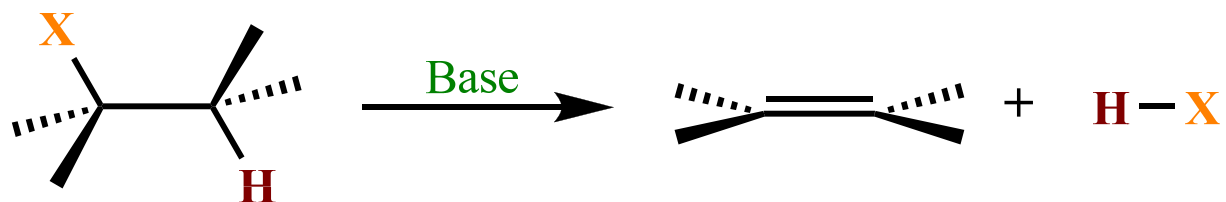


Elimination Reactions



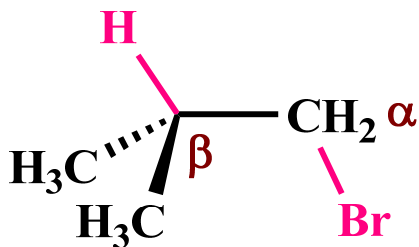
Just as there are two mechanisms of substitution (S_N2 and S_N1), there are two mechanisms of elimination (E2 and E1).

E2 mechanism — bimolecular elimination

E1 mechanism — unimolecular elimination

The E2 and E1 mechanisms differ in the timing of bond cleavage and bond formation, analogous to the S_N2 and S_N1 mechanisms.

E2 and S_N2 reactions have some features in common, as do E1 and S_N1 reactions.

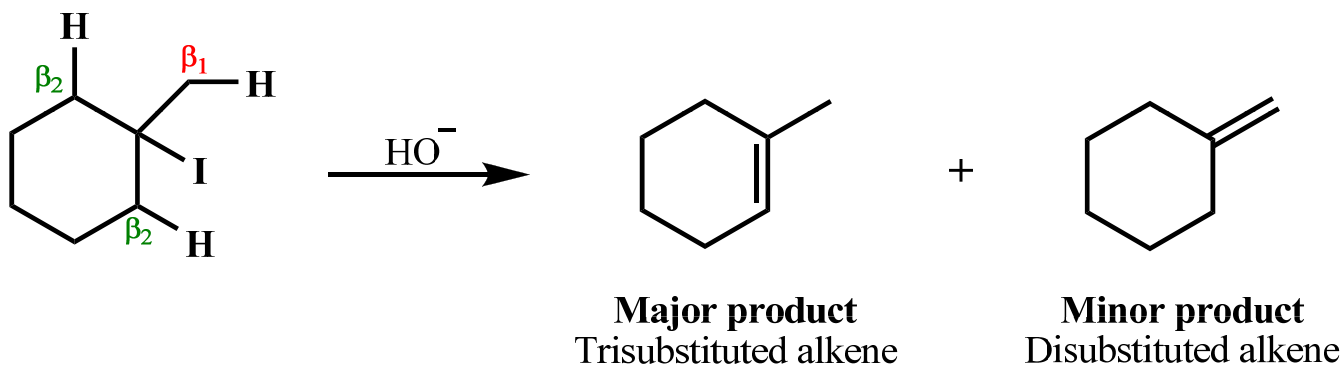


Base removes a proton from the β -carbon atom, while the halogen atom leaves from the α -carbon resulting in the formation of a π -bond. Such eliminations are also called β -elimination reactions

The Zaitsev (Saytseff) Rule

When alkyl halides have two or more different β carbons, more than one alkene product is formed.

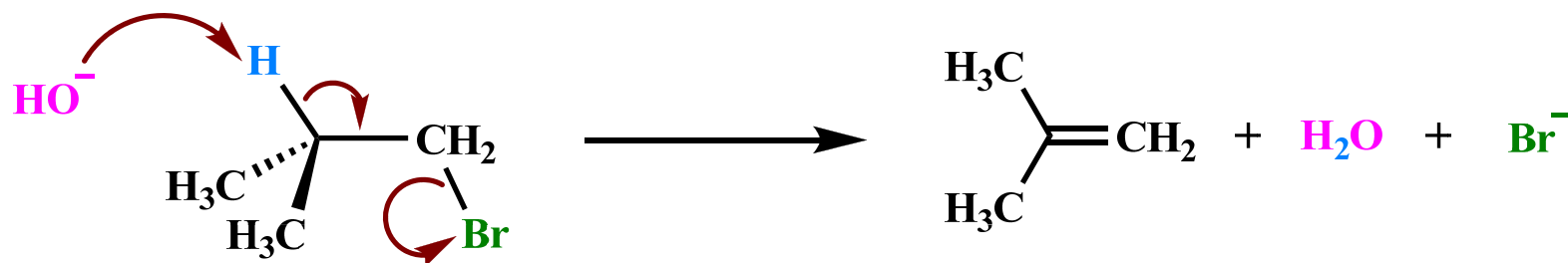
In such cases, the major product is the more stable product—the one with the more substituted double bond. This phenomenon is called the Zaitsev rule.



