

UNIT-II ELIMINATION REACTIONS:-

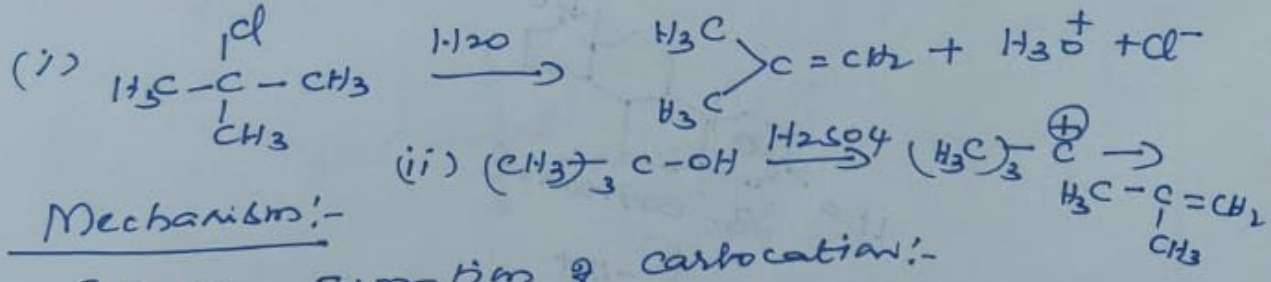
Elimination reaction involves the loss of two groups or atoms from a molecule. Multiple bonds are formed through the loss of groups bonded to adjacent atoms. These are known as 1,2-elimination, termed as E₁ + E₂ elimination.

A third mechanism is designated as E₁CB (Elimination, unimolecular of conjugate base) ^{which is} less common. The substrate undergoing E₁CB has a leaving group which is β to the carbanion intermediate formed.

E₁ Mechanism - UNIMOLECULAR ELIMINATION:-

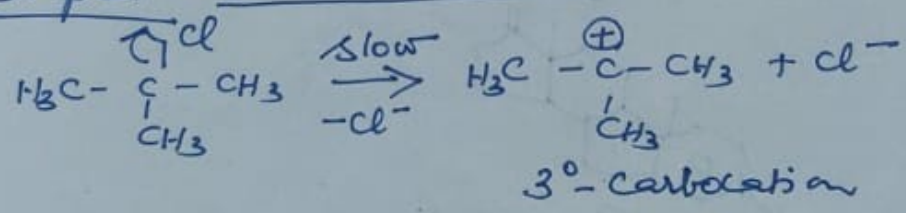
Definition:- Elimination reaction, in which an atom/group from α-carbon atom and a proton from β-carbon are eliminated in two steps.

E.g. Dehydrohalogenation of (CH₃)₃CCl with H₂O to form (CH₃)₂C=CH₂ follows E₁ mechanism.

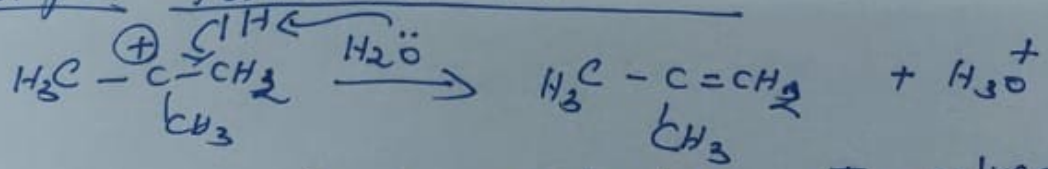


Mechanism:-

Step I:- formation of carbocation:-



Step II:- Formation of product:-

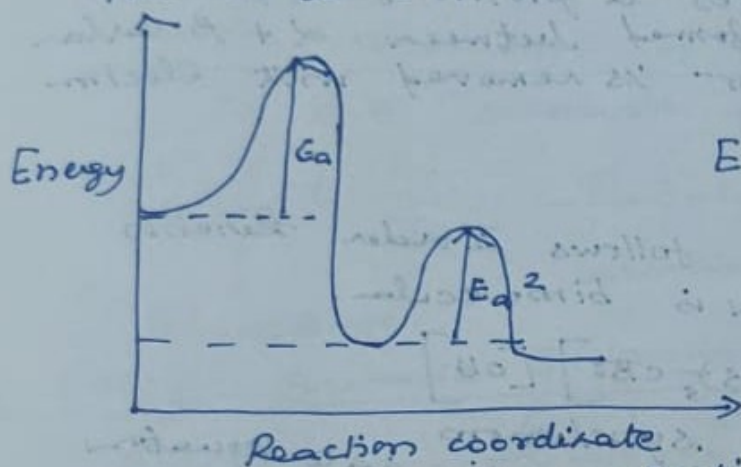


In E₁ mechanism, the solvent

acts as a base, accepts one of the β -protons. The initial step for S_N1 and $E1$ reactions are same. But in S_N1 reactions the solvent acts as a nucleophile to form carbocation intermediate.

CHARACTERISTICS:

- 1) $E1$ reaction follows first order kinetics. Slow step involves only alkyl halide.
- 2) $E1$ mechanism has two steps and there are two energy barriers.



$$E_{a1} > E_{a2}$$

3) Since carbocation stability decreases in the order $3^\circ > 2^\circ > 1^\circ$, the rate of $E1$ reaction also follows the same order.

4) Whenever the intermediate permits, rearrangement takes place.

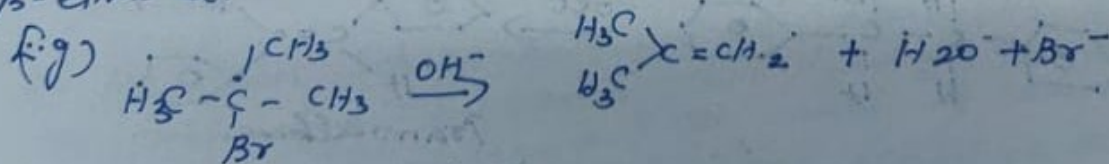
5) $E1$ reactions are non-stereospecific.

6) $E1$ reactions are regioselective.

$E2$ -Mechanism:-

Definition:-

The groups eliminated are trans to each other and this is also β -elimination or H_2 -elimination or β -elimination or β -trans elimination.

