmann pdt. ratio increases from $1^\circ \rightarrow 2^\circ \rightarrow 3^\circ$
Saytzeff

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