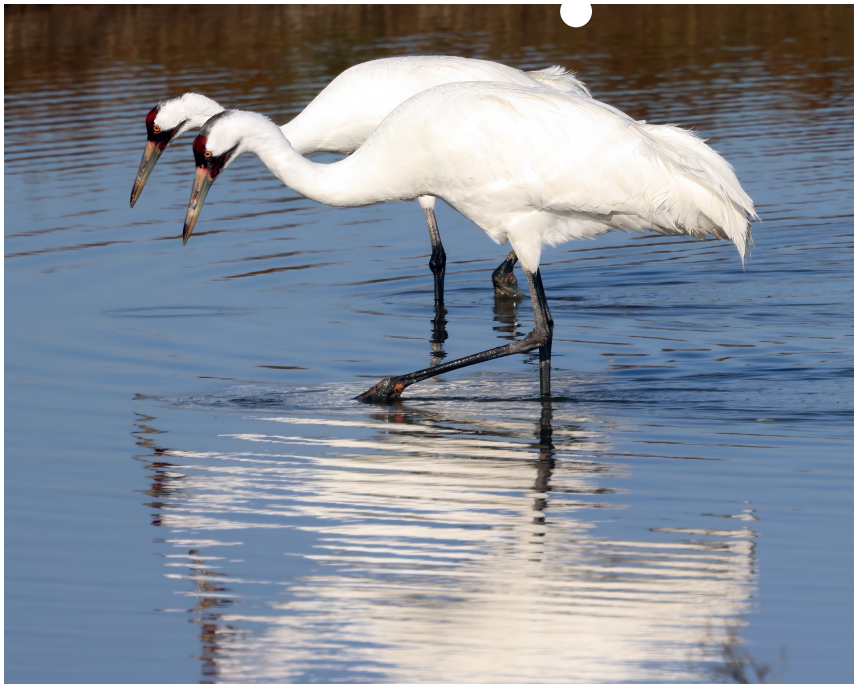
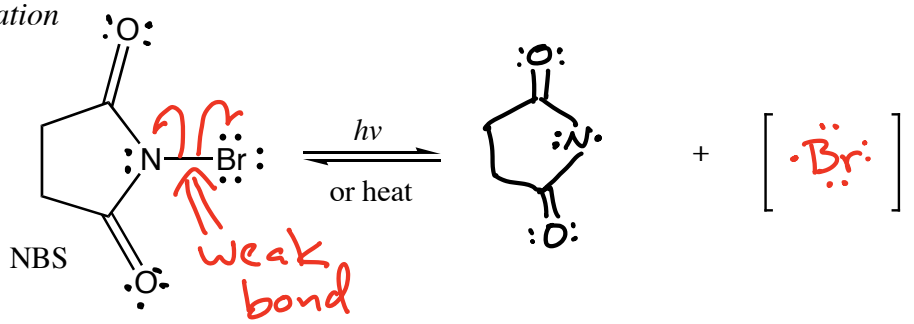




