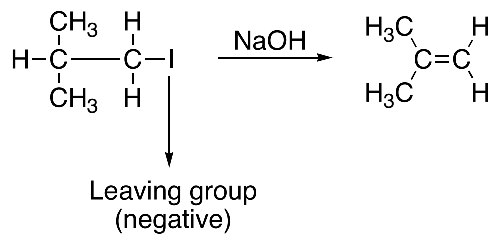
Elimination Reactions: E_2 and E_1

1) Dehydrohalogenation (removal of HX, X = Cl, Br, I, *can be E_1 or E_2*)
2) Dehalogenation (removal of X_2, *always E_2*)
3) Dehydration of alcohols (removal of HOH, reverse of addition of H_2O with alkenes *can be E_1 or E_2*).



Leaving Group Ability

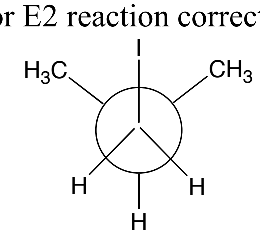
$I^- > Br^- > Cl^- >> F^- > {}^-OH, {}^-OR$
Good Bad

- depends on size, solvation of anion, and bond length. Iodide is large and more solvated than Fluoride. C-I bond is longer and easier to break. Note that hydroxide anion (OH^-) and alkoxide anion (OR^-) are terrible leaving groups, but their protonated forms, water (HOH) and alcohol (HOR) are good leaving groups – hence those eliminations usually require acid

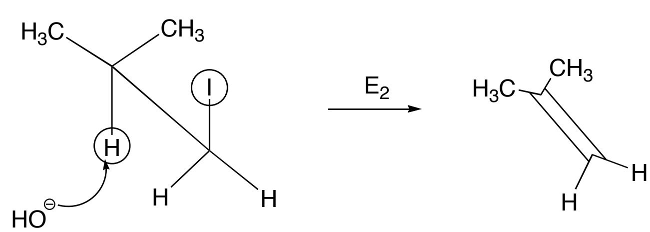
Reactivity of halide anions: As expected based on electronegativity

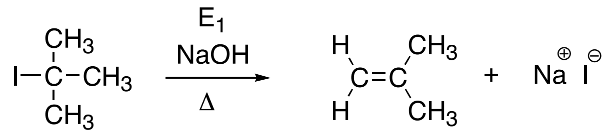
$I^- > Br^- > Cl^- > F^-$

For E2 reaction correct alignment (antiperiplanar) favours eleimination

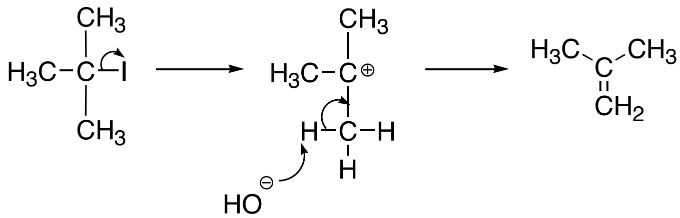


- Leaving groups and H-removed in anti-periplanar arrangement



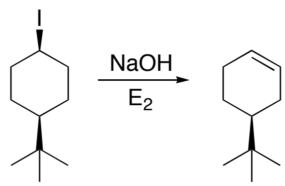


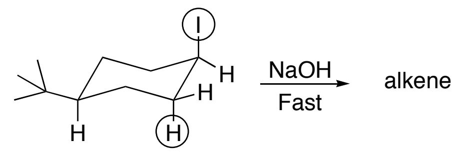
- not concerted, mostly E1
- carbocation intermediate.



- 3^{o} leaving group good for E_1

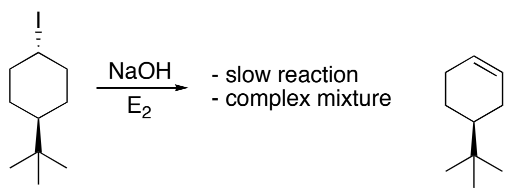
Cis



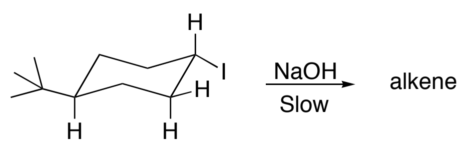


anti-periplanar

Trans

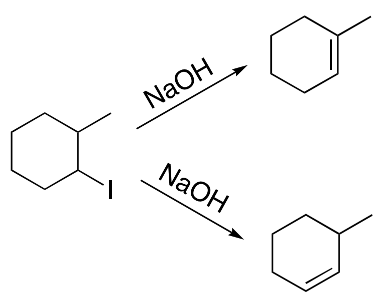


low yield



The trans isomer must assume an unfavorable conformation to allow alignment of H which is removed and iodide leaving group

