



CSIR-NET

Council of Scientific & Industrial Research

CHEMICAL SCIENCE

VOLUME - II

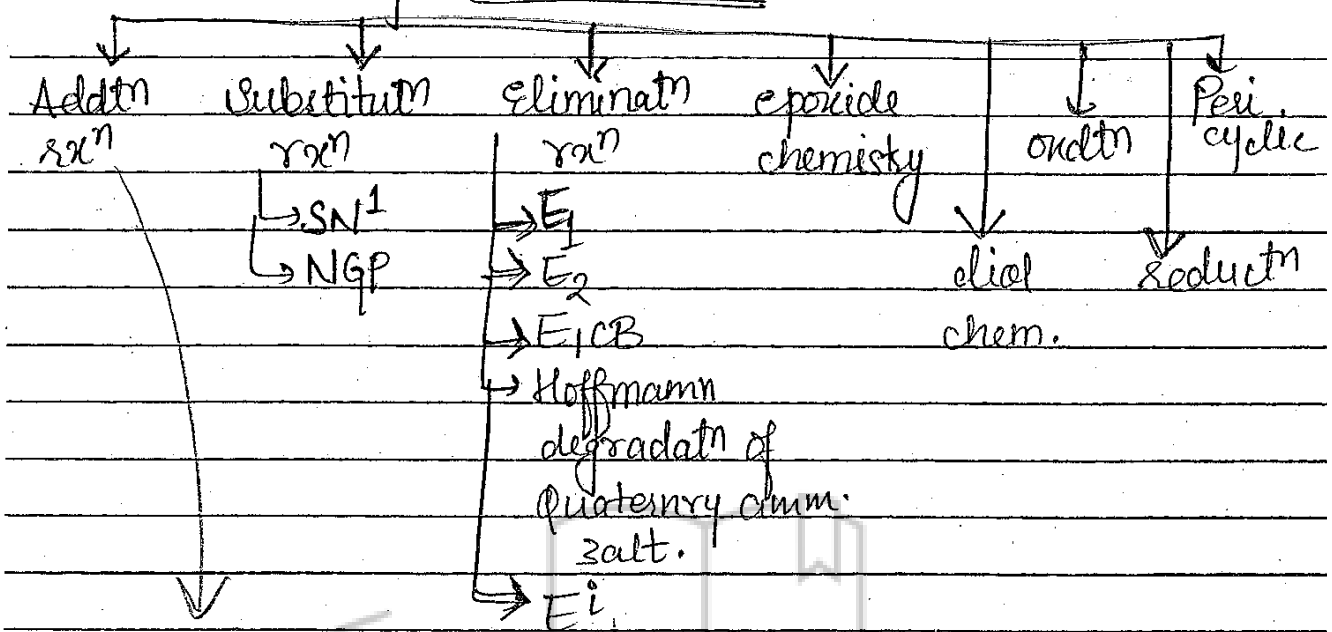
ORGANIC CHEMISTRY



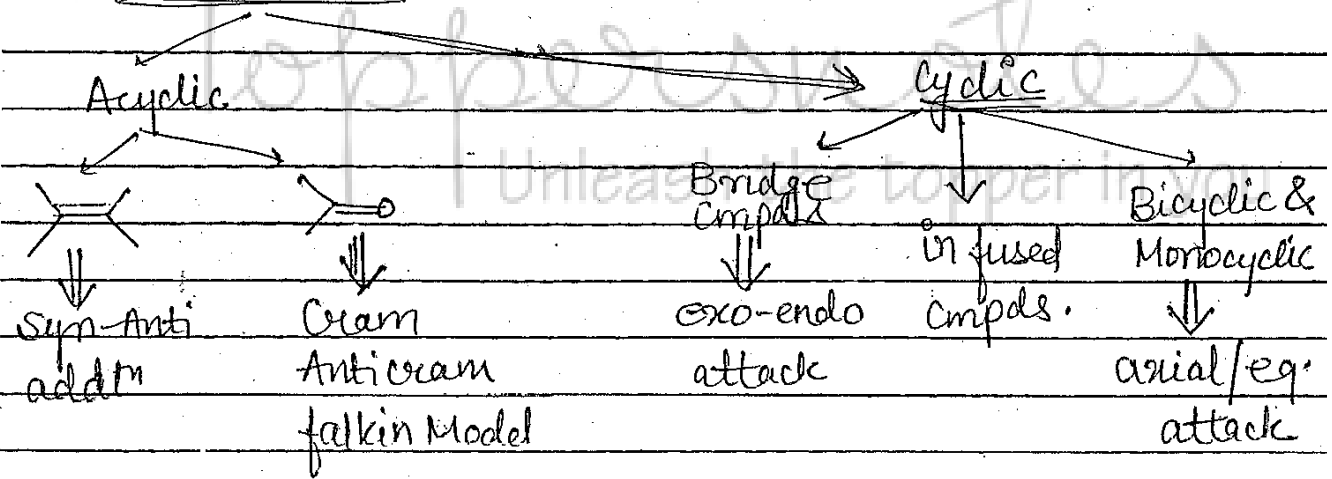
Index

(1) Dynamic stereo	1
• Addition reaction	1
• Elimination reaction	66
• Epoxide chemistry	109
• Diol chemistry	135
• Oxidants	163
• Reduction	178
(2) LDA(Lithium Di isopropyl amide)	220
(3) Fragmentation	243
(4) Pericyclic Rxⁿ	261
• Cyloddt ⁿ Rx ⁿ	263
• Claisen Rearrangement	284
(5) Group transfer Reaction	297
(6) Torque selectivity	313
(7) Aromaticity	334
• High degree of stability	335
• Relative Stability	347
• Quasi aromatic compound	353
• Annelation effect	361

Dynamic Stereo



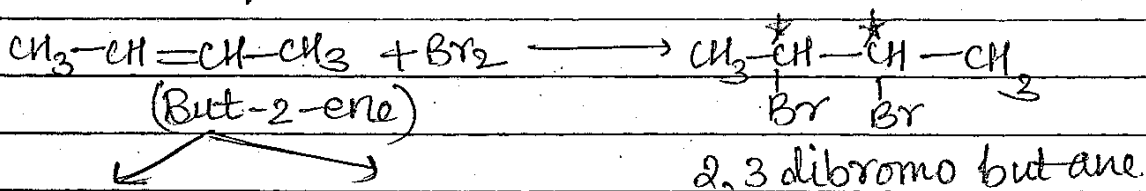
Addition Rxn



Stereochem. of Addition Rxn :-

Addition in Acyclic system :

• Addition on C=C



Cis
Trans
Meso
Threo

stereoselective \rightarrow cost lobes & crowding (wedge, dash)

\rightarrow the stereochem. diff. reactant, react differently & gives stereochemically diff prod. It is k/o stereospecific rxⁿ. (In the sense of reactants).

\rightarrow In the sense of prod, if only one stereo-isomer is formed as product in the rxⁿ, then rxⁿ k/o stereospecific rxⁿ. (prod $\hat{=}$ sense $\hat{=}$)

\Rightarrow 100% stereo selective

\rightarrow If during the rxⁿ more than 1 type of stereo-isomers are formed in unequal amount then, rxⁿ k/o stereoselective rxⁿ.

Reactant \rightarrow A + B

		Stereo isomers obtain in unequal amount.		
Stereo selective Rx ^{ns} :		80%	20%	} stereo selective reactant.
		60%	40%	
		10%	90%	
Enantio selective	Diastereo selective	25%	25%	
\downarrow	\downarrow	(50%)	(50%)	
one of the enantiomers is formed as major prod.	one of the diastereomer is formed as major prod.	when prod obtained in equal amount		then stereoselective word is rarely used.