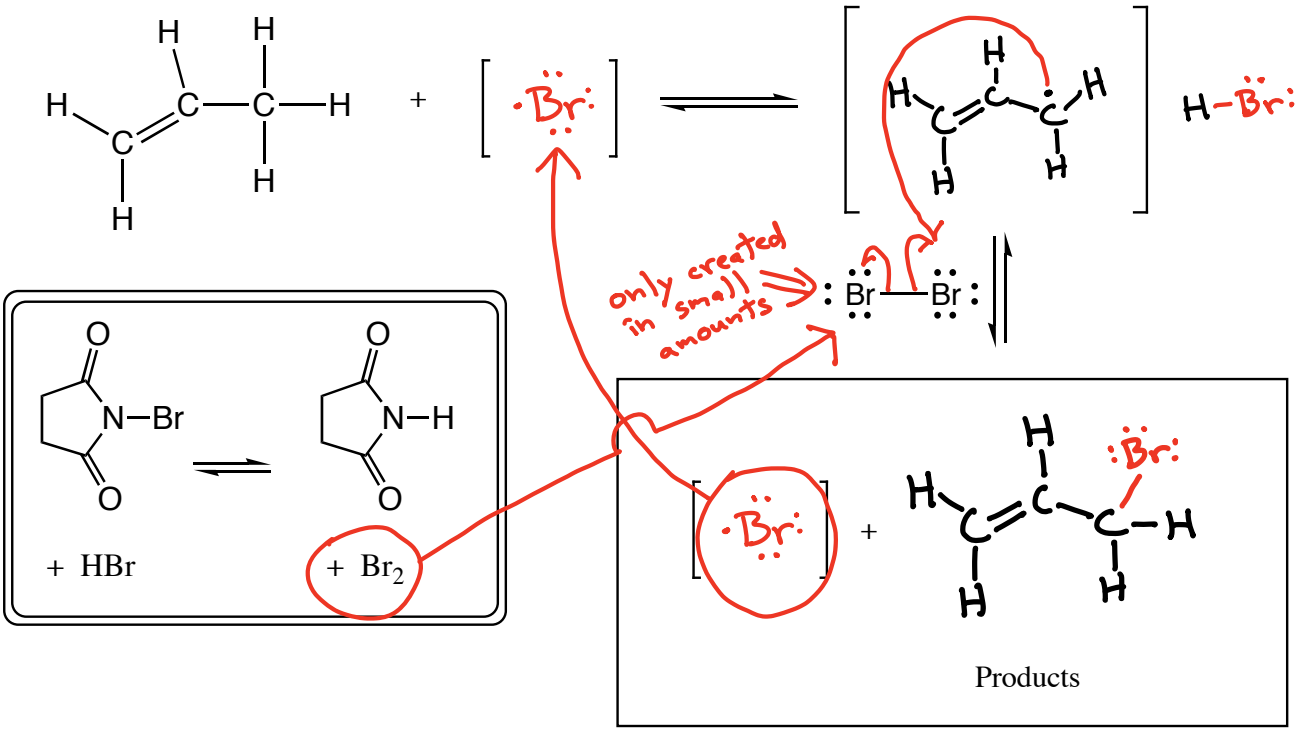


Allylic Halogenation

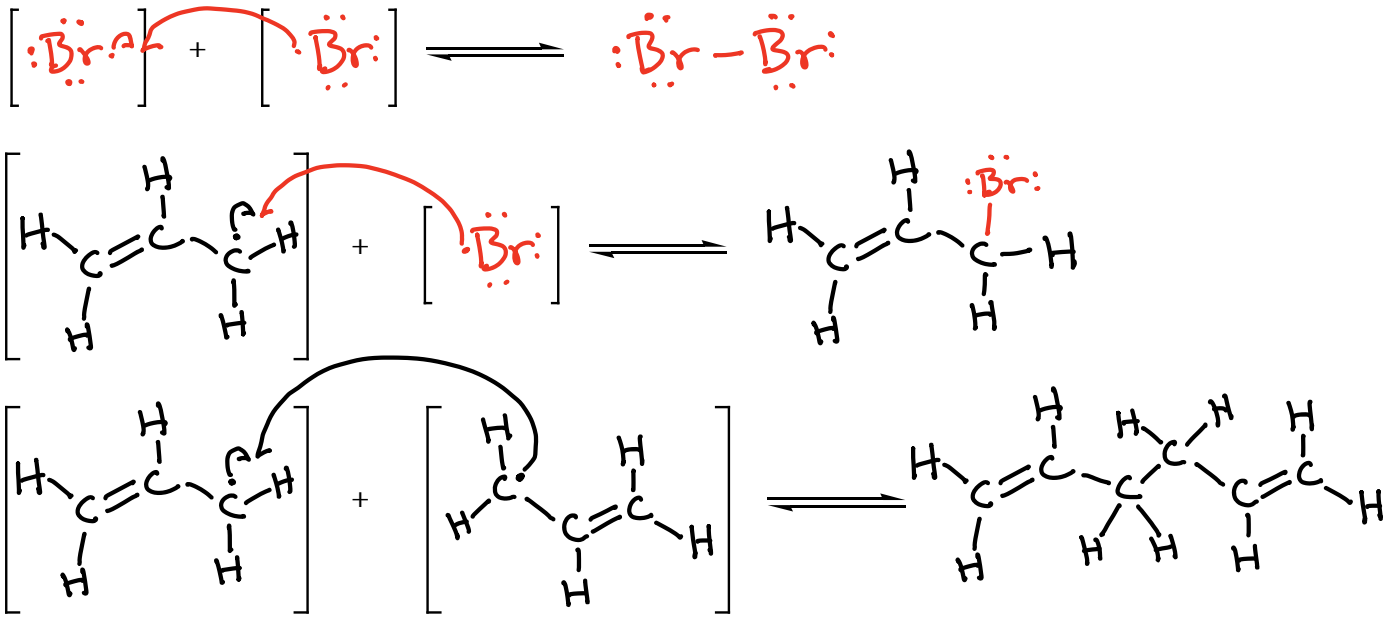
Initiation



Propagation



Termination





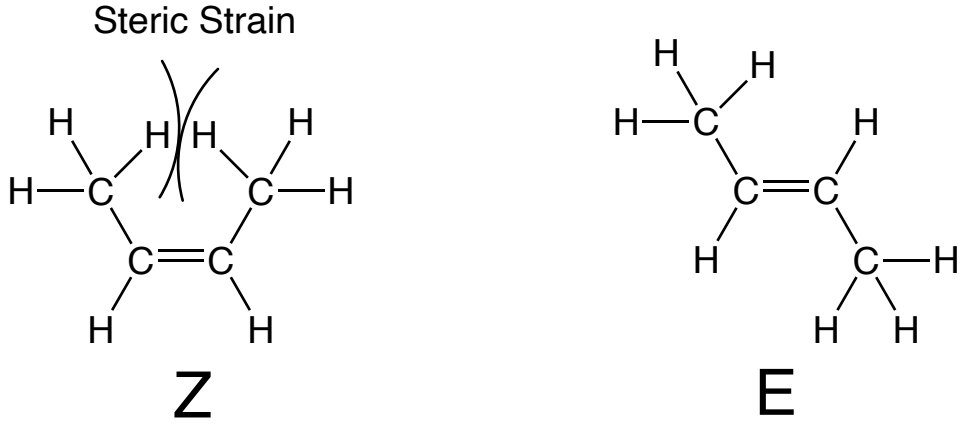
Big Change — For this reaction you need to choose the most stable product, NOT worrying about the most stable contributing structure of an allylic radical intermediate.



From Week 6

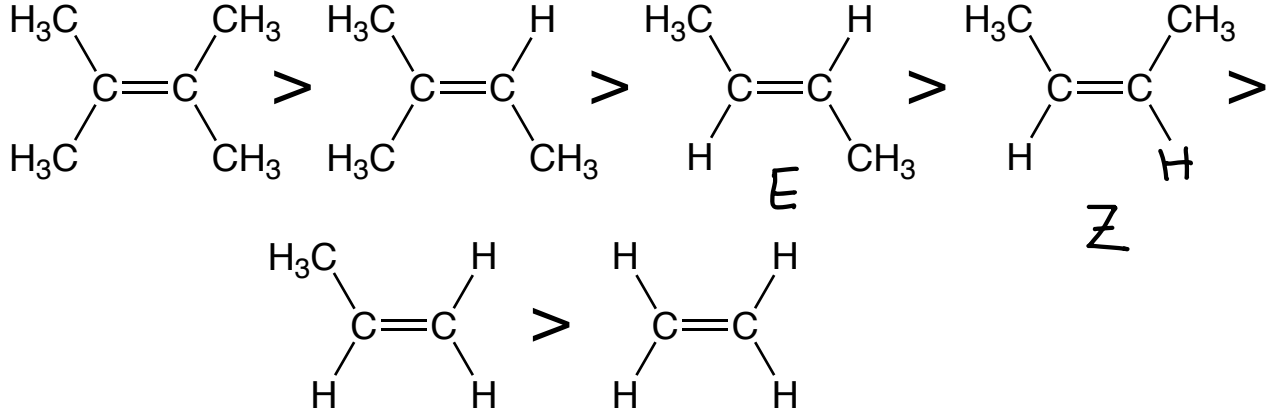
Special Alkene Bonus: Important material you will need to know!

Alkene stability part 1: Z (cis) groups larger than H atoms will crunch into each other causing steric strain.



Alkene stability part 2: For reasons we are not able to tell you, more substituted alkenes have more stable (stronger) pi bonds than alkenes with more H atoms on their sp^2-hybridized C atoms (despite there being steric strain present in the most substituted alkenes).