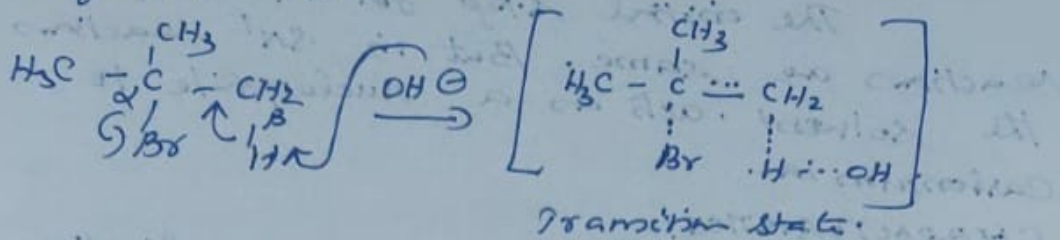


Mechanism:-

Like S_N2 reaction, $E2$ reaction also

having one step only.

(3)



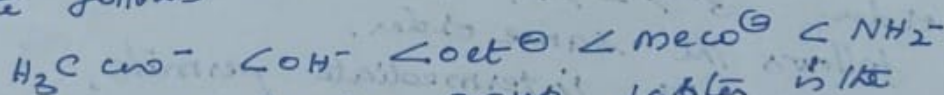
- The base removes a proton from β -carbon
- New bond is formed between $\alpha + \beta$ carbon
- Leaving group Br^- is removed with electron pair.

CHARACTERISTICS-

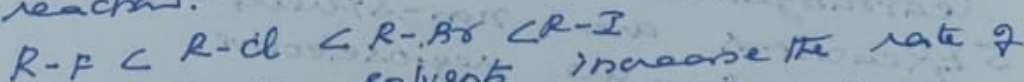
- 1) E_2 mechanism follows II order kinetics and the reaction is bimolecular.

$$\text{Rate} = k [(\text{CH}_3)_3\text{CBr}] [\text{OH}^-]$$

- 2) The reaction is synchronous
- 3) Since the base appears in rate equation rate follows

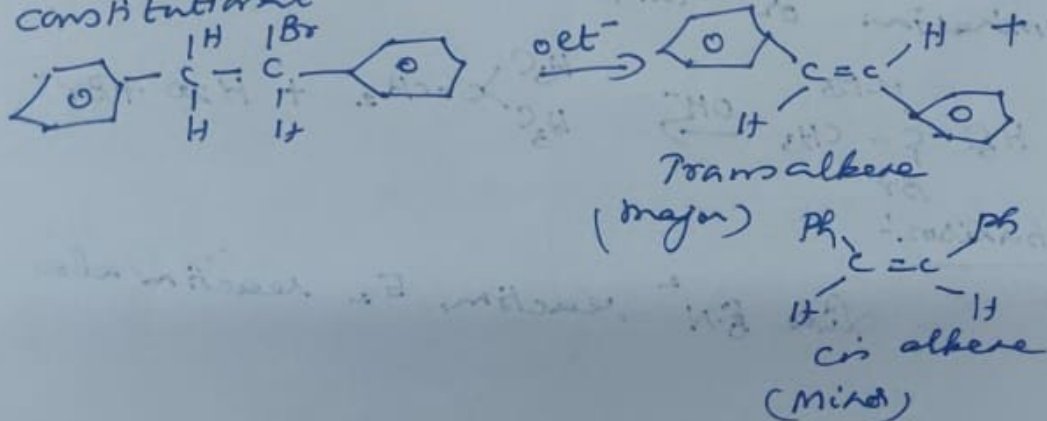


- 4) Better the leaving group, faster is the E_2 reaction.



- 5) Polar aprotic solvents increase the rate of E_2 reaction. These solvents (example CH_3COCH_3) do not solvate the anion as well as no interaction with the base. So base is stronger, which increases the reaction rate.

- 6) E_2 reaction is regioselective, and constitutional isomer predominates.



7. E_2 -reaction is stereoselective - one stereoisomer is formed preferentially. (4)

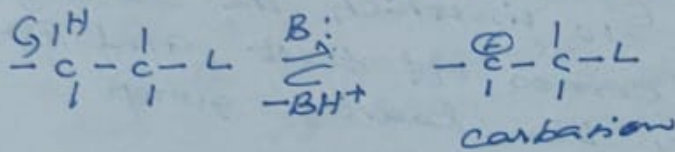
E1CB MECHANISM:-

Definition:-

Bond to the hydrogen breaks during the first step to give carbanion and the bond to the leaving group breaks in the second step. This is unimolecular reaction of the conjugated base.

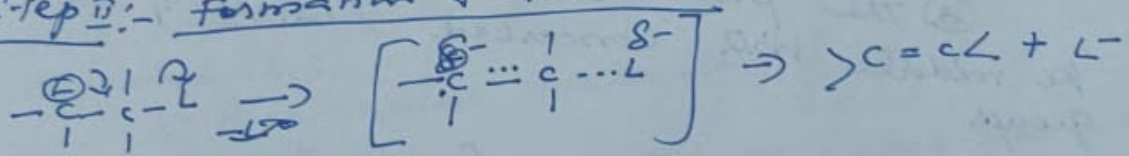
Step I:- Formation of carbanion:-

It is a reversible fast step.



B: \rightarrow Base.

Step II:- Formation of product:-

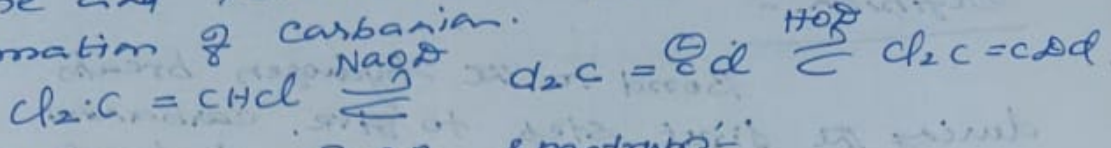


CHARACTERISTICS:-

- 1) Rate $(r) = k [\text{Base}] [\text{substrate}]$
- 2) E_1CB reaction usually proceed in the presence of concentrated strong bases in polar media at elevated temperature.
- 3) E_1CB reactions are non-stereospecific.
- 4) Intermediates are carbanions.
- 5) The most acidic β -H is abstracted by the base before the leaving group departs the substrate.
- 6) Hoffmann product is expected to be formed.
- 7) E_1CB reactions are regioselective.
- 8) Reaction depends on the stability of the carbanion. Electron withdrawing groups on β -C will increase the rate of reaction.
- 9) Non-hydroxy polar solvents stabilize the carbanion. Use of DMSO moves the mechanism towards E_1CB pathway.
- 10) Rate depends on acidity of β -H.

