Toppersnotes
Unleash the topper in you

CSIR-NET

Council of Scientific & Industrial Research

CHEMICAL SCIENCE

VOLUME - III

ORGANIC CHEMISTRY

SIERRA INNOVATIONS

Index

Rxn of Carbocation :-

Imp ① REARRANGEMENT : यदि reassangement होता है तो पहले carbocation का।

② Electrophilic addition.

③ Sn^1

④ E^1 (unimolecular elimination.

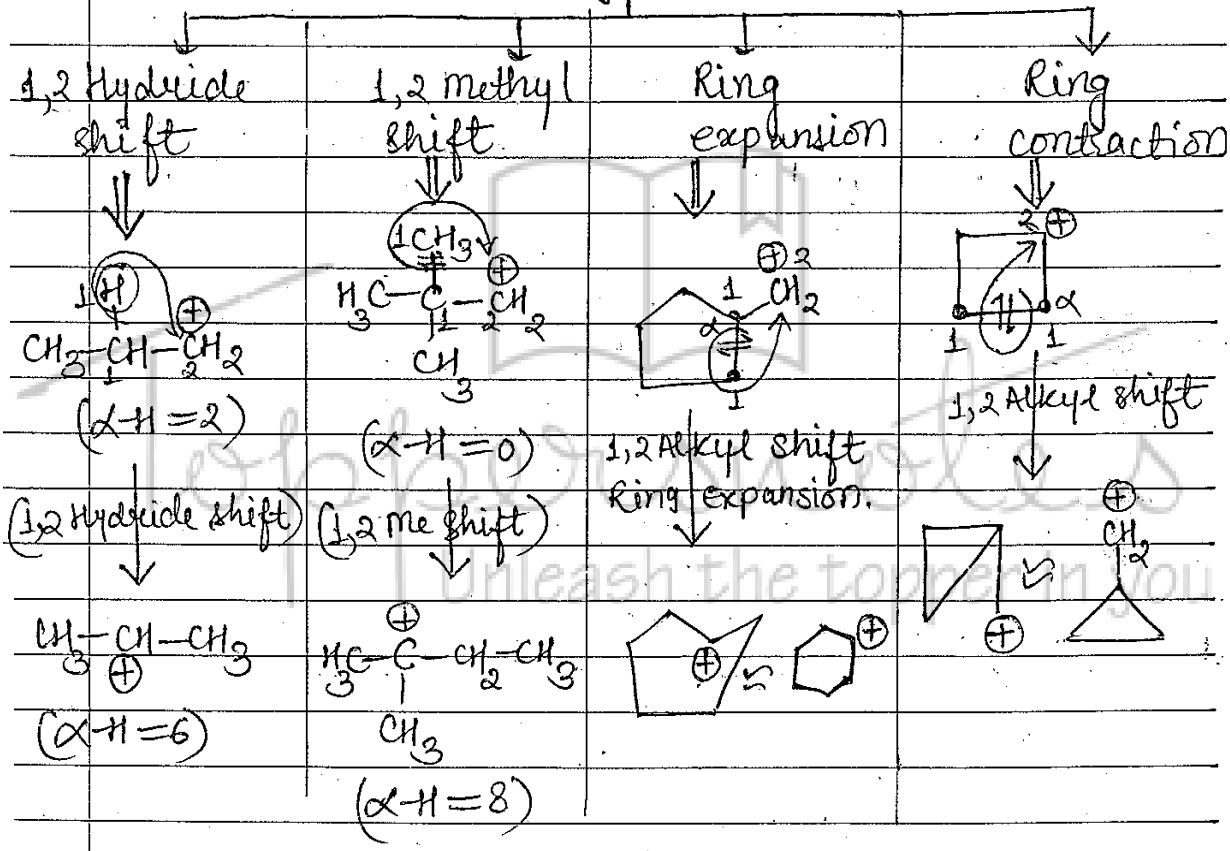
⑤ A_ESE

⑥ Isomerisation of Alkene

⑦ Dimerisation of Alkene.
⑧ Some Name Rxn.

REARRANGEMENT :- (in Carbocation)

Less stable carbocation → (rearrangement) More stable carbocation.