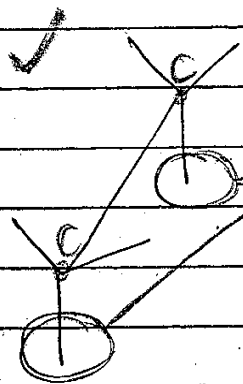
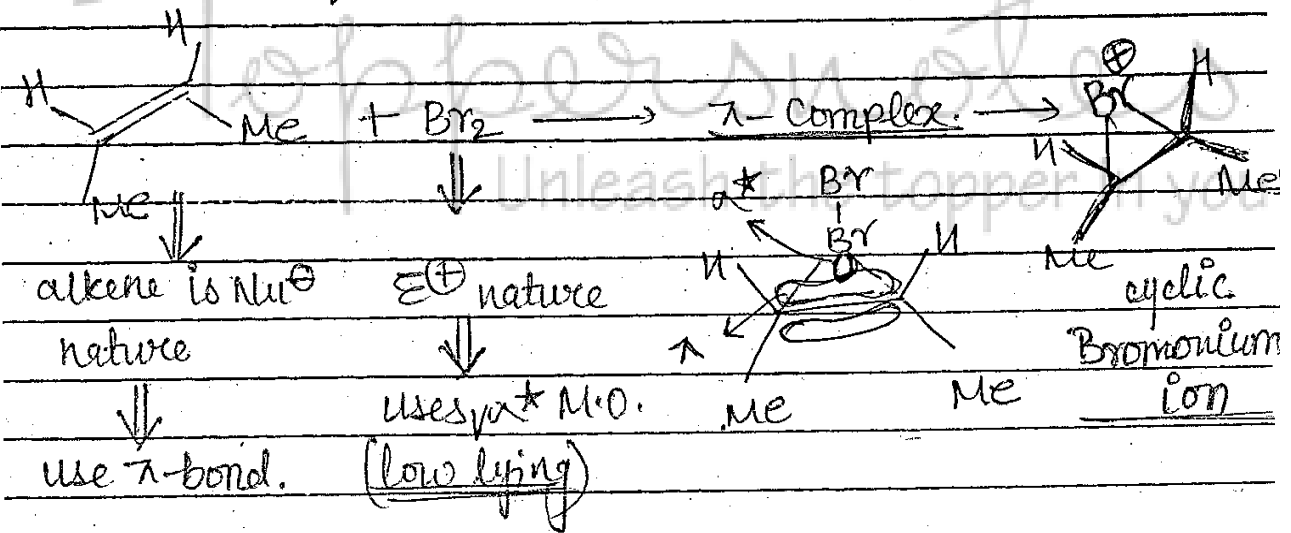
Enantiospecific Rxⁿ:-
(100% enantio selective)

→ If during the rxⁿ only one enantiomer is formed then it is k/o enantiospecific rxⁿ.

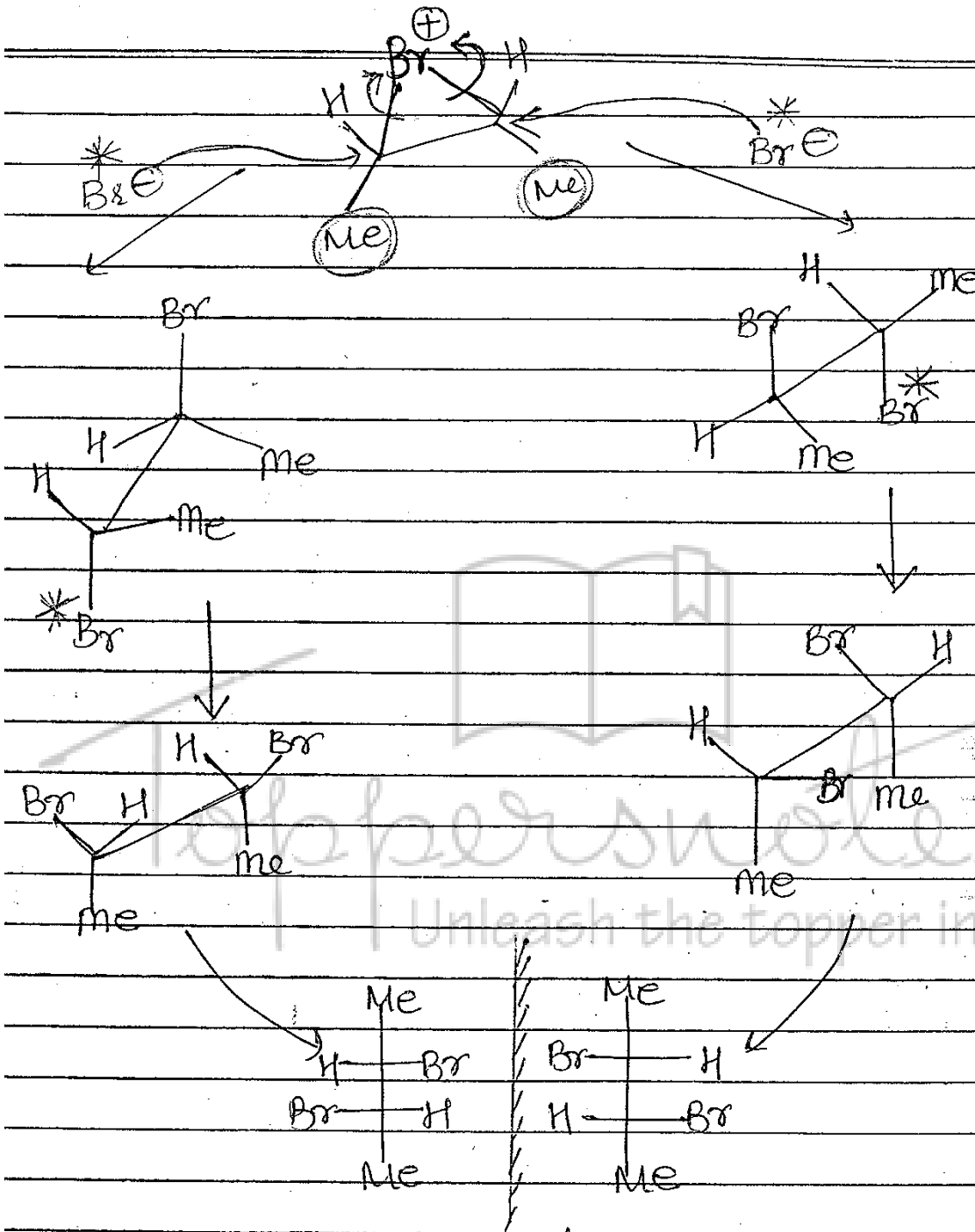
Diastereospecific rxⁿ:-
(100% diastereoselective)

→ If during the rxⁿ, only one diastereomer is formed as product then rxⁿ is diastereospecific

Case I Rxⁿ of cis-2-butene with Bromine:



जब दोनों carbon पे जोर same हो तब इस position पे वो likhe jate है जिसे हम principal chain दिखाई दे।
जब दोनों C पे सब grp alg हो तब इस position पे ऊँचे रखते है जो आपस में alg हो।



Three; pair of enantiomers
 Racemic mixture.

