Hello Dr. Iverson,
You may not remember me, but I was in your organic chemistry class last semester,… I hope you can appreciate my unique story.

This past summer I was diagnosed with lymphoma cancer. Initially I had lost all hope, I kept asking myself "why me?" and kept thinking of all things I hadn't accomplished in my lifetime. Nevertheless, I soon got over that fact and started my chemotherapy treatments. Each treatment got worse and worse as I experienced more and more of the side effects. At night I couldn't fall asleep from all psychological and financial stress, couldn't eat because of mouth sores, and when I did eat I would feel sick and nauseated. It wasn't until my third treatment that I remembered the many times you told the class that running could help quality of life. It took a couple of weeks for me to convince myself to start running but I eventually started slowly.I never thought how great of an affect physical activity could have. I was never obese so I never gave running or cardio any thought. As I started running on a regular basis I started seeing my symptoms disappear slowly. Soon when I would come back from running I suddenly had an appetite, regardless of the mouth sores I was hungry enough to eat. My sleeping schedule was started falling into place because I was so tired after running. My stress levels decreased enough that I could see the difference. Best of all it gave me something to do during my days at home, saving me from depression.

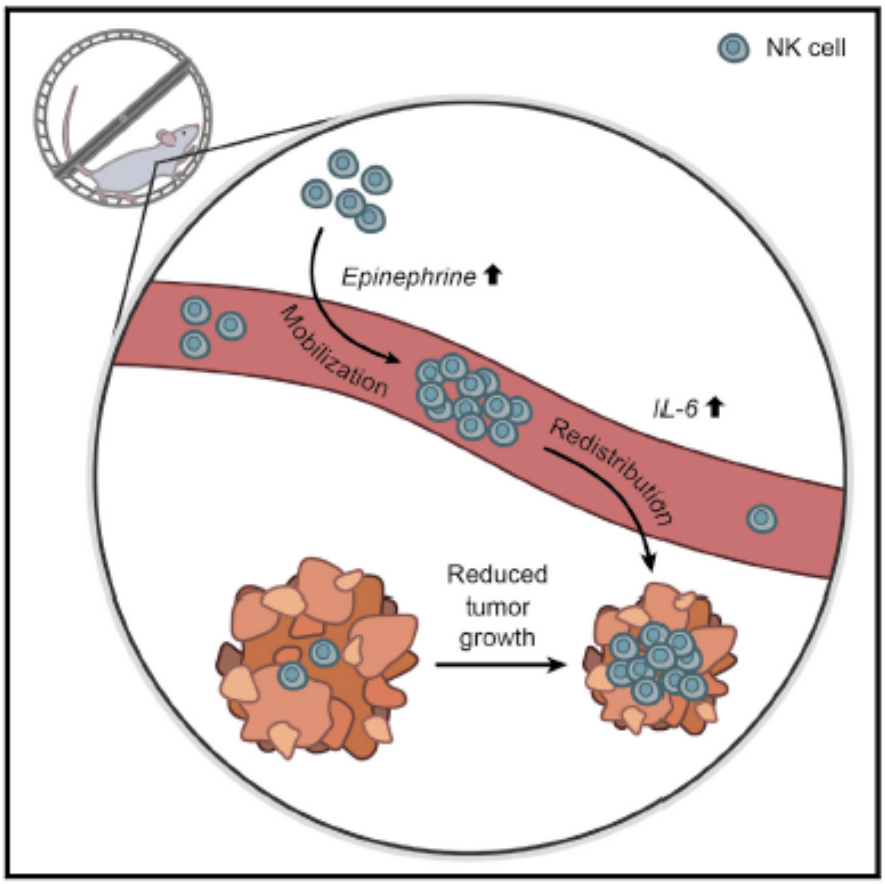
Running saved my life Dr. Iverson.