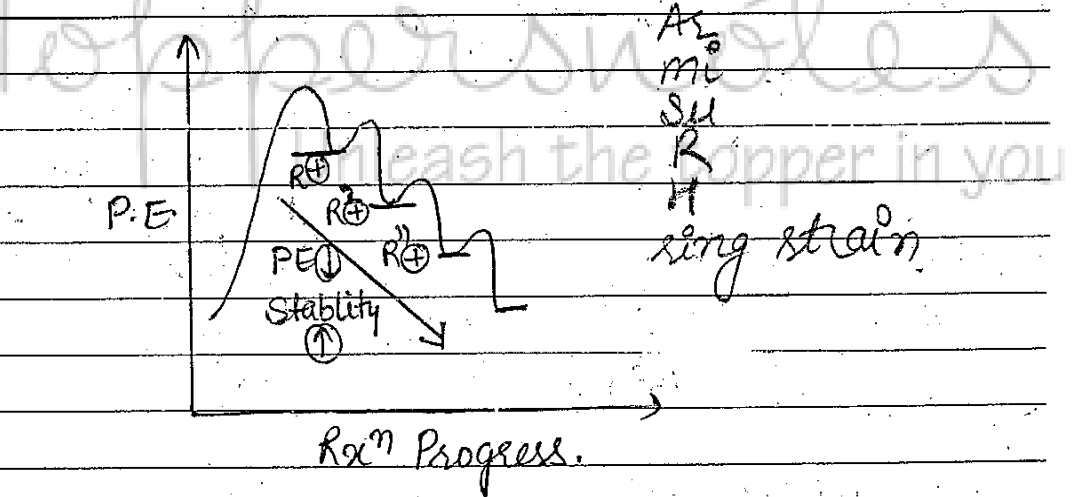
Key Points About Reavrangement :-

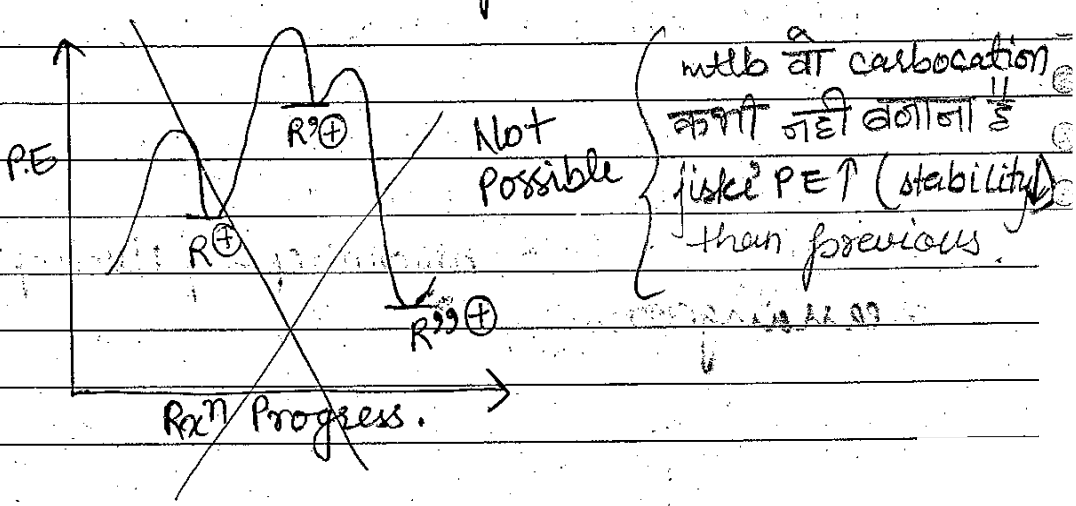
→ Since Carbocation is e⁻ deficient sp. so migrating gp mitrates e⁻ its Bond pair, such type rearrangement c/o Anionotropic / Nucleophilic rearrangement.

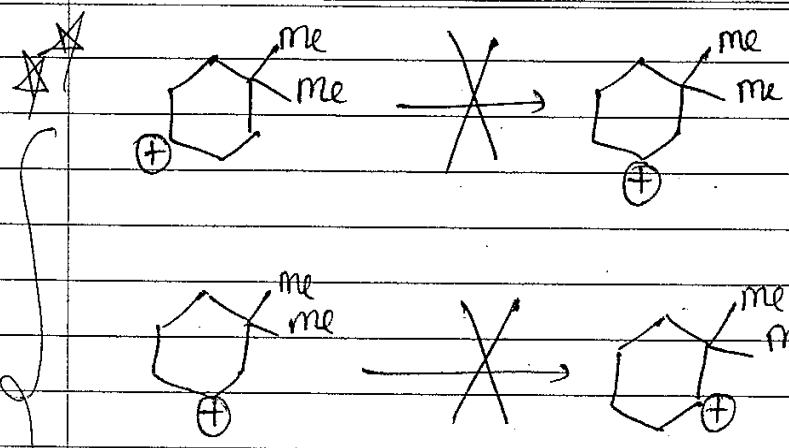
- Rearrangement in Carbocation is Spontaneous: (possible है तो store नहीं करना है)

→ Ring expansion & Contraction, is also eg of 1,2 Alkyl shift.

→ In a Carbocation, no. of rearrangements are possible but the condition is after each rearrangement the newly formed carbocation shud be more stable than previous one; & their stability shud be compared by:
ring strain, Hyperconjugn, reso,.....
(reso के ऊपर लिखे गए)