Strongest Pi Bond



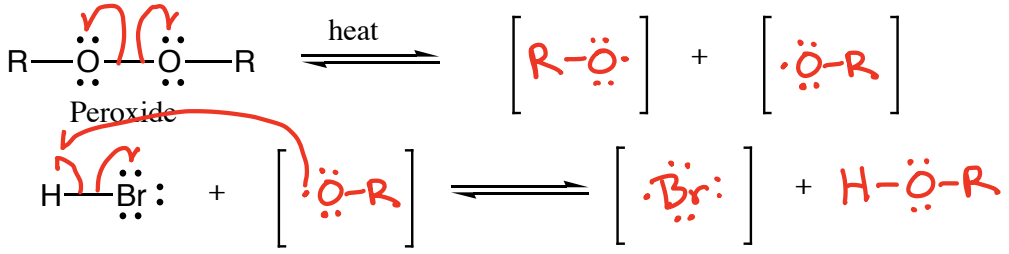
Weakest Pi Bond



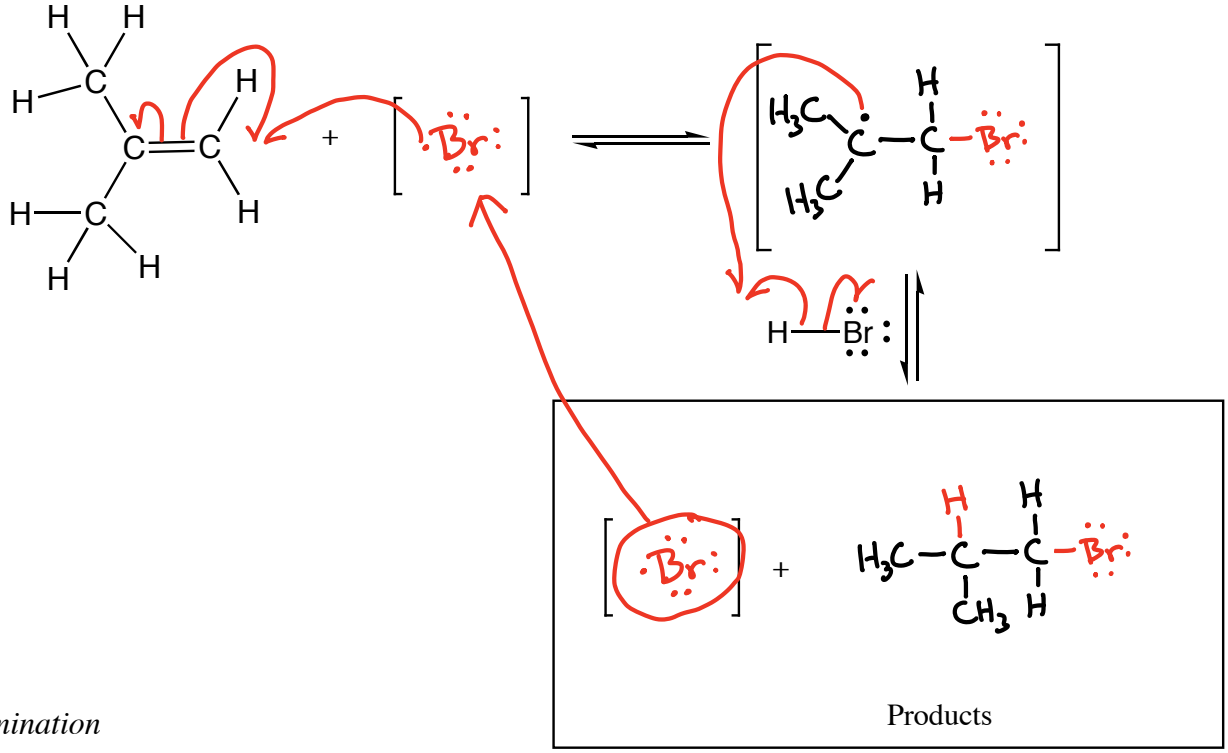
Time Capsule: Zaitsev's rule follows this trend!!