Substrate
Sym

Addition
Anti^o

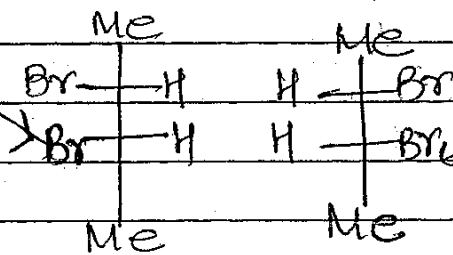
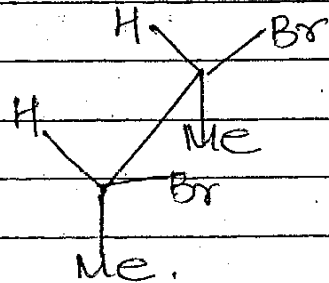
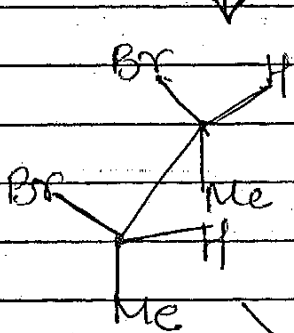
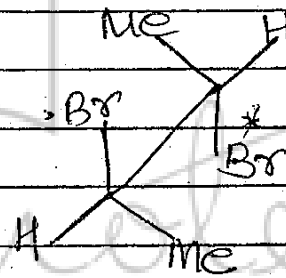
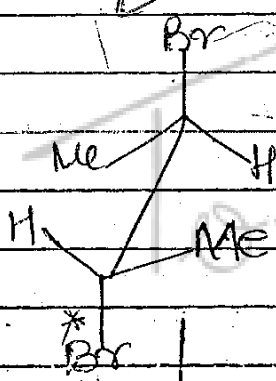
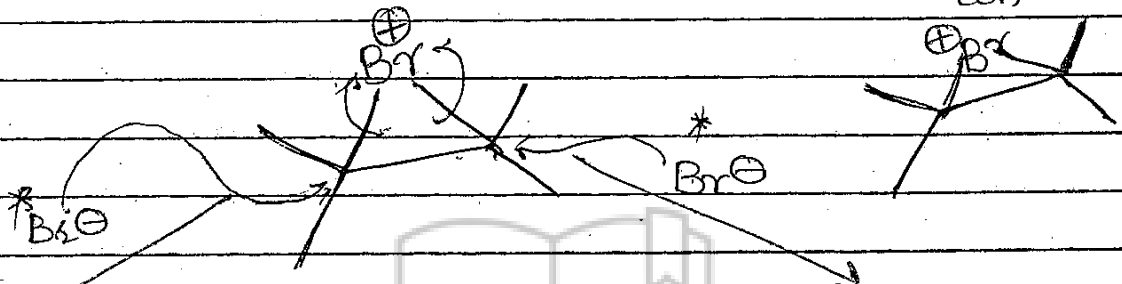
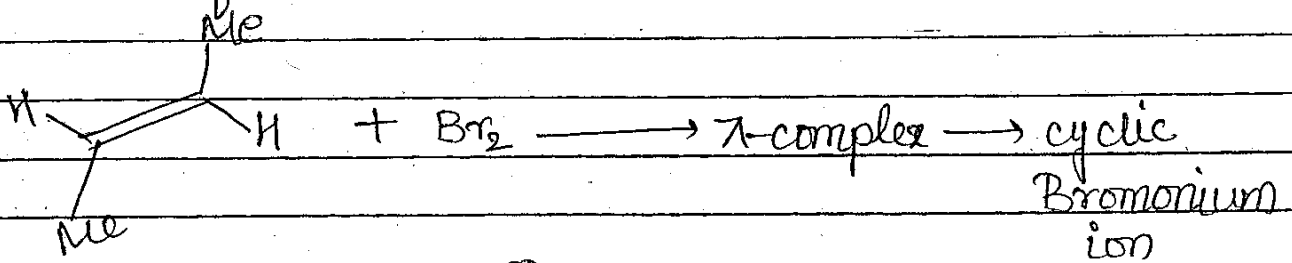
Product.

Three always
 Pair of enantiomers always.

↓
Racemic mixture.

Case-II

Rxnⁿ of Trans-2-butene + Bromine



same side
 erythro condition is meso

Meso

Substrate
Anti

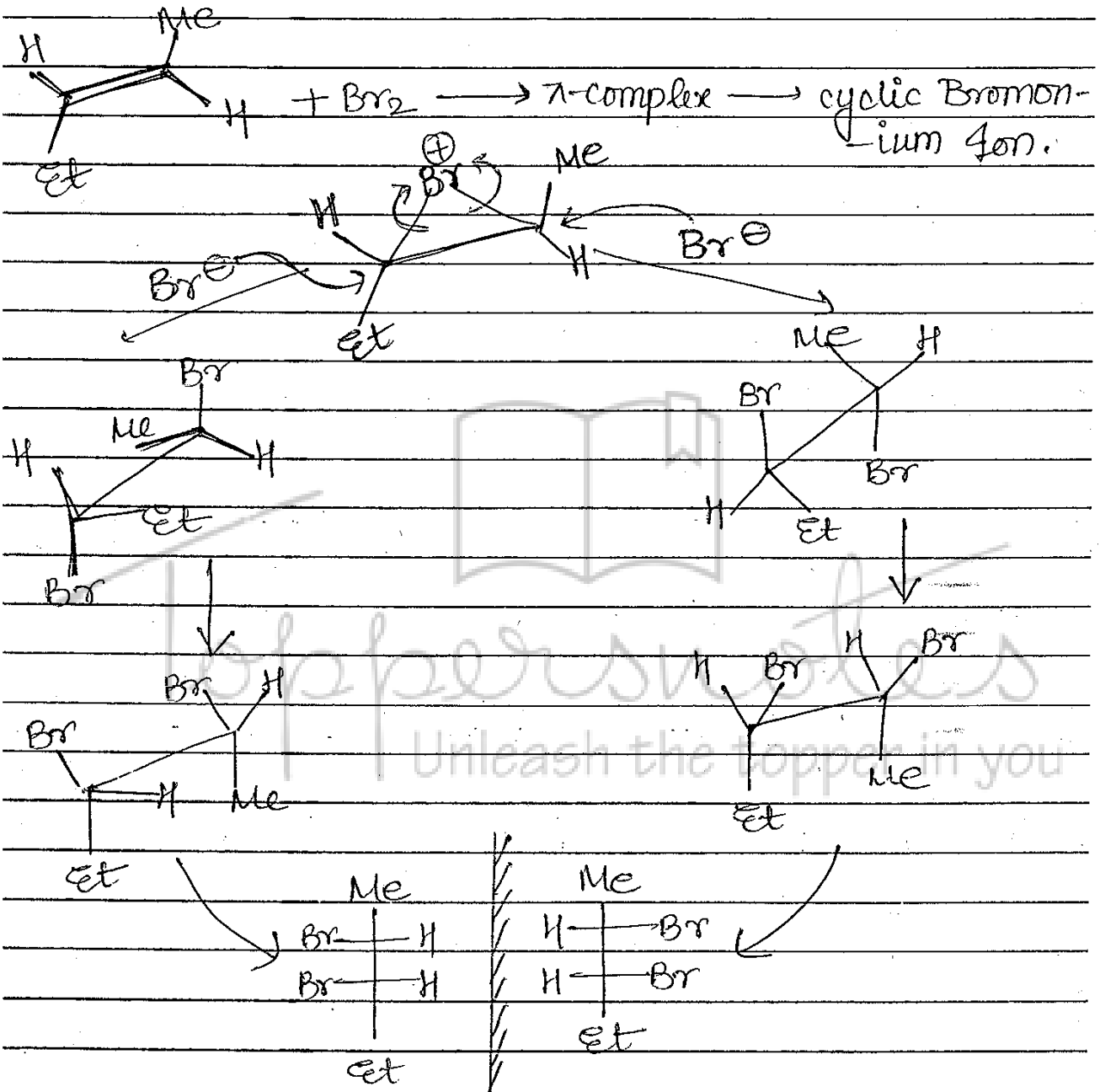
Addition
Anti

Product.

