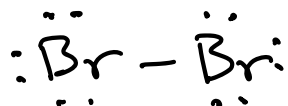
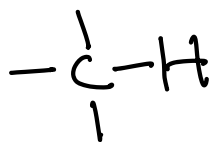
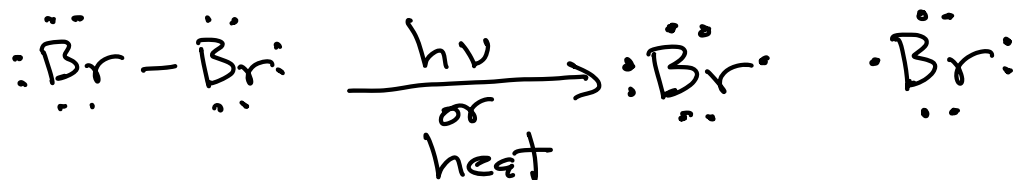
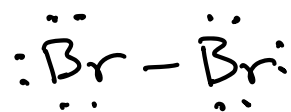
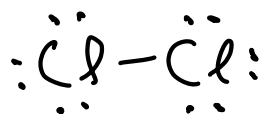
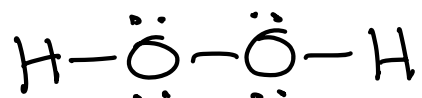
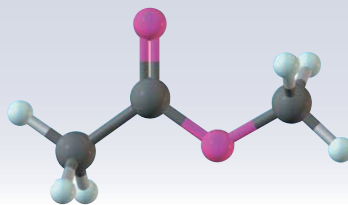




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Appendix 3 Bond Dissociation Enthalpies



Bond dissociation enthalpy (BDE) is defined as the amount of energy required to break a bond homolytically into two radicals in the gas phase at 25°C.



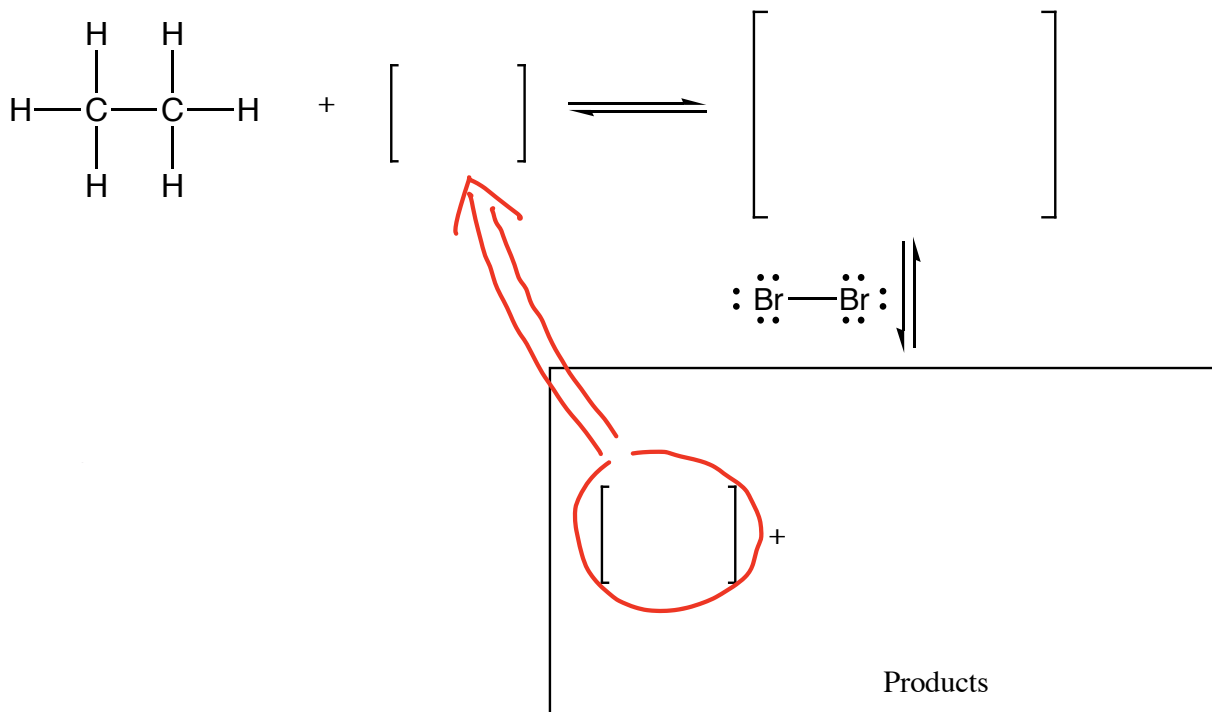
Bond	ΔH^0	Bond	ΔH^0	Bond	ΔH^0
H—H bonds		C—C multiple bonds		C—Br bonds	
H—H	435 (104)	CH ₂ =CH ₂	727 (174)	CH ₃ —Br	301 (72)
D—D	444 (106)	HC≡CH	966 (231)	C ₂ H ₅ —Br	301 (72)
X—X bonds		C—H bonds		(CH ₃) ₂ CH—Br	309 (74)
F—F	159 (38)	CH ₃ —H	439 (105)	(CH ₃) ₃ C—Br	305 (73)
Cl—Cl	247 (59)	C ₂ H ₅ —H	422 (101)	CH ₂ =CHCH ₂ —Br	247 (59)
Br—Br	192 (46)	(CH ₃) ₂ CH—H	414 (99)	C ₆ H ₅ —Br	351 (84)
I—I	151 (36)	(CH ₃) ₃ C—H	405 (97)	C ₆ H ₅ CH ₂ —Br	263 (63)
H—X bonds		CH ₂ =CH—H	464 (111)	C—I bonds	
H—F	568 (136)	CH ₂ =CHCH ₂ —H	372 (89)	CH ₃ —I	242 (58)
H—Cl	431 (103)	C ₆ H ₅ —H	472 (113)	C ₂ H ₅ —I	238 (57)
H—Br	368 (88)	C ₆ H ₅ CH ₂ —H	376 (90)	(CH ₃) ₂ CH—I	238 (57)
H—I	297 (71)	HC≡C—H	556 (133)	(CH ₃) ₃ C—I	234 (56)
O—H bonds		C—F bonds		CH ₂ =CHCH ₂ —I	192 (46)
HO—H	497 (119)	CH ₃ —F	481 (115)	C ₆ H ₅ —I	280 (67)
CH ₃ O—H	439 (105)	C ₂ H ₅ —F	472 (113)	C ₆ H ₅ CH ₂ —I	213 (51)
C ₆ H ₅ O—H	376 (90)	(CH ₃) ₂ CH—F	464 (111)	C—N single bonds	
O—O bonds		C ₆ H ₅ —F	531 (127)	CH ₃ —NH ₂	355 (85)
HO—OH	213 (51)	C—Cl bonds		C ₆ H ₅ —NH ₂	435 (104)
CH ₃ O—OCH ₃	159 (38)	CH ₃ —Cl	351 (84)	C—O single bonds	
(CH ₃) ₃ CO—OC(CH ₃) ₃	159 (38)	C ₂ H ₅ —Cl	355 (85)	CH ₃ —OH	385 (92)
C—C single bonds		(CH ₃) ₂ CH—Cl	355 (85)	C ₆ H ₅ —OH	468 (112)
CH ₃ —CH ₃	376 (90)	(CH ₃) ₃ C—Cl	355 (85)		
C ₂ H ₅ —CH ₃	372 (89)	CH ₂ =CHCH ₂ —Cl	288 (69)		
CH ₂ =CH—CH ₃	422 (101)	C ₆ H ₅ —Cl	405 (97)		
CH ₂ =CHCH ₂ —CH ₃	322 (77)	C ₆ H ₅ CH ₂ —Cl	309 (74)		
C ₆ H ₅ —CH ₃	435 (104)				
C ₆ H ₅ CH ₂ —CH ₃	326 (78)				