The Zaitsev product or the more substituted alkene product is more stable than the less substituted product. The stability of the more substituted alkene is a result of number of different contributing factors, including hyperconjugation.

Each alkyl group that can involve in hyperconjugation with the double bond stabilizes it by approximately 6 kcal/mol

The E2 Mechanism



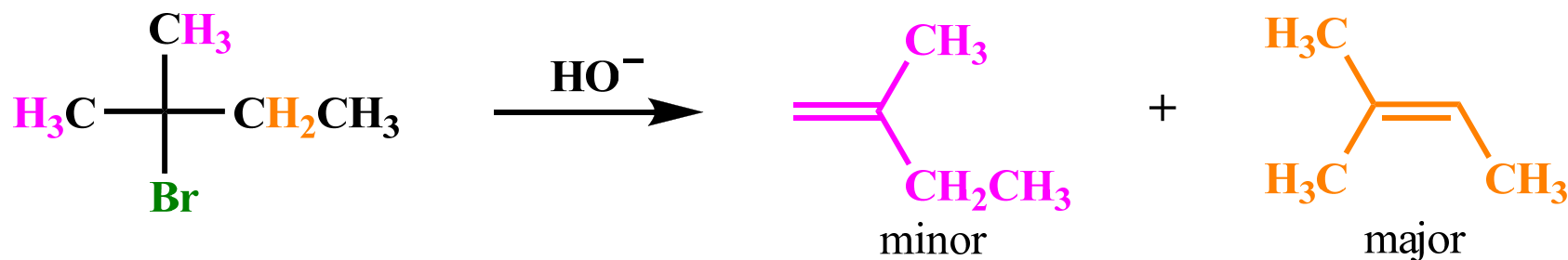
The most common mechanism for dehydrohalogenation is the E2 mechanism.

It exhibits second-order kinetics, and both the alkyl halide and the base appear in the rate equation

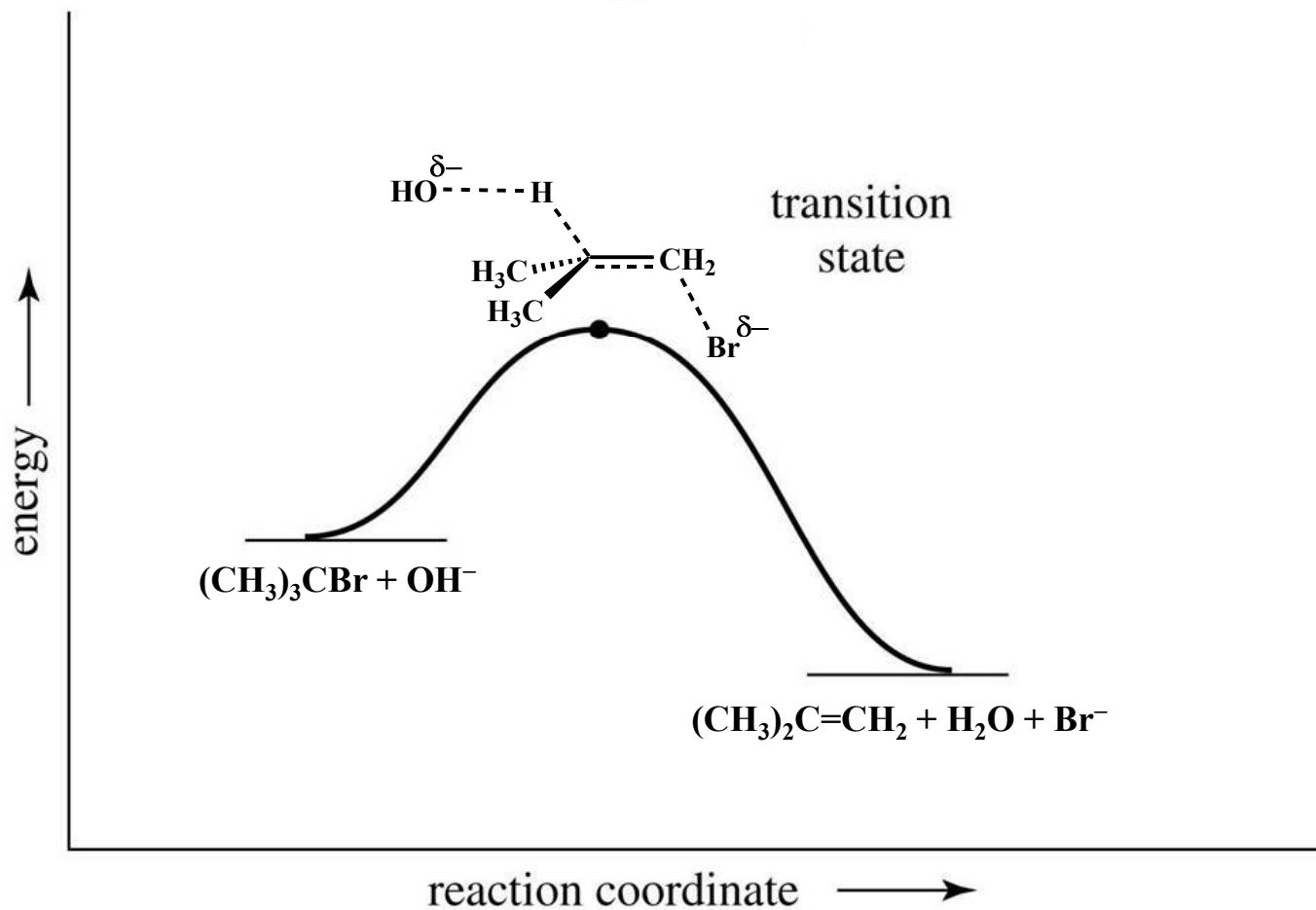
$$\text{rate} = k[(\text{CH}_3)_3\text{CBr}][\text{HO}^-]$$

