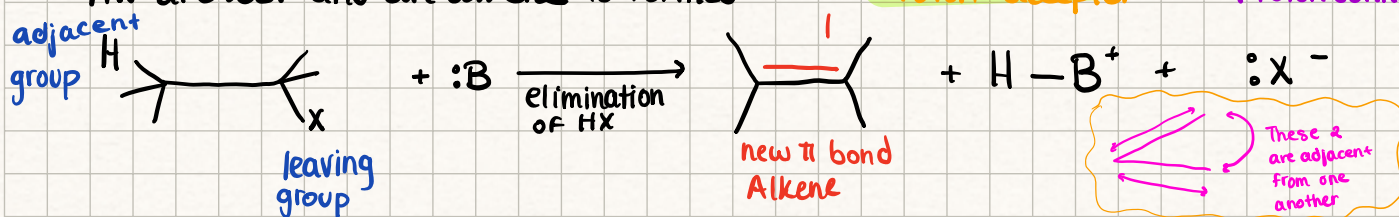


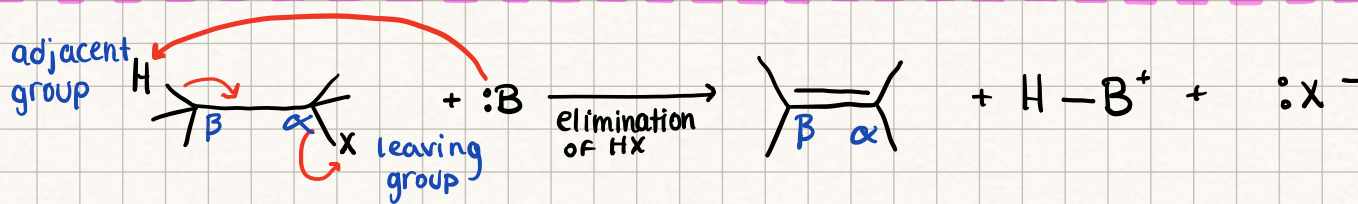
Elimination Reactions: All involve loss of elements from the starting material to form a new π bond in the product

↳ Alkyl halides undergo elimination reactions with **Brønsted-Lowry bases**. The elements of HX are lost and an alkene is formed



Dehydrohalogenation: Method of removing elements of HX which introduces a π bond & prepare an alkene

↳ Is an example of **β elimination** since it requires a loss of elements from 2 adjacent atoms. The **α carbon** is bonded to the leaving group and the **β group** is adjacent to it

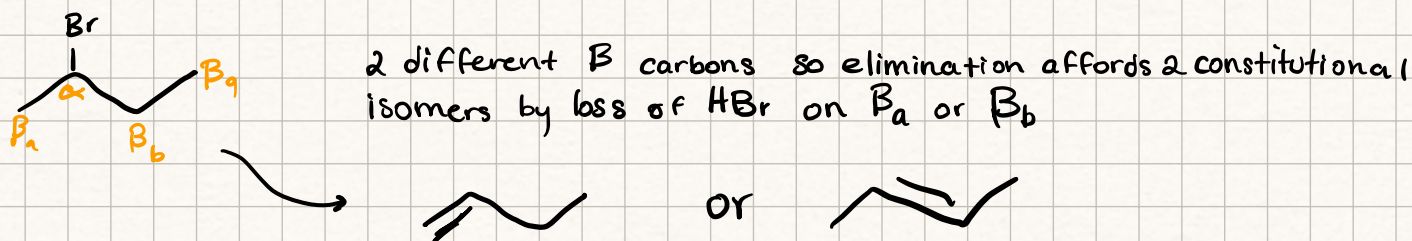
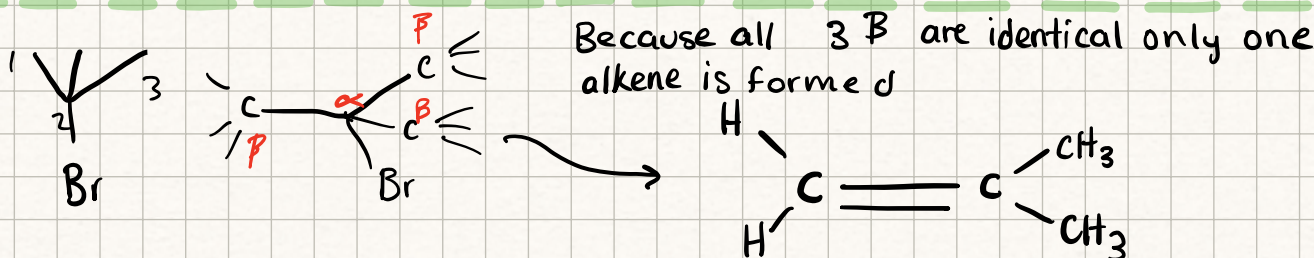