Alkane Free Radical Halogenation

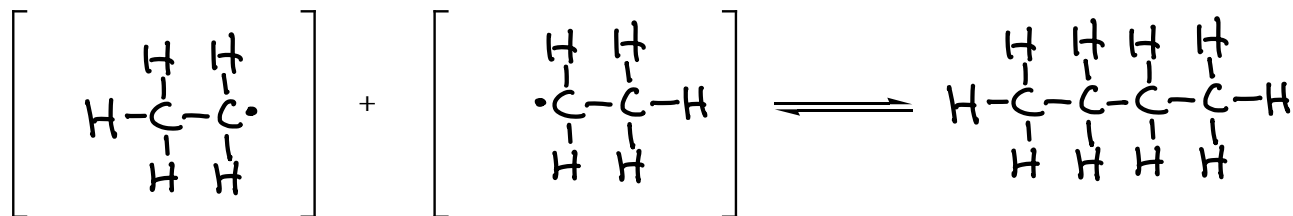
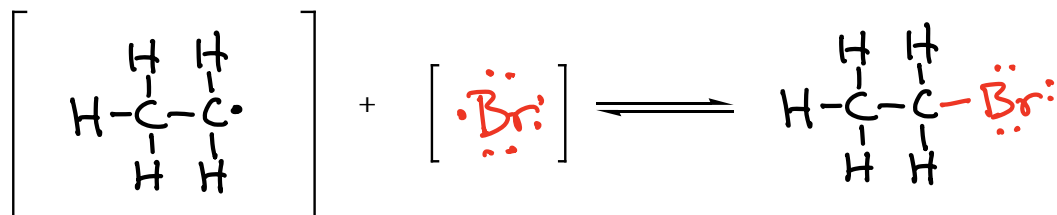
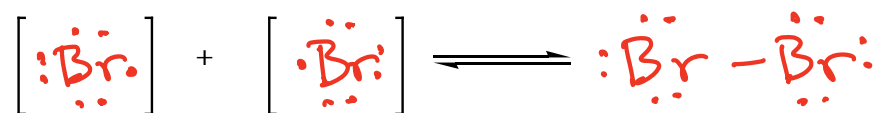
Initiation