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.



Energy Profile for an E2 Reaction



Factors Affecting the Rate of an E2 Reaction

There are close parallels between E2 and S_N2 mechanisms in how the identity of the base, the leaving group and the solvent affect the rate.

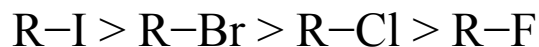
The base appears in the rate equation, so the rate of the E2 reaction increases as the strength of the base increases.

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.

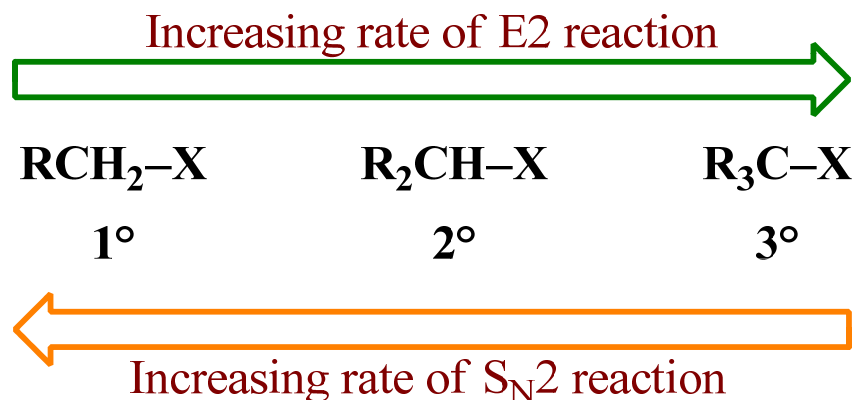
Rate of reaction follows the order,



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.



The increase in E2 reaction rate with increasing alkyl substitution can be rationalized in terms of transition state stability.

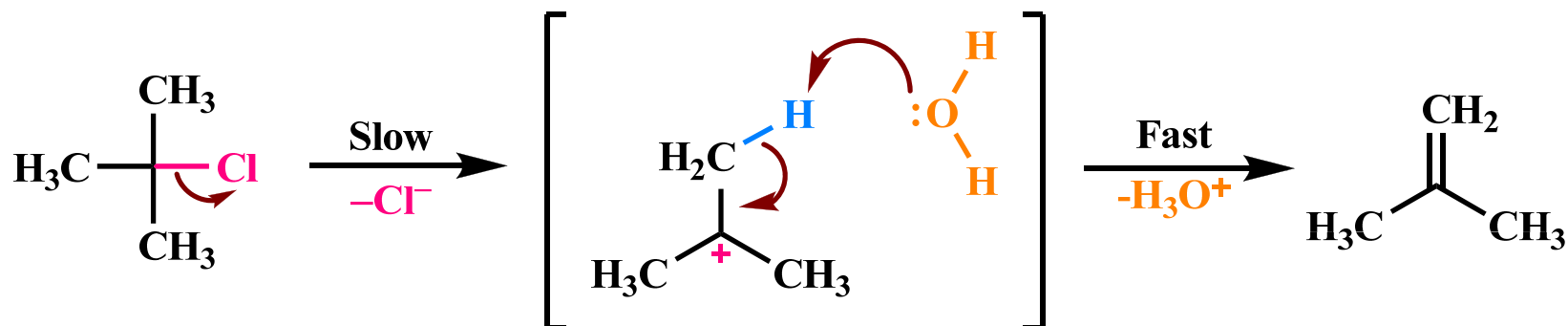
In the transition state, the double bond is partially formed. Thus, the transition state for a more substituted alkene is lower in energy, reducing the activation energy for the reaction and making the reaction faster.

