ELIMINATION REACTION (Part-III)

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Unimolecular Elimination Reaction (E1)

☐ It is two step reaction:

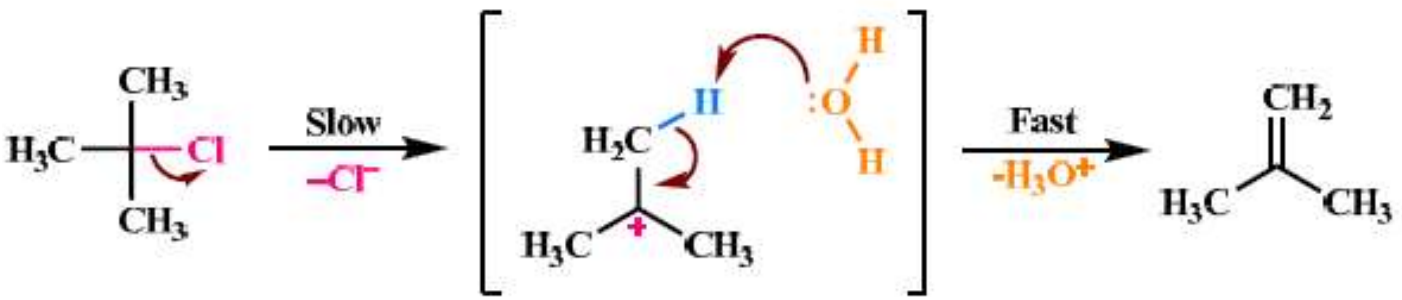
First step is similar to that of $S_N1$reaction i.e., the generation of carbocation intermediate. In second step, hydrogen is abstracted by the base rather than attack on the carbocation as in S_N1.

☐ Only one of the substrates is involved in the rate determining step i.e., unimolecular reaction.

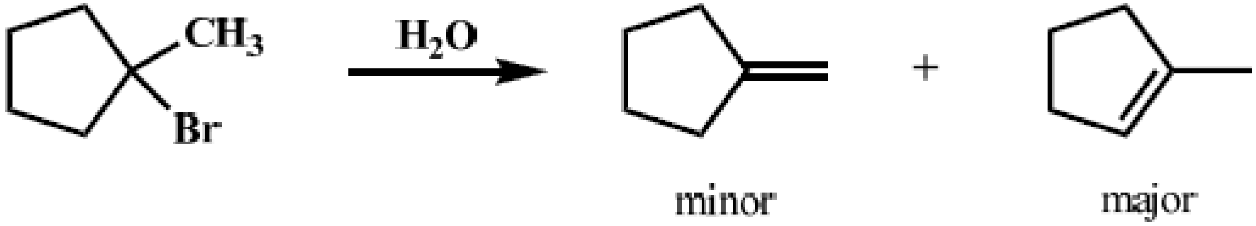
☐ It exhibits first-order kinetics:

$$\text{rate} = k[(CH_3)_3CCl]$$

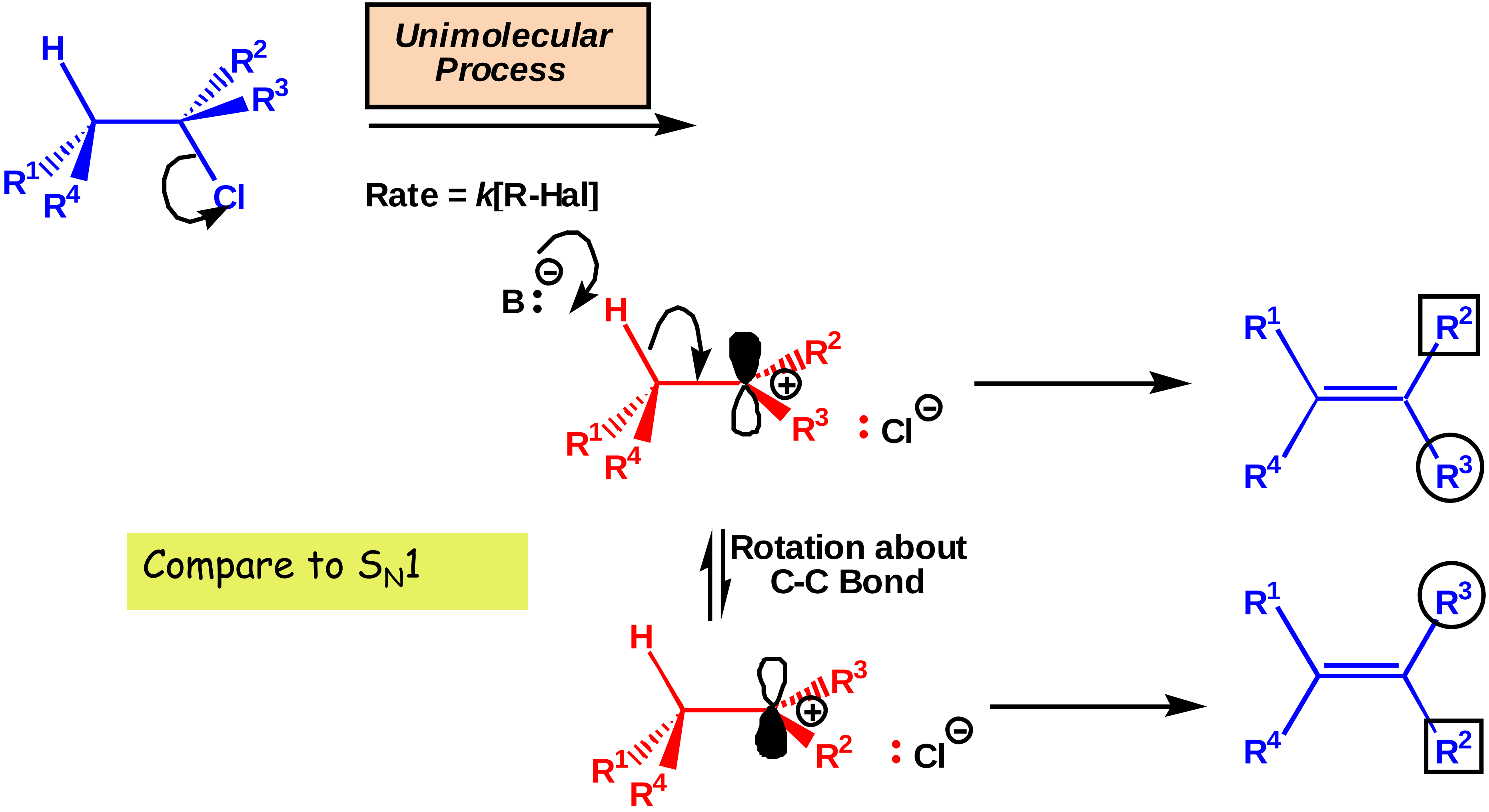
The E1 Reaction Mechanism



- The E1 reaction proceeds via a two-step mechanism: the bond to the leaving group breaks first before the π bond is formed. The slow step is unimolecular, involving only the alkyl halide..
- E1 reactions also are regioselective and follow Zaitsev rule.



The E1 Reaction Mechanism



Unimolecular Process

Rate = *k*[R-Hal]