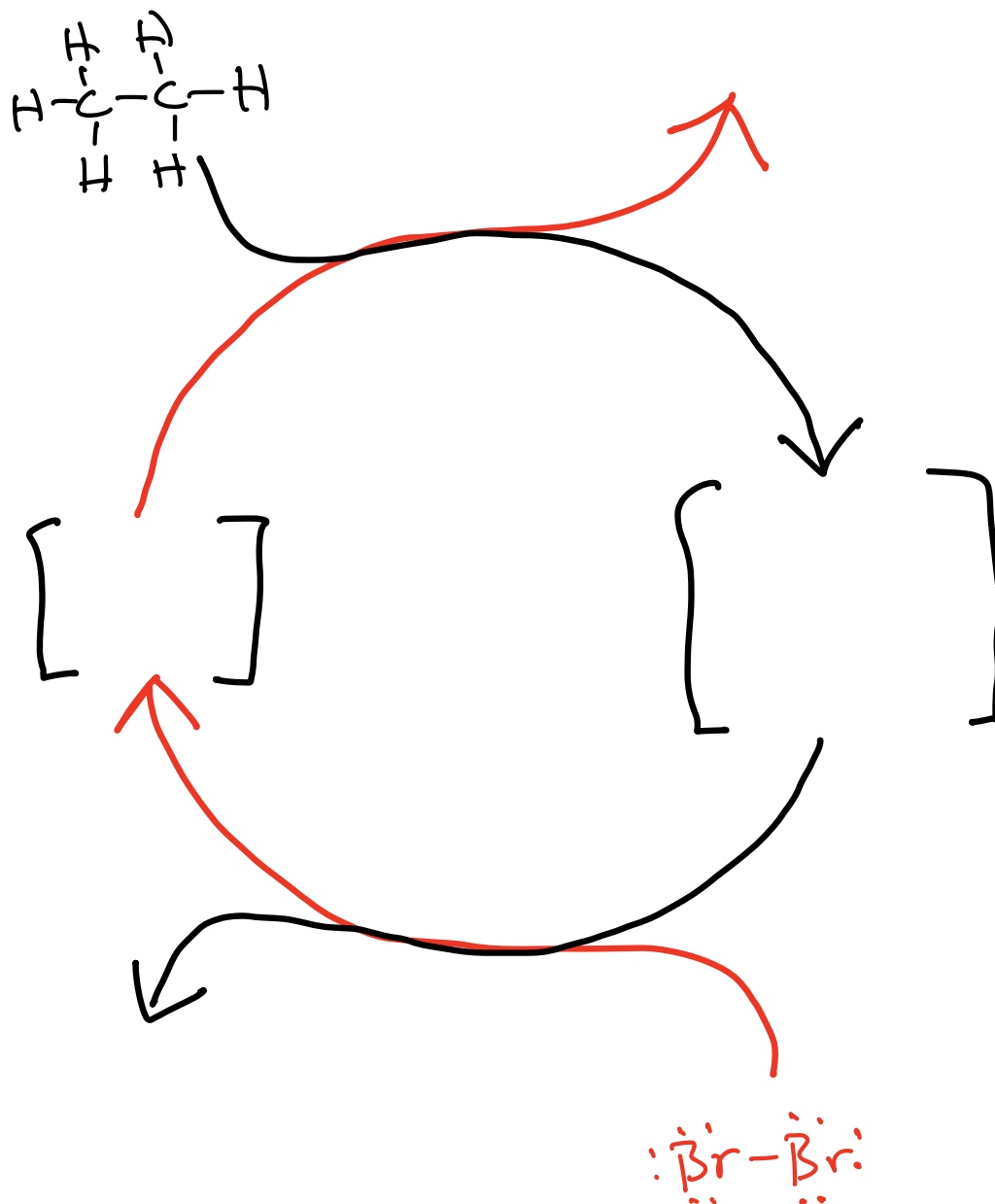
Propagation



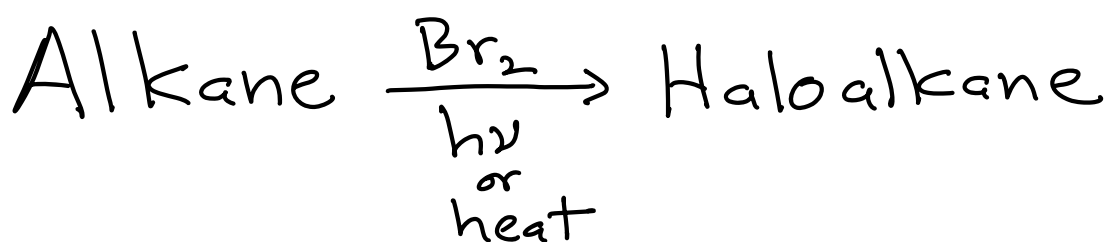
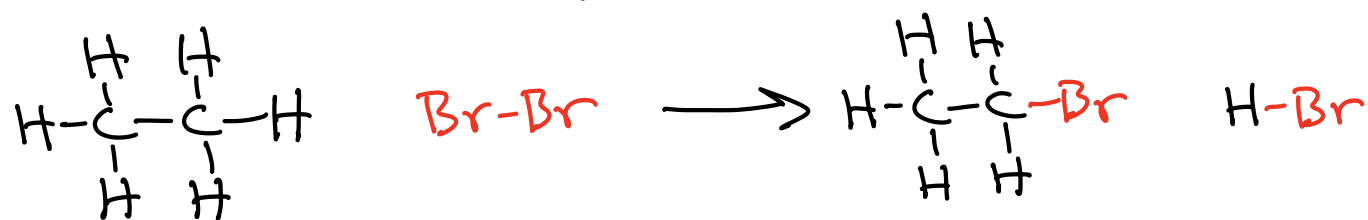
Termination



Propagation Process Diagram

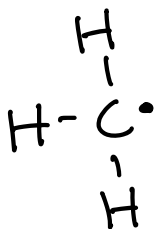


Motive for overall process



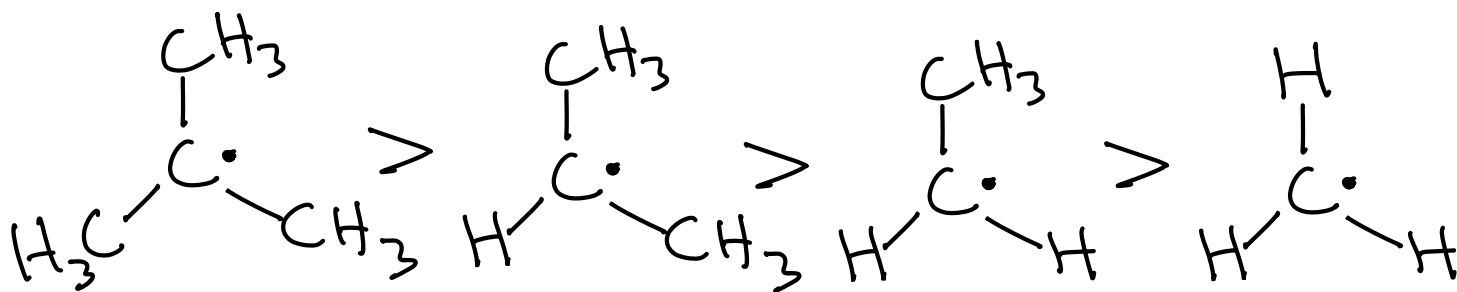
This is the only reaction
you will learn that starts
with an alkane!

Radical $\rightarrow$ species with an unpaired electron $\rightarrow$ very reactive $\rightarrow$



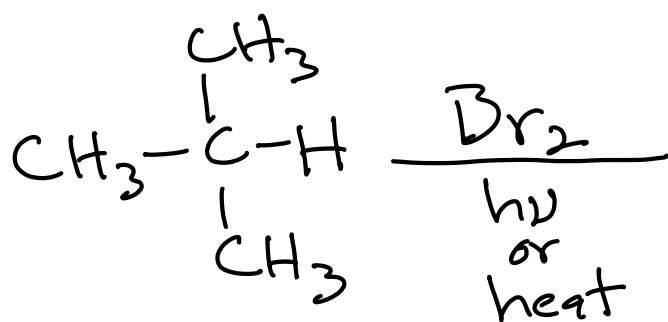
Think of a radical as being
"analogous to a carbocation without

Think of a radical as being
"analogous to a carbocation"



Radical Stability

* $\Rightarrow$ When there is a choice in a radical reaction with an alkane the Br atom will end up on the most substituted C atom that had an H atom



Br₂ is more selective than Cl₂ (I₂ does, not work at all)

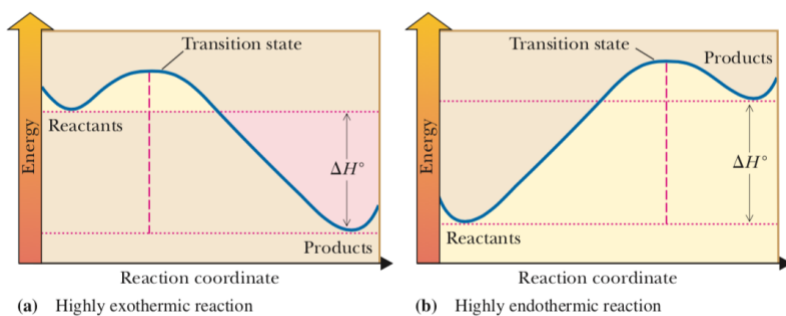


Figure 8.2

Hammond's postulate. Energy diagrams for two one-step reactions. In the exothermic reaction, the transition state occurs early, and its structure resembles that of the reactants. In the endothermic reaction, the transition state occurs late, and its structure resembles that of the products.

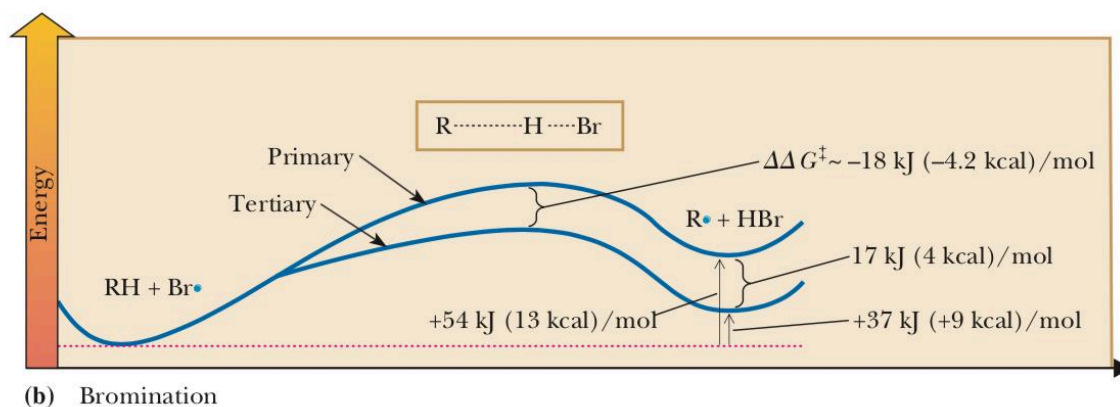
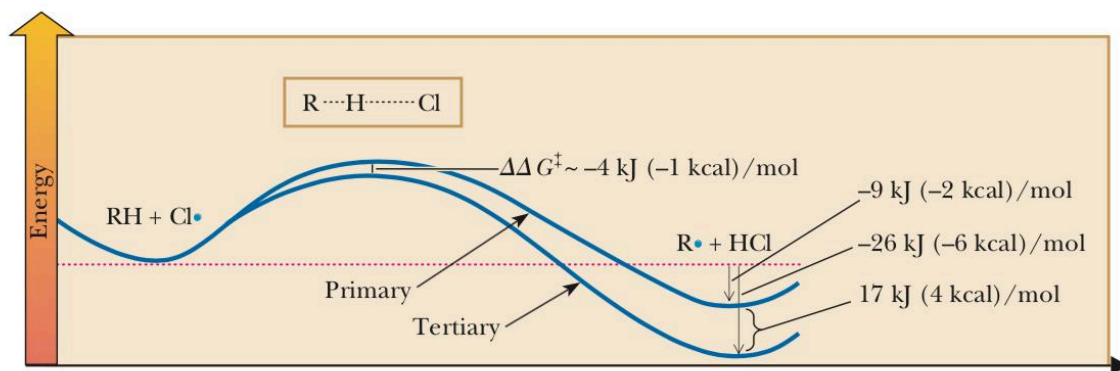
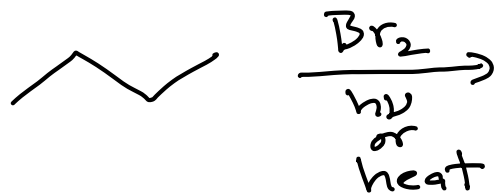
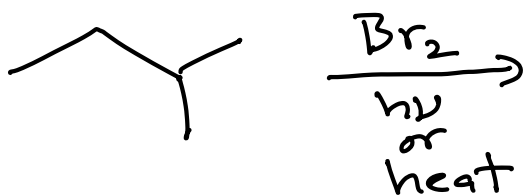
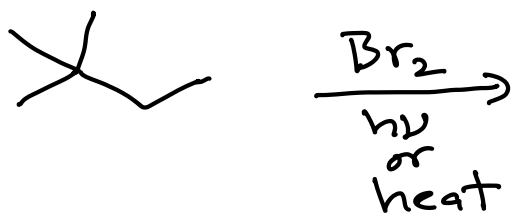