Non-Markovnikov Addition of HBr to an Alkene

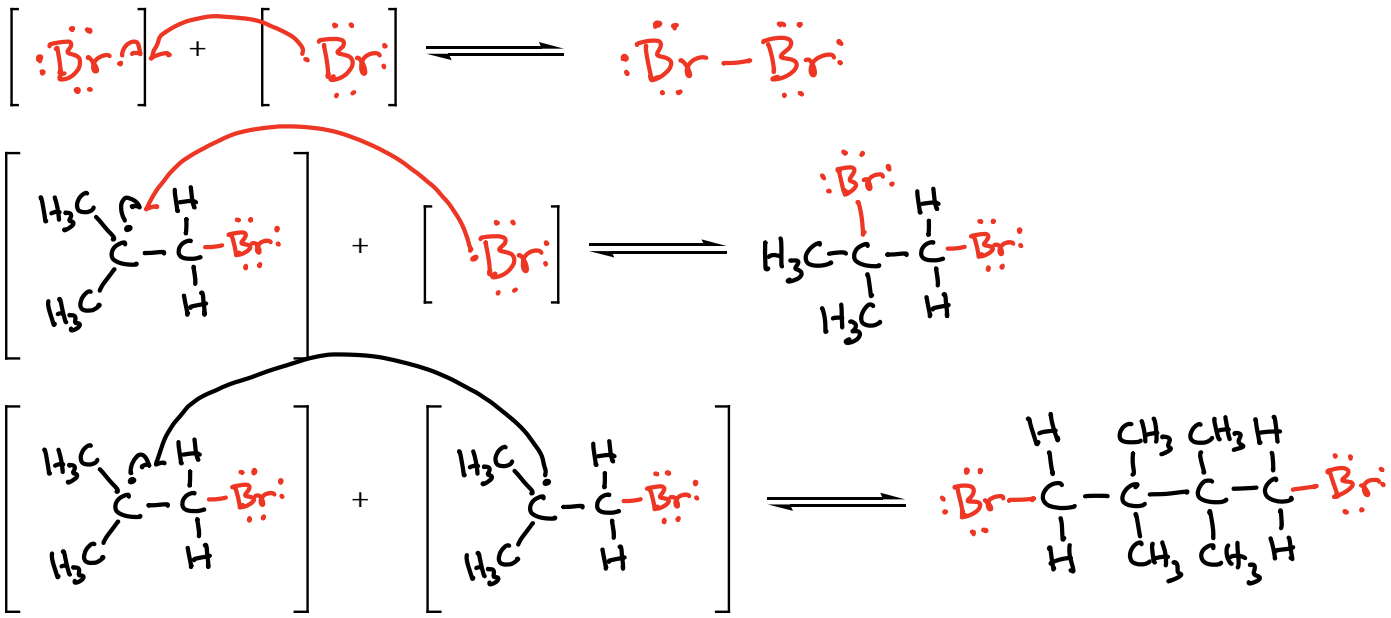
Initiation



Propagation



Termination





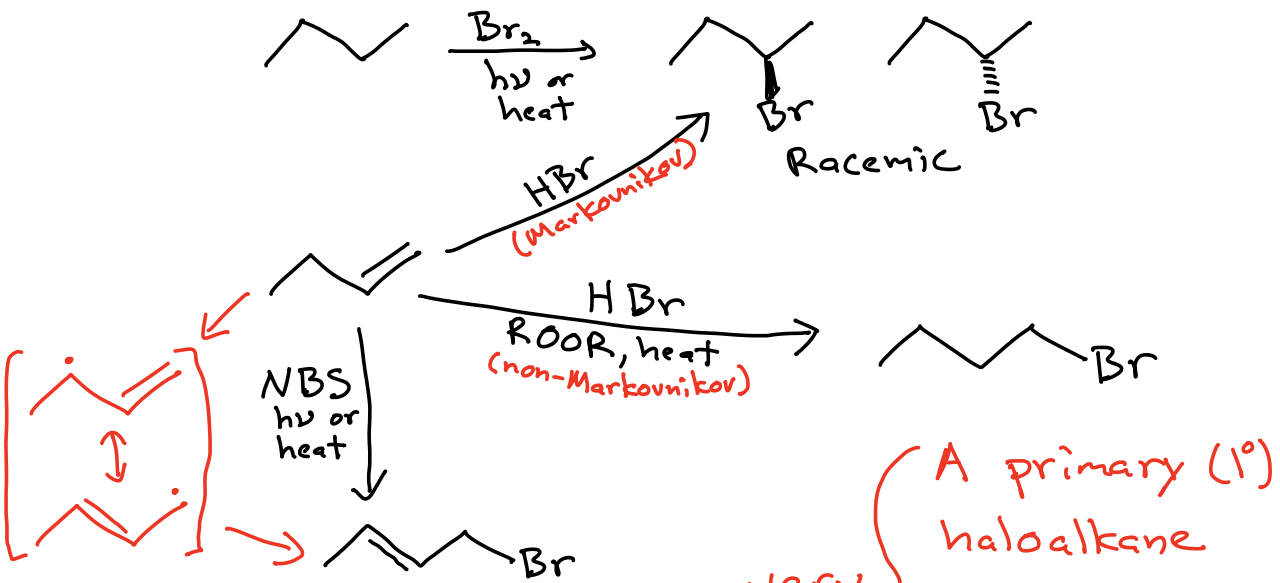
For subtle reasons (not discussed) H-Br, ROOR and heat gives very little allylic halogenation, and NBS/hν or heat gives very little alkene addition even though they both involve $[\cdot\ddot{\underset{\cdot\cdot}{Br}}:]$ and an alkene starting material.

Please accept this

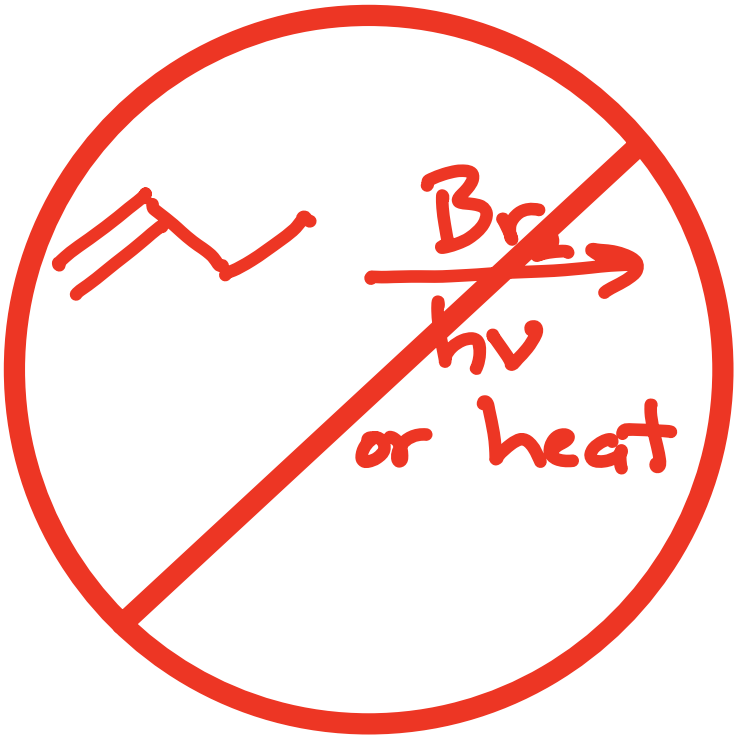
This is huge ↘

HBr
ROOR
heat
→ Non-Markovnikov Regiochemistry

Making Haloalkanes



very useful } A primary (1°) haloalkane product from a terminal alkene



Never use Br_2 and hv or heat with an alkene!



