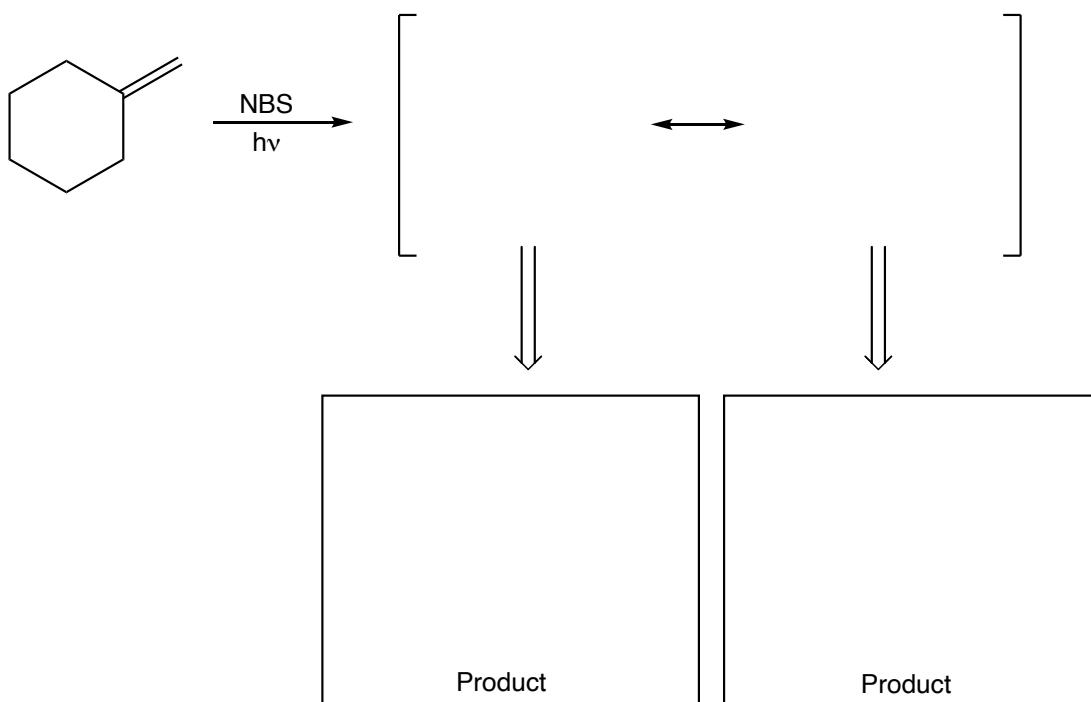
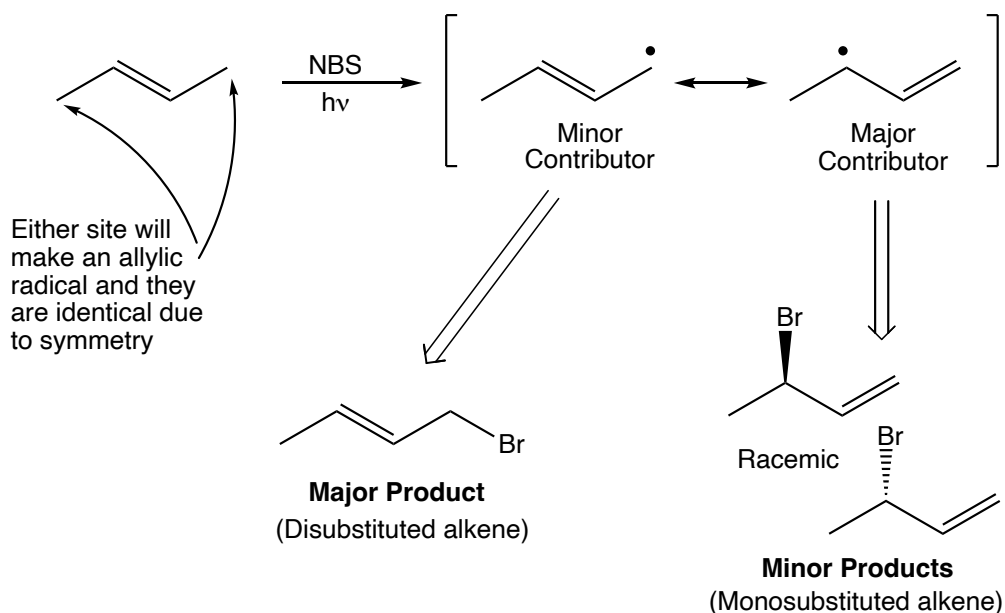