Figure 8.3

Transition states and energetics for hydrogen abstraction in the radical chlorination and bromination of 2-methylpropane (isobutane). The product is the intermediate radical, $R\cdot$.

Examples



Organic Chemistry is the study of carbon-containing molecules.

This class has two points.

The first point of the class is to understand the organic chemistry of living systems. We will teach you how to think about and understand the most amazing things on the planet!!

Water is essential for life, you will learn why water has such special properties. 8/27/25

You will learn the secret structural reason proteins, the most important molecular machines in our bodies, can support the chemistry of life. 9/10/25

You will learn why when you take Advil for pain, exactly half of what you take works, and the other half does nothing. 9/24/25

You will learn how toothpaste works. 10/6/25

You will learn how a single chlorofluorocarbon refrigerant molecule released into the atmosphere can destroy many, many ozone molecules, leading to an enlargement of the ozone hole.

You will learn how medicines like Benadryl, Seldane, and Lipitor work.

You will learn how Naloxone is an antidote for an opioid overdose.

You will learn why Magic Johnson is still alive, decades after contracting HIV.

You will learn how MRI scans work.

The second point of organic chemistry is the synthesis of complex molecules from simpler ones by making and breaking specific bonds.

You will learn how to understand movies of reaction mechanisms like alkene hydration.

You will learn reactions that once begun, will continue reacting such that each product molecule created starts a new reaction until all the starting material is used up.

You will learn reactions that can make antifreeze from vodka.

You will learn a reaction that can make nail polish remover from rubbing alcohol.

You will learn how to look at a molecule and accurately predict which atoms will react to make new bonds, and which bonds will break during reactions.

You will learn how to analyze a complex molecule's structure so that you can predict ways to make it via multiple reactions starting with less complex starting molecules.

Allylic Halogenation

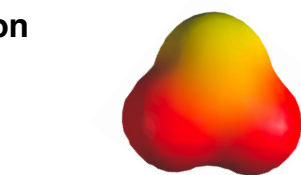
2 New ideas



B) When there is a choice in allylic halogenation reactions you always make the most product!

How to think about allyl radicals and allyl cations

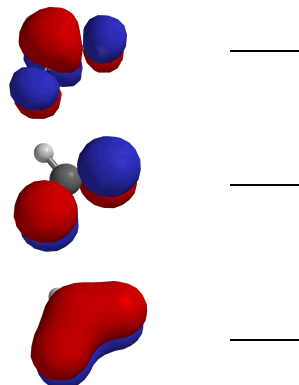
Carboxylate anion



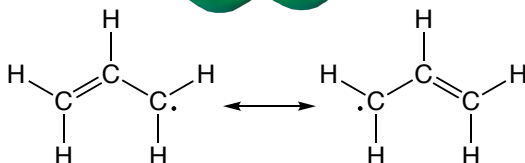
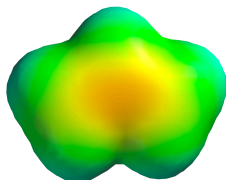
Total # of electrons in the π bond = _____

Total # of electrons in the 2p orbital of the other O atom = _____

Total # of electrons in the π -way =



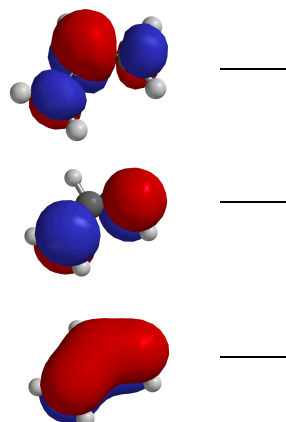
Allyl radical



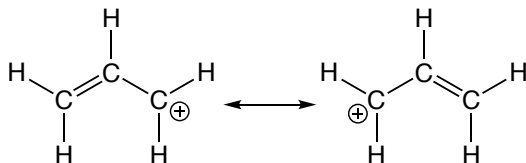
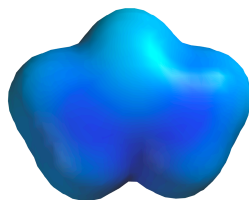
Total # of electrons in the π bond = _____

Total # of electrons in the 2p orbital of the other C atom = _____

Total # of electrons in the π -way =



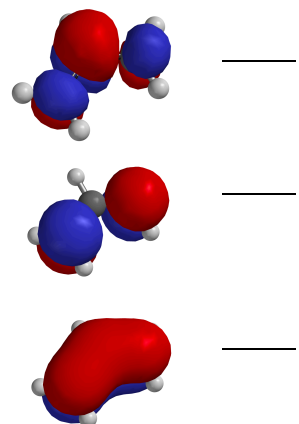
Allyl cation



Total # of electrons in the π bond = _____

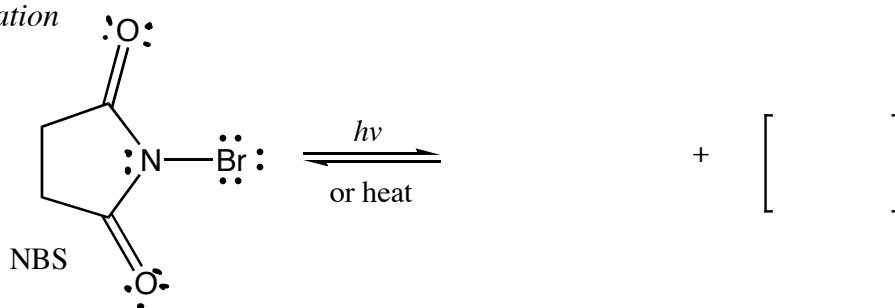
Total # of electrons in the 2p orbital of the other C atom = _____