Evidences for the formation of carbanion: - ⑤

In the following reactions, exchange between ^{of} deuterium and proton between base and substrate supports the formation of carbanion.



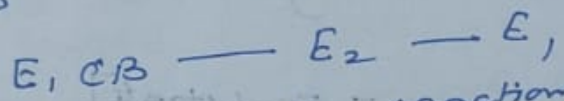
E₁, E₂ and E₁CB Spectrums:-

① In E₁, E₂ & E₁CB mechanisms, the similarities are greater than the differences

② There is a spectrum of mechanisms ranging from one extreme in which the leaving group departs well before the proton, that is E₁, in which the leaving group

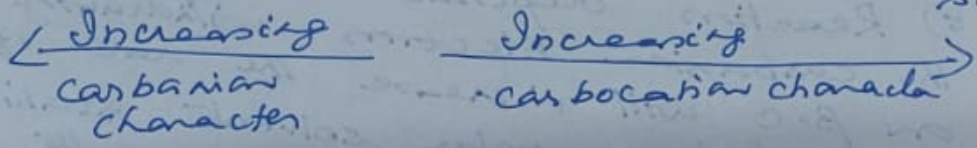
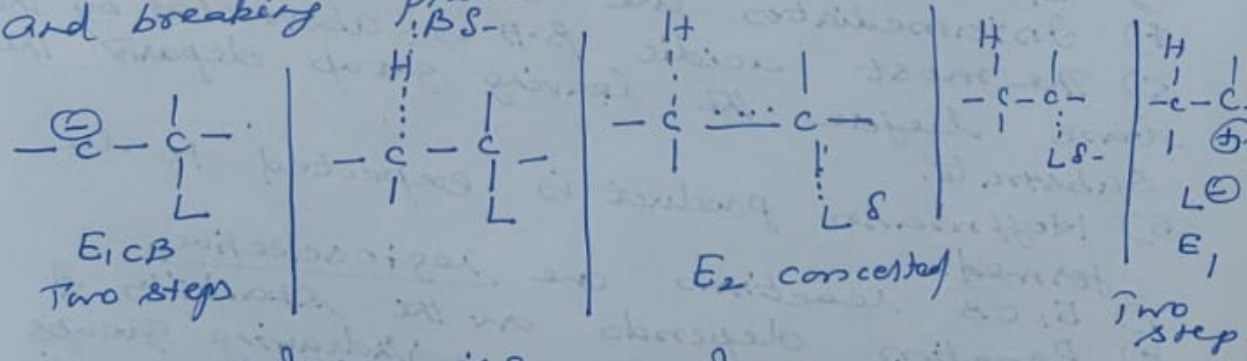
proton comes off first and then after some time, the leaving group follows, that is E₁CB.

③ The pure E₂ case is placed in the middle with concerted leaving of both groups



④ However, E₂ reactions are not exactly in the middle, but somewhere to one side or other.

⑤ These three mechanisms differ mainly in the timing of various bond making and breaking processes.



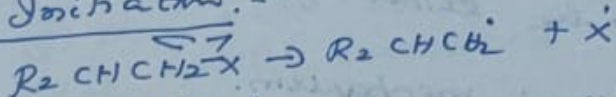
③ Evidences for E_c mechanism :-

- (i) follow first order kinetics since only one molecule of the substrate is involved in the reaction.
- (ii) Free radical inhibitors do not slow down the reaction.
- (iii) Follows exclusive syn elimination.
- (iv) The intermediate has more steric crowding compared to starting material and so these eliminations have negative entropy of activation.
- (v) K_c isotope effects indicate that both C-H & C-O/C-N bonds break in the transition state.

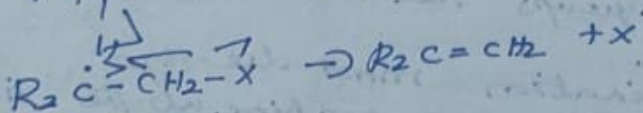
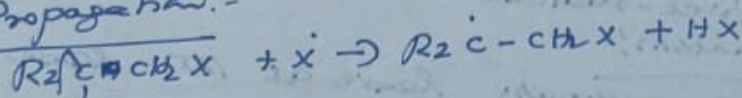
④ Free-radical mechanism:-

- (i) Homolytic cleavage produce free radicals.
- (ii) Free-radical mechanism is followed mostly in pyrolysis of polyhalides and of primary monohalides.