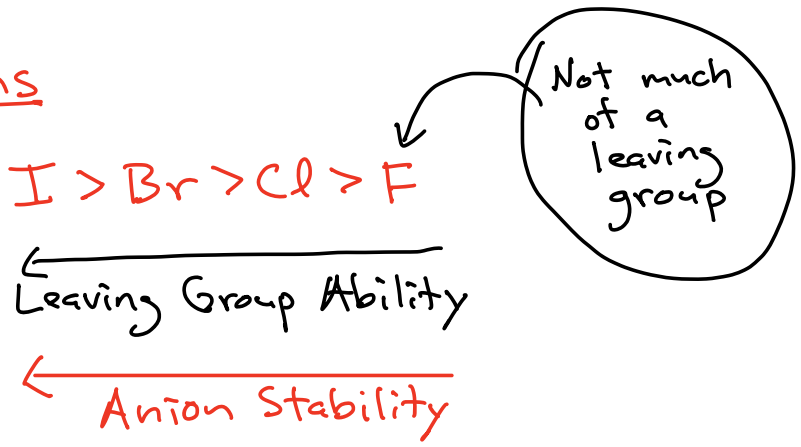


New Concept → Leaving Group

A group that can make a single bond to carbon that can make a stable species when it departs

nucleophiles/bases

Halogens



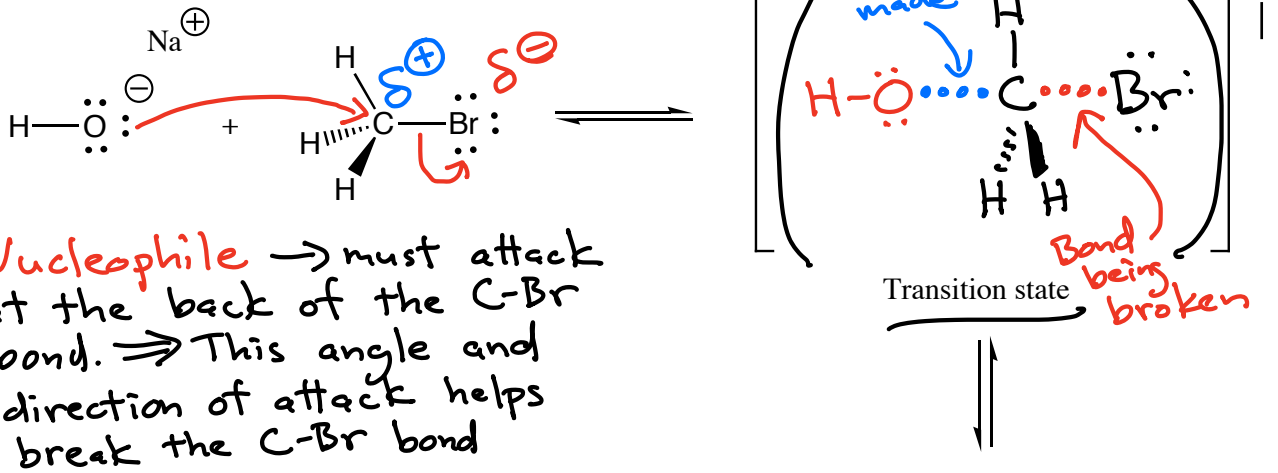
1st New Mechanism

S_N2 ← Bimolecular → both the haloalkane and nucleophile are involved in the rate-determining (slow) step of the reaction

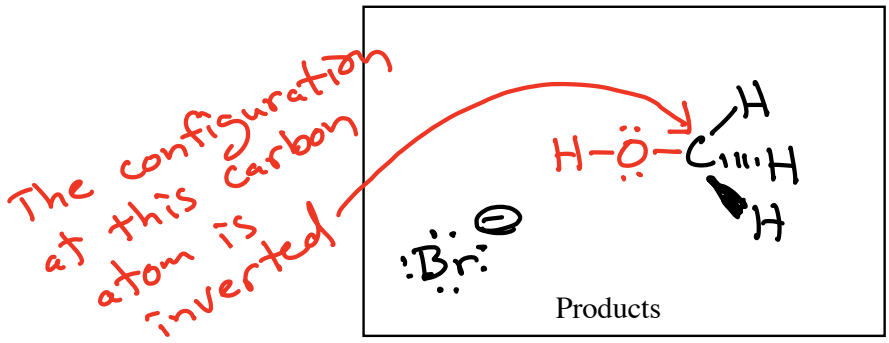
Substitution

Nucleophilic

The S_N2 Mechanism



Nucleophile → must attack at the back of the C-Br bond. ⇒ This angle and direction of attack helps break the C-Br bond