Total # of electrons in the π -way =

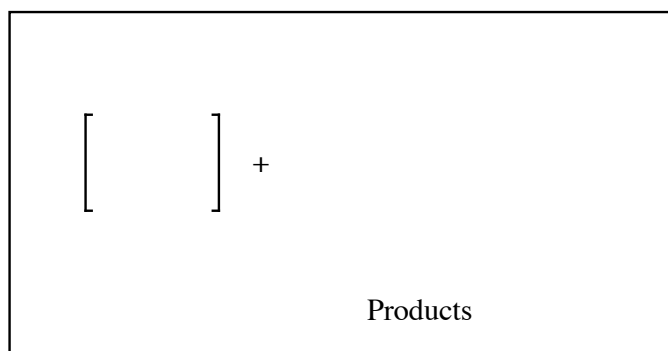
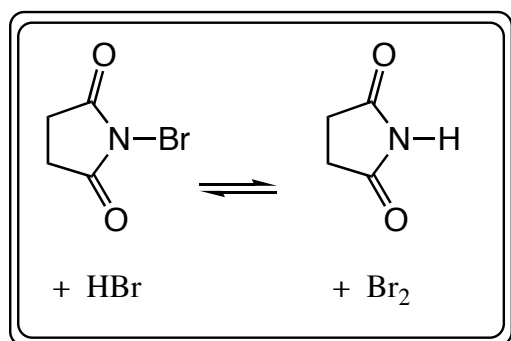
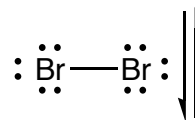
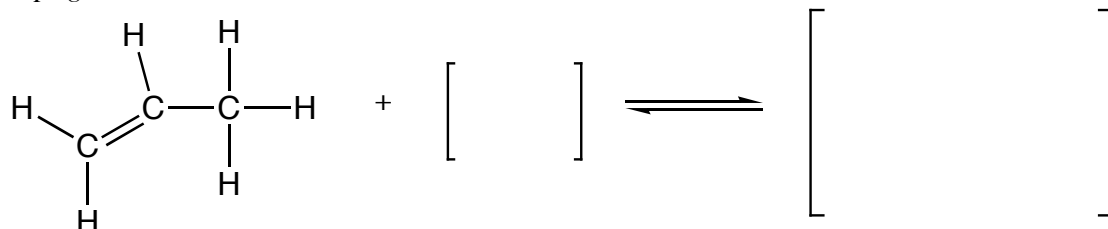


Allylic Halogenation

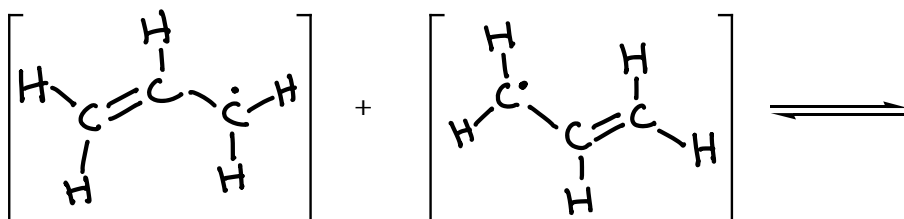
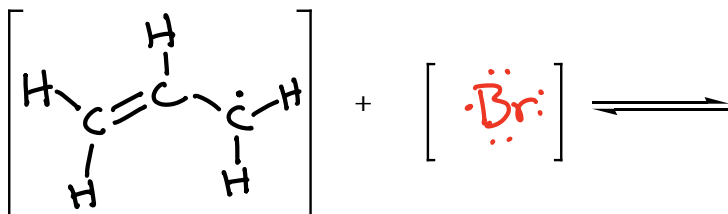
Initiation



Propagation



Termination



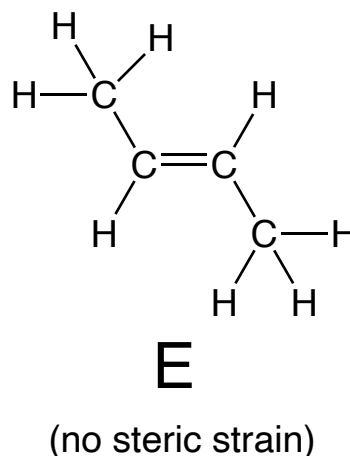
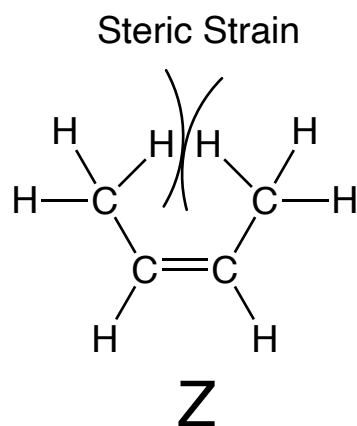


Big Change — For this reaction you need to choose the most stable product, NOT worrying about the most stable contributing structure of an allylic radical intermediate. 99)



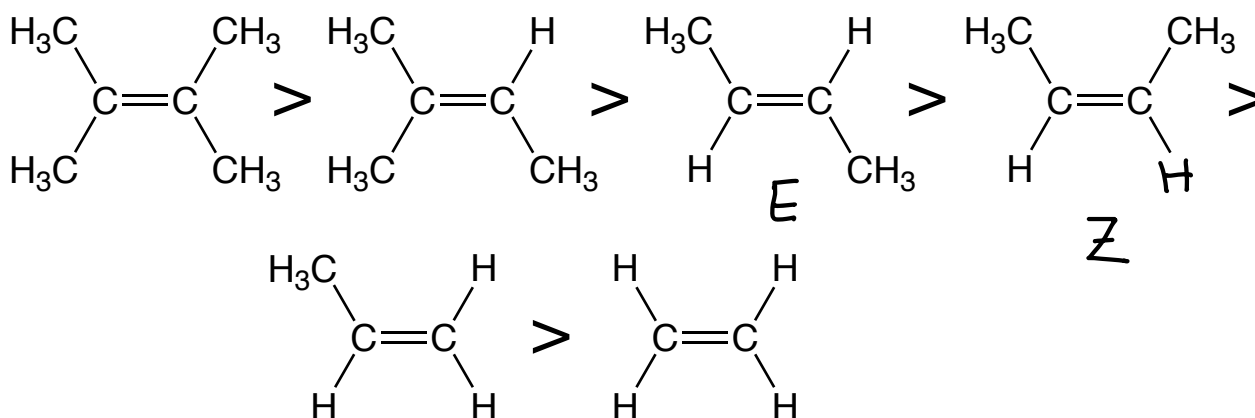
Special Alkene Bonus: Important material you will need to know!

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).

