ELIMINATION REACTION (Part-II)

By

Dr. JYOTI CHANDRA

Assistant Professor

Department of Chemistry

Email ID- jyotic09@gmail.com

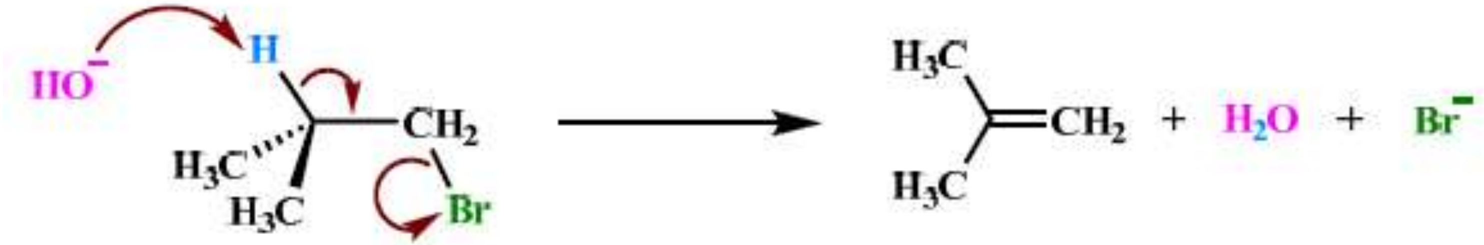
B.Sc-Ist Year (SEM-II)

Patna Women's College

Patna University

Bimolecular Elimination Reaction (E2)

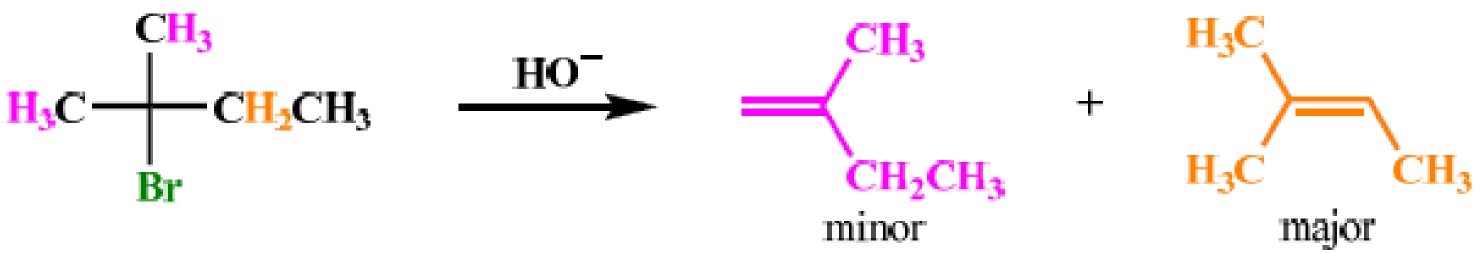
- Two groups depart simultaneously.
- Involves only one step (in other words, no intermediates are involved).
- Bimolecular reaction i.e., both substrate and nucleophile participate in a single step
- The base abstracts the β-hydrogen and leaving group simultaneously leaves such that it forms a multiple bond between α and β-carbon atoms.



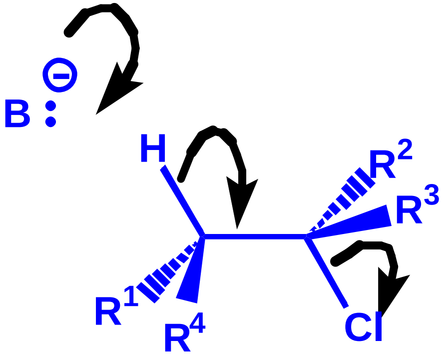
- Exhibits second-order kinetics, and both the alkyl halide and the base appear in the rate equation as:

$$\text{Rate} = k[(CH_3)_3CBr][HO]$$

- The reaction is concerted—all bonds are broken and formed in a single step.
- E2 reactions are regioselective and favor the formation of **Zaitsev products**