Characteristics 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

E2 reactions are stereoselective, resulting in the formation of trans-double bonds preferably.

The E1 Mechanism

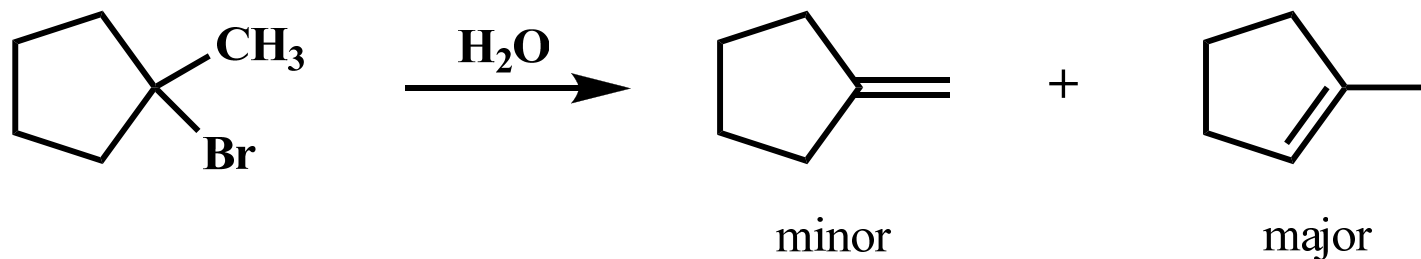


The E1 reaction proceeds via a two-step mechanism: the bond to the leaving group breaks first before the π bond is formed. The slow step is unimolecular, involving only the alkyl halide.