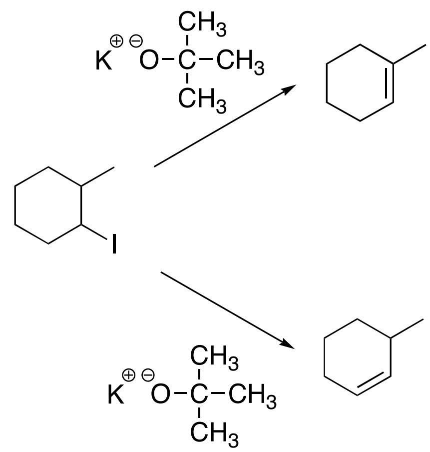
- Zaitsev (Saytzeff) rule: elimination reactions give most highly substituted alkene



Tri-substituted alkene (major) - more stable

Di-substituted alkene (minor) - less stable

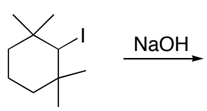
- Hoffman elimination: Removes least hindered hydrogen, usually uses bulky base.



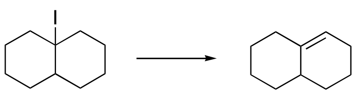
Minor

Major

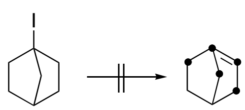
Limitations to Eliminations



- No elimination
- No H on adjacent carbon

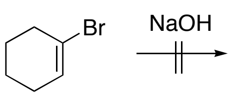


eliminates readily
(one bridge has 0 carbons)

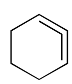


cannot eliminate

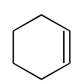
• atoms with dot should be in plane
- too strained to form (Bredt's rule)
- cannot form alkene on bridgehead carbon if rings are small and each bridge has at least one carbon



- No elimination

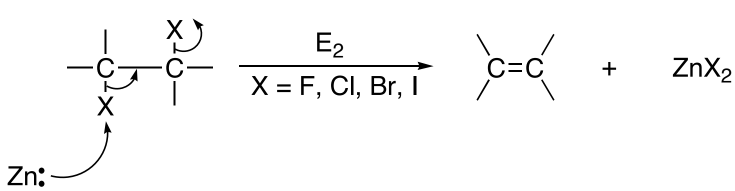


- too strained to form

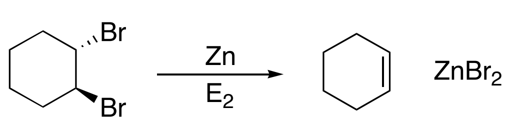


- too unstable to form

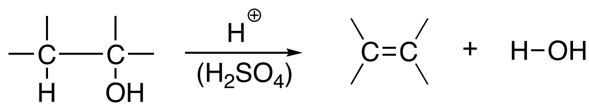
Dehalogenation

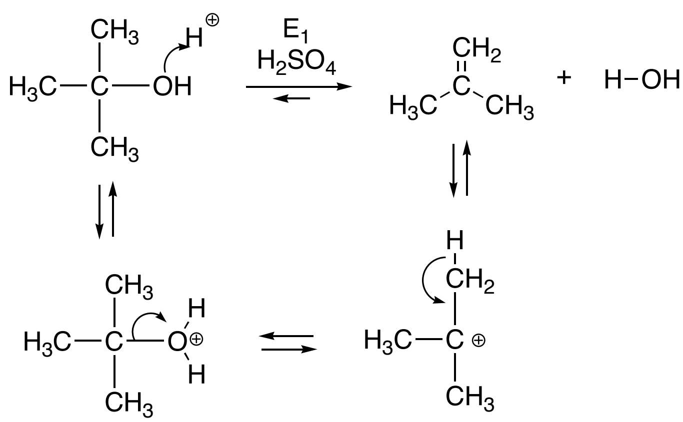


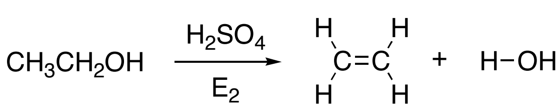
ex)

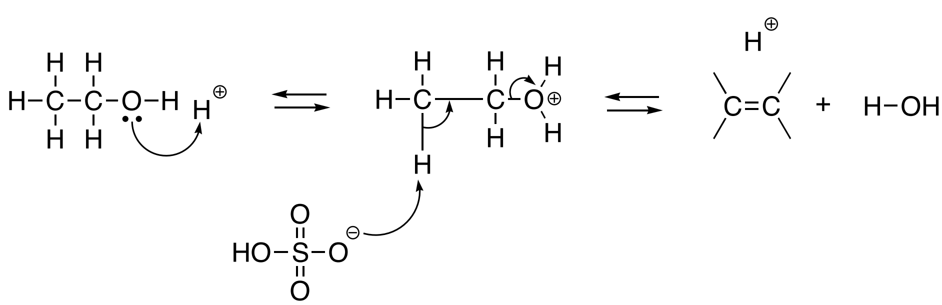


Dehydration:









Polymers and Polymerization

Poly = many

Meros = parts

Nature has many polymers, for example: nucleic acids (DNA, RNA), proteins and peptides (from amino acids), fat (from acetate), polysaccharides (sugar polymers).

H_2SO_4 + HNO_3 + Cotton → Explosion (no smoke) = gun cotton (nitrocellulose)