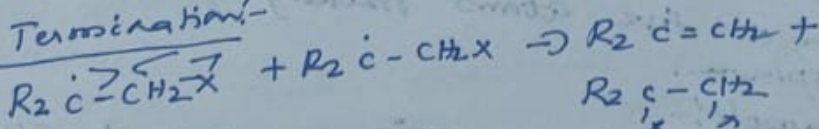
(iii) Initiation:-



(iv) Propagation:-



(v) Termination:-



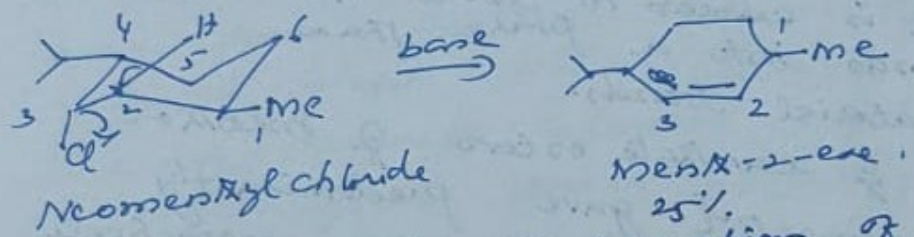
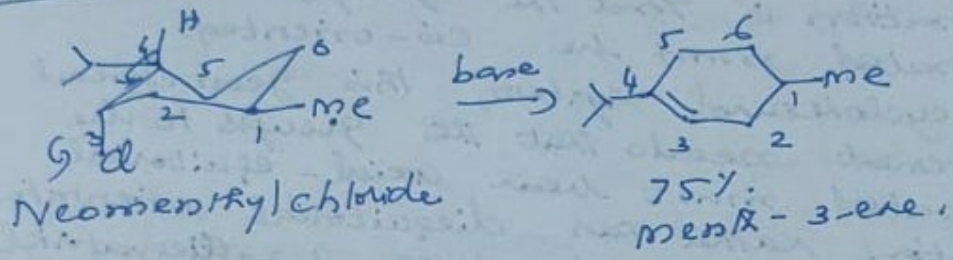
STEREOCHEMISTRY OF E₂ Elimination in Cyclohexane systems:-

- (i) E₂ eliminations readily take place when the groups to be eliminated bear antiplanar arrangement. In cyclohexane system, this relationship requires that the groups being eliminated bear trans diaxial arrangement and not trans diequatorial arrangement.
- (ii) The principle of diaxial elimination by E₂ mechanism is illustrated in menthyl and neomenthyl chloride by a base.

(iii) Neomenthyl chloride readily eliminates HCl to give menth-3-ene

(iv) The most stable conformation of neomenthyl chloride has axial chlorine atom (3) with two other axial hydrogens on adjacent carbons (C2 + 4)

(v) The stereoelectronic requirement for E2 elimination is satisfied by this conformation and the major product of elimination is the thermodynamically more stable menth-3-ene (Saytzev product)

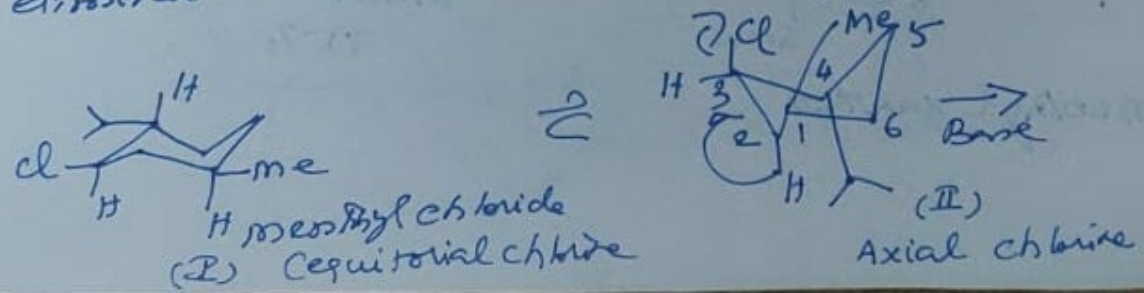


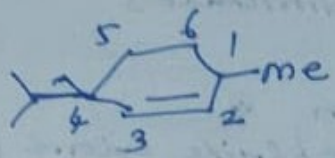
(vi) The most stable conformation of menthyl chloride (I) has equatorial chlorine atom which is not suitably oriented for E2 elimination.

(vii) In its alternative conformation (II) of menthyl chloride, obtained by ring inversion, the chlorine and hydrogen atoms on adjacent carbon atoms (C4 + C2) are trans diaxial.

(viii) Although this conformation satisfies the stereoelectronic requirement for E2 elimination, it is so unfavorable due to the presence of bulky axial isopropyl and methyl groups.

(ix) The rate of elimination is very slow and since there is only one axial hydrogen on C2 adjacent to the axial chlorine, the product of elimination is menth-2-ene (anti-Saytzev product).





ment-2-ene (100%)

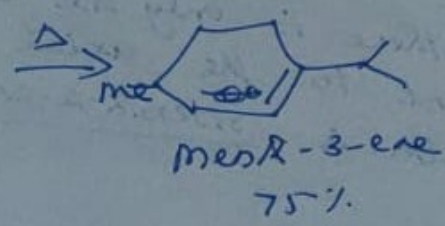
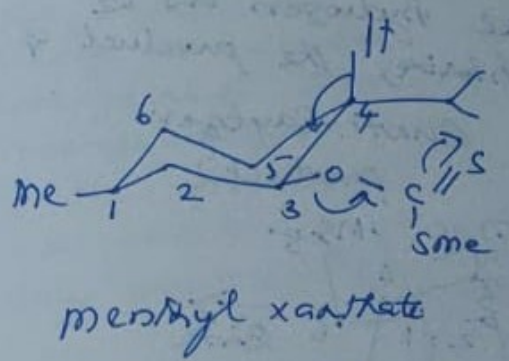
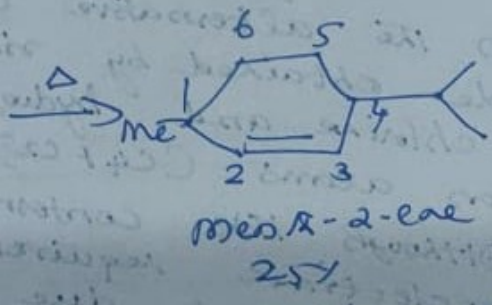
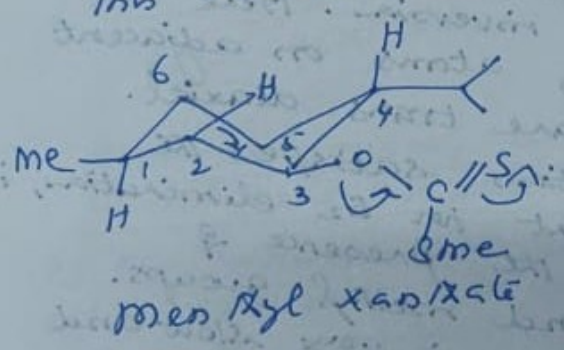
CHUGAEV REACTION:-