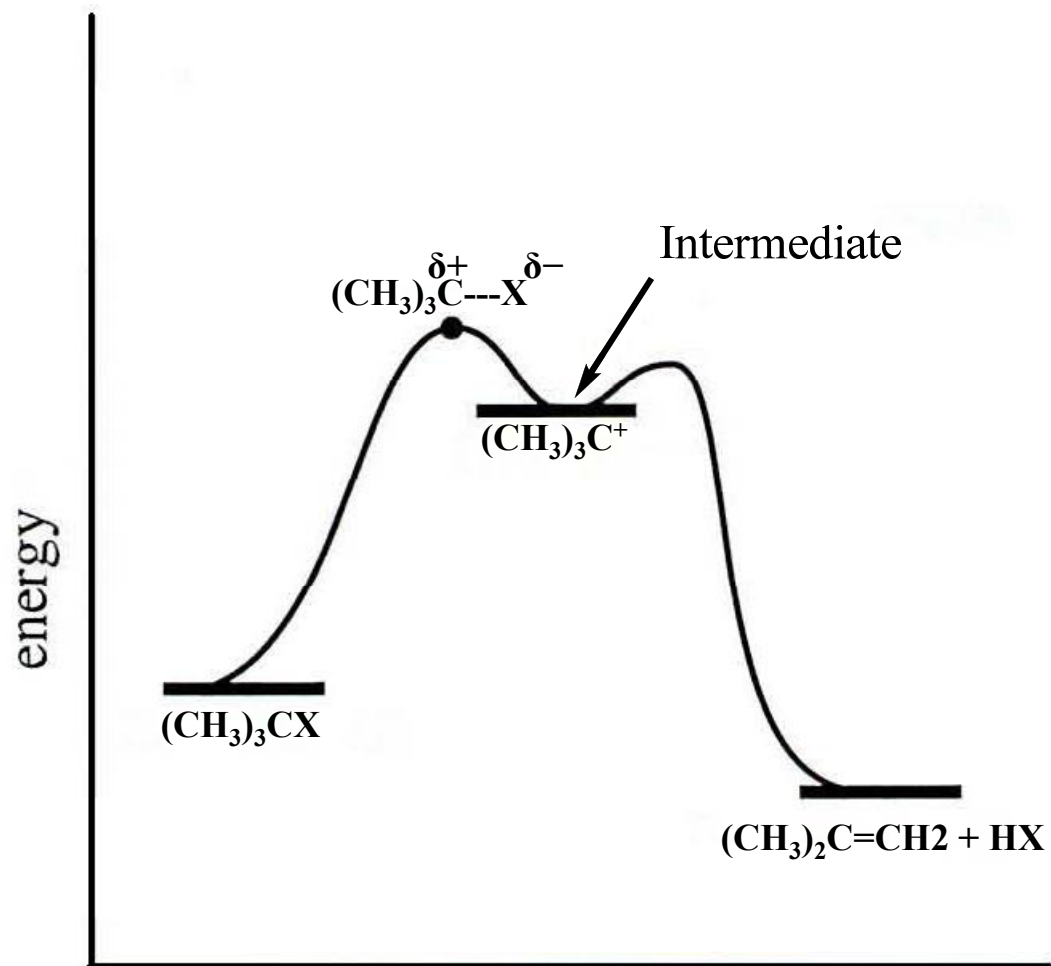
It exhibits first-order kinetics,

$$\text{rate} = k[(\text{CH}_3)_3\text{CCl}]$$

E1 reactions also are regioselective and follow Zaitsev rule

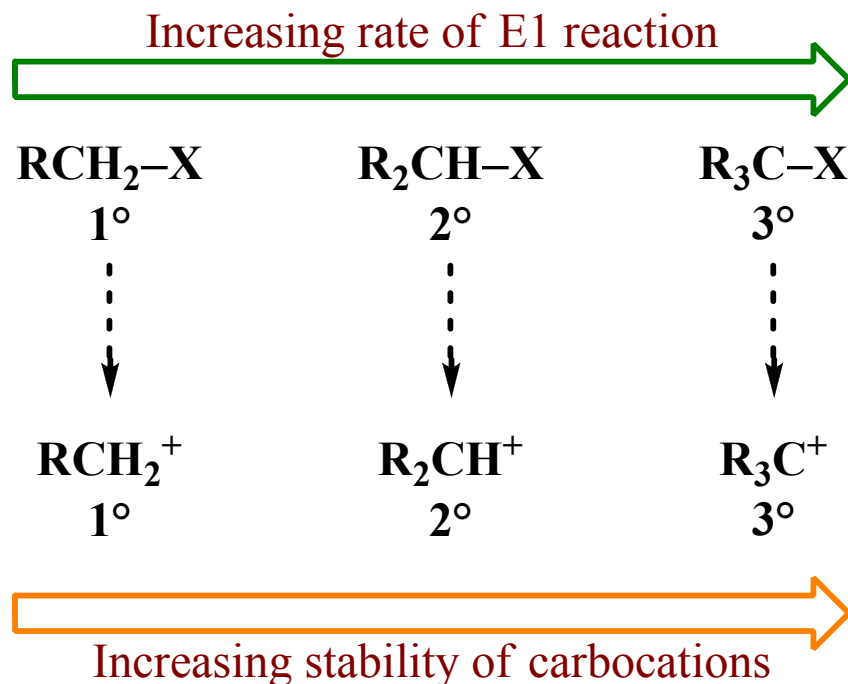


Energy Profile for an E1 Reaction



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.



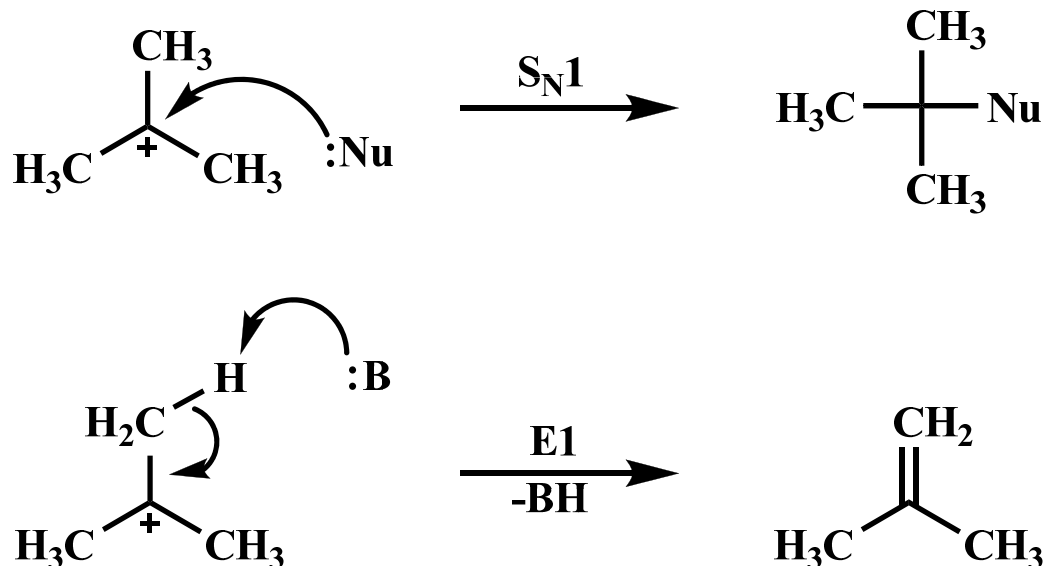
The strength of the base usually determines whether a reaction follows the E1 or E2 mechanism. Strong bases like OH^- and OR^- favor E2 reactions, whereas weaker bases like H_2O and ROH favor E1 reactions.