Erythro ∇ always
 Meso ∇

Case \Rightarrow III

Rxn of Trans-2-Pentene \vec{c} Br₂

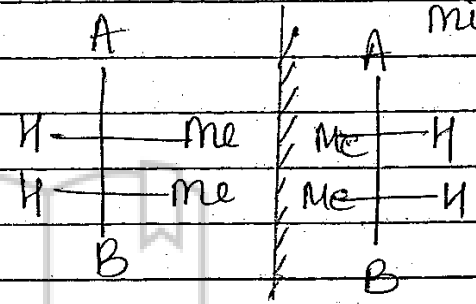
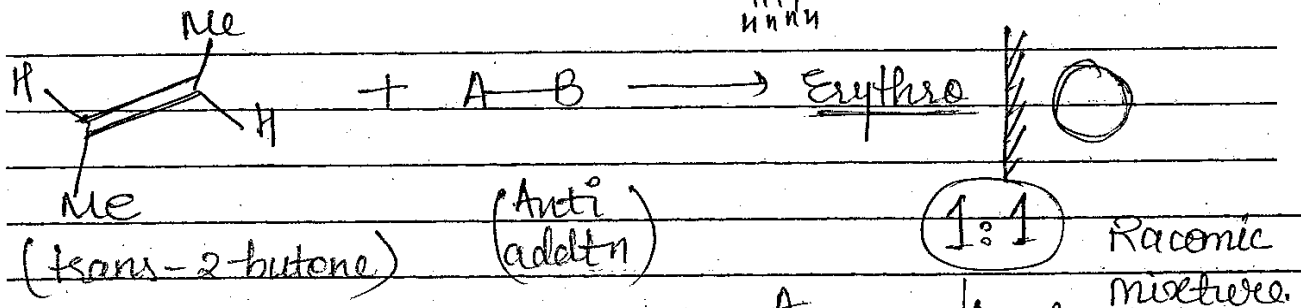


Erythro ; pair of enantio.
Racemic Mix.

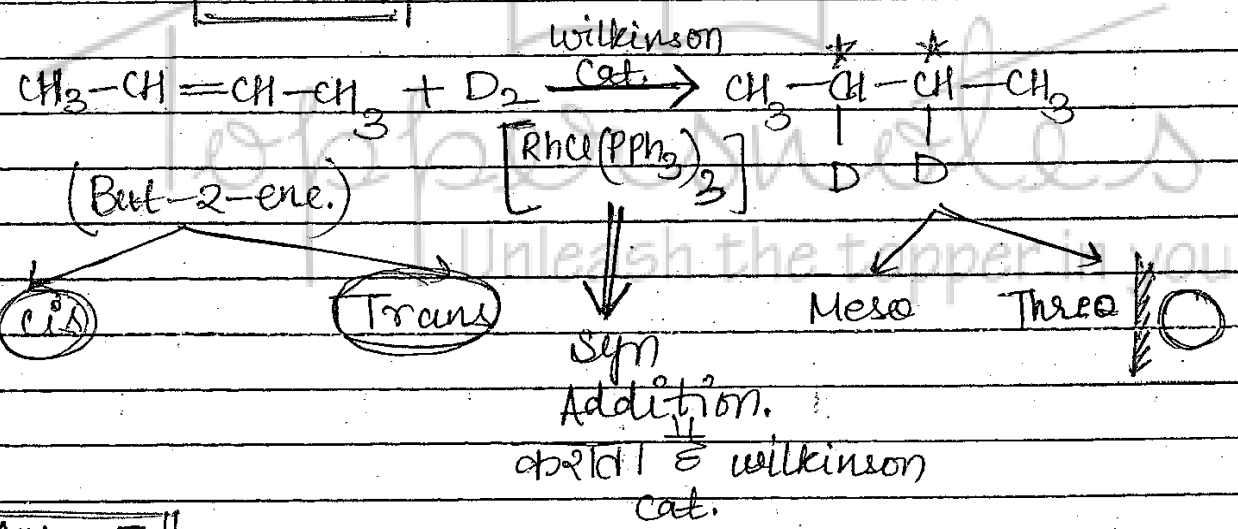
Substrate	Addn	Prod.
Anti	Anti	Erythro
		↓
		Pair of enantio.
		↓
		Racemic Mix.

दोनों side same crowding है ∴ H दोनों side से adsorb हो सकती है।

Case-4

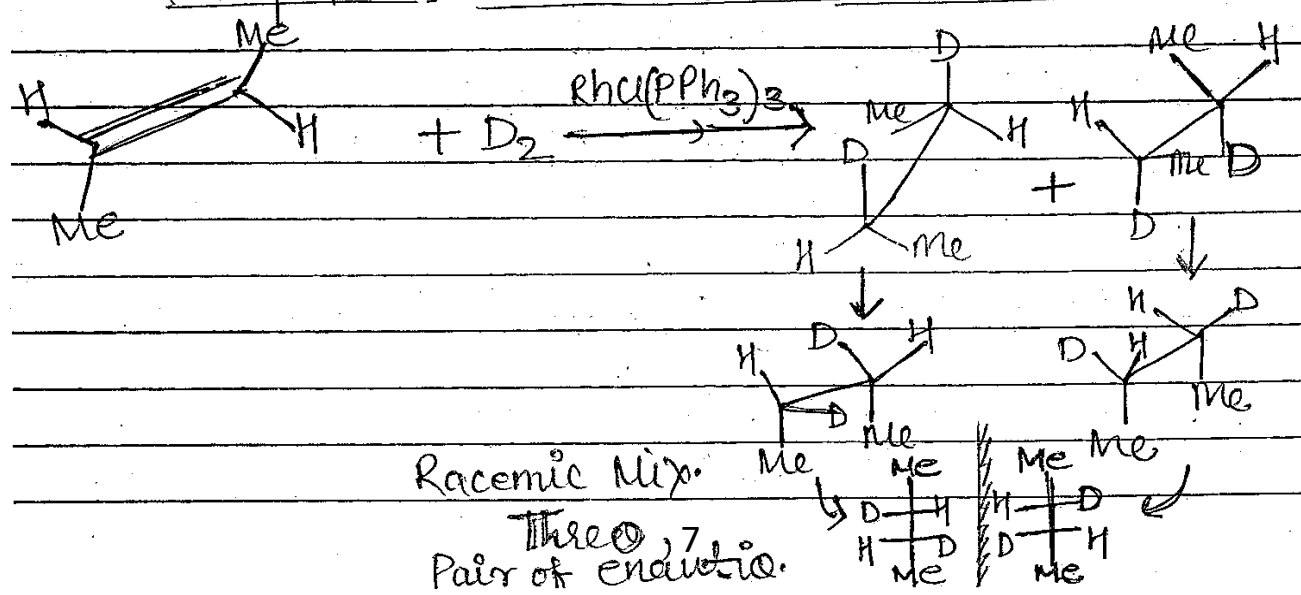


Case 5 CONCEPT



Case-5

Rxn of Trans-2-butene with Deuterium:



Substrate

Addn

Prod.