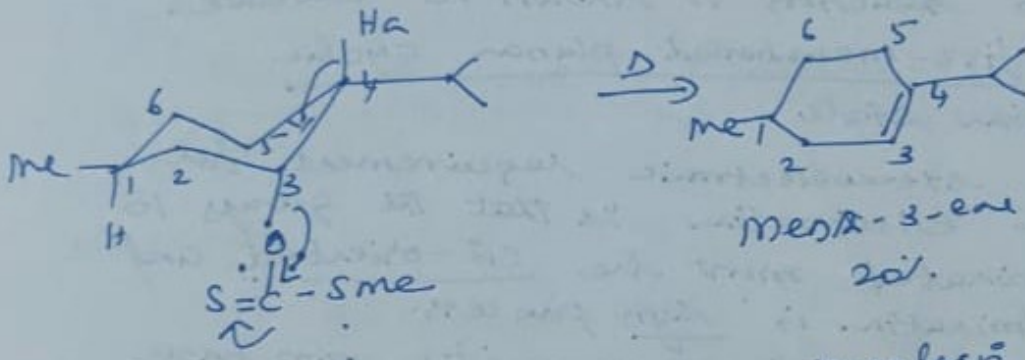
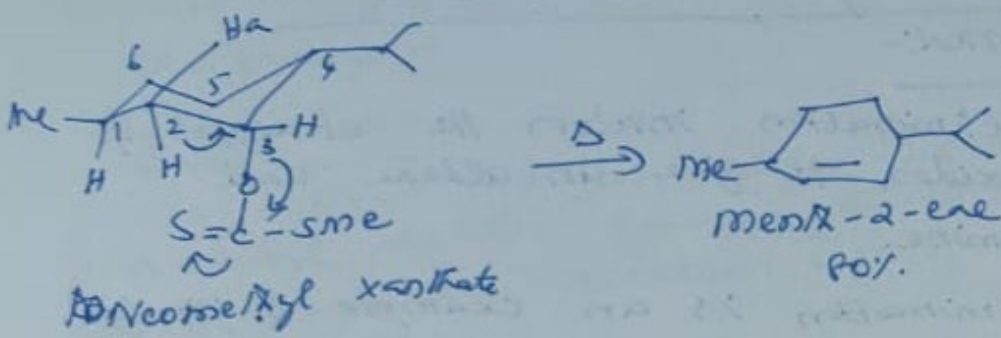
(i) Pyrolysis of acetates, xanthates and amine oxides produce olefins. These reactions are shown to produce through six and five membered planar cyclic transition states.

(ii) The stereoelectronic requirement for pyrolytic elimination is that the groups to be eliminated must be cis-oriented.

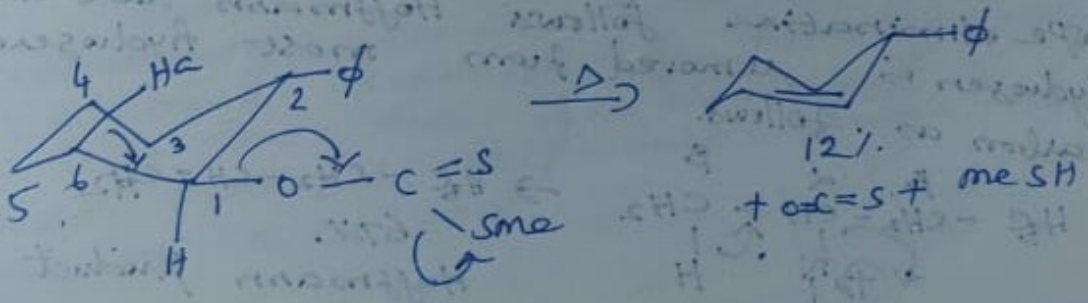
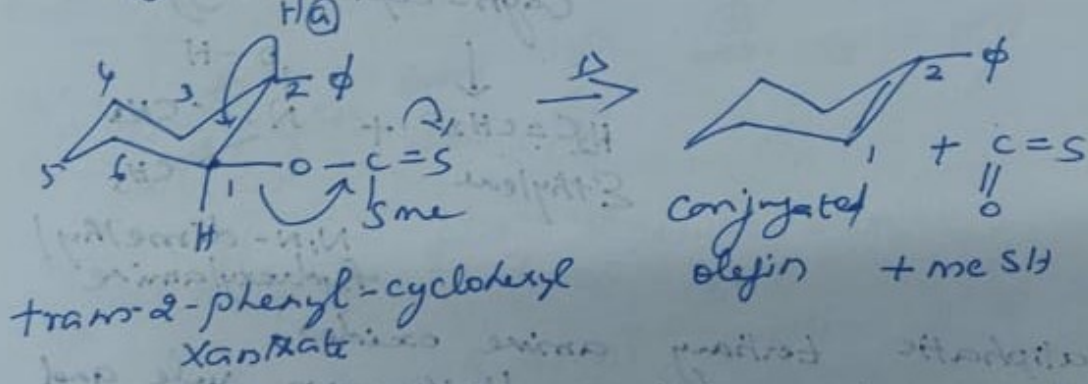
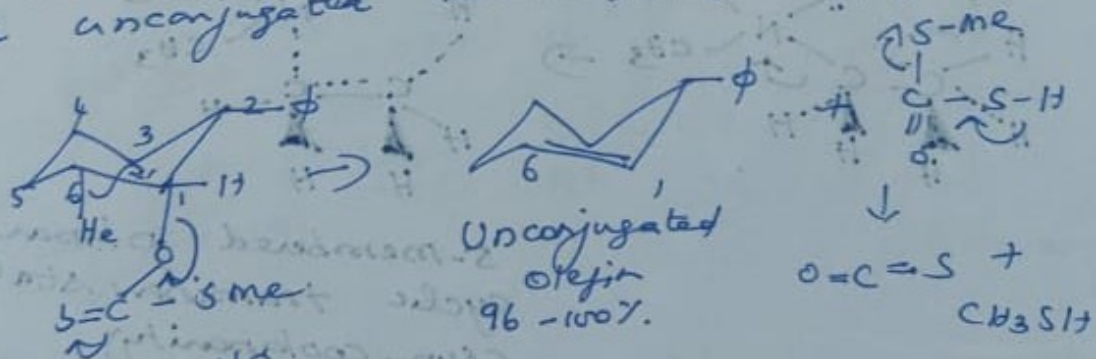
(iii) In cyclohexanol system, this geometrical requirement needs that the groups to be eliminated must bear axial-equatorial orientation rather than diequatorial orientation. Since it is easier to force 1,2-diequatorial-axial bonds into a plane than 1,2-diequatorial bonds.