Characteristics 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 S_N1 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

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

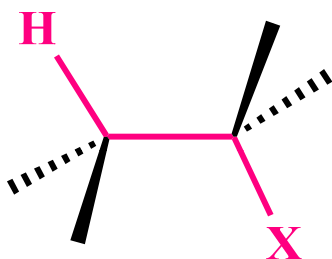
With strong bases and nucleophiles: A mixture of S_N2 and E2 reaction products are formed

With strong sterically hindered bases: Elimination occurs by an E2 mechanism

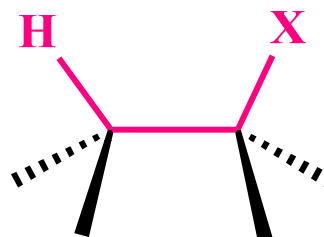
With weak nucleophiles or bases: A mixture of S_N1 and E1 products results

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

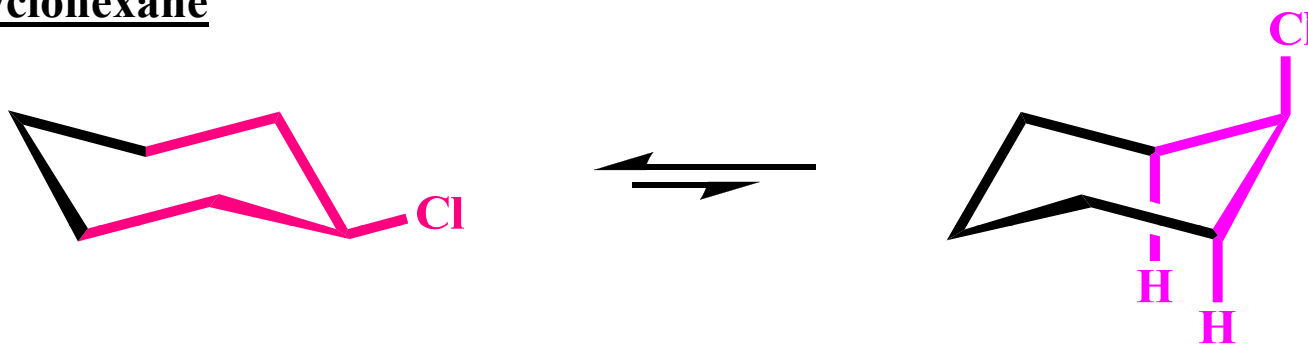
E2 elimination occurs most often in the anti periplanar geometry. This arrangement allows the molecule to react in the lower energy staggered conformation, and allows the incoming base and leaving group to be further away from each other.

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.

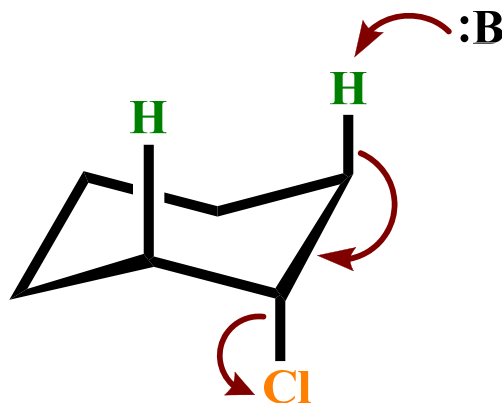
E2 Reactions in 6-Membered Rings

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

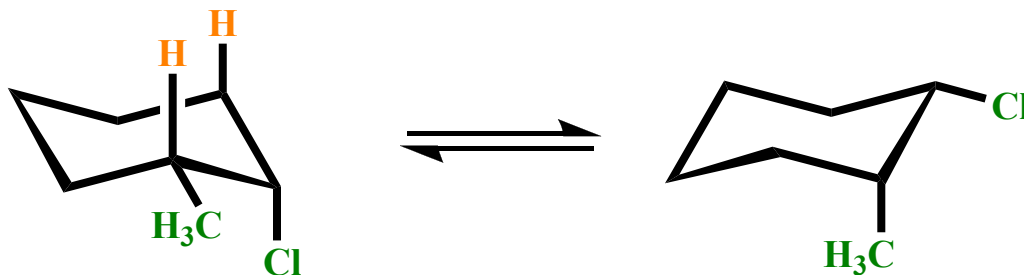
Chlorocyclohexane



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.