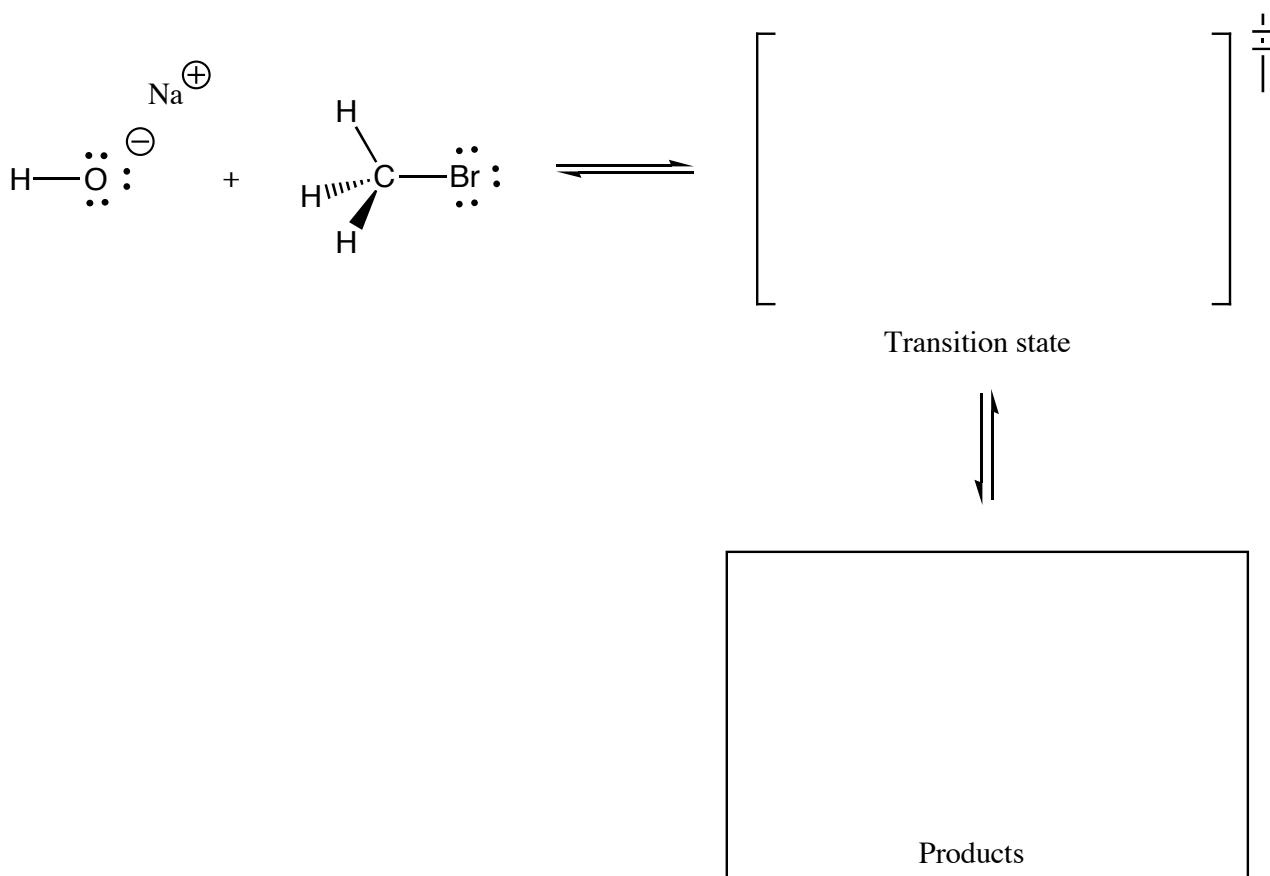