Anti

Syn

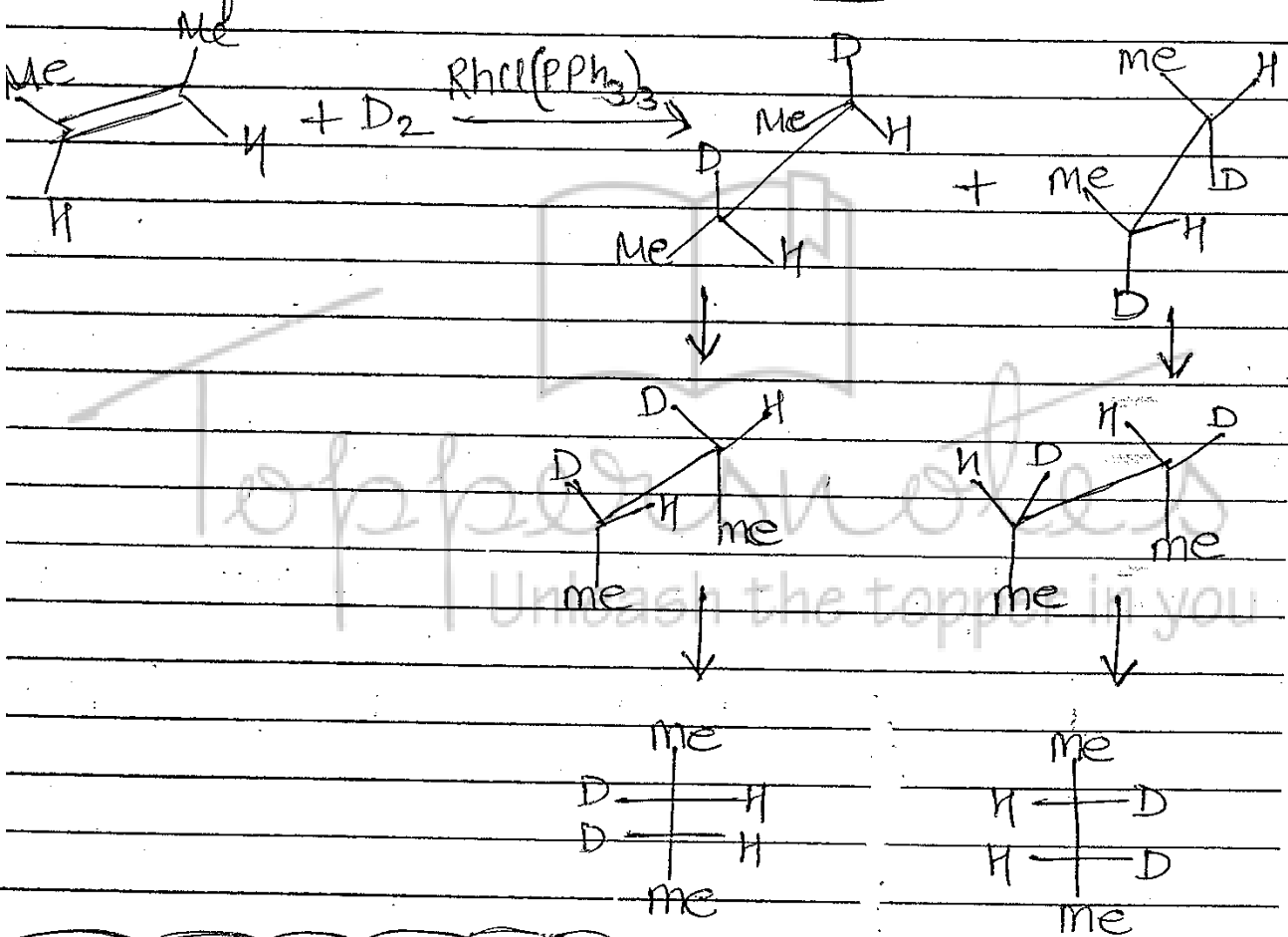
Threo

Pair of enantio.

Racemic mixture.

Case (6)

Redn of cis-2-butene + Deuterium



Substrate	Addn	Prod
Syn	Syn	erythro
		↓
		Meso.

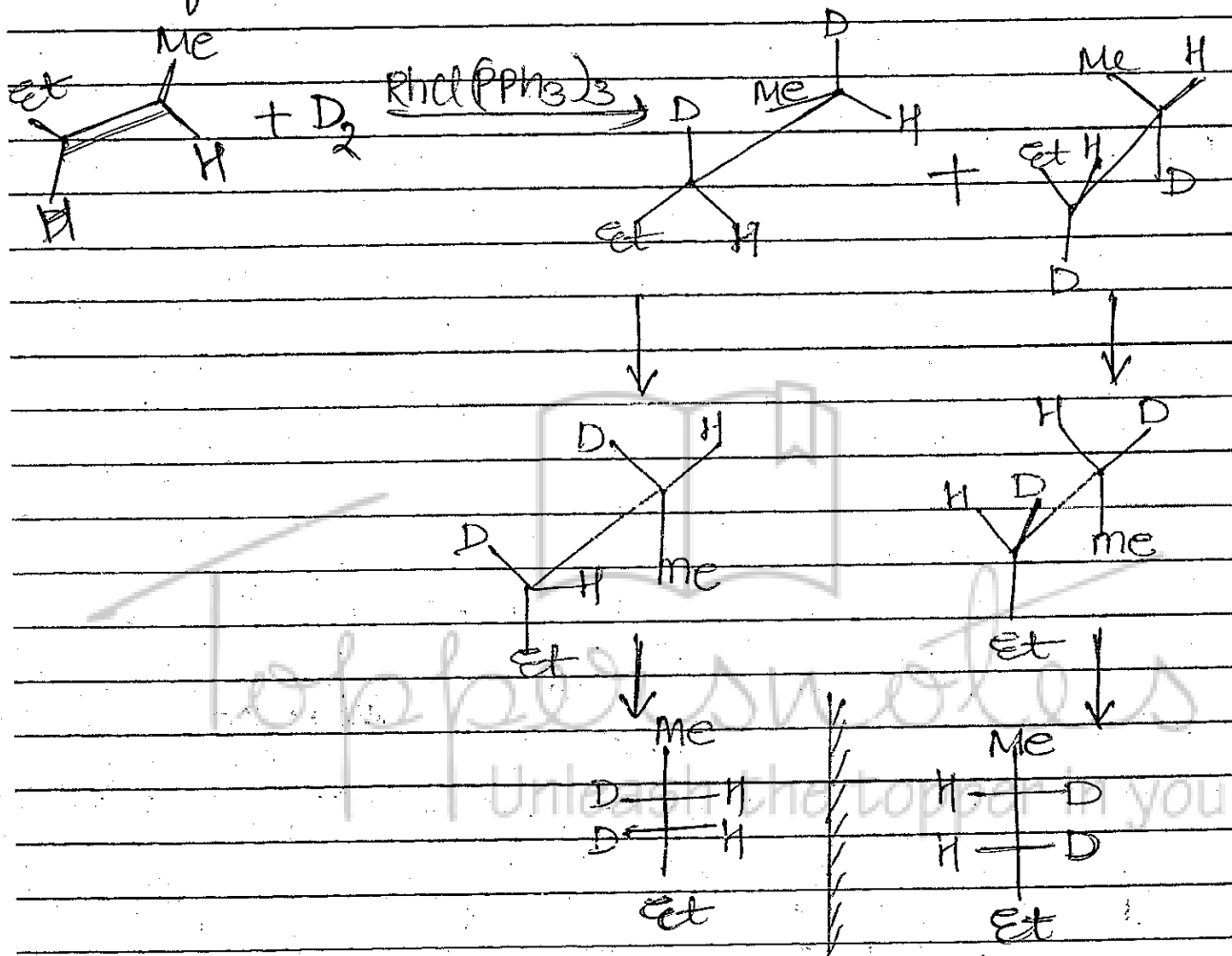
Erythro

↓

MESO

Case-7

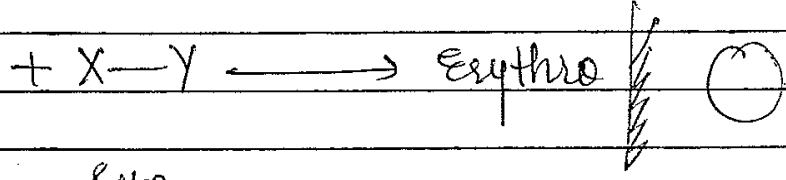
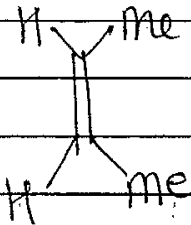
Rxn of cis-2-Pentene with Deuterium:



enythra
 Pair of enantio.
 Racemic mix.

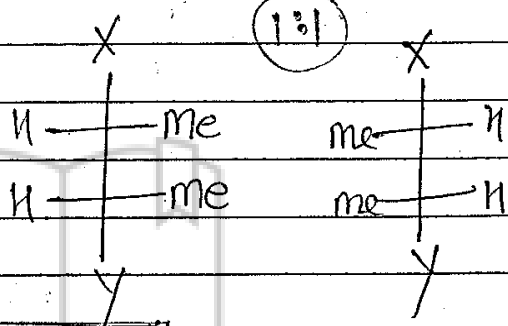
Substrate	Additn	Prod.
Syn	Syn	Enythra
		↓
		Pair of enantio
		Racemic Mix.