(iv) Pyrolysis of xanthate esters of menthol and neomenthol gave predominantly ment-3-ene and ment-2-ene respectively which involves cyclic transition state. This reaction is known as CHUGAEV reaction.





(v) Another example is the pyrolysis of cis and trans-2-phenylcyclohexyl xanthates. Trans isomer produces predominantly conjugated olefin 1-phenylcyclohexene, whereas cis-isomer produces almost entirely the unconjugated isomer, 3-phenylcyclohexene



STEREOCHEMISTRY & MECHANISM OF COPE

ELIMINATION:-

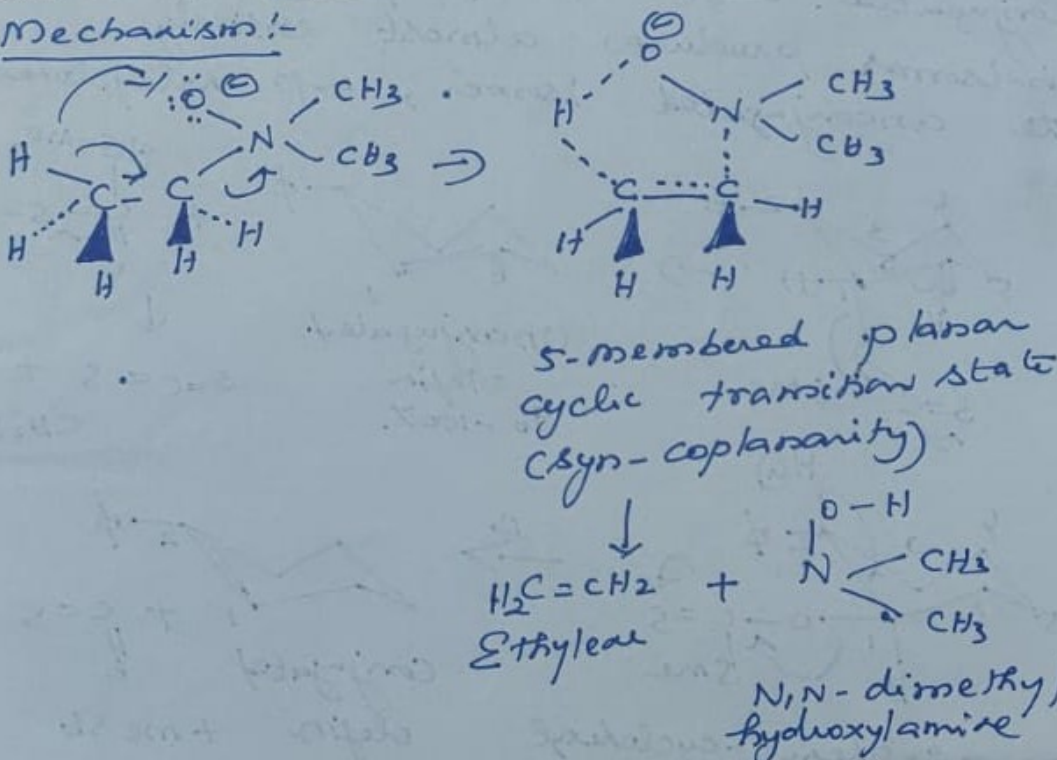
(i) Cope elimination involves the cleavage of amine oxides to give an alkene and hydroxylamine.

(ii) This elimination is an example of pyrolysis and this reaction is shown to produce through five-membered planar cyclic transition state.

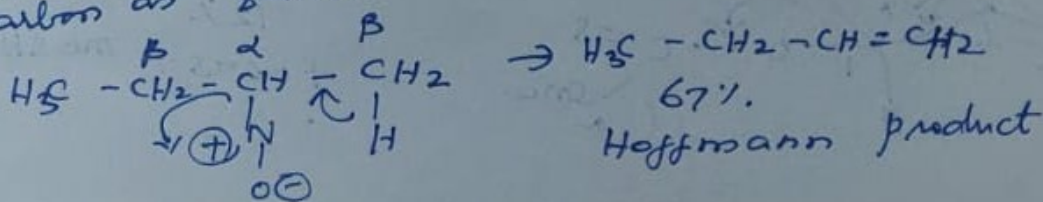
(iii) The stereoelectronic requirement for pyrolytic elimination is that the groups to be eliminated must be cis-oriented and the elimination is syn process.

(iv) The amine oxide acts as its own base. No external base or solvent is needed for pyrolytic eliminations and hence they are termed as Elimination internal E_i.

(v) Mechanism:-



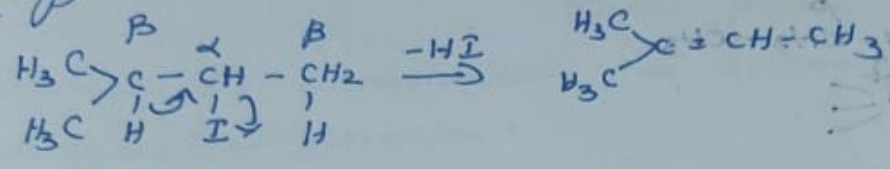
(vi) In aliphatic tertiary amine oxides, Cope elimination follows Hoffmann rule and hydrogen is removed from most hindered carbon as follows.



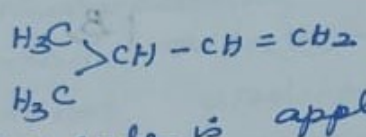
Explain Saytzeff and Hoffmann rule with examples.

Saytzeff rule
 When hydrogens, halides are eliminated from alkyl halides, hydrogen leaves from the least hydrogenated β -carbon atom.