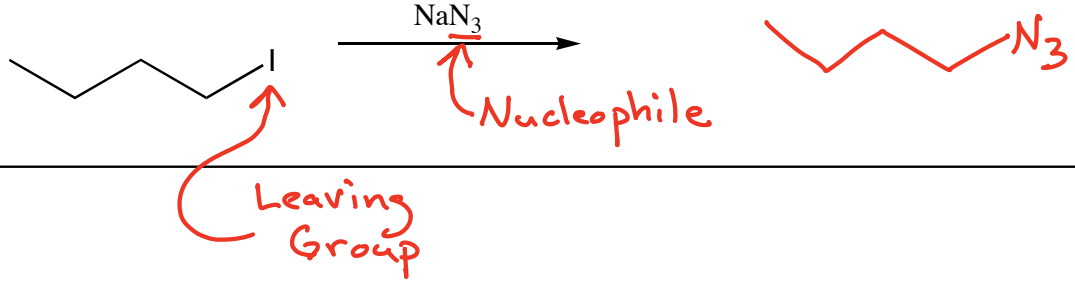


Summary: The nucleophile attacks by making a new bond to C from the back of the C-X bond just as X leaves

Regiochemistry: N/A

Stereochemistry: INVERSION at the site of reaction

Example:

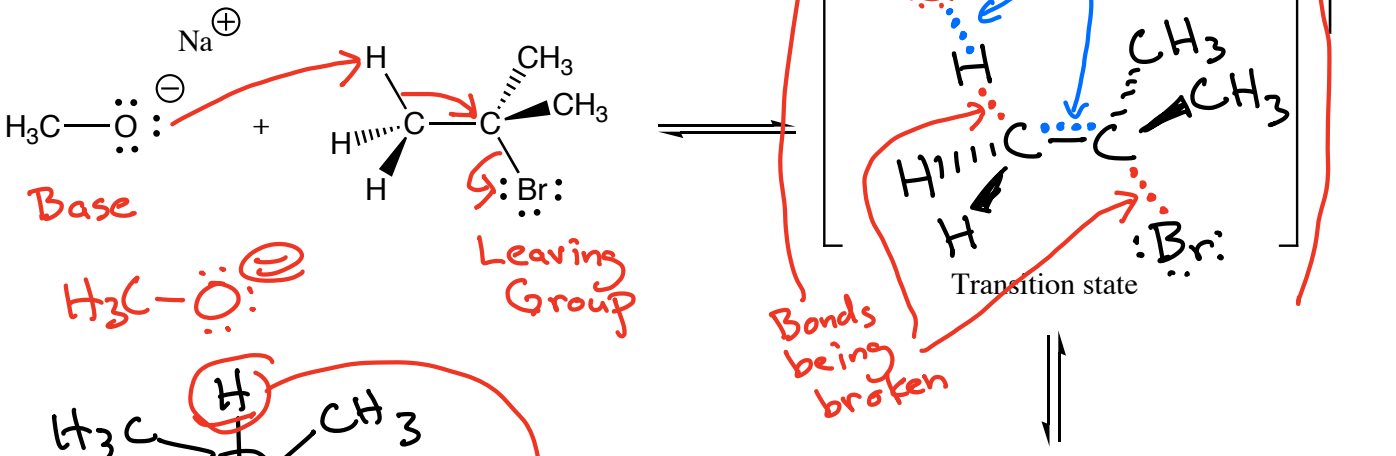


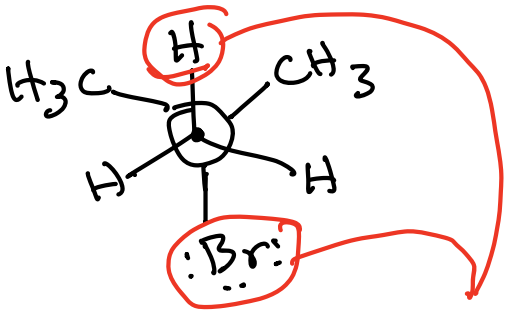
2nd New Mechanism

E2 ← Bimolecular → both the haloalkane and the base are involved in the rate-determining (slow) step of the reaction