-Bases commonly used in elimination are negatively charged oxygen compounds like OH^- & its alkyl derivatives, OR^- called **alkoxides**

↳ Potassium tert-butoxide, $K^+ ^-OC(CH_3)_3$ a bulky nonnucleophilic base, is especially useful

How to draw any product of dehydrohalogenation

1. Find the α carbon - is sp^3 hybridized carbon which is bonded to the leaving group
2. Identify all β carbons with H atoms
3. Remove the Elements of H and X from the α and β carbon and form a π bond



Alkenes

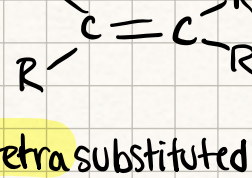
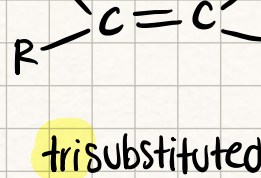
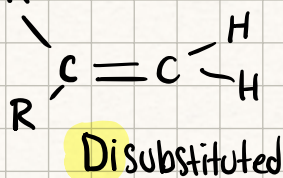
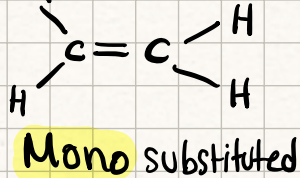
◦ Alkenes are hydrocarbon containing a carbon-carbon double bond therefore are $sp^2 \rightarrow 120^\circ$ and trigonal planar

◦ Are classified according to the number of carbon atoms bonded to the carbons of the double bond

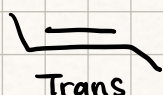
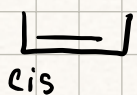
↳ **Monosubstituted alkene** has one carbon attached to the double bond carbons

Disubstituted alkene has two



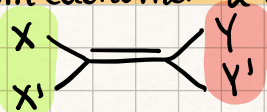


- Cis isomers have two groups on the same side of the double bond
- Trans isomers have two groups on opposite sides of the double bond



* These are isomers of each other but not superimposable therefore are diastomers of one another

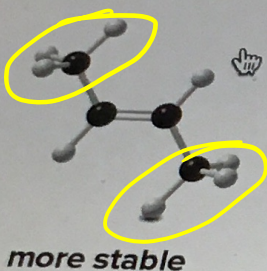
- Whenever the 2 groups on each end of the carbon-carbon double bond are different from each other 2 diastomers are possible



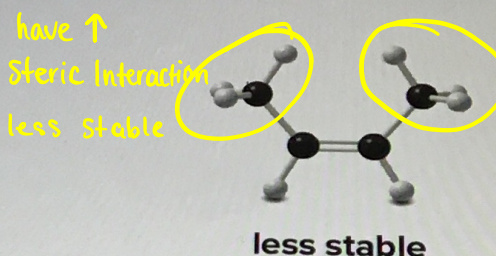
- X' & X must be different from each other and Y and Y' must be different from each other two have 2 diastomers
- All 4 have to be different

- Trans Alkenes are generally more stable than cis Alkenes b/c larger groups bonded to the double bond carbons are further apart reducing steric interactions

The trans isomer has the CH₃ groups farther away from each other.