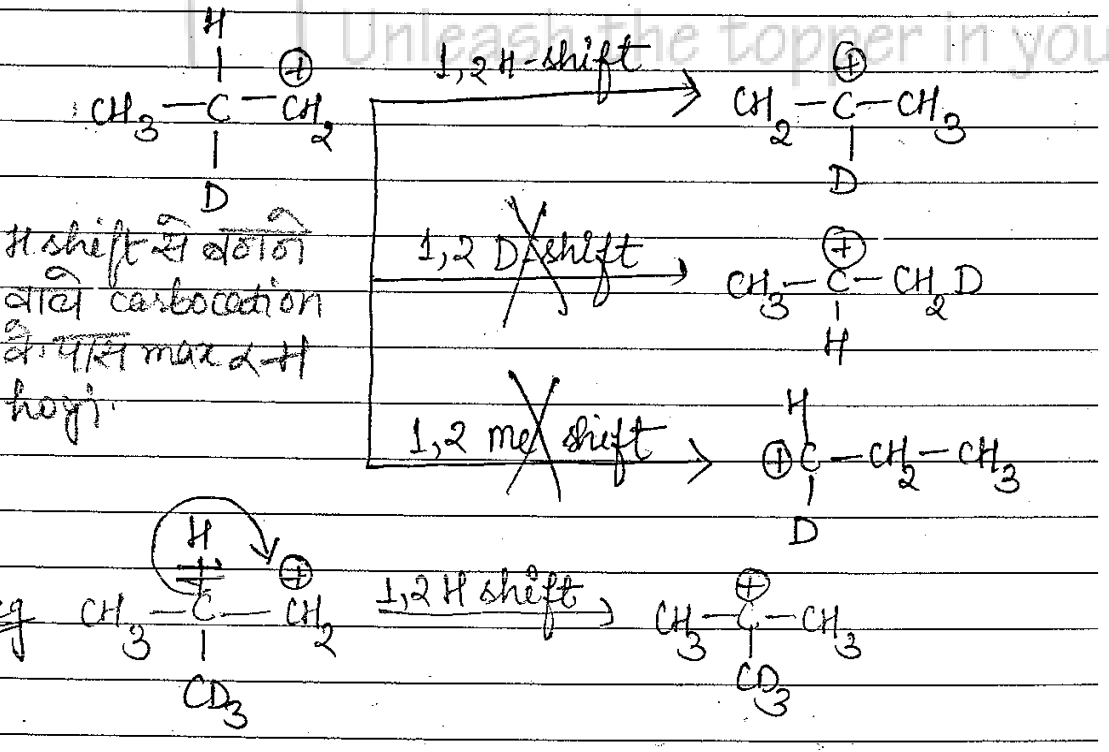






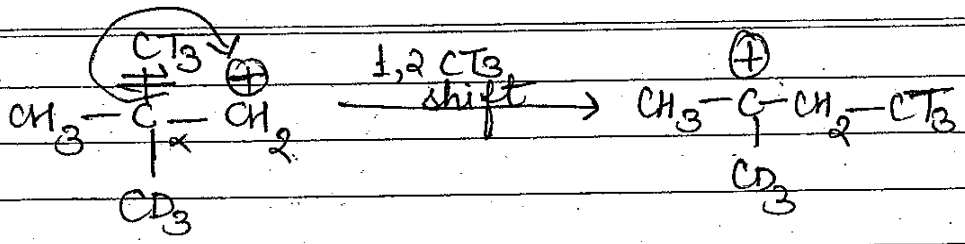
+I ↑ hora hai but Inductive effect is not Driving Force for Rearrang. ∴ ये rearrang. NOT possible.

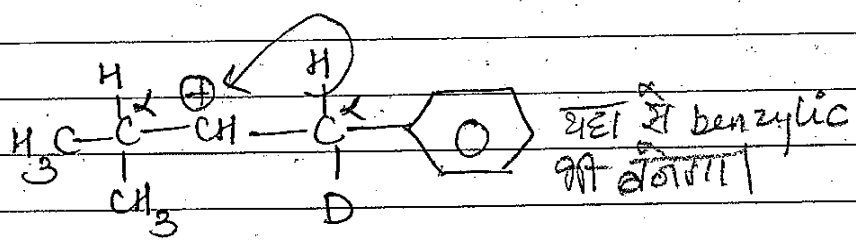
→ If in a carbocation, more than 1 type of gps are available for migration then the gp migrates & gives more stable carbocation.

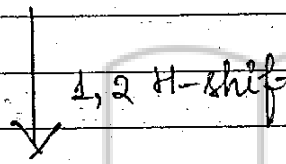


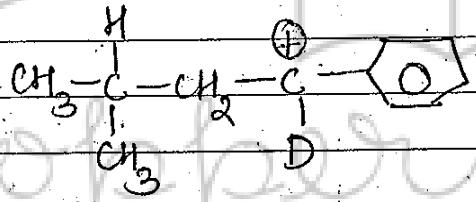
H shift से बनने वाले carbocation से ↑ max α-H होंगे।

eg

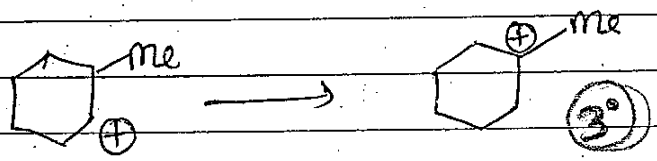
eg: 

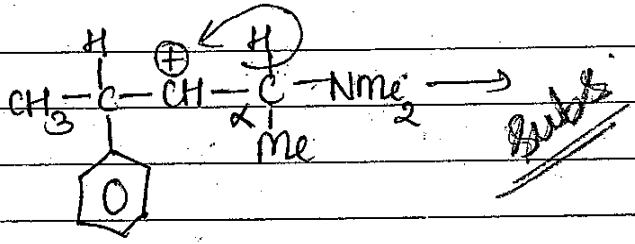
eg: 