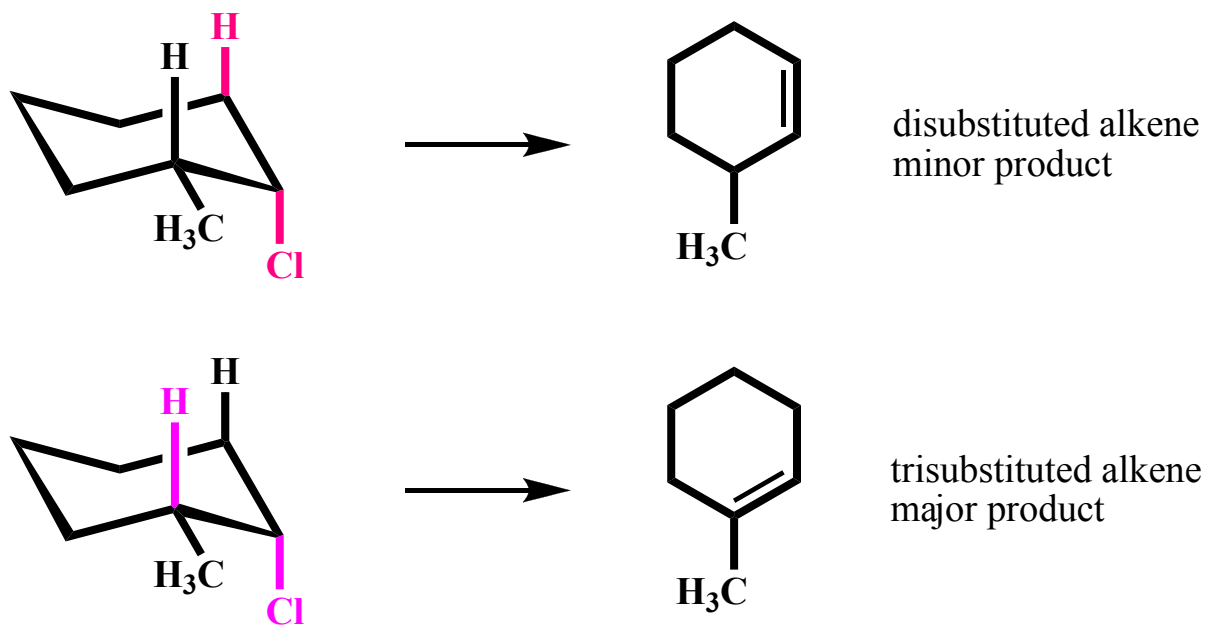
Dehydrohalogenation of *cis*-1-Chloro-2-methylcyclohexane



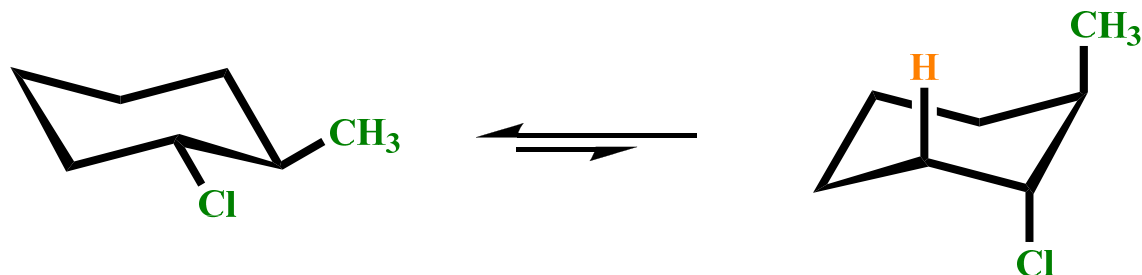
In this conformer two Hs are anti periplanar to the Cl.

In this conformer Cl is in an equatorial position 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.



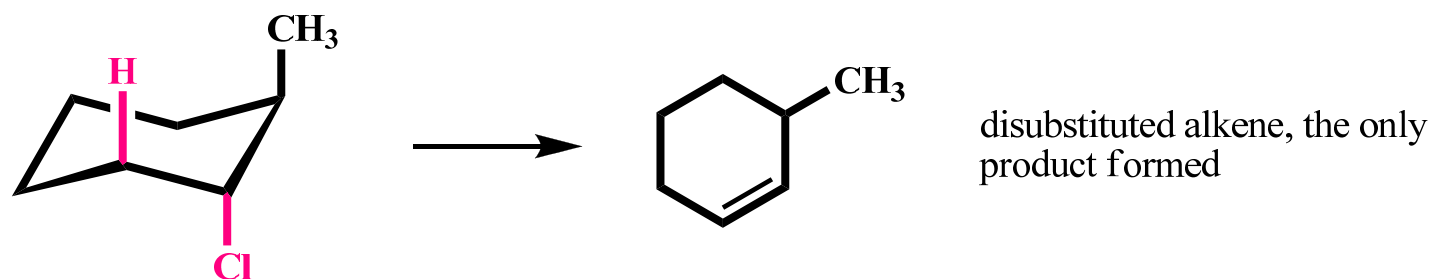
Dehydrohalogenation of *trans*-1-Chloro-2-methylcyclohexane



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

In this conformer one H and one CH₃ are anti periplanar to the Cl.

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.