E2 Reaction Mechanism

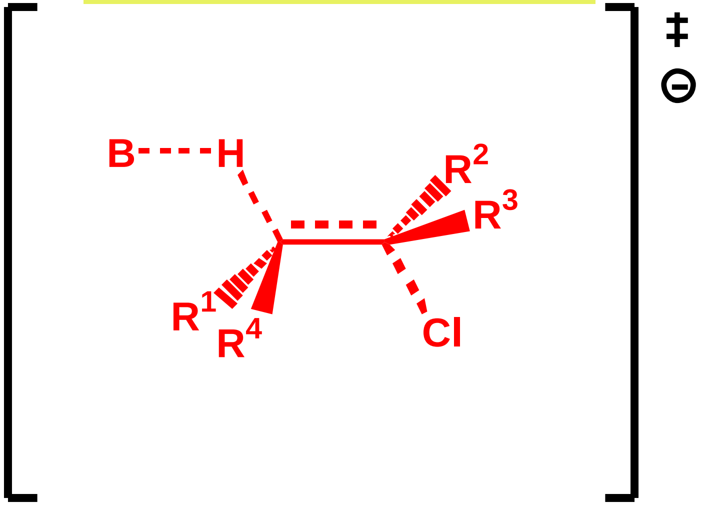


Bimolecular Process

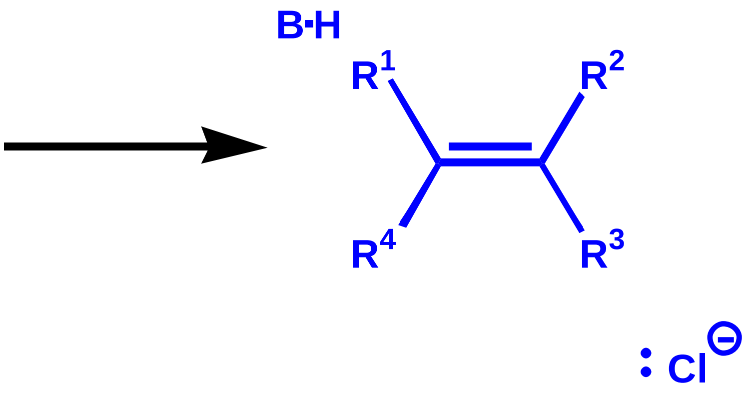
Rate = *k*[R-Hal][B]