Short Article

Cell Metabolism

Voluntary Running Suppresses Tumor Growth through Epinephrine- and IL-6-Dependent NK Cell Mobilization and Redistribution

Graphical Abstract



Authors

Line Pedersen, Manja Idorn, Gitte H. Olofsson, ..., Bente K. Pedersen, Per thor Straten, Pernille Hojman

Correspondence

phojman@inflammation-metabolism.dk

In Brief

The beneficial effects of exercise are countless. Pedersen et al. now link exercise, cancer, and immunity and reveal that exercise decreases tumor incidence and growth by over 60% across several mouse tumor models through a direct regulation of NK cell mobilization and trafficking in an epinephrine- and IL-6-dependent manner.

Highlights

- Exercise reduces tumor incidence and growth in several mouse models
- Exercise increases NK cell infiltration, thereby controlling tumor growth
- Epinephrine mobilizes NK cells and β-blockade blunts the tumor suppression
- Exercise-induced muscle-derived IL-6 is involved in NK cell redistribution

Accession Numbers

GSE62628

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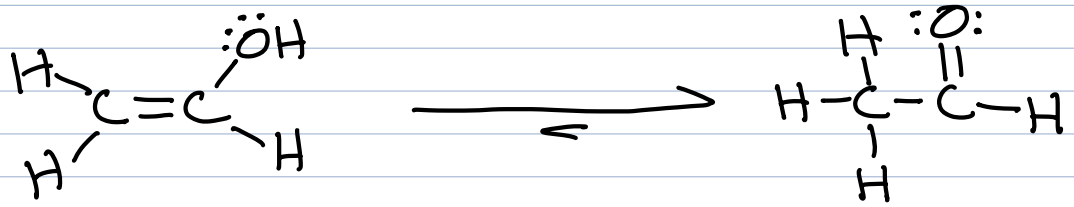
New Concept → The following species are in equilibrium, and the more stable species is the keto form

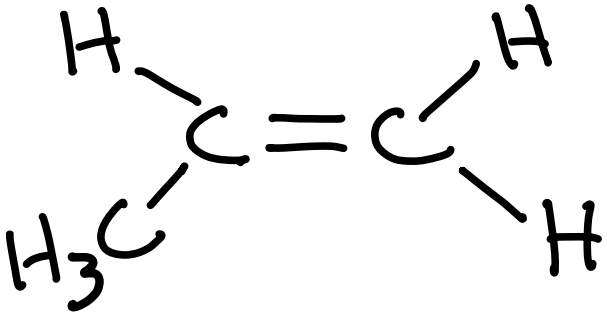


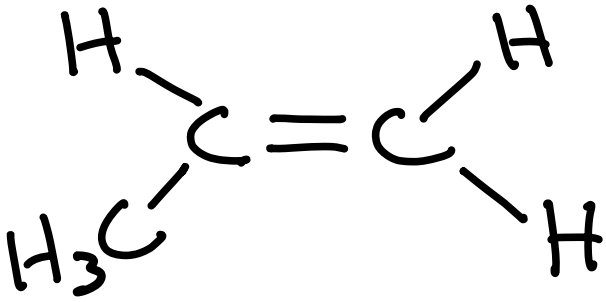
enol form

keto form

Favored (a C=O pi bond is stronger than a C=C pi bond)

This process is called "tautomerization" as in "keto-enol tautomerization"