When analyzing allylic halogenation reactions (NBS and $h\nu$)

1. Consider all possible allylic radicals that can be formed.
2. Analyze all contributing structures for all of the allylic radicals.
3. Add a Br atom at the site of the unpaired electron for all contributing structures for all of the allylic radicals.
4. From all of the possible products, the predominant product is the one **THAT IS THE MOST STABLE ALKENE** – the most substituted alkene – alkyl groups stabilize alkenes – *trans* over *cis*.
5. Note: It is OK if the product you choose derives from an allylic radical contributing structure that is a minor contributor. **FOR THIS REACTION WE ONLY CARE ABOUT THE RELATIVE STABILITIES OF THE PRODUCT ALKENES.**



The S_N2 Mechanism

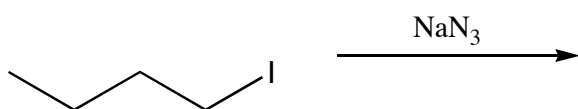


Summary:

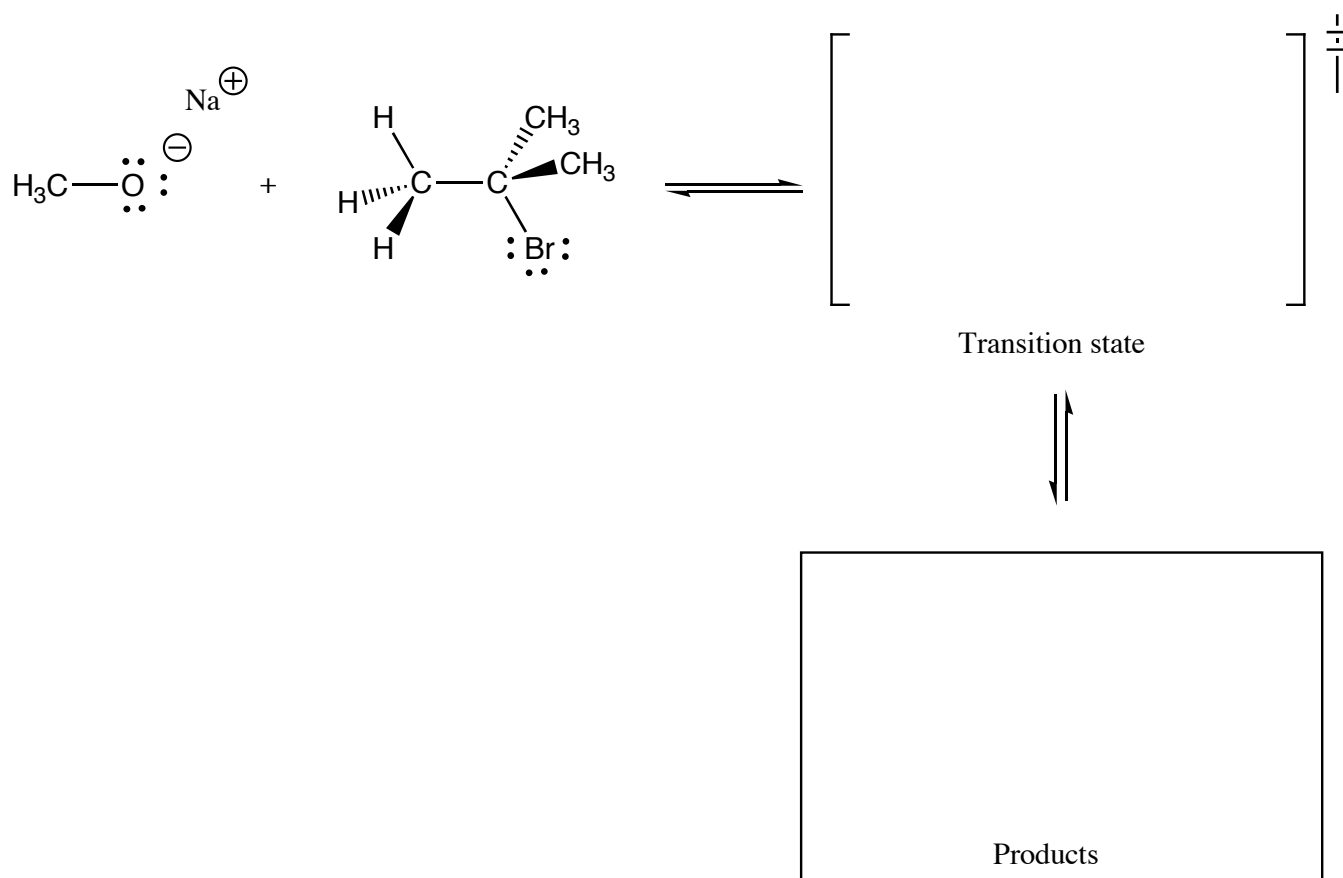
Regiochemistry:

Stereochemistry:

Example:



The E2 Mechanism

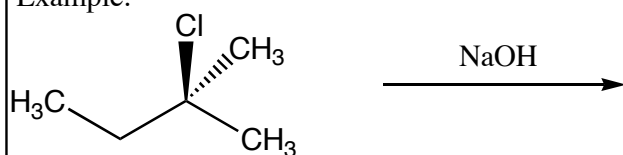


Summary:

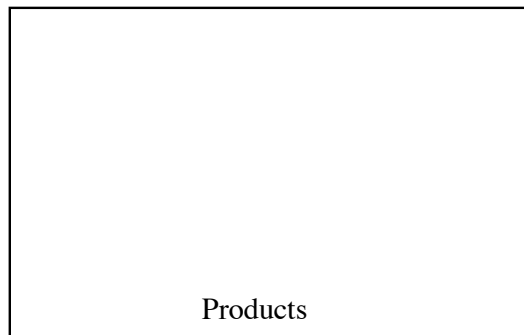
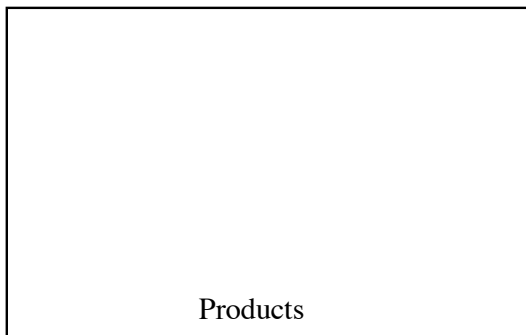
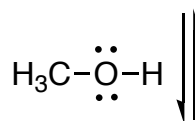
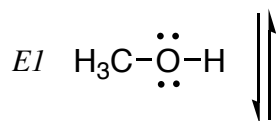
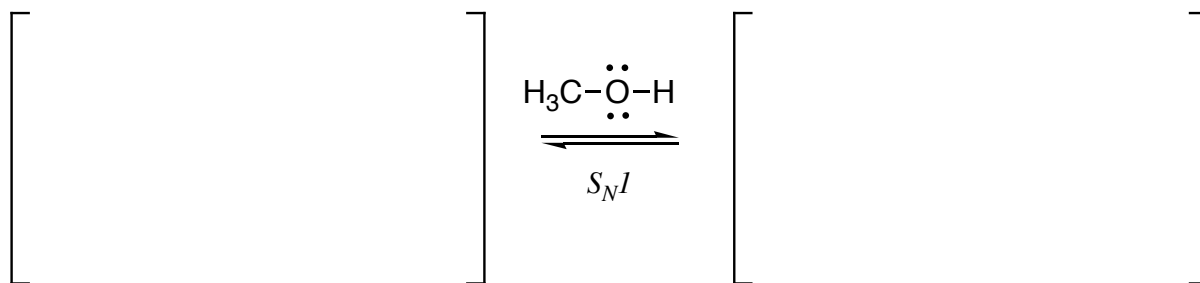
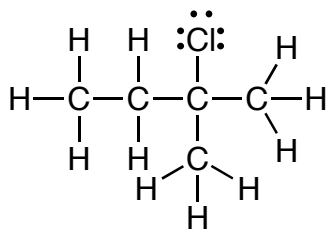
Regiochemistry:

Stereochemistry:

Example:



The S_N1 and $E1$ Mechanisms



Summary:

Regiochemistry:

Stereochemistry:

Example:

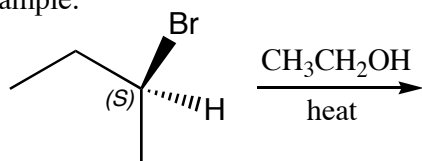
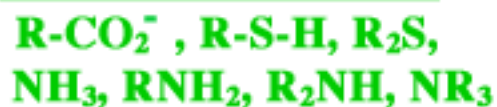


Table of Nucleophiles

Strong Nucleophiles



Medium Nucleophiles



Weak Nucleophiles



Special Case

Tert-Butoxide (tBuO^-) is a strong base, but is not a nucleophile due to steric hindrance.

Substitution/Elimination Decision Map

Methyl Halide \Rightarrow S_N2

Primary Haloalkane \Rightarrow $t\text{BuOK ?}$ \Rightarrow Yes \Rightarrow E2
 \downarrow
No \Rightarrow S_N2

Secondary Haloalkane
or
Allylic/Benzylic Halides \Rightarrow Very Weak Base ? \Rightarrow Yes \Rightarrow $S_N1/E1$ *
 \downarrow
Very Strong Base ? \Rightarrow Yes \Rightarrow E2 **
 \downarrow
No \Rightarrow S_N2

Tertiary Haloalkane \Rightarrow Very Weak Base ? \Rightarrow Yes \Rightarrow $S_N1/E1$
 \downarrow
No \Rightarrow E2

For S_N2 Remember Chiral Center INVERSiON
For E2 Remember anti-periplanar and Zaitsev
For S_N1 Remember Chiral Center Scrambling
For E1 Remember Zaitsev

* Note: With Very Weak Bases, S_N2 can compete here, but for the purposes of this class, assume $S_N1 / E1$ predominate

** Note: If $t\text{BuOK}$ is the very strong base, an appreciable amount of a non-Zaitsev product can be formed because the bulky $t\text{BuOK}$ will tend to react with the most accessible H atom.