H and Cl must be *antiperiplanar*

Compare to S_N2



Transition State – Energy Maxima



Retension of Stereochemistry

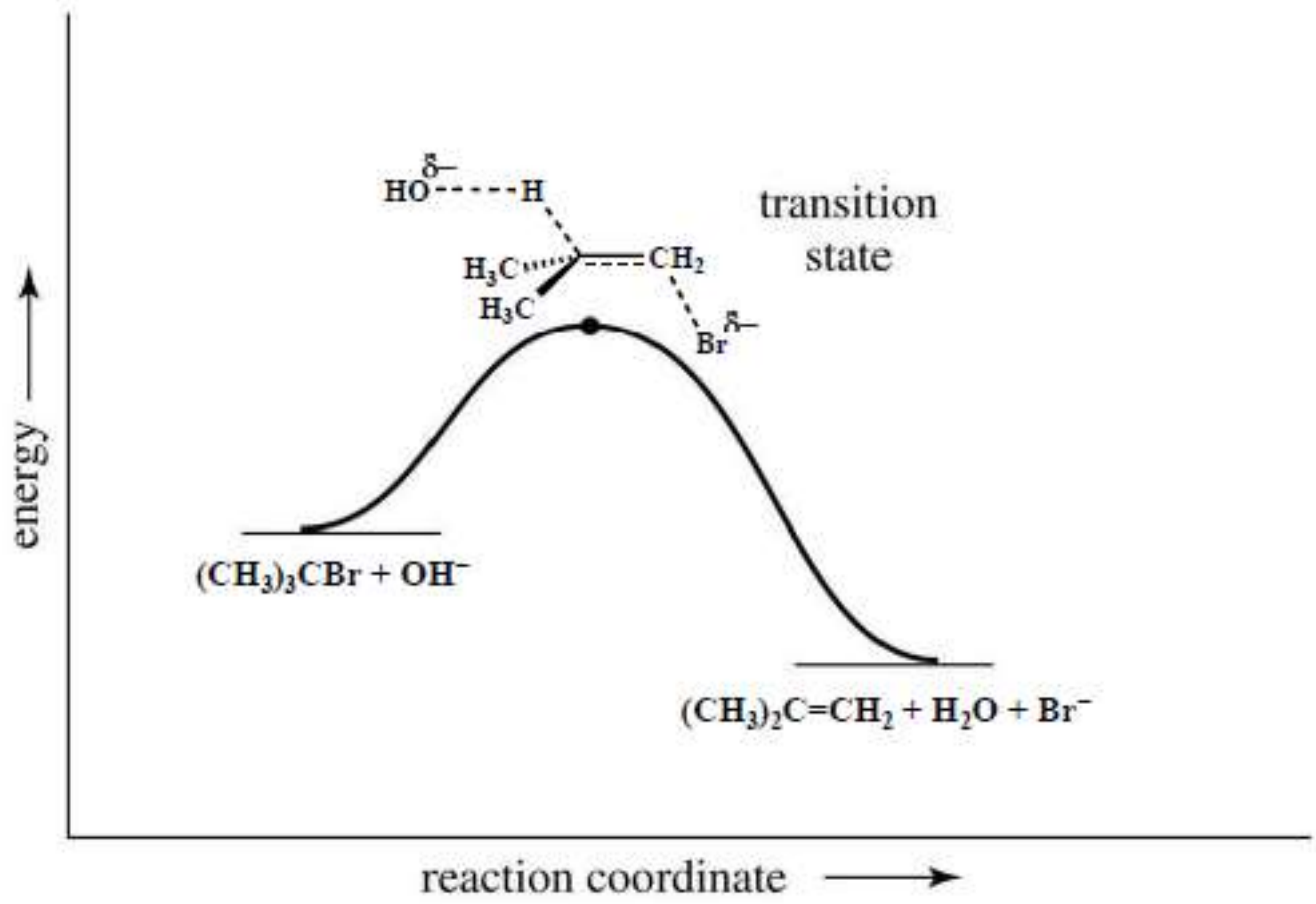
E2 Reaction Mechanism

- ☐ The sequence of mechanisms involved are:

1) The attack of base on β-hydrogen and its abstraction as a proton is the first event. This will leave two electrons of the C-H bond available for the formation of a new double bond between the carbon atoms.

2) As the new double bond is created, the C-Cl bond begins to break away (leaving group). This will result in the departure of the chloride ion.

Energy Profile for an E2 Reaction



Factors Affecting the Rate of an E2 Reaction

There are close parallels between E2 and S_N2 mechanisms.

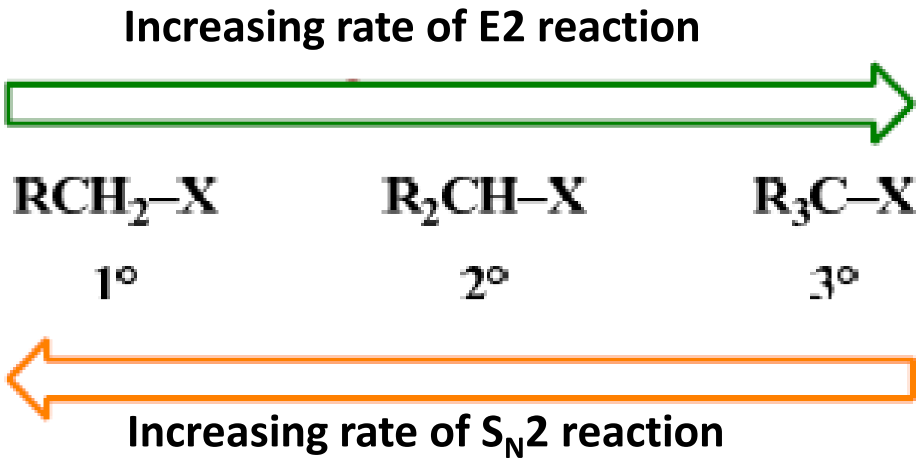
- ☐ The base appears in the rate equation, so the rate of the E2 reaction increases as the strength of the base increases.
- ☐ E2 reactions are generally run with strong, negatively charged bases like OH^- and OR^-.
- ☐ Polar aprotic solvents increase the rate of E2 reactions
- ☐ There is a partial breaking of the bond to the leaving group in the transition state. So, the better the leaving group the faster the E2 reaction.
- ☐ Rate of reaction follows the order,