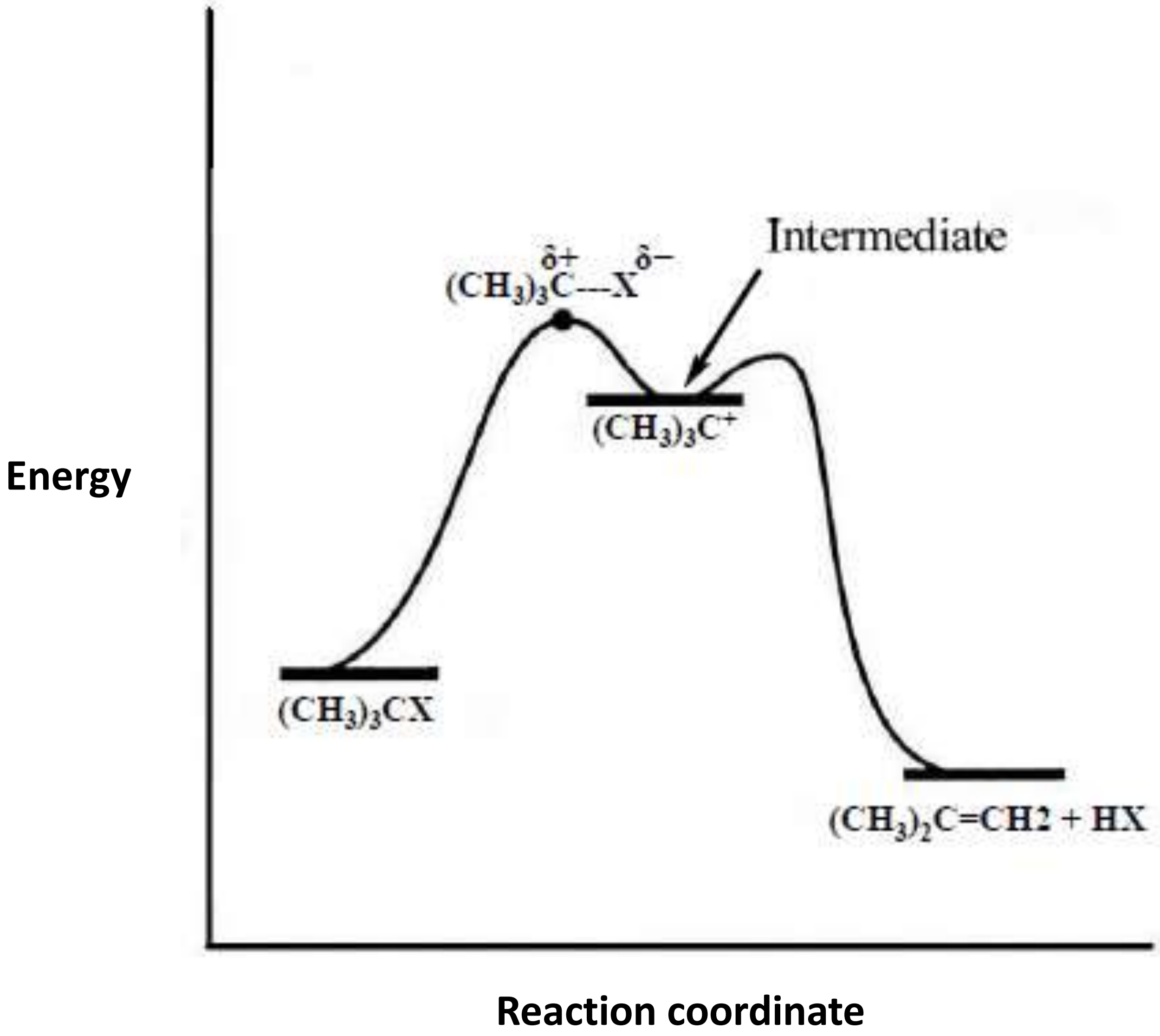
Rotation about C-C Bond

Compare to S_N1

Reactive Intermediate – Energy Minima

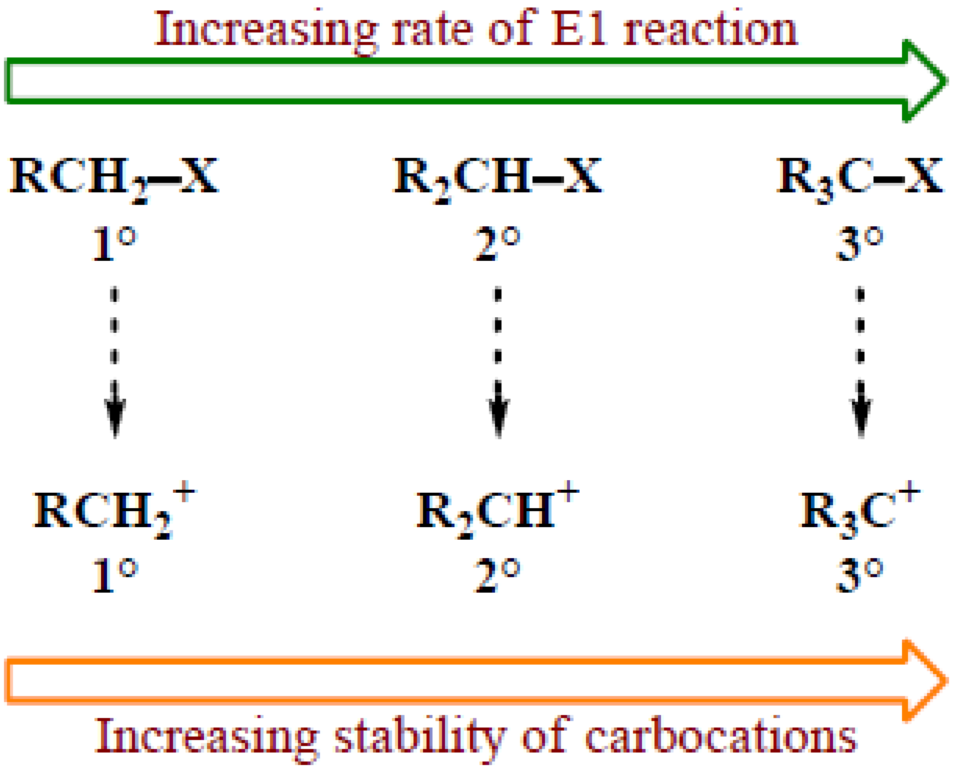
Loss of Stereochemistry

Energy Profile for an E1 Reaction



Factors Affecting the Rate of an E1 Reaction

- ❑ The rate of an E1 reaction increases as the number of R groups on the carbon with the leaving group increases.



Increasing rate of E1 reaction

$RCH_2{-}X$ 1°

$R_2CH{-}X$ 2°

$R_3C{-}X$ 3°

RCH_2^+ 1°

R_2CH^+ 2°

R_3C^+ 3°

Increasing stability of carbocations

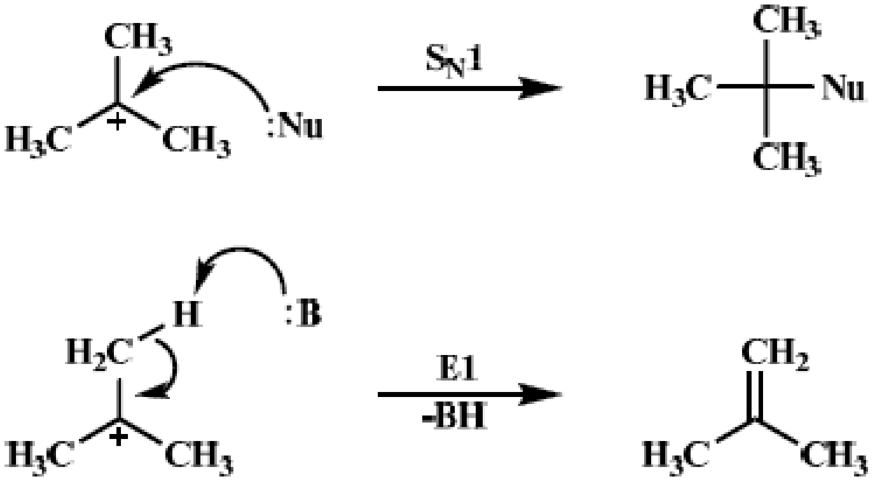
Summary of an E1 Reaction

- ✓ Kinetics – First order
- ✓ Mechanism – Two steps
- ✓ Identity of R group – More substituted halides react faster

  Rate: $R_3CX > R_2CHX > RCH_2X$
- ✓ Strength of the base – Favored by weaker bases such as H_2O and ROH
- ✓ Leaving group – Better leaving group leads to faster reaction rates. Just as in SN1 reactions, the rate determining step involves the C—X bond cleavage
- ✓ Type of solvent – Favored by polar protic solvents, which can stabilize the ionic intermediates

S_N1 and E1 Reactions

- S_N1 and E1 reactions have exactly the same first step—formation of a carbocation. They differ in what happens to the carbocation.



- Since in both the reactions, the rate determining steps are the same, they cannot be individually controlled. Because E1 reactions often occur with a competing S_N1 reaction, E1 reactions of alkyl halides are much less useful than E2 reactions.