Steric interactions of the CH₃ groups destabilize the cis isomer.



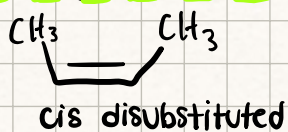
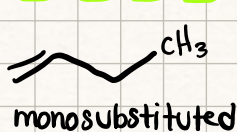
least stable

Most stable



* More R groups more stable Alkene because R groups are sp³ hybridized and the C=C is sp². The percent s-character of a hybrid orbital increases from 25% to 33% in going from sp³ to sp². The higher the percentage of s-character the more it accepts electron density.

↳ sp² hybridized Carbon atoms accept more electron density & sp³ are more able to donate electron density



Increased Stability

- Trans Alkenes are more stable than cis Alkenes because they have less steric interactions
- Increasing alkyl substitution stabilizes an alkene by an electron-donating inductive effect

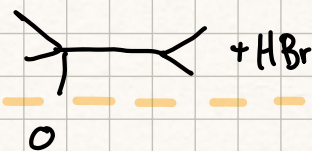
Mechanisms of Elimination

- 2 Methods of elimination E2 and E1 just like 2 methods of nucleophilic substitution SN1 and SN2
- E2 mechanism is bimolecular elimination } differ in timing of bond cleavage and bond

- E1 mechanism is unimolecular elimination] formation, are analogous to SN1 & SN2

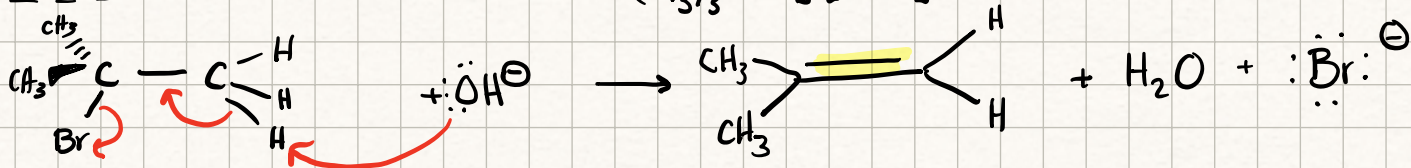
E2 Mechanism

- Most common mechanism for dehydrohalogenation is the E2 mechanism



E2 Reaction

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



E2 reaction is a 2nd order kinetics meaning is bimolecular therefore both the alkyl halide and base appear in rate equation

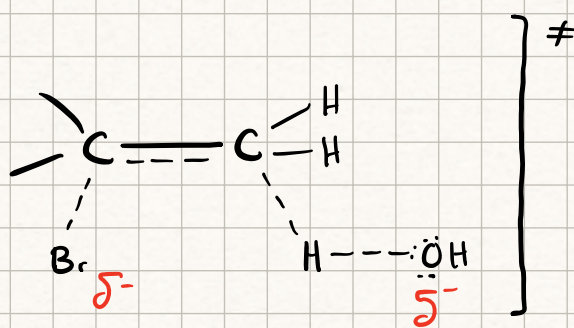
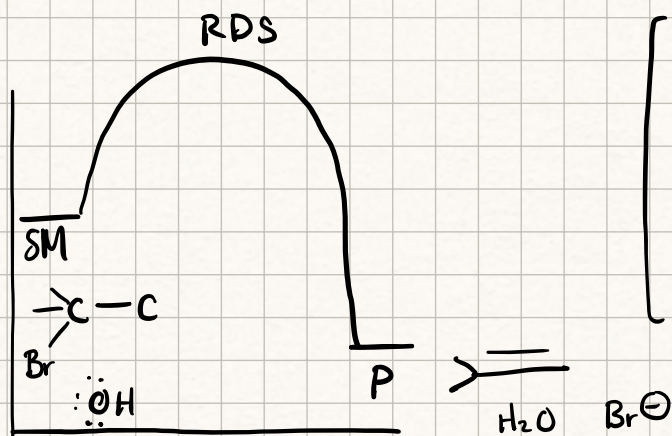
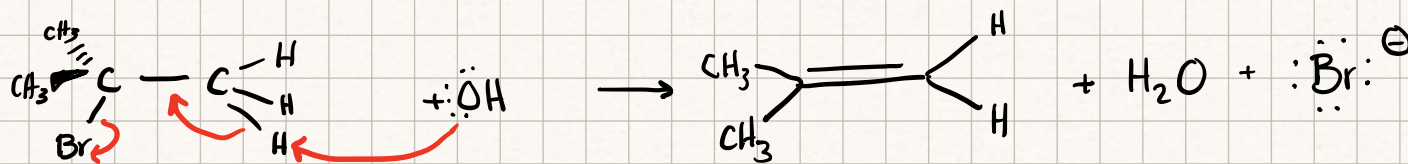
↳ 2nd order explained b/c is a concerted reaction: All bonds are broken and formed in a single step