$$R{-}I > R{-}Br > R{-}Cl > R{-}F$$

Factors Affecting the Rate of an E2 Reaction

The S_N2 and E2 mechanisms differ in how the R group affects the reaction rate.

- As the number of R groups on the carbon with the leaving group increases, the rate of the E2 reaction increases.



Increasing rate of E2 reaction

$RCH_2–X$ $R_2CH–X$ $R_3C–X$

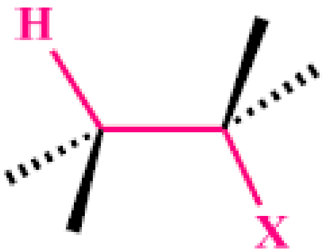
1° 2° 3°

Increasing rate of S_N2 reaction

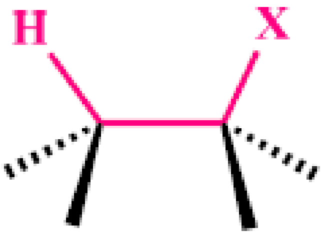
- The increase in E2 reaction rate with increasing alkyl substitution can be rationalized in terms of transition state stability.
- In the transition state, the double bond is partially formed. Thus, the transition state for a more substituted alkenes is lower in energy, reducing the activation energy for the reaction and making the reaction faster.
- E2 reactions are stereoselective, resulting in the formation of trans-double bonds preferably.

Stereochemistry of the E2 Reaction

- The transition state of an E2 reaction consists of four atoms from the substrate (one hydrogen atom, two carbon atoms, and the leaving group, X) aligned in a plane. There are two ways for the C—H and C—X bonds to be coplanar.



anti periplanar
H and X are on the opposite side



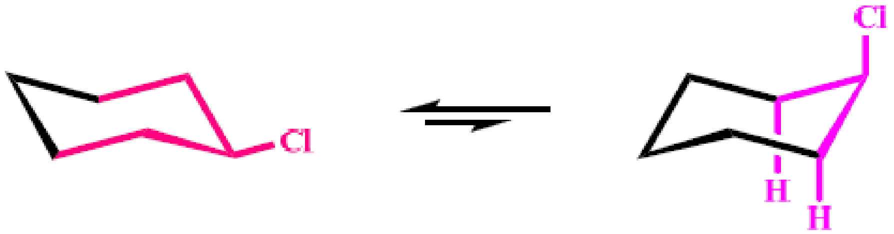
syn periplanar
H and X are on the same side

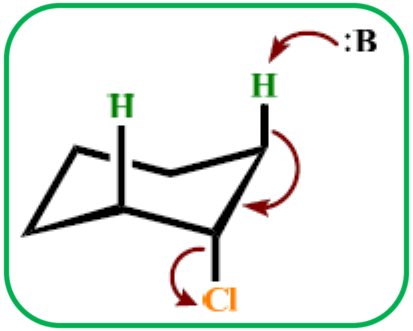
- E2 elimination occurs most often in the anti periplanar geometry. This arrangement allows the molecule to react in the lower energy staggered conformation, and allows the incoming base and leaving group to be further away from each other.
- The anti periplanar geometry also allows direct interaction between the bonding electrons of C—H bond and the anti-bonding orbital of the C—X bond.

E2 Reactions in 6-Membered Rings

- The stereochemical requirement of an anti periplanar geometry in an E2 reaction has important consequences for compounds containing six-membered rings.