S_N1, S_N2, E1 or E2 Reaction

✓ **3°Alkyl Halides**

- With strong bases: E2 elimination occurs
- With weak nucleophiles or bases: A mixture of products from S_N1 and E1 reactions

✓ **1°Alkyl Halides**

- With strong nucleophiles: Substitution occurs by an S_N2 mechanism
- With strong sterically hindered bases: Elimination occurs by an E2 mechanism

✓ **2°Alkyl Halides**

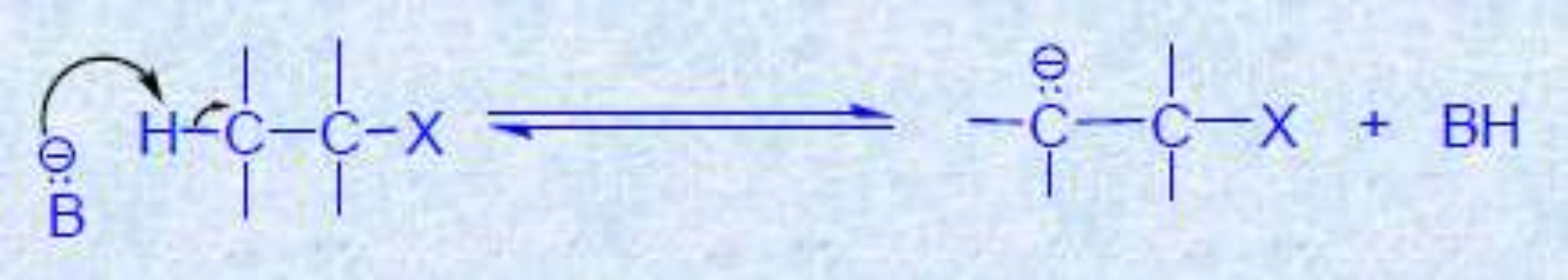
- **With strong bases and nucleophiles**: A mixture of S_N2 and E2 reaction products are formed .
- **With strong sterically hindered bases**: Elimination occurs by an E2 mechanism.
- **With weak nucleophiles or bases**: A mixture of S_N1 and E1 products results

Elimination Unimolecular conjugate Base (E1cB Reaction)

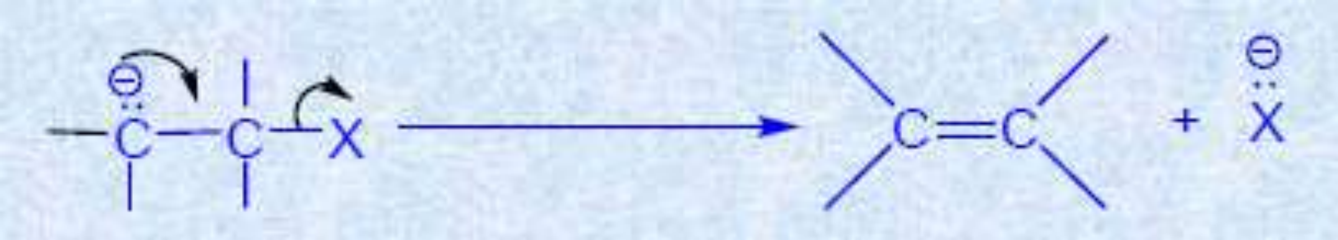
- ☐ This is a two step base-induced β-elimination.
- ☐ In this reaction base first abstracts the β-hydrogen, giving rise to a carbanion or **conjugate base of the substrate from which the leaving group departs subsequently to form the product.**
- ☐ In E1cB, the deprotonation occurs ahead of leaving group departure
- ☐ Reaction usually follows second order kinetics but is designated as E1cB to indicate that the departure of the leaving group is from the initially formed conjugate base (i.e., carbanion).

E1cB mechanism

- **Step 1:** attack of the base on the β-hydrogen. B-hydrogen leaves without its carbon electron pair forming a carbanion. The electron pair then move towards the new C-C double bond to be generated.



- **Step 2 :** Departure of the leaving group to give product.



Details on E1cB

- ☐ Depending on the nature of the rate-determining step, there are different ways by which reaction can proceed:

1) Carbanion returns to the starting material faster than the product formation. Step 1 is reversible and step 2 is slow. It is designated as $(\text{E1cB})_R$.
2) Product formation is faster as compared to return of proton to carbanion. Step 2 is irrevererersible and step 1 is slow. It is designated as $(\text{E1cB})_I$.