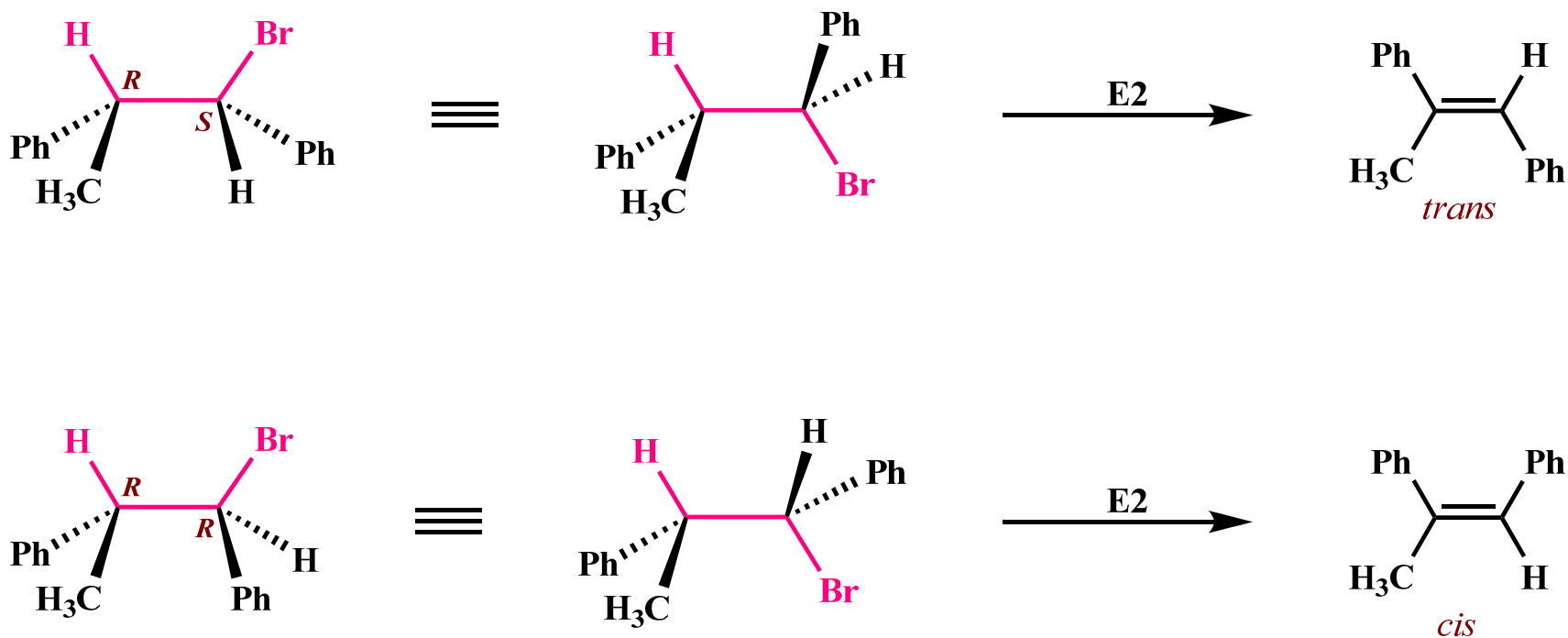


disubstituted alkene, the only product formed

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.

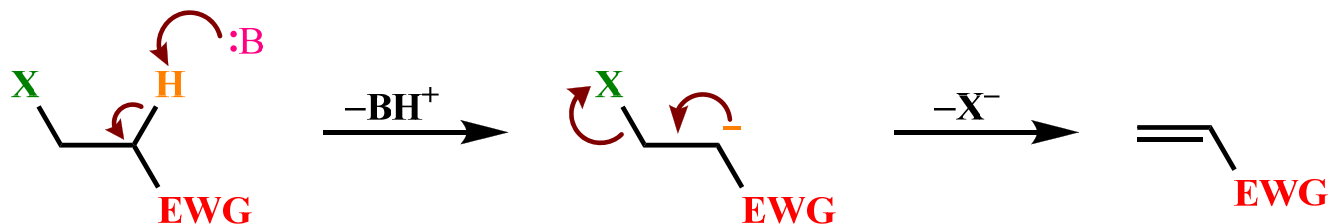
Stereospecificity in E2 reactions

Diastereomeric starting compounds yield diastereomeric products after an E2 reaction



E1cB Reaction

An elimination reaction that happens when a compound bearing a poor leaving group and an acidic hydrogen is treated with a base.



E1cB stands for **Elimination Unimolecular conjugate Base**. The reaction is unimolecular from the conjugate base of the starting compound, which in turn is formed by deprotonation of the starting compound by a suitable base.

The electron withdrawing group (EWG) can be a carbonyl group (keto, aldehyde, ester), a nitro group, an electron deficient aromatic group etc. Dehydration of aldol is the most common E1cB reaction