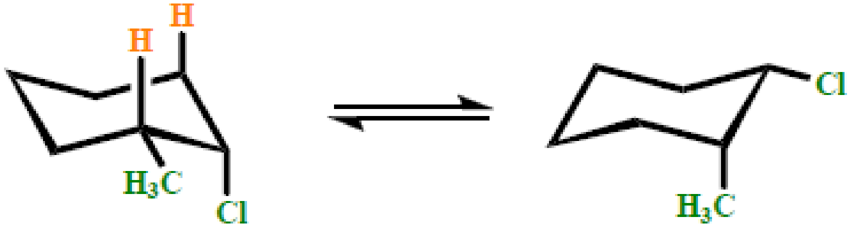
- **Chlorocyclohexane**





- For E2 elimination, the C—Cl bond must be anti periplanar to the C—H bond on a β-carbon, and this occurs only when the H and Cl atoms are both in the axial position. The requirement for trans-diaxial geometry means that elimination must occur from the less stable conformer.

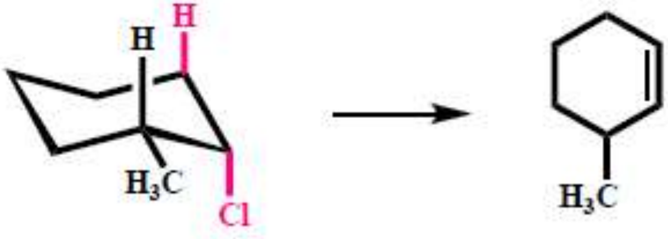
Dehydrohalogenation of cis-1-Chloro-2-methylcyclohexane



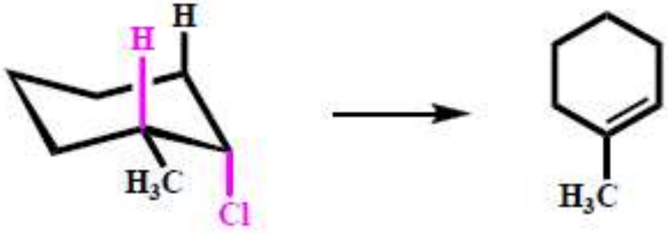
In this conformer two Hs are anti periplanar to the Cl.

In this conformer Cl is in an equatorial psition and has no Hs periplanar to it.

- The conformer with Cl in an axial orientation reacts to give two alkenes. The alkene that is more substituted is the major product.



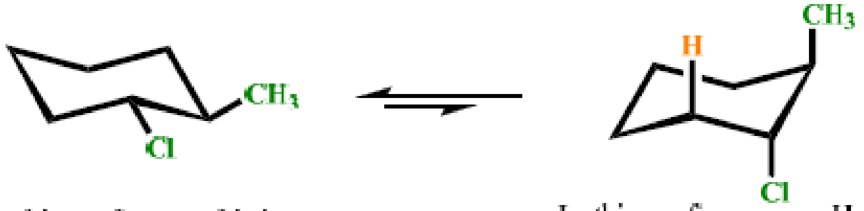
disubstituted alkene
minor product



trisubstituted alkene
major product

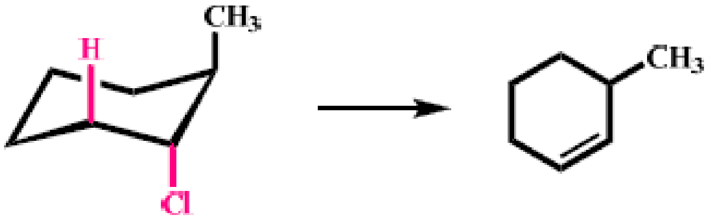
Dehydrohalogenation of trans-1-Chloro-2-methylcyclohexane

- ❖ The conformer with Cl in an axial orientation has just one β-H atom. Only one product is formed, which is not what is predicted by the Zaitsev rule.



In this conformer Cl is in an equatorial psition and has no Hs periplanar to it.

In this conformer one H and one CH_3 are anti periplanar to the Cl.