- B/c is one step there is one energy barrier between reactants and products. You're breaking 2 bonds & forming 2 bonds (C-Br, C-H) (H₂O and π bond)

↳ Therefore transition state has **broken** **Formed**

4 partial bonds have δ⁻ distributed around leaving group & base

* Entropy favors the products of an E2 Reaction b/c 2 molecules of SM form 3 molecules of P

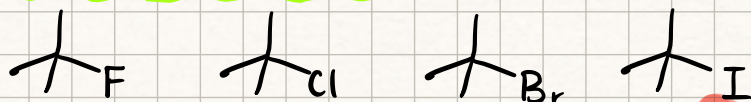


Question: Do the dots not matter here anymore distance wise?

- Because the base appears in the rate equation the rate of E2 will increase as the strength of the base increases

↳ E2 usually occurs w/ strong negatively charged bases like -OH and -OR
Sometimes use strong sterically hindered nitrogens bases called DBN & DBU

* Because bond to leaving group is partially broken in the transition state, the better the leaving group the faster the E2 reaction



* leaving group better acid = better leaving group

Increased leaving group ability increasing rate of E2 reaction

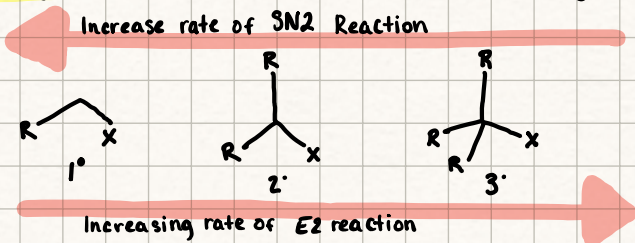
Solvents

Polar aprotic solvents do not solvate well with anions like -OH , a negatively charged base will not be hidden by strong interactions w/ solvent and the base is stronger. Stronger base means faster reaction

Polar Aprotic Solvent favors E2

How SN2 and E2 differ

- Reactions differ as the number of R groups on the carbon w/ leaving group increases the rate of E2 increases rate of SN2 ↓



- R groups increase rate b/c in TS the double bond is partially formed so has increasing stability of double bond w/ alkyl substituents stabilizes the TS which increases rate of the reaction essentially more bonds are formed

The Zaitzev rule

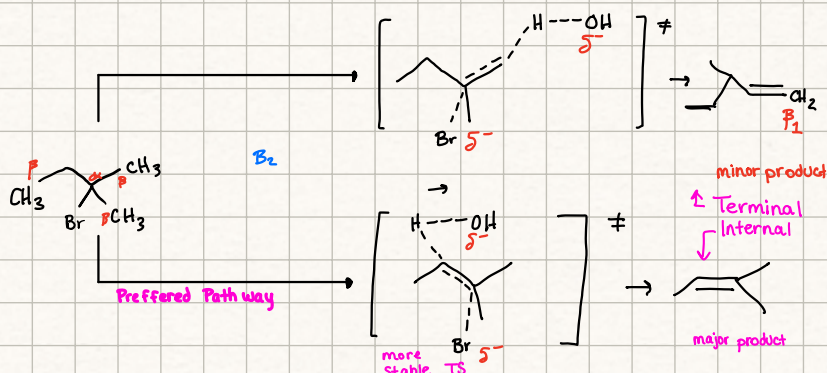
The Zaitzev rule major production in E2 elimination has the more substituted double bond