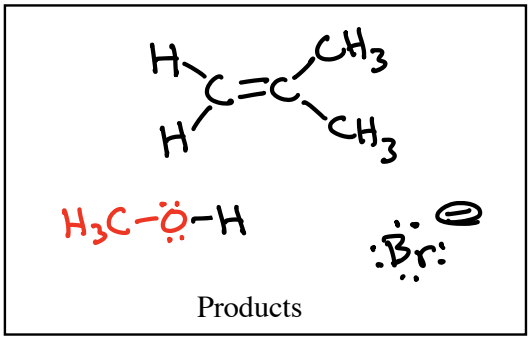
Elimination

The E2 Mechanism





The H that is leaving and the Br must be anti-periplanar

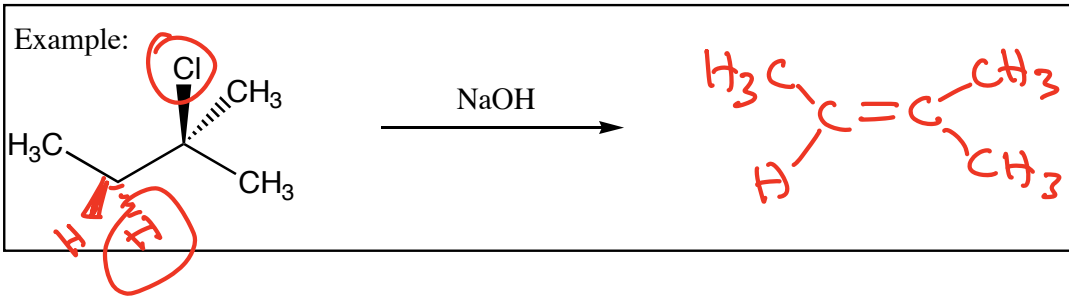


Summary: Base removes an H atom as a pi bond forms and the Br atom leaves → The H and Br must be anti-periplanar

Regiochemistry: Zaitsev's Rule → most stable alkene product

Stereochemistry: Determined by anti-periplanar transition state

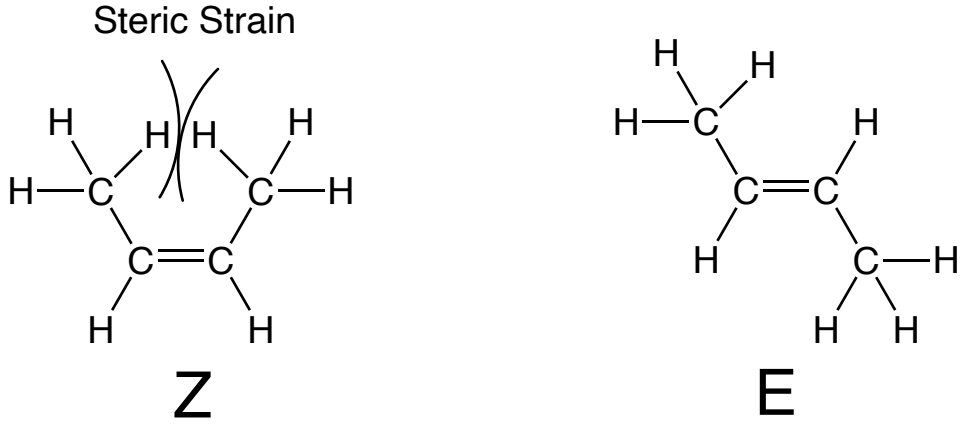
Example:



From Week 6

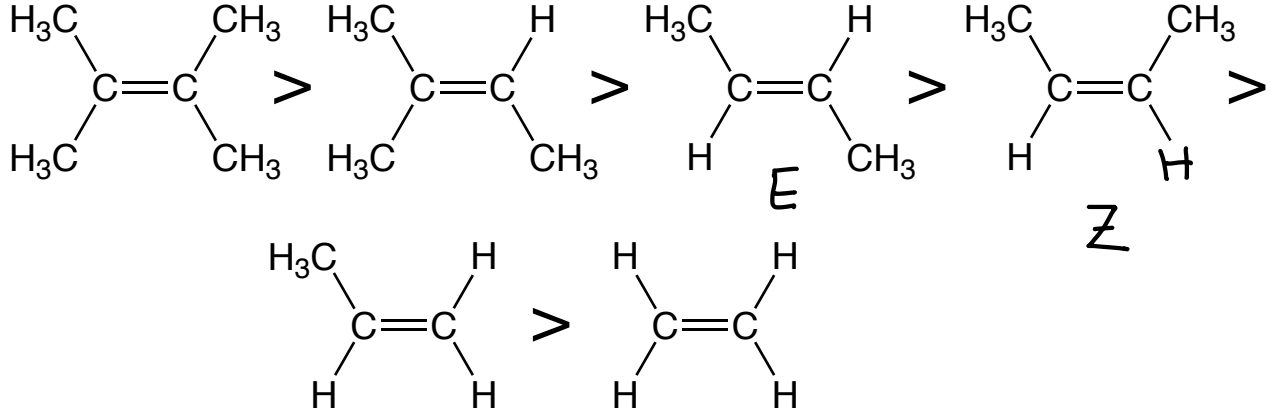
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