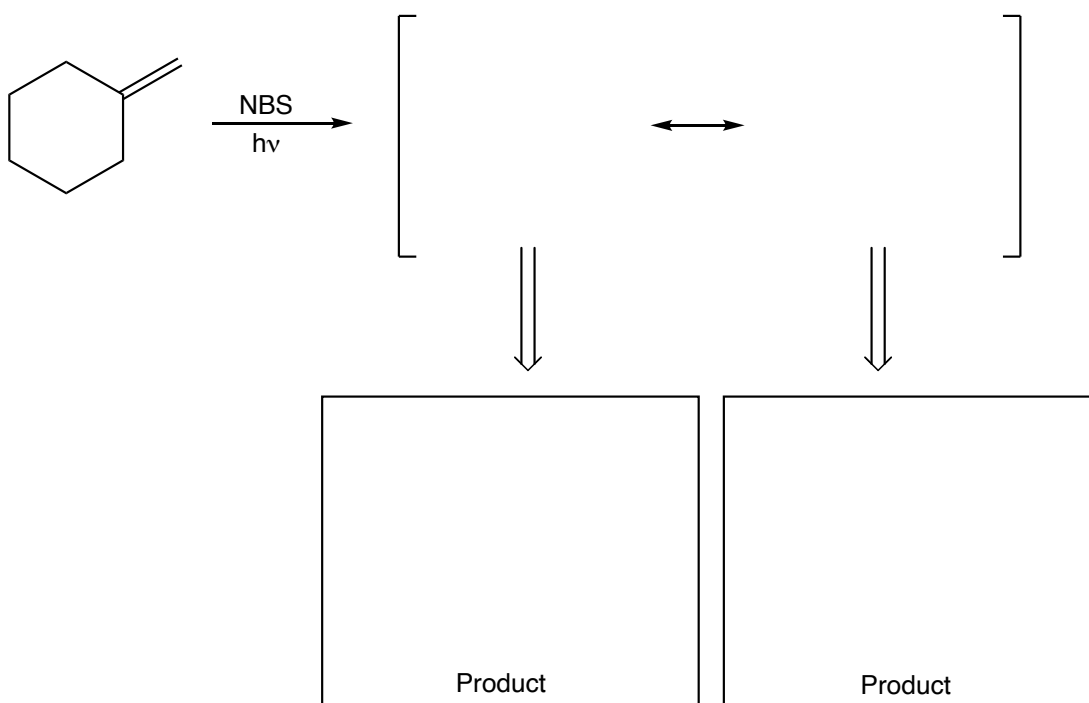
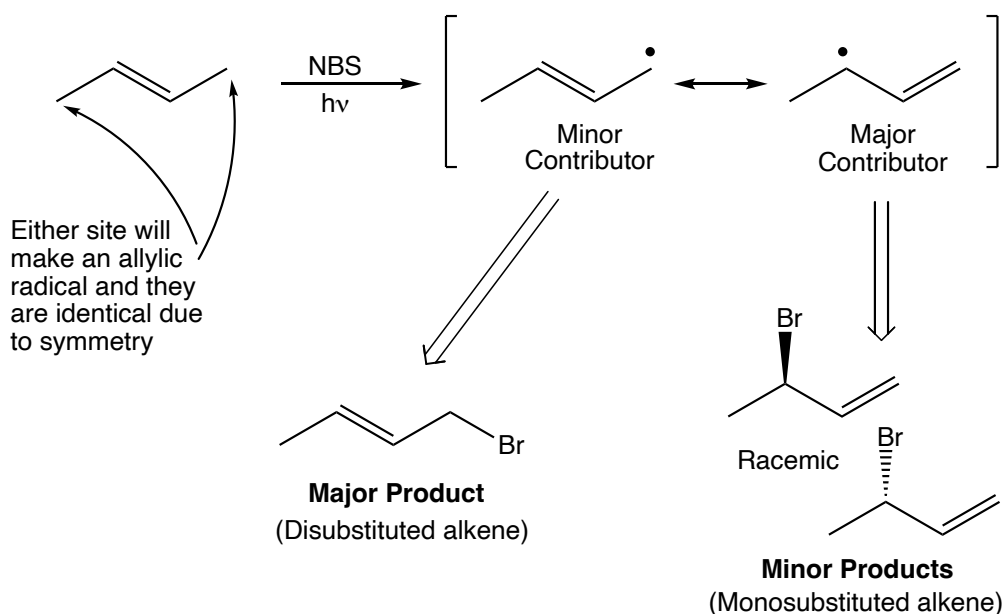
Strongest Pi Bond



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

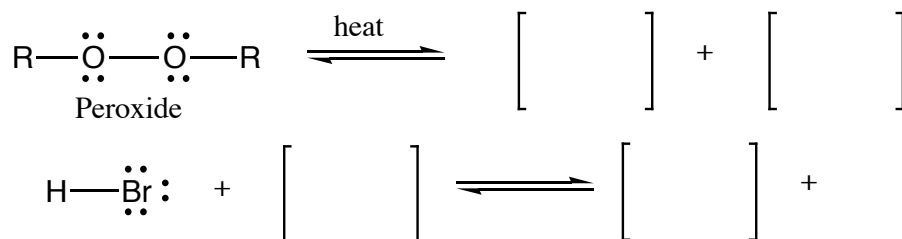
When analyzing allylic halogenation reactions (NBS and $h\nu$)

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.**

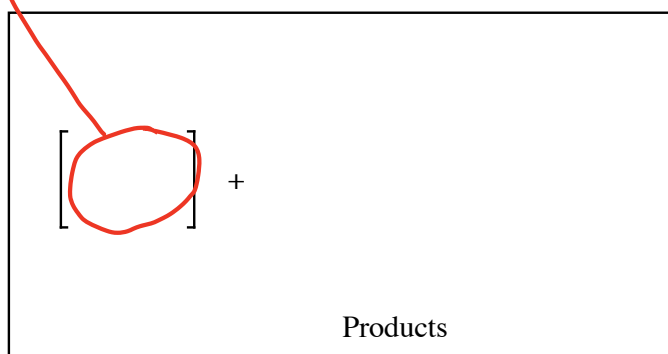
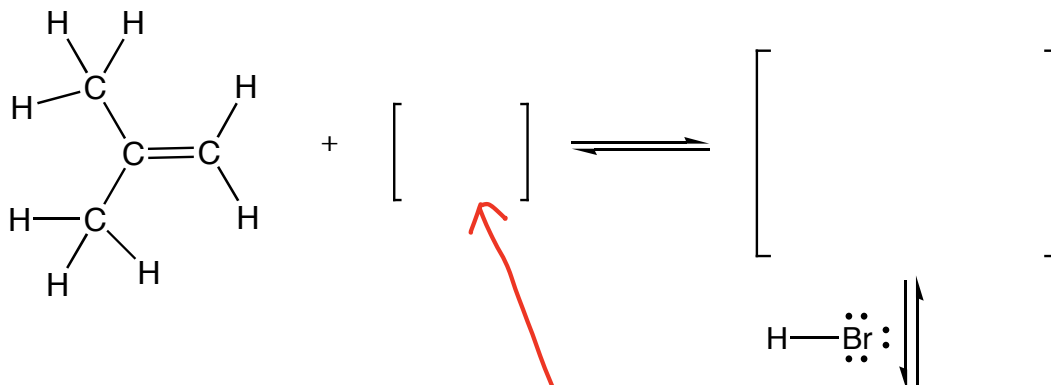