(E.g)



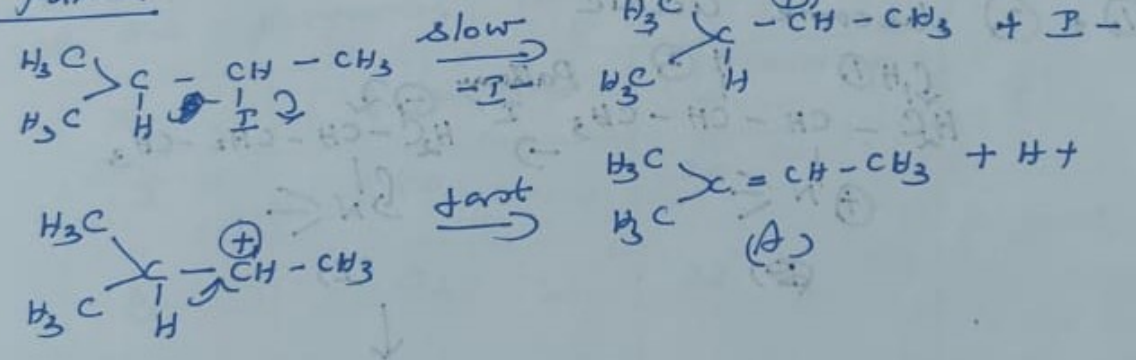
and not



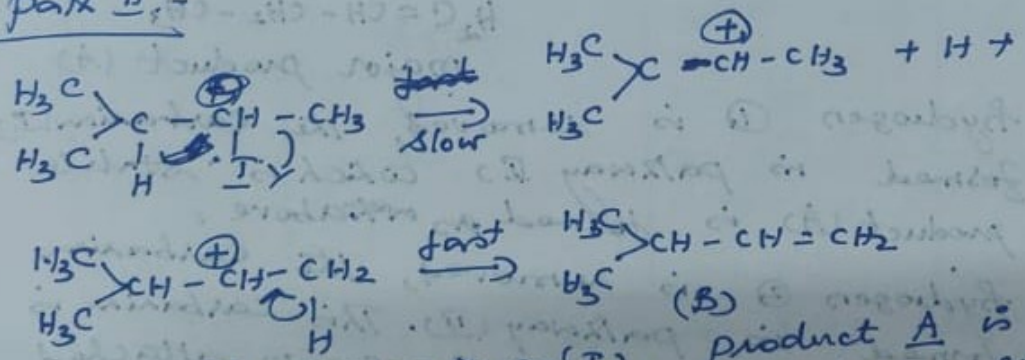
This rule is applicable to both E_1 & E_2

mechanism:
 when the mechanism is E_1

Path I:-



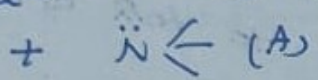
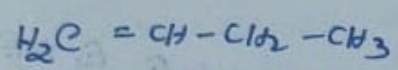
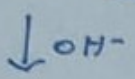
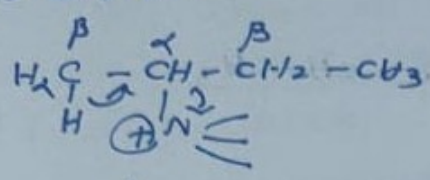
Path II:-



Though pathway (I), product A is formed predominantly according to Saytzeff rule, since it is more stabilised by hyperconjugation since it has three α CH bonds. But through pathway II, the product formed has only one α CH bond.

Hoffmann's rule:-

When quaternary ammonium bases are decomposed, the olefin formed is that whose unsaturated carbon atoms are linked to the least number of alkyl groups. Hydrogen is removed from the most hydrogenated β -carbon.

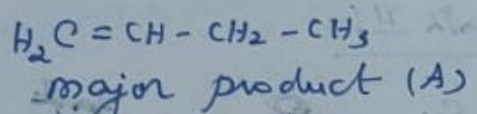
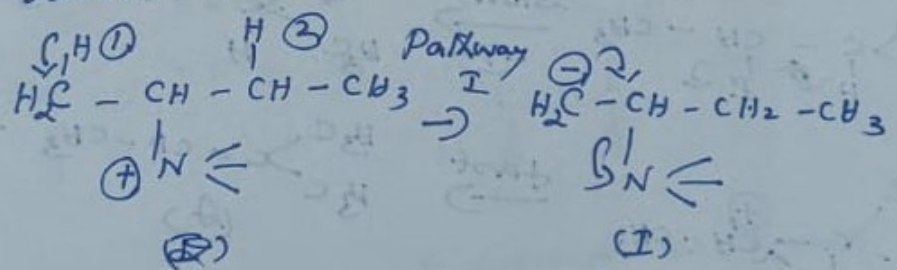


and not $\text{H}_3\text{C} - \text{CH} = \text{CH} - \text{CH}_3$

(B)

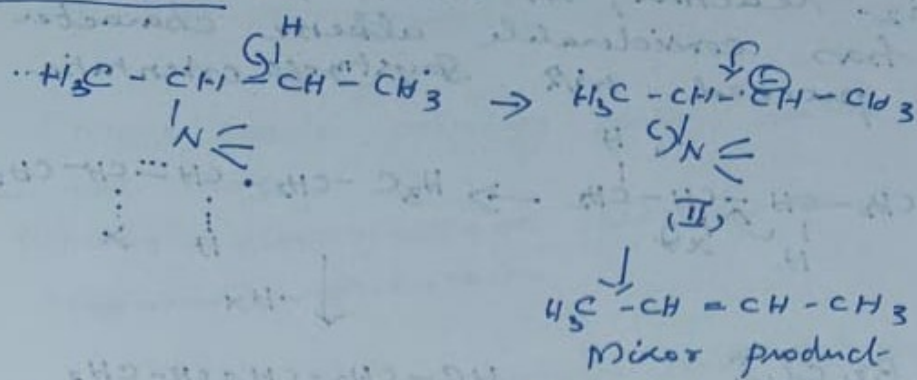
Explanation:-

- ① leaving group $\text{N} \equiv$ will exert a powerful electron withdrawing inductive effect on both β -carbon atoms and hydrogens marked as ① & ② become acidic



- ② If hydrogen ① is removed, the carbanion (I) is formed in pathway (I) which is stable and product (A) is formed as above.
- ③ If hydrogen ② is removed, the carbanion (II) is formed in pathway (II). This carbanion is destabilised by the methyl group attached to β -carbon.