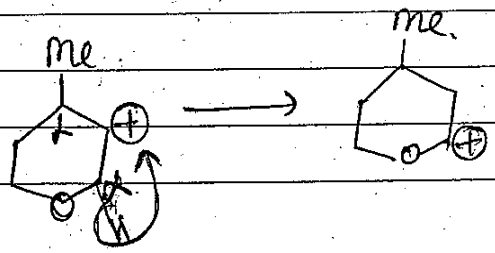


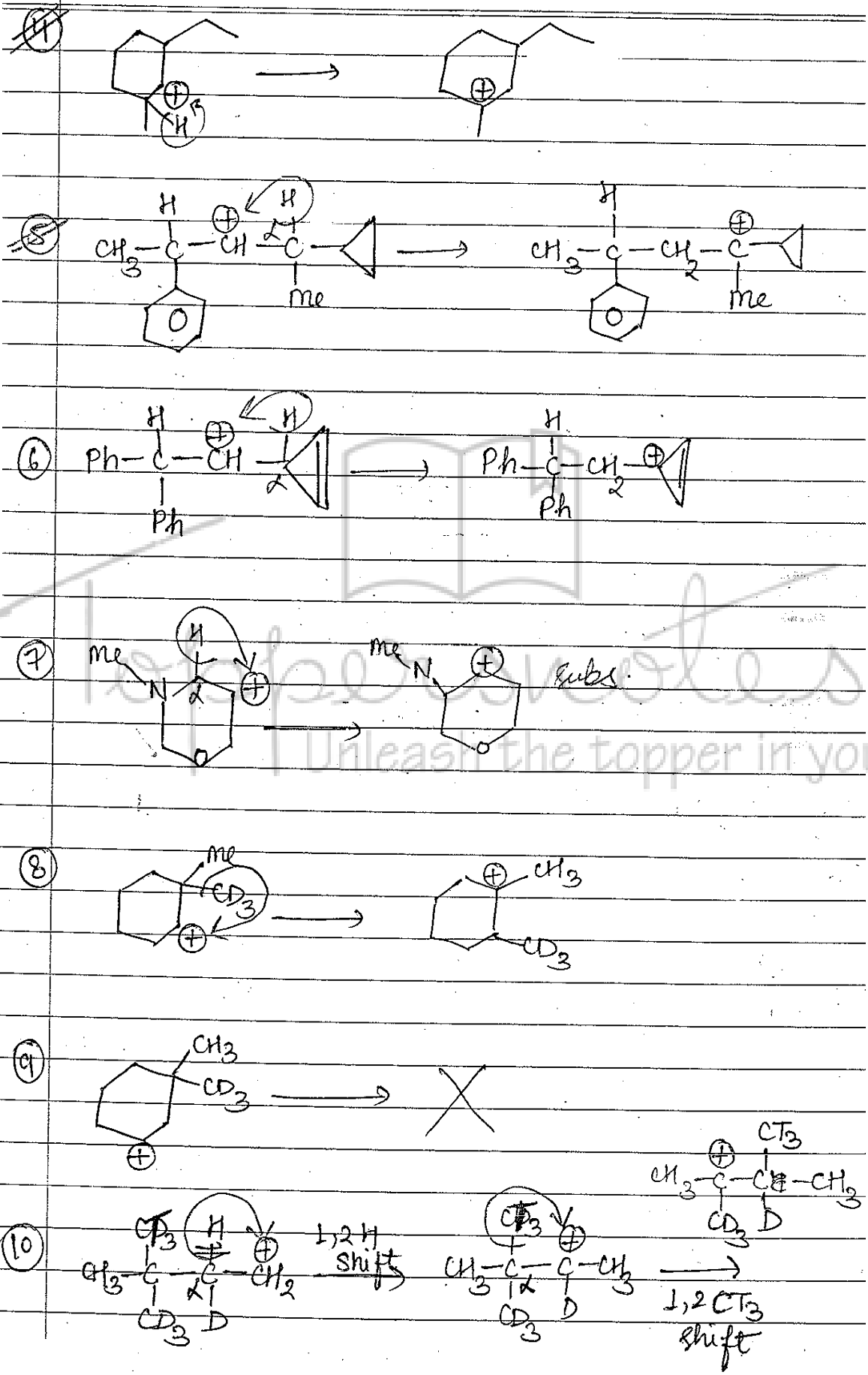


Q. Convert to most stable Carbocation:-

(1) 

(2) 

(3) 



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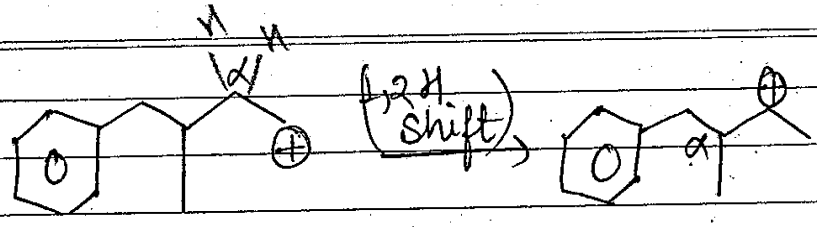
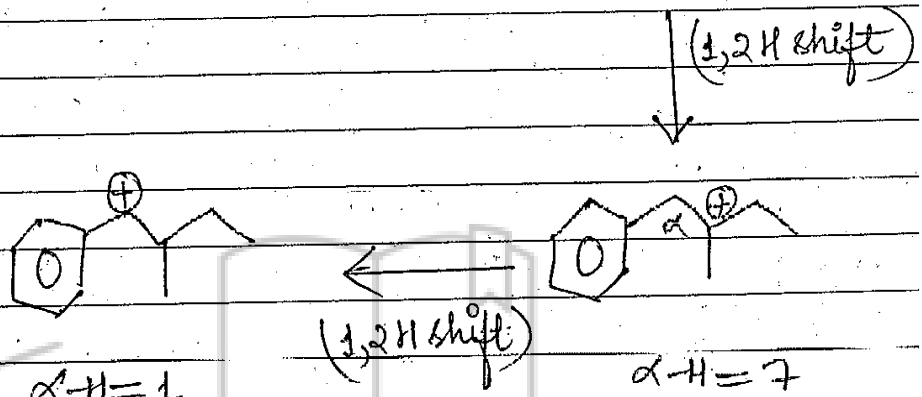


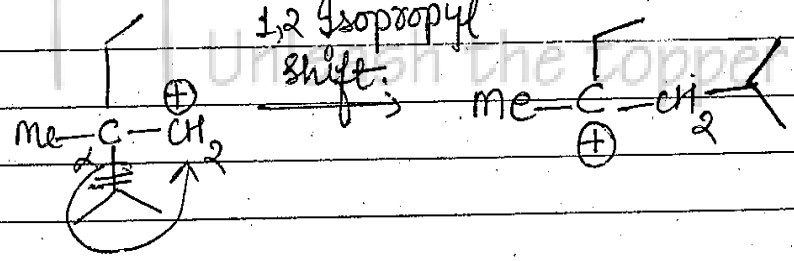
(α-H = 2) (α-H = 4)



α-H = 1 and Benzylic

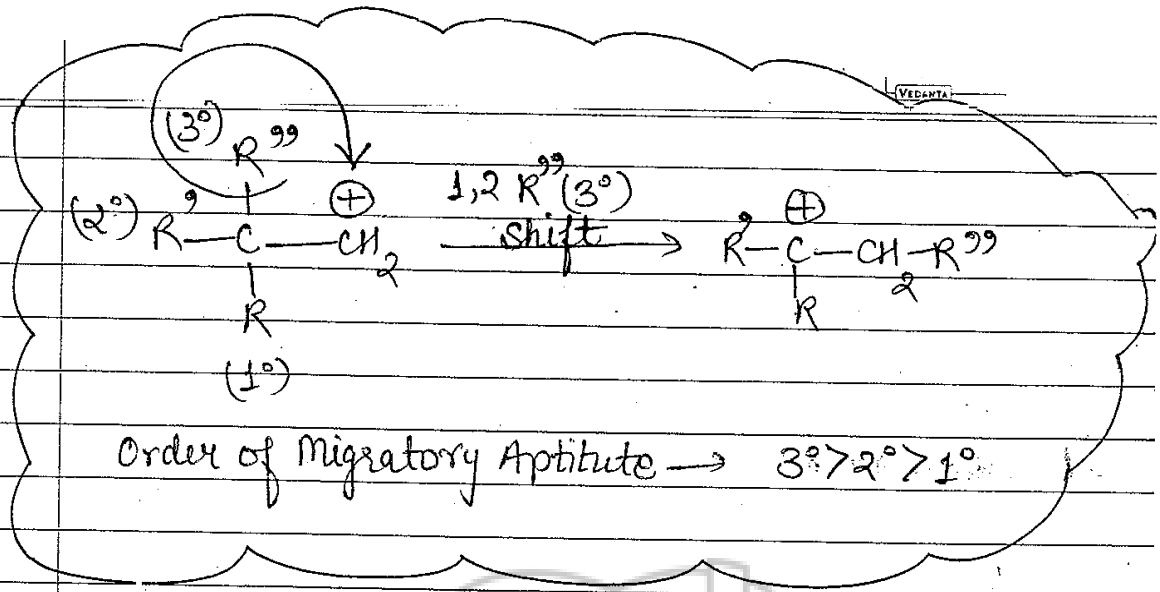
α-H = 7

(12)



Carbocation ko me & Et wala stable karenge compared to isopropyl ∴ usko nikala.