Non-Markovnikov Addition of HBr to an Alkene

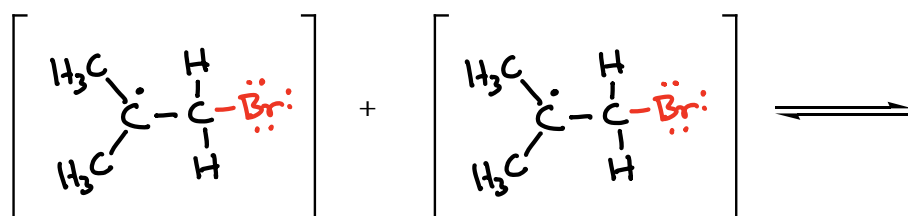
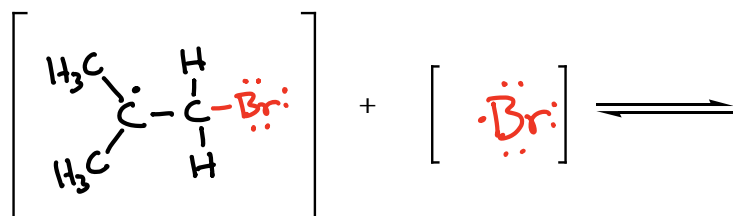
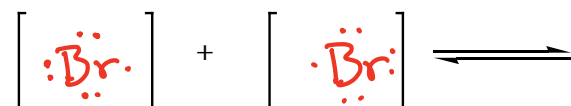
Initiation



Propagation



Termination





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

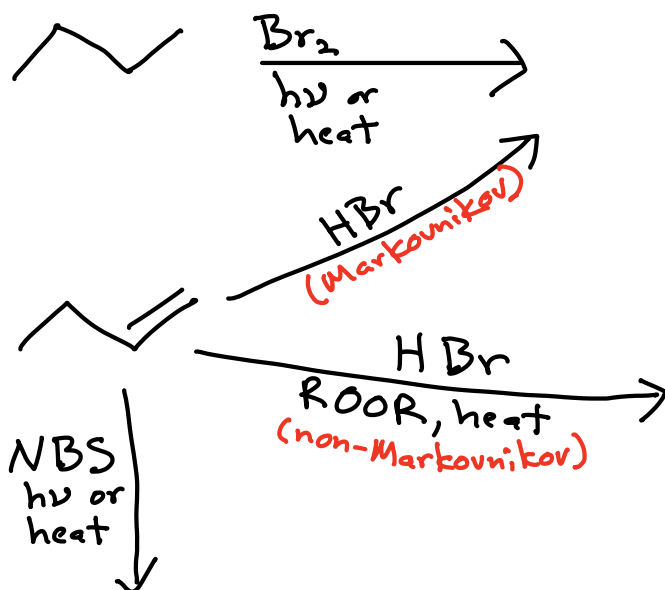
This is huge →

HBr
ROOR
hv or
heat



Non-Markovnikov
Rejochemistry

Making Haloalkanes





Never use
 Br_2 and $h\nu$
or heat
with an
alkene!





New Concept → Leaving Group

Halogens



← Leaving Group Ability

← Anion Stability

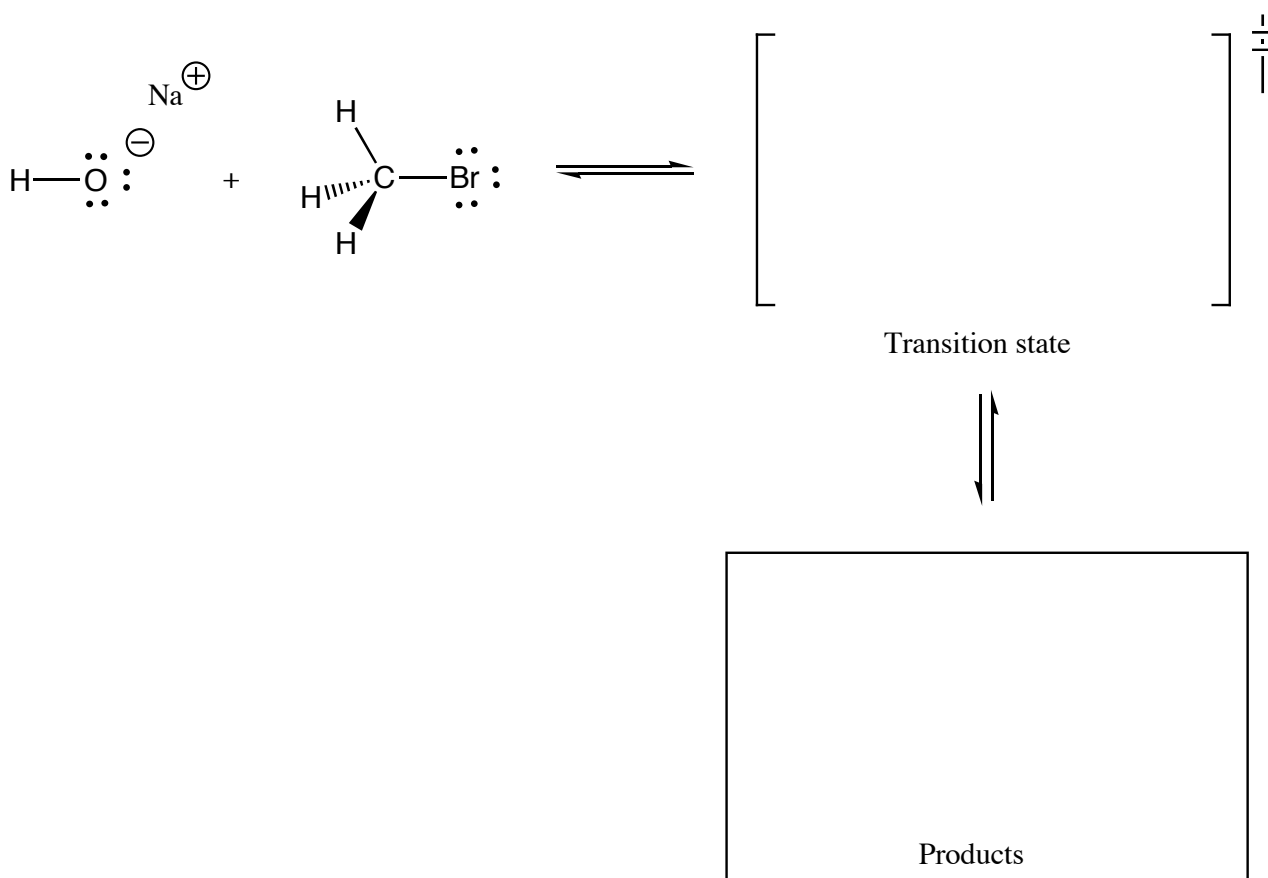
1st New Mechanism

→ S_N2

Substitution

↗
Nucleophile

The S_N2 Mechanism



Summary:

Regiochemistry:

Stereochemistry:

Example:

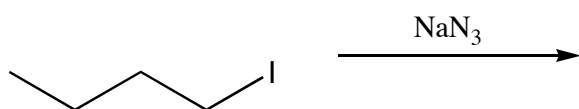


Table of Nucleophiles

Strong Nucleophiles

Br^- , I^- , R-S^- , H-S^- , $\text{N}\equiv\text{C}^-$, N_3^-

$\text{R-C}\equiv\text{C}^-$, R-O^- , H-O^- Strong Bases

Medium Nucleophiles

**R-CO_2^- , R-S-H , R_2S ,
 NH_3 , RNH_2 , R_2NH , NR_3**

Weak Nucleophiles

$\text{R-CO}_2\text{H}$, R-O-H , H_2O Very Weak Bases

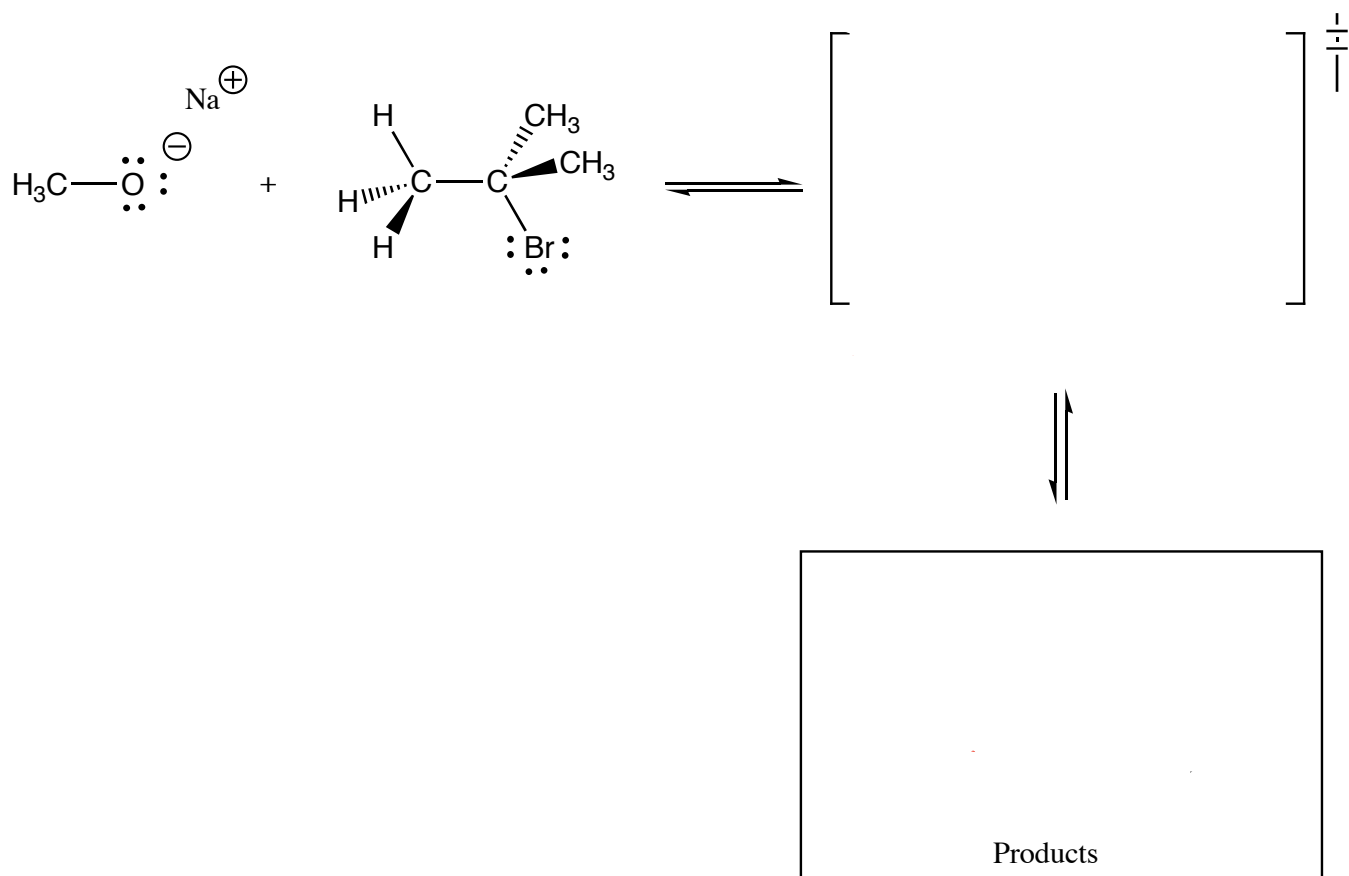
Special Case

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

2nd New Mechanism

E2

The E2 Mechanism

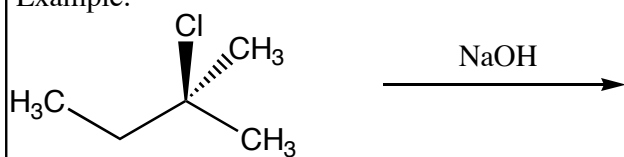


Summary:

Regiochemistry:

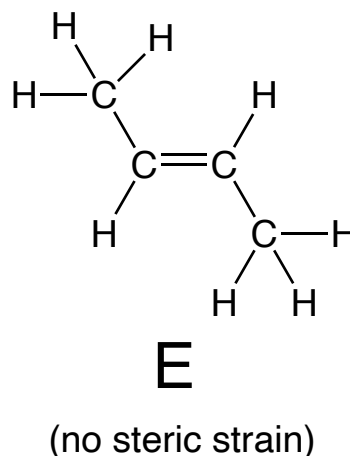
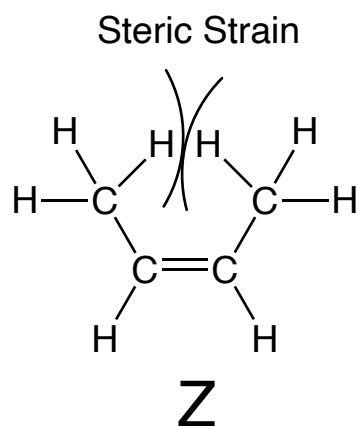
Stereochemistry:

Example:



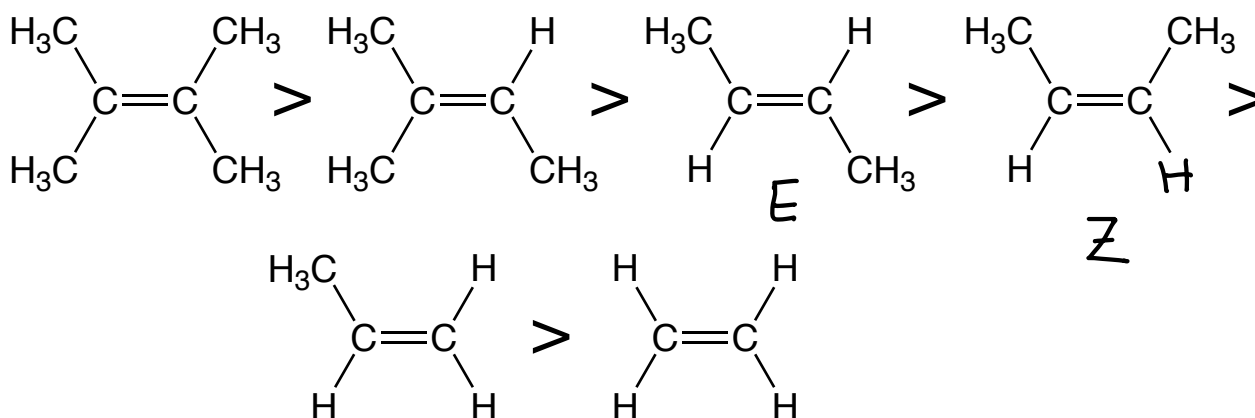
Special Alkene Bonus: Important material you will need to know!

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!!***

Zaitsev's Rule $\rightarrow$

3rd and 4th mechanism $\rightarrow$
these must be considered
together

S_N1 and $E1$