Case (8)



cis-but-2-ene
syn anti

Pair of enantio.
Racemic mix.



Type of Reagent

Syn-Addition

~~Anti Addition~~

- (1) $i) \text{OsO}_4$
- } 2-OH
- } supply H
- } chiral E
- (ii) NaHSO_3

- (4) Diimide reduction
- $\text{N}_2\text{H}_2 / \text{N}_2\text{D}_2 / \text{N}_2\text{T}_2$
- (5)
- $\text{N}_2\text{H}_4 + \text{H}_2\text{O}$
- $2\text{H} / 2\text{D} / 2\text{T}$

- (2) 1% alk. KMnO_4
- (Baeyer's reagent)
- 2-OH

- (5) Ni / H_2
- Pd / H_2 (2H)
- Pt / H_2

- (3) Woodward Rxn
- $\text{I}_2 / \text{AgO} / \text{COCl}_2 (\text{aq})$
- 2-OH

- (6) $[\text{RhCl}(\text{PPh}_3)_3] / \text{H}_2$
- $[\text{RhCl}(\text{PPh}_3)_3] / \text{D}_2$
- $2\text{D} / 2\text{H}$

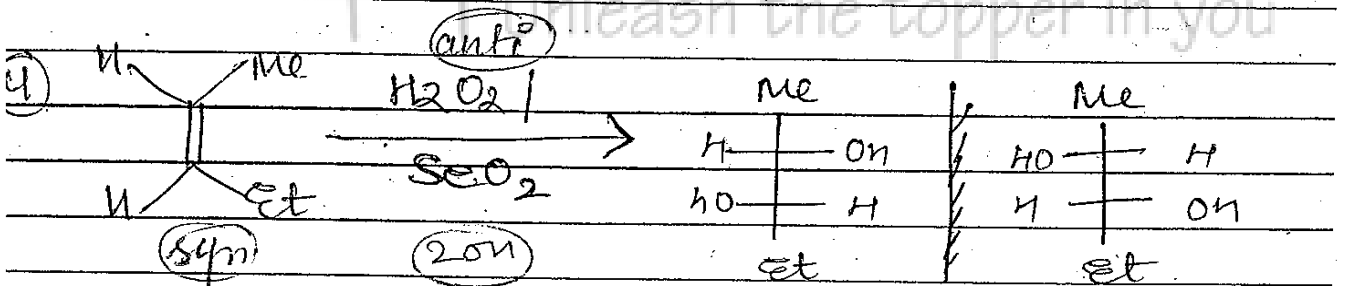
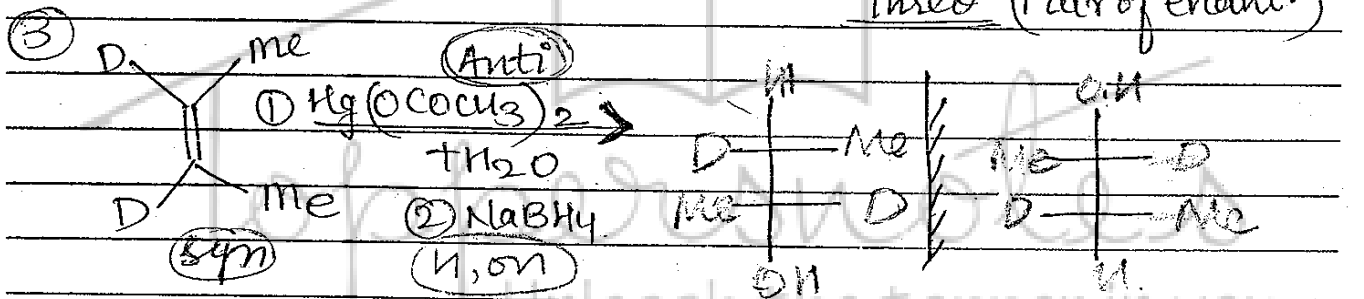
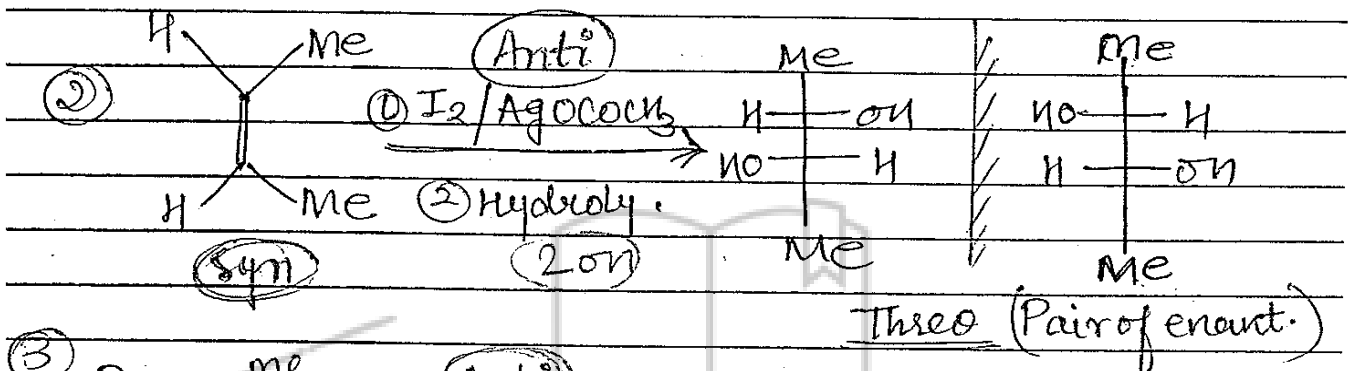
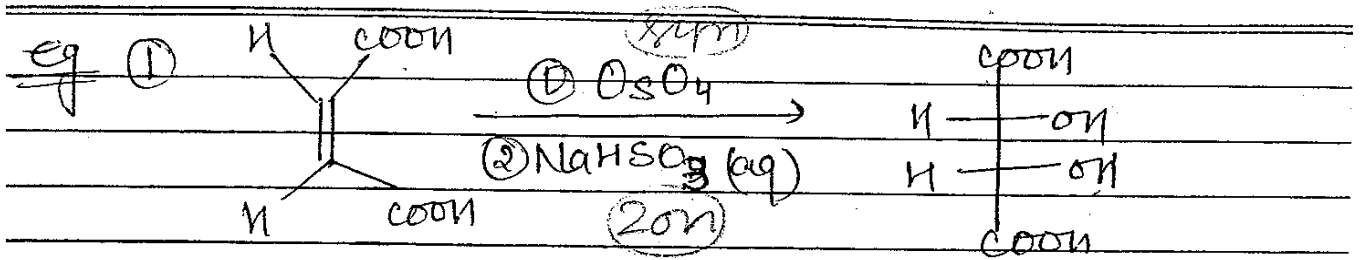
- (7) Hydroboration
- (i) $\text{B}_2\text{H}_6 / \text{THF}$
- oxidation
- H_2O_2
- (ii) $\text{H}_2\text{O}_2 / \text{OH}^-$

Threo \hat{H} C₂ hoti h. (simi gp opp. side)
Meso \hat{H} C₂ $\sigma\tau\epsilon\eta$ hoti.