आने वाले carbocation को वो group वाला stable करता है jiske पास α-H max hoti hai. ∴ jiske पास α-H कम हो उसको nikalte h.



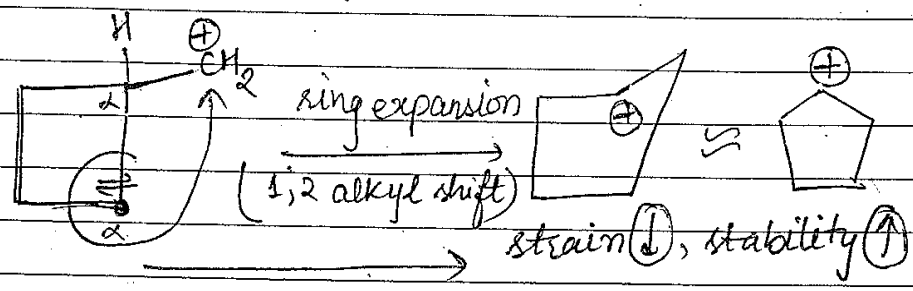
Order of Migratory Aptitute → 3°>2°>1°

** Ring expansion is dominant over Gp transfer but expansion takes place upto 5-memb.

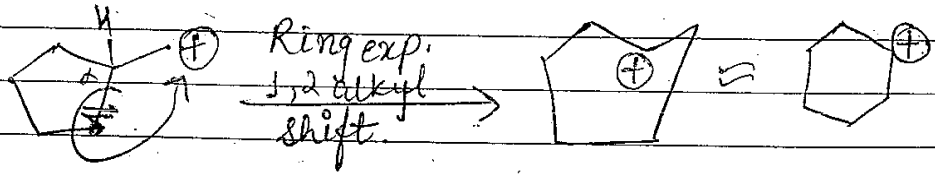
4 memb ⟶ 5 memb ✓
5 memb ⟶ 6 memb ✓
6 memb ⟶ 7 memb ✗ Not possible. ring expansion.

** But if there is a driving force then expansion in 6-memb ring is also possible.

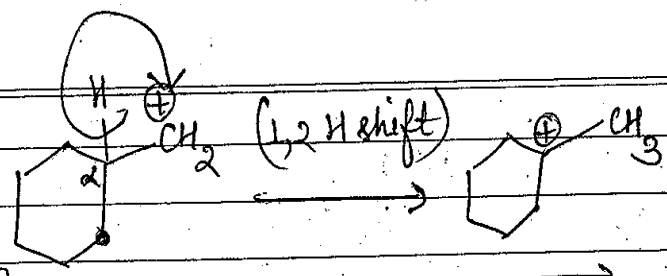
eg ①



②

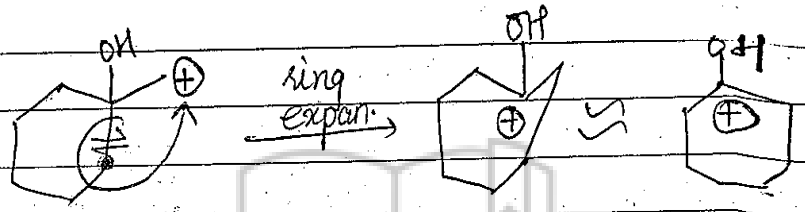


strain ↓, stability ↑

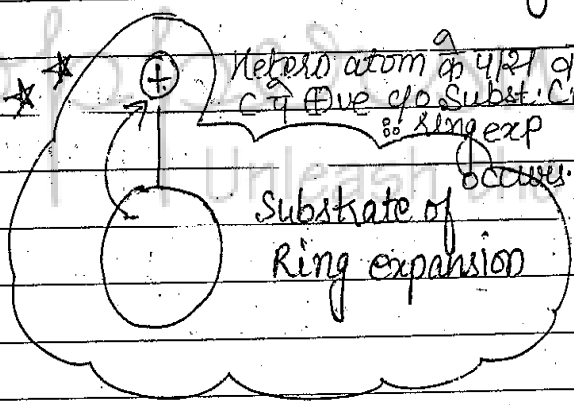
(3) 

6 memb ring का expansion not possible ∴ H को migrate करने के as Driving force नहीं है.

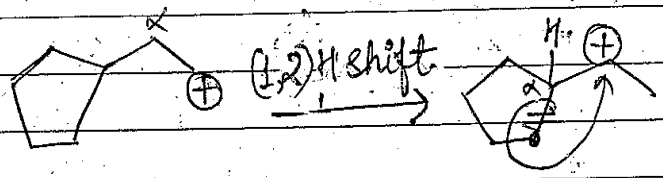
α-H ↑, stability ↑

(4) 

(Due to this D.F. 6 memb converted to 7 memb ring) ← Substituted carbo cation (max stable)