- If reaction is regioselective when it yields predominantly or exclusively one constitutional isomer when more than one is possible.

↳ E2 is regioselective b/c the more substituted alkene predominates

- Zaitzev rule results b/c the double bond is partially formed in the transition state for the E2 reaction. These double bonds create more stability of double bond by increasing R groups and lowering its energy of the TS which increases the rate of reaction

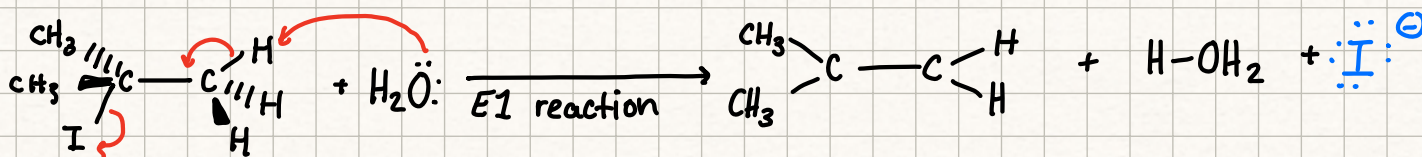
- E2 will create alkenes C and D. D will have the more substituted double bond, is the major product, because the TS leading to its formation is lower in energy



- Reaction is stereoselective when it forms predominantly or exclusively one stereoisomer when 2 or more are possible. E2 is stereoselective

The E1 Mechanism

The dehydrohalogenation with H_2O to form $(\text{CH}_3)_2\text{C}=\text{CH}_2$ can be used to illustrate the second general mechanism of elimination the E1 mechanism

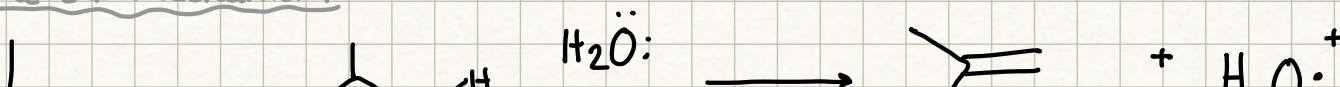


* An E1 reaction exhibits first-order kinetics meaning is unimolecular

↳ rate = $k[\text{electrophile}]$

- The reaction like SN1 kinetics suggest the reaction mechanism involves more than one step & the slow step is unimolecular involving only the alkyl halide