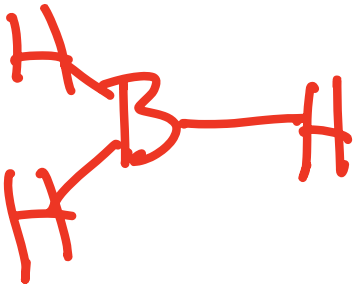


$H_3C-C\equiv C-H$

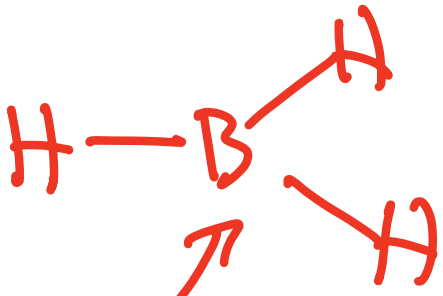
$H_3C-C\equiv C-H$

$H_3C-C\equiv C-H$

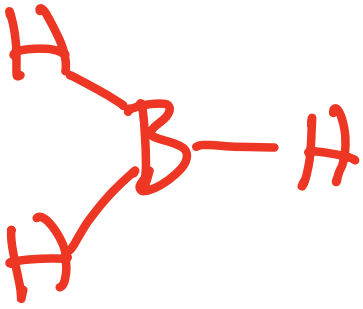
$H_3C-C\equiv C-H$

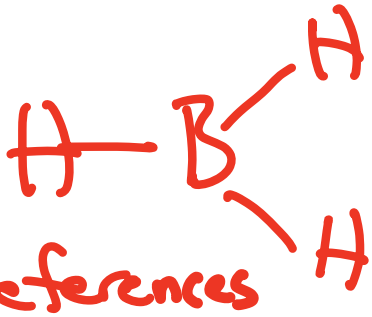


steric strain

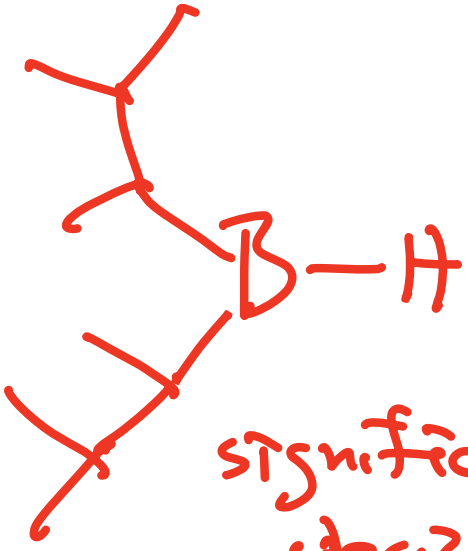


Little steric strain

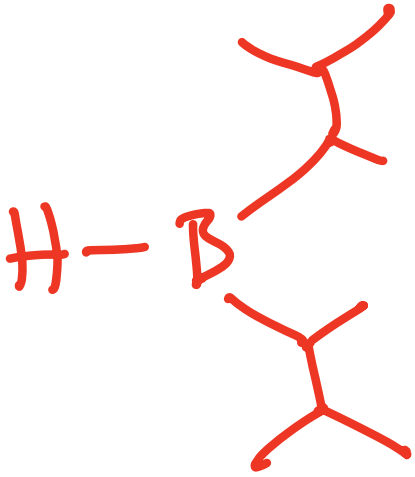




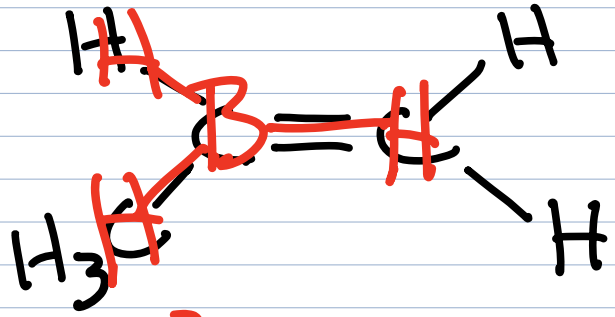
No real preferences



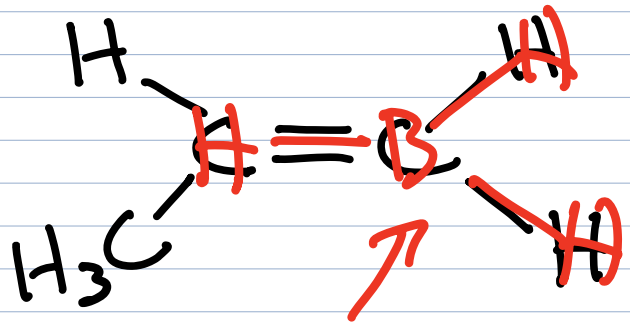