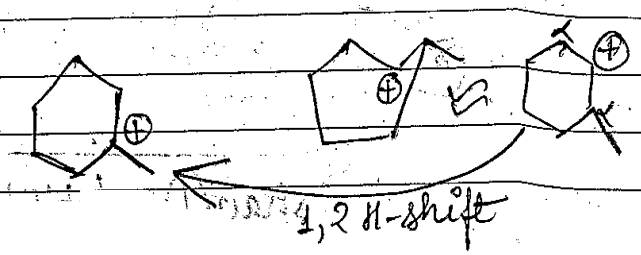


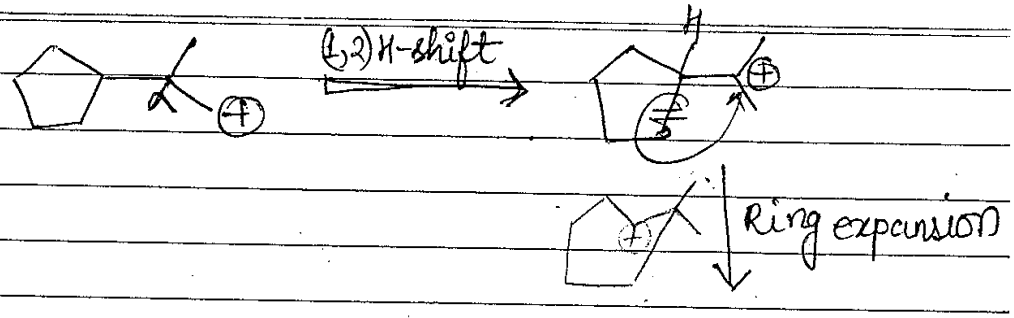
charged C के to nearby atom पर substrate ⊕nt then only ring expansion.

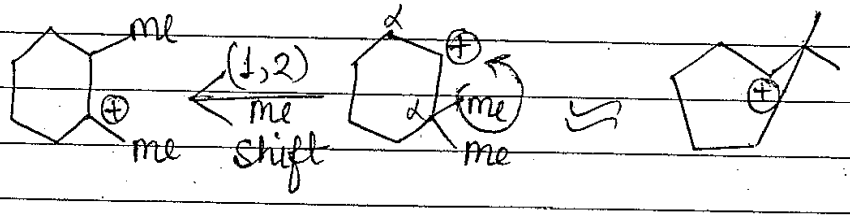
Eg: 

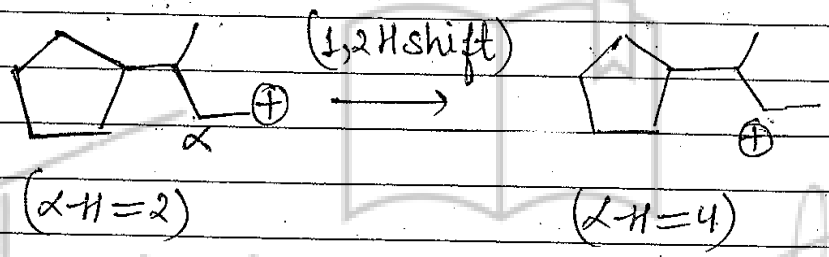
1,2 Shift = 3
1,2 Hydride = 2
1,2 Alkyl = 1 shift

Ring expansion



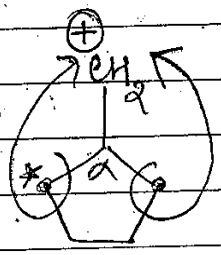
eg 



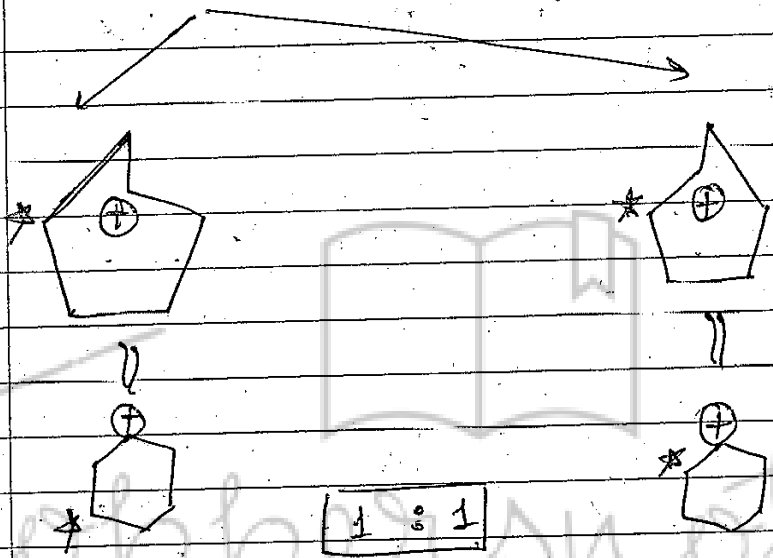
eg: 

Direction of Ring expansion :-

eg

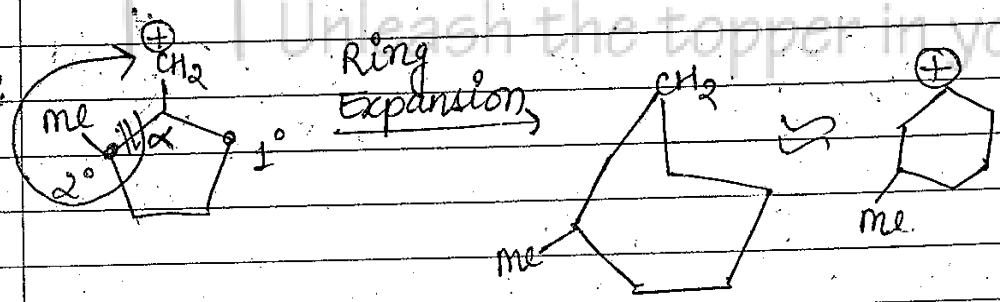


50% 50% दोनो तरफ से ring expansion possible है (equally)