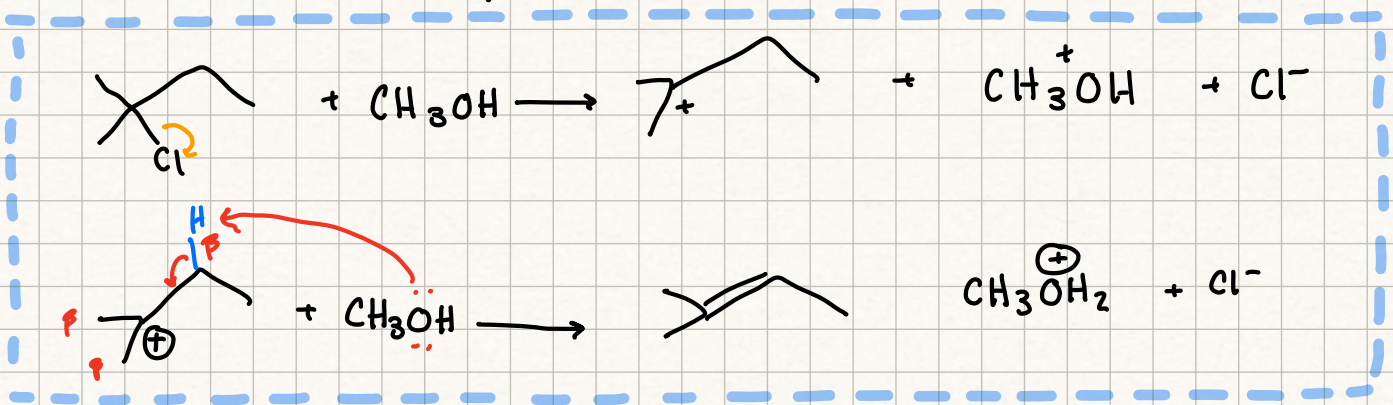
The E1 Mechanism





Both E1 and E2 require 2 bonds broken and 2 bonds formed, only difference is time
 ↳ E1 reaction the leaving group comes off first before the β proton is removed, & reaction occurs in 2 steps

↳ E2 reaction the leaving group comes off as the β proton is removed and the reaction occurs in one step



- The rate of an E1 reaction increases as the number of R groups on the carbon w/ the leaving group increase

Increasing Rate of an E1 reaction



Increasing Carbocation Stability

- Strong bases like OH^- and OR^- favor E2 whereas weaker bases like H_2O and ROH favor E1 reactions

- E1 reactions are regioselective favoring formation of the more substituted more stable alkene

↳ Regioselective mean have multiple possible stereoisomers however one is favored

- Zaitsev rule (double bond w/ more substituted β is favored) applies to E1 reaction as well

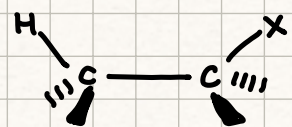
* $\text{S}_{\text{N}}1$ and E1 have the same first step-formation of carbocation, however what happens to carbocation differs

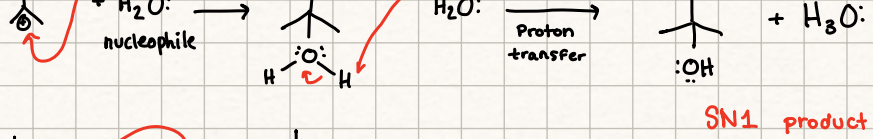


- Same conditions which favor $\text{S}_{\text{N}}1$ mechanism will favor elimination by an E1 mechanism
 ↳ a 3° alkyl halide as substrate
 a weak nucleophile or base as reagent
 a polar protic solvent

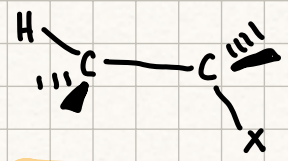
* As result both reactions usually occur in the same reaction mixture to afford a mixture of product

Stereochemical Features

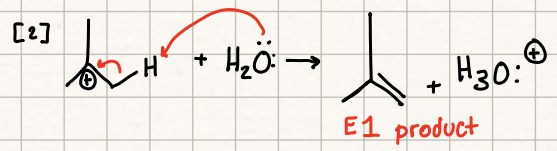




Syn periplanar



anti periplanar



- The H and X atoms can be orientated on the same side of the molecule, this geometry is called **Syn periplanar**
- The H and X atoms can be orientated on opposite side of the molecule, the geometry is called **anti periplanar**
- All evidence suggests that E2 elimination occurs most often in the anti periplanar geometry
- * **Anti periplanar arrangement has a staggered confirmation** \rightarrow 2 electron rich groups are far apart
- * **Syn periplanar arrangement has an eclipsed confirmation** \rightarrow 2 electron rich groups are close
- Need to be in axial confirmation in order for E2 to occur (less stable will occur)
- **Strength of base is the most important factor in determining the mechanism for elimination. Strong bases favor the E2 mechanism. Weak bases favor E1 mechanism.**