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Pathway II:-



Explain E₂ elimination in 2-halopentanes / dehydrohalogenation.

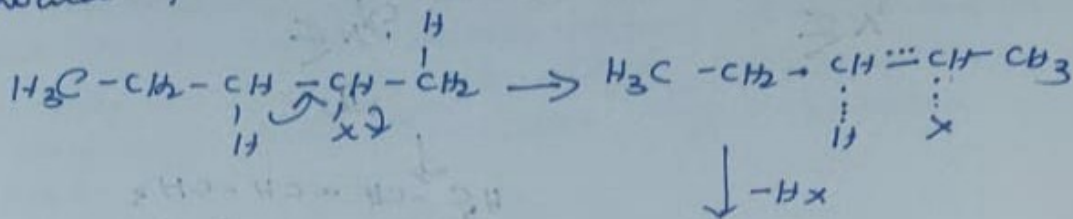
(or)
 Why 2-fluoropentane undergoes E₂-elimination by Hoffmann orientation though all 2-halopentanes undergo E₂-elimination by Saytzeff orientation.

① when 2-halopentanes are treated with strong base sodium methoxide, elimination follows E₂-mechanism and the proportion of the two pentanes vary as follows:

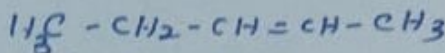
X	2-pentene %	1-pentene %
I	80	20
Br	72	28
Cl	65	35
F	30	70

- ② E₂-Elimination is a one-step elimination in which the C-H and C-X bonds get broken in the same transition state.
- ③ The cleavage of C-H & C-X bonds in an E₂ elimination need not be completely synchronised always.

④ In E₂ reaction, in which the transition state has considerable alkene character should proceed with Saytzeff orientation.



X = Br, Cl, I



2-pentene

(Saytzeff rule)

⑤ When the cleavage of C-H bond exceeds that of C-X bond (as in C-F bond due to greater bond energy and poor leaving group of F), the E₂ transition state would have little alkene character.

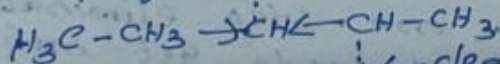
⑥ Rather a negative charge will develop on the carbon losing the proton.

⑦ E₂-transition state will have more carbanion character and its stability will be determined by factors which disperse or intensify this negative charge.

⑧ When a terminal primary hydrogen is abstracted in 2-fluoropentane, the negative charge develops on the primary carbon bearing only one e⁻ releasing and destabilising alkyl group.

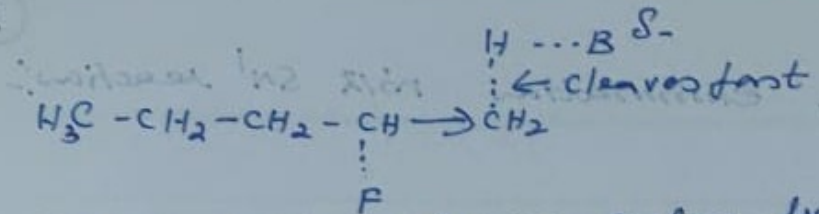
⑨ On the other hand, if a secondary hydrogen is abstracted, the negative charge will develop on the secondary carbon bearing two e⁻ releasing and destabilising alkyl groups.

⑩ Primary carbanion is more stable than secondary carbanion.



← leaves slowly.

(Less stable 2^o carbon bears partial -ve charge).



(More stable primary carbon bears partial -ve charge)

(1) So, 2 fluoropentane should react with Hoffmann orientation

Comparison E_2 mechanism with S_N2 mechanism.

S.No. Factors	S_N2	E_2
1. Reagent	Strong nucleophile	Strong base.
2. Solvent	Non-hydroxylic solvent of high low polarity increases the rate.	Non-hydroxylic solvents of high polarity increase the rate.
3. Rate	Rate follows the order $1^\circ > 2^\circ > 3^\circ$	Rate follows the order $3^\circ > 2^\circ > 1^\circ$
4. Transition state	$ \begin{array}{c} \text{S}^- \\ \vdots \\ \text{Nu} \dots \text{C} \dots \text{L} \text{S}^- \\ \\ \text{L} \end{array} $	$ \begin{array}{c} \text{B} \dots \text{H} \\ \vdots \\ > \text{C} \dots \text{C} < \\ \vdots \\ \text{L} \end{array} $
5. Kinetics	Rate = k [Substrate] [Nucleophile ⁻]	Rate = k [Substrate] [Base]
6. Stereochemistry	Inversion of configuration takes place.	Trans. elimination takes place.
7. Temperature.	Low temperature favours S_N2 reaction.	High temperature favours E_2 elimination.
8. Rearranged products	Rearranged products are formed.	No rearranged products are formed.

Compare E₁ elimination with S_N¹ reaction:-

S.No.	FACTOR	E ₁ Elimination	S _N ¹ reaction
①	Order of reactivity	Order follows in alkyl halides is 3° > 2° > 1°	Order follows in alkyl halides is 1° > 2° > 3°
②	Rate of the reaction	Formation of carbonium ion is the rate determining step Rate ∝ [Alkyl halide]	Formation of carbocation ion is the rate determining step. Rate ∝ [Alkyl halide]
③	Conc of the reagent	Low	High
④	Stereochemistry	Non-stereospecific	Racemization occurs
⑤	Temperature	Since elimination reaction needs more energy, high temperature increases the rate	Low temperature is enough
⑥	Solvent	polar hydroxylic solvents & low dielectric constant are required	polar hydroxylic solvents & high dielectric constant are needed
⑦	Rearranged products	Rearranged products are got	No rearranged products
⑧	Transition state	$\begin{array}{c} \delta- \\ \\ -C-C-\delta- \\ \quad \end{array}$	$\begin{array}{c} \delta+ \quad \delta- \\ \quad \\ -C \cdots C- \\ \end{array}$