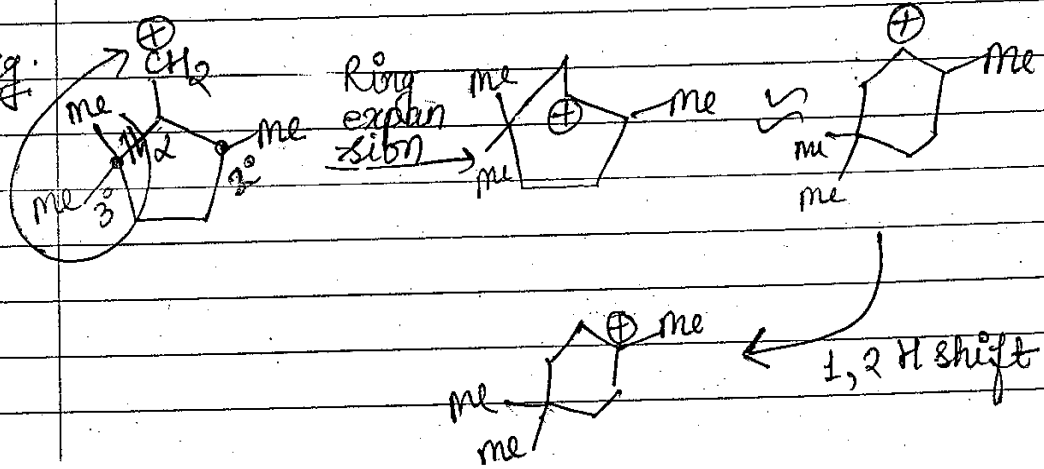


1 : 1

eg:



eg:



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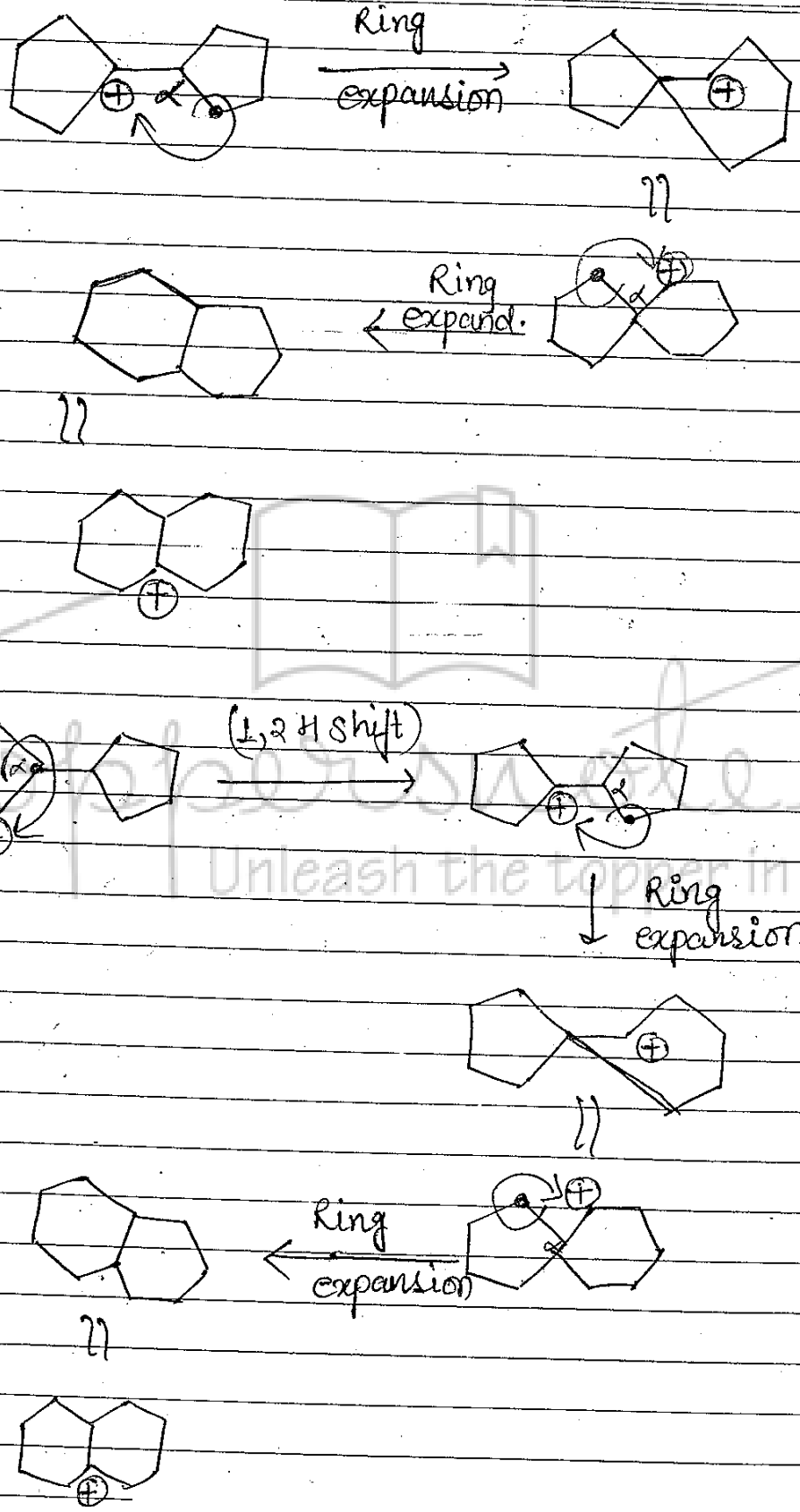

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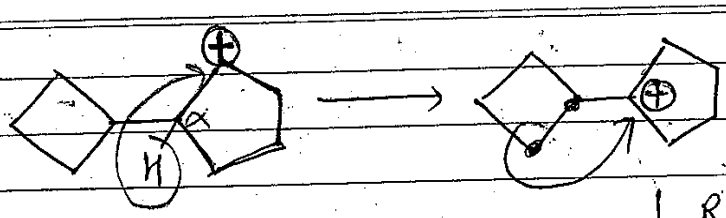
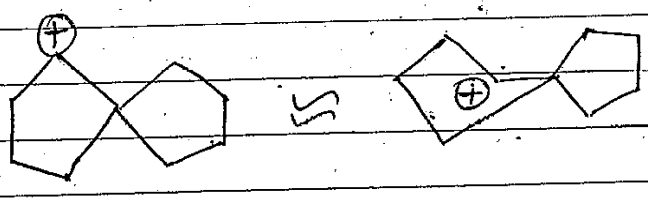
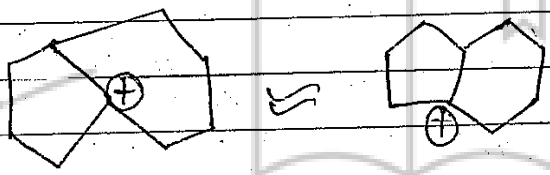