Anti Addn

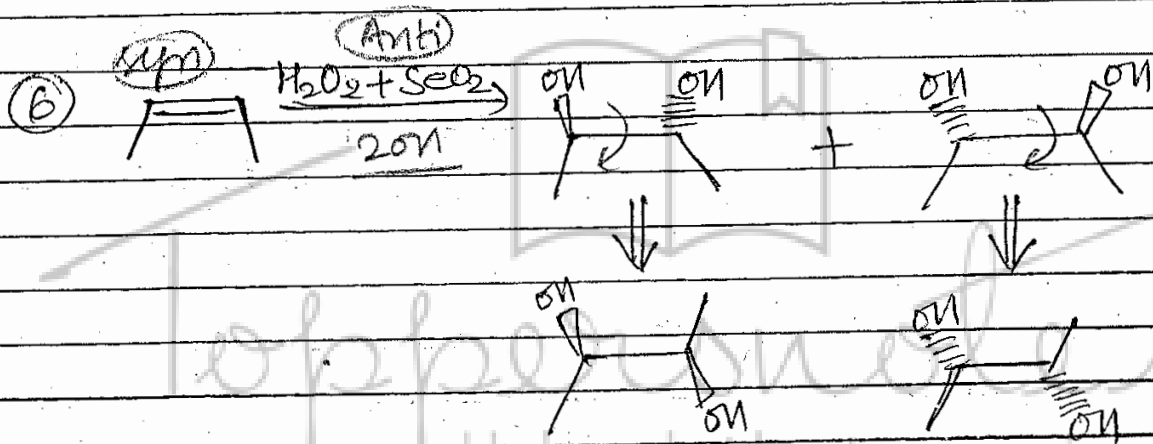
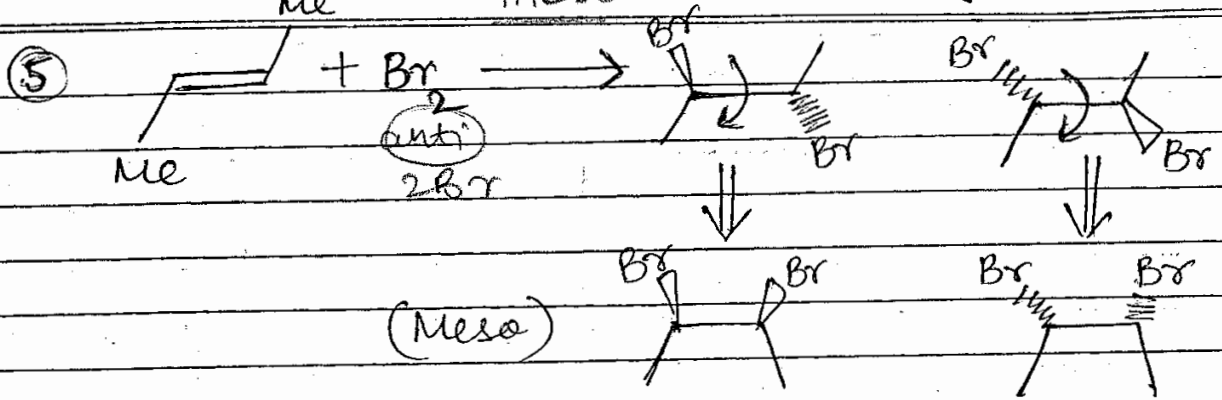
<p>① Br₂ ; I₂ (2 Br) (2-I)</p>	<p>⑥ Interhalogen compd ICl (I⁺, Cl⁻) IBr (I⁺, Br⁻)</p>
<p>② Br₂ / Nu[⊖] ; (Br, Nu)</p> <p>eg: Br₂ + H₂O (Br, OH) Br₂ + ROH (Br, OR) Br₂ + NaCl (Br, Cl)</p>	<p>⑦ H₂O₂ / seq₂ (2OH)</p>
<p>③ NBS / Nu[⊖] ; (Br, Nu)</p> <p>eg: NBS / H₂O (Br[⊕], OH[⊖]) NBS / ROH (Br, OR)</p>	<p>⑧ Prevost Rzn. i) I₂ / AgO COCH₃ ii) Hydrolysis (2-OH)</p>
<p>④ $\text{CH}_3 - \overset{\text{O}}{\parallel}{\text{C}} - \text{N} \begin{matrix} \nearrow \text{H} \\ \searrow \text{Br} \end{matrix} / \text{H}_2\text{O}$ (Br, OH)</p>	<p>⑨ oxymercuration i) Hg(OAc)₂ + H₂O demercuration NaBH₄ (H, OH)</p>
<p>⑤ HOX (OH[⊖], X[⊕]) HOBr (OH[⊖], Br[⊕]) HOI (OH[⊖], I[⊕])</p>	

fisher formulae is eclipsed conformation

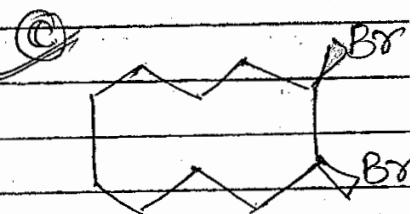
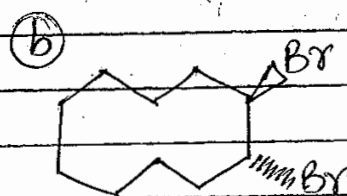
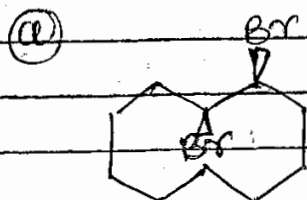
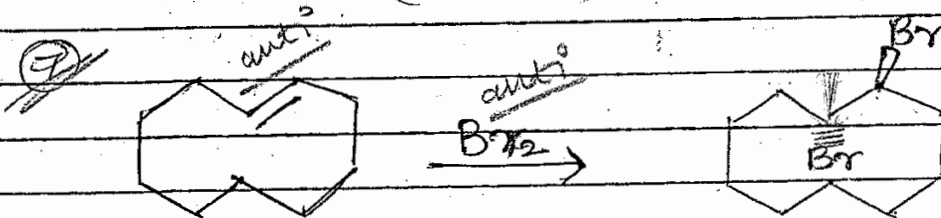


Substrate	Addtn	Prod.
Syn	Anti	Threo (Racemic Pair of enantiom. mix)
Anti	Syn	————— 99 —————
Syn	Syn	Erythro meso Pair of enantiom.
Anti	Anti	

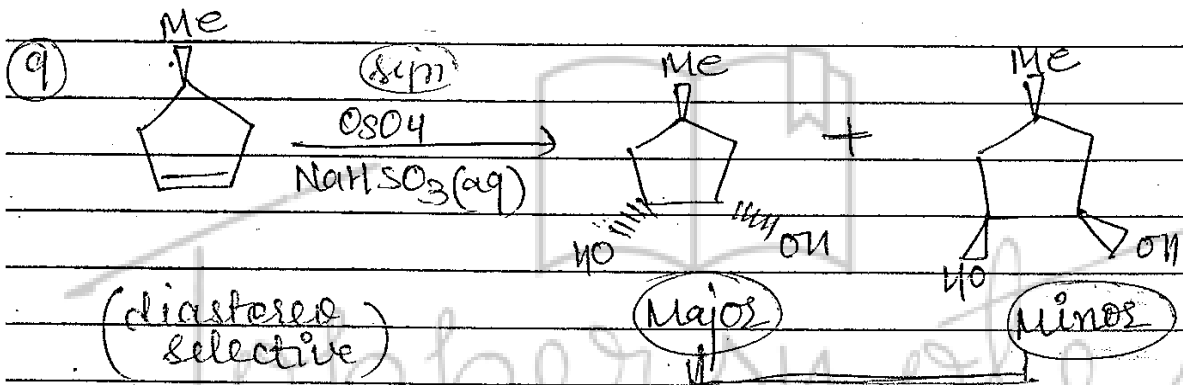
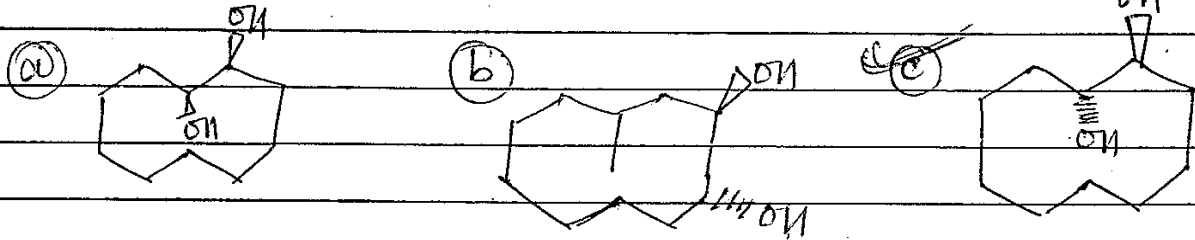
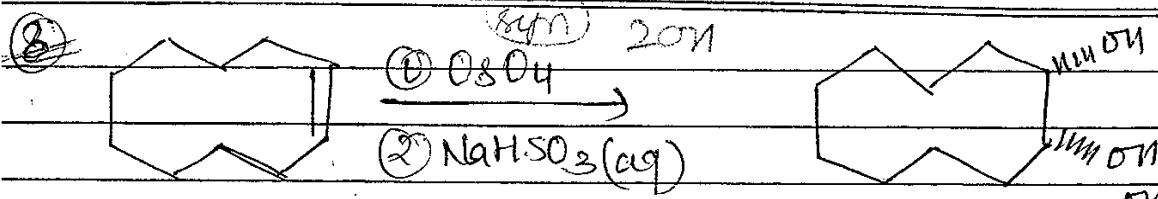
Anti + Anti \rightarrow **Erythro** \rightarrow same gp. same side
 Me meso