significant steric strain



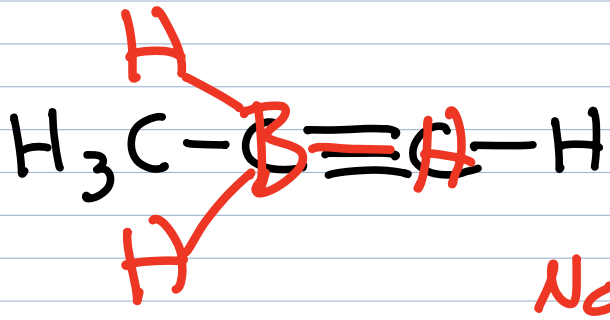
Highly Preferred

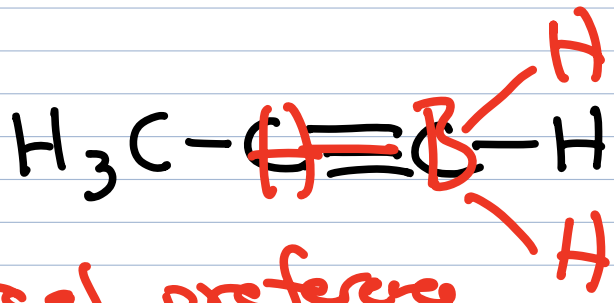


steric strain

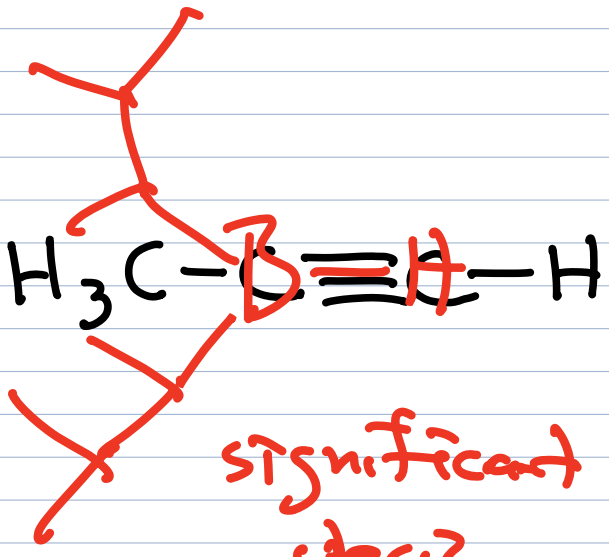


Little steric strain

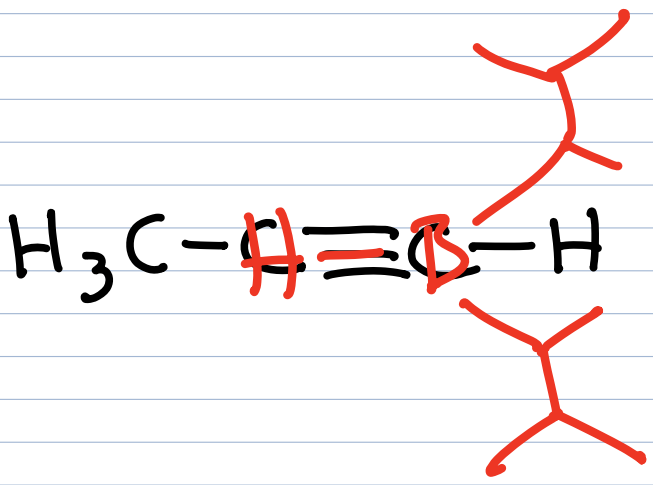




No real preference

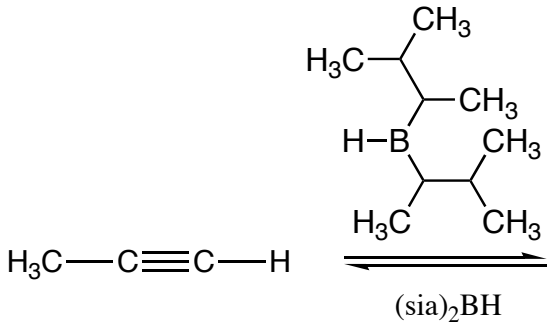


significant steric strain



Highly Preferred

Terminal Alkyne Hydroboration



transition state

2. H_2O_2 / $HO^{\ominus}$

(Chemist opens flask and adds new reagent)

Keto-enol tautomerization

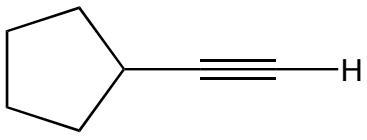
Products

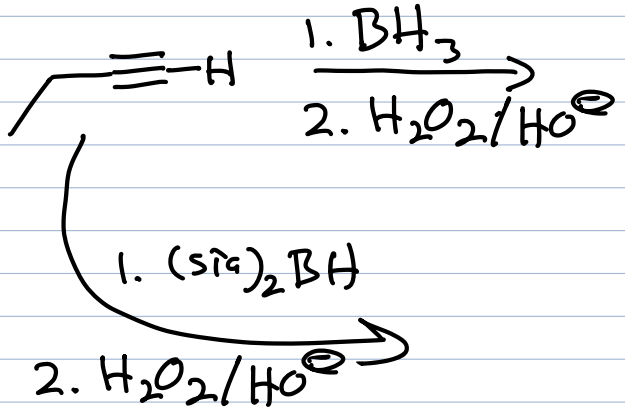
Summary:

Regiochemistry:

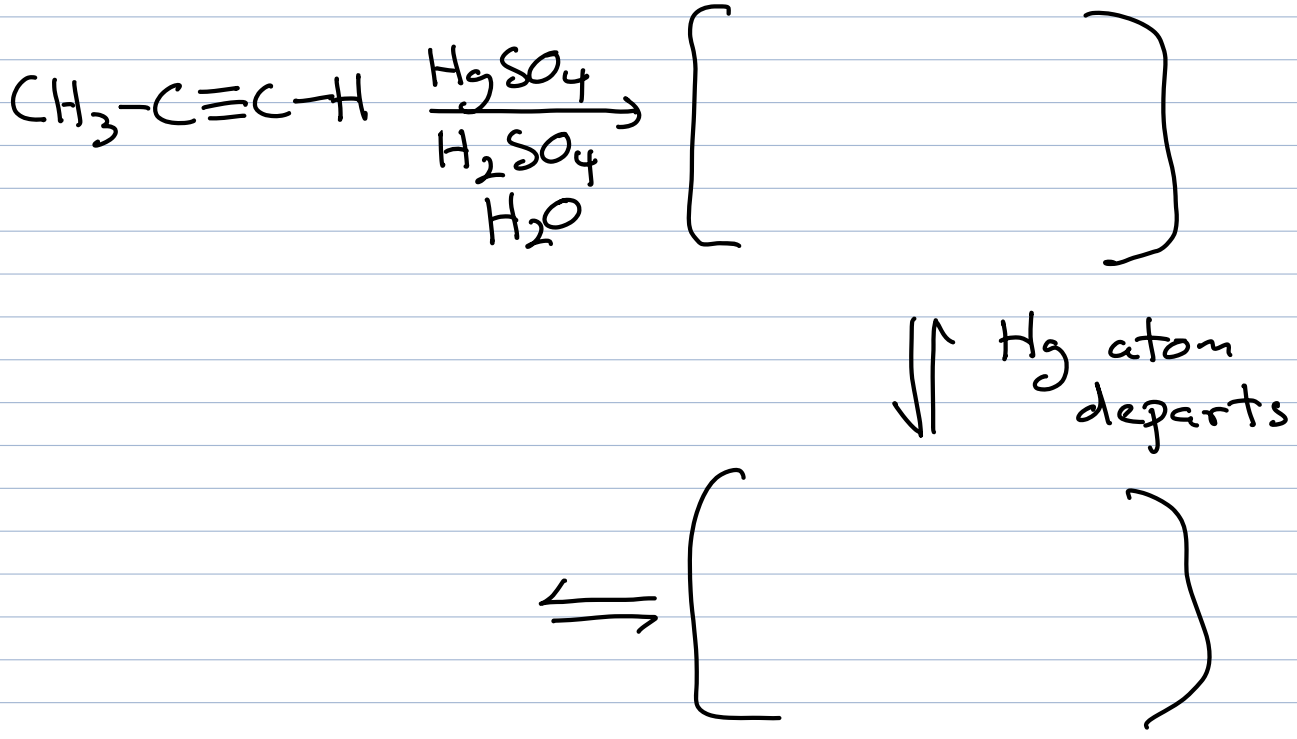
Stereochemistry:

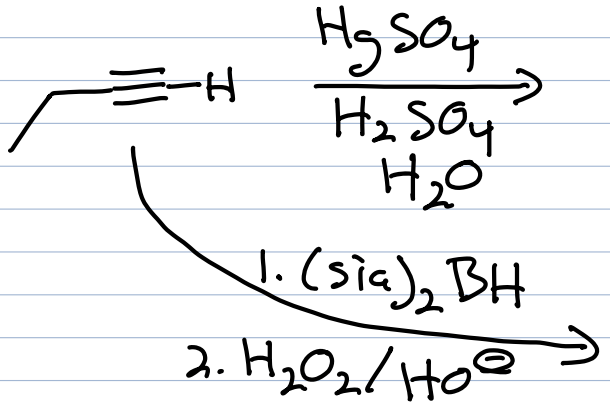
Example:




1. BH_3
2. $H_2O_2/HO^{\ominus}$
1. $(sia)_2BH$
2. $H_2O_2/HO^{\ominus}$

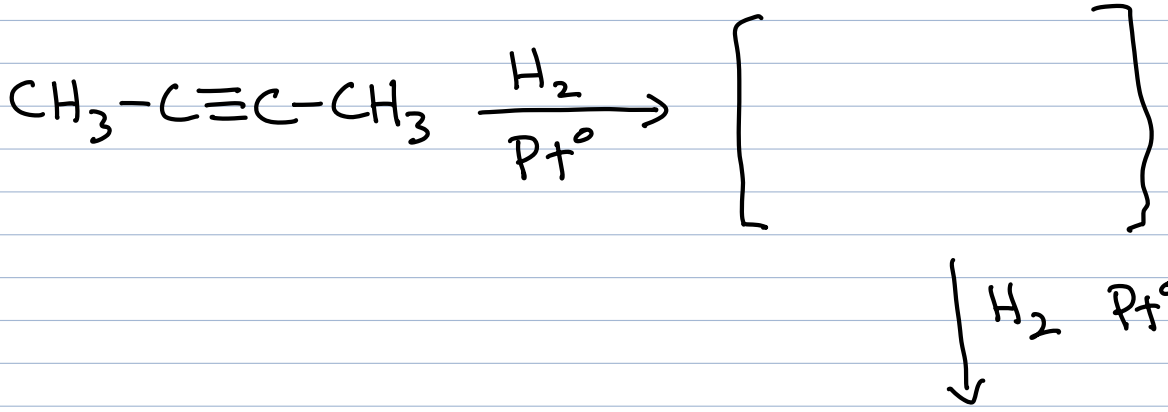
Hydration of an alkyne using $HgSO_4$, H_2SO_4, H_2O



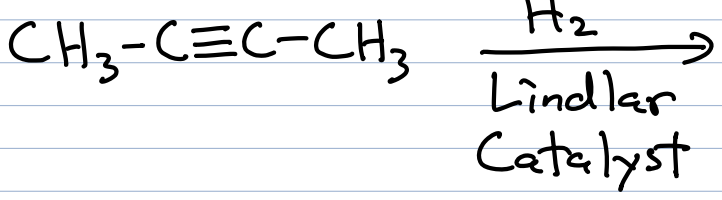


Reduction of Alkynes

1) Hydrogenation H_2 Pt°, Pd°, Ni°

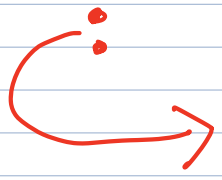


Lindlar Catalyst → special catalyst that stops the hydrogenation at the syn addition



Time Out:

Regular Arrows



"Fish hook" Arrows

Radical → a species with an electron

Time In:

2) Dissolving metal reductions of alkynes

Na^0 in NH_3