Ring expansion

Ring expansion





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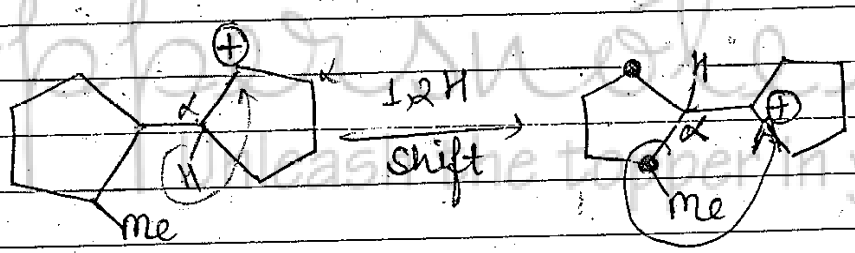
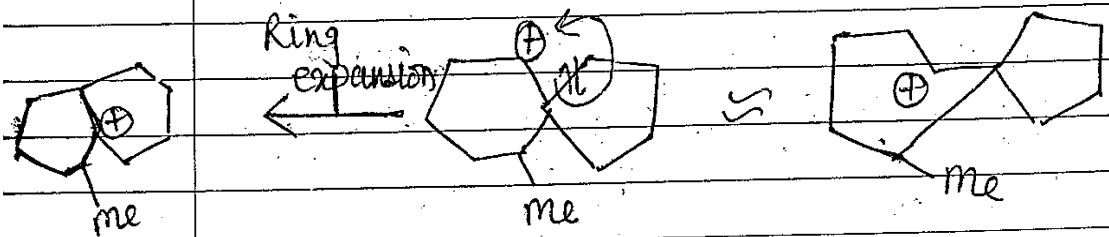
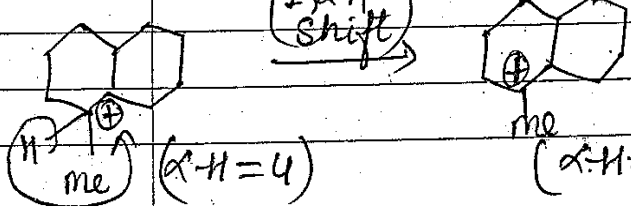


Ring expansion

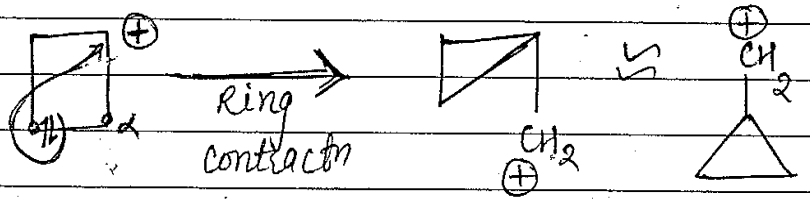
Ring expansion





★★ Key Point ⑦ ring के C पे ही ⊕ve है।

Case 1 : In this case, ring contraction occurs



Case ② :

9 memb. ring —Ring contraction→ 8 memb

8 memb ring —〃→ 7 memb

7 memb ring —〃→ 6 memb ring

α-H shud (↑) during this ring contraction hoga.

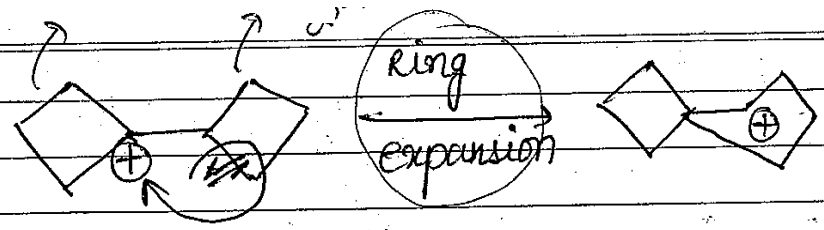
Case ③ :

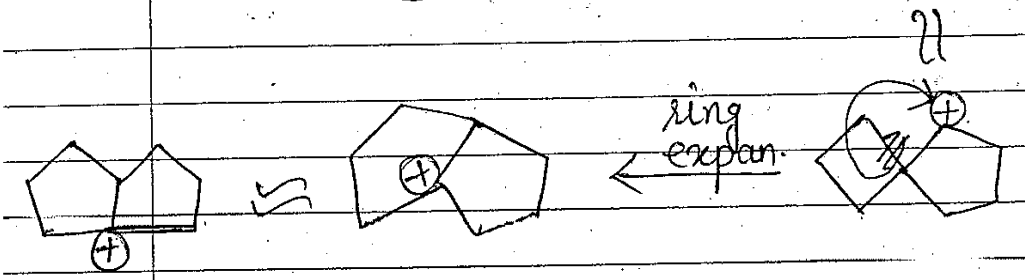
→ Sometimes bcz of the stereochem reason, also ring Contraction occurs. (will be discussed in Pindcol – Pinacolone rearrang.)

★★ Key-point ⑧

→ If in the Carbocation, both ring expansion as well as ring contraction is possible then ring expansion is dominant over contraction.

eg:





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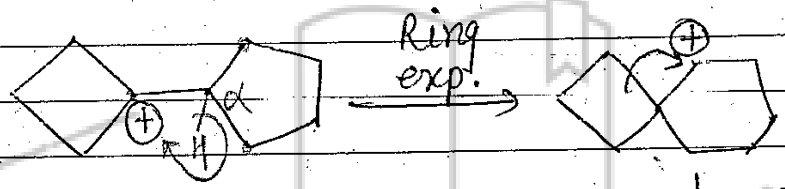

Isomerisation of Alkene :-

→ Carried out in ⊕nce of Acidic medium. The acid used are :-

i) Conc. H_2SO_4
ii) TsOH (PTSA)

★ less stable alkene → more stable alkene.

★ less substituted → more substituted.

→ (more DB वाली alkene)

α-H ↑