(simi gps opp. side) **Threo**

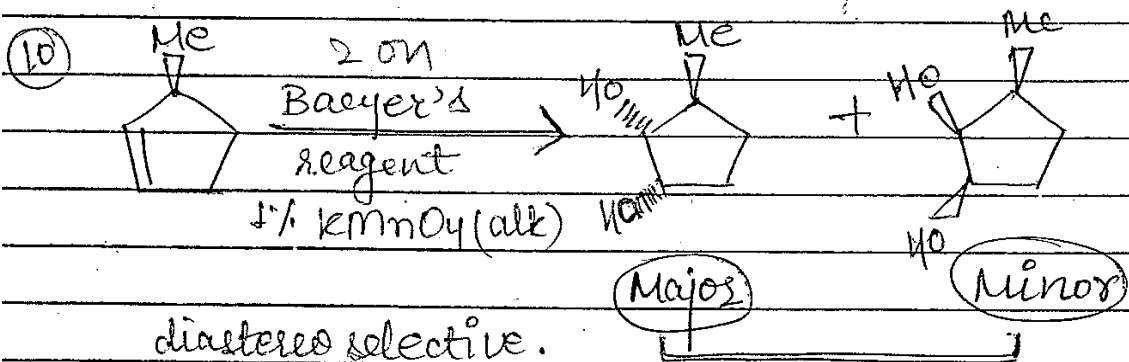


Anti + Anti \rightarrow **Erythro** \rightarrow same gp same side.

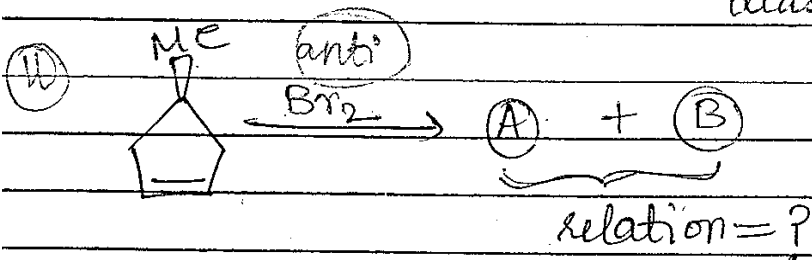


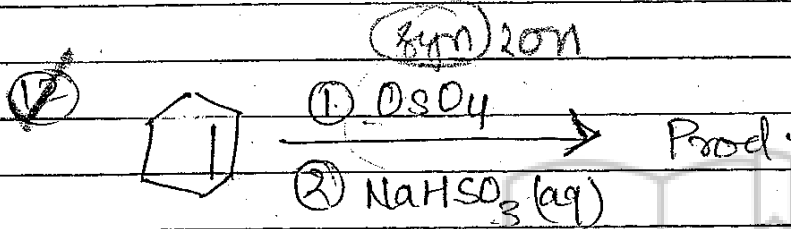
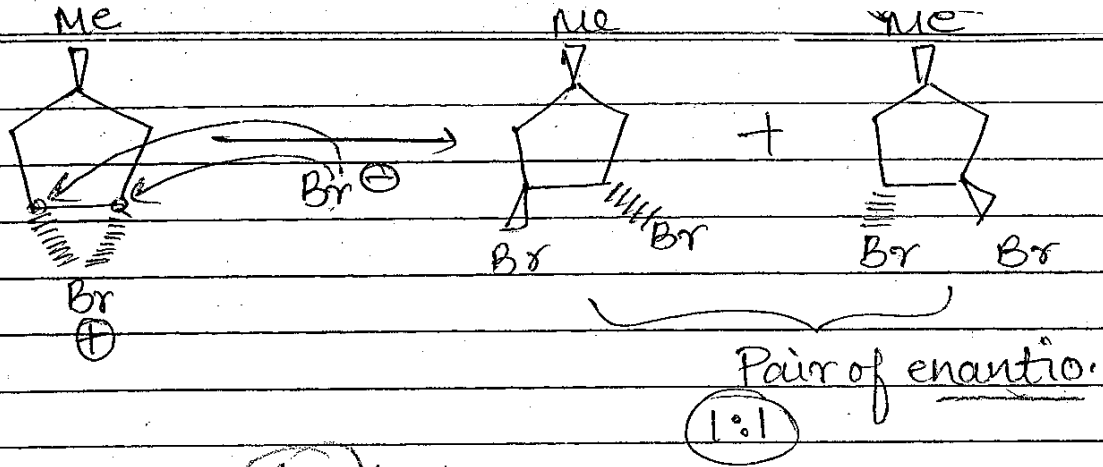
Diastereomers

(Me wedge पे या :: (prod) attack)
(dash से होता)



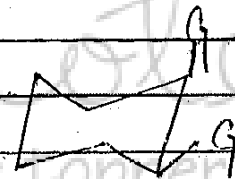
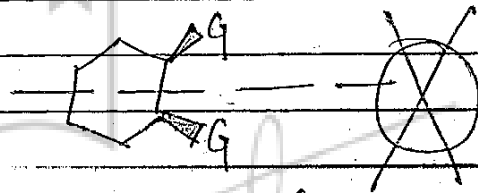
diastereomers





Which is true for prod

- 1) Prod is chiral.
- 2) Non-resolvable prod.
- 3) Optical Active prod.
- 4) O.I. prod.

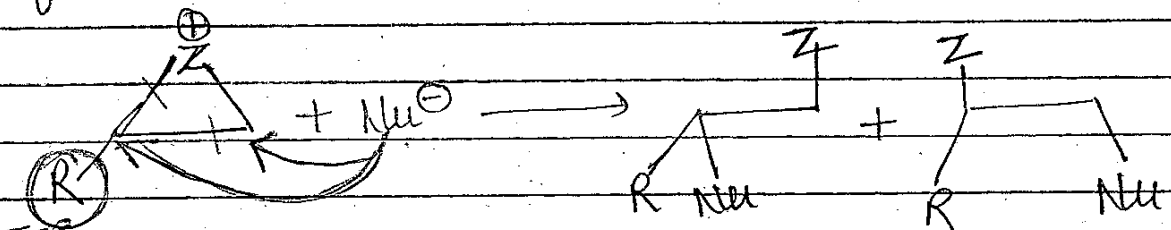


axial \rightleftharpoons eq.

\therefore Plane absent; so chiral $\frac{1}{2}$

Some key Points :-

* Identification of regio selectivity in following type of ions.



** Ring opening वहाँ से करते
 जहाँ से stable carbocation बँगा
 दिखे। जहाँ (ERG) लगा होता है

Regio Isomers
(Major)
(Minor)