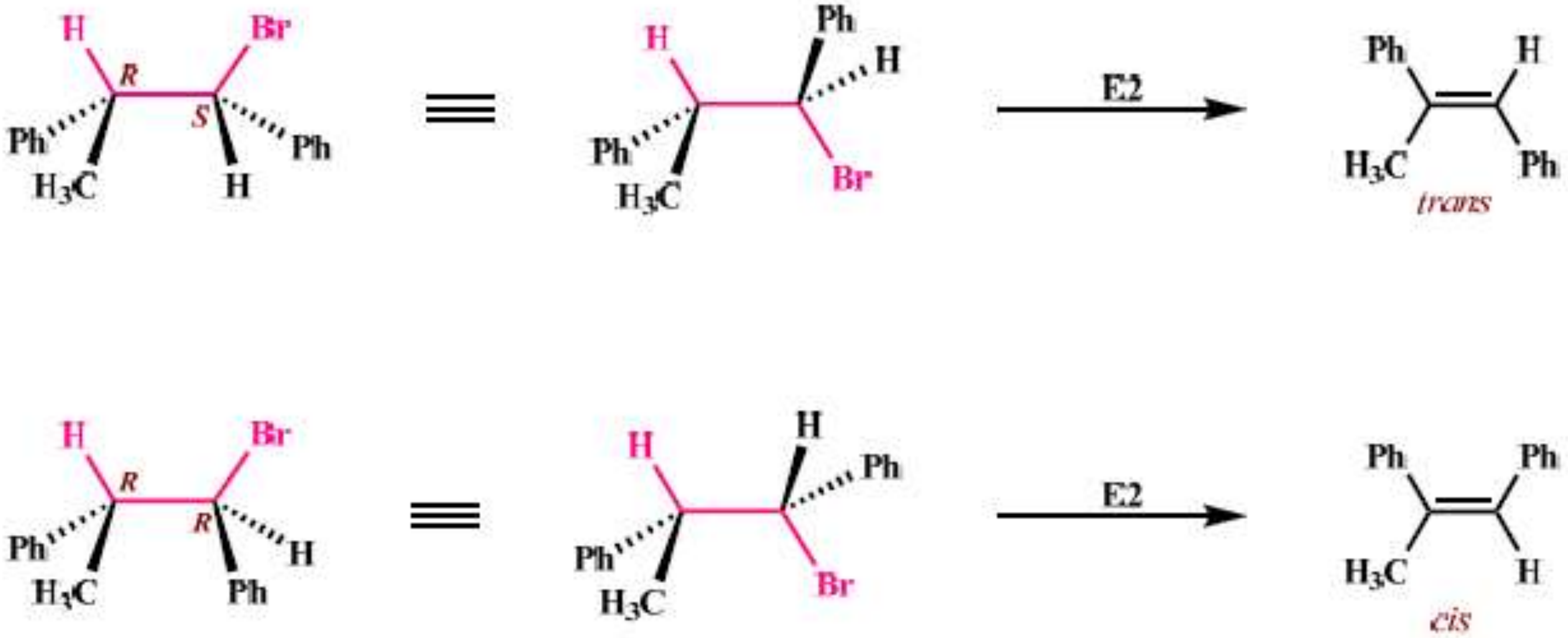


disubstituted alkene, the only product formed

- ❖ In conclusion, with substituted cyclohexanes, E2 elimination should occur with a trans diaxial arrangement of the leaving group and the β-H, and as a result of this requirement, the more substituted alkene is not necessarily the major product.

Stereospecificity in E2 reactions

- Diastereomeric starting compounds yield diastereomeric products after an E2 reaction.



Summary of an E2 Reaction

- ✓ Kinetics – Second order
- ✓ Mechanism – Single step
- ✓ Identity of R group – More substituted halides react faster

Rate: $R_3CX > R_2CHX > RCH_2X$

- ✓ Strength of the base – Stronger bases favor the reaction
- ✓ Leaving group – Better leaving group leads to faster reaction rates
- ✓ Type of solvent – Favored by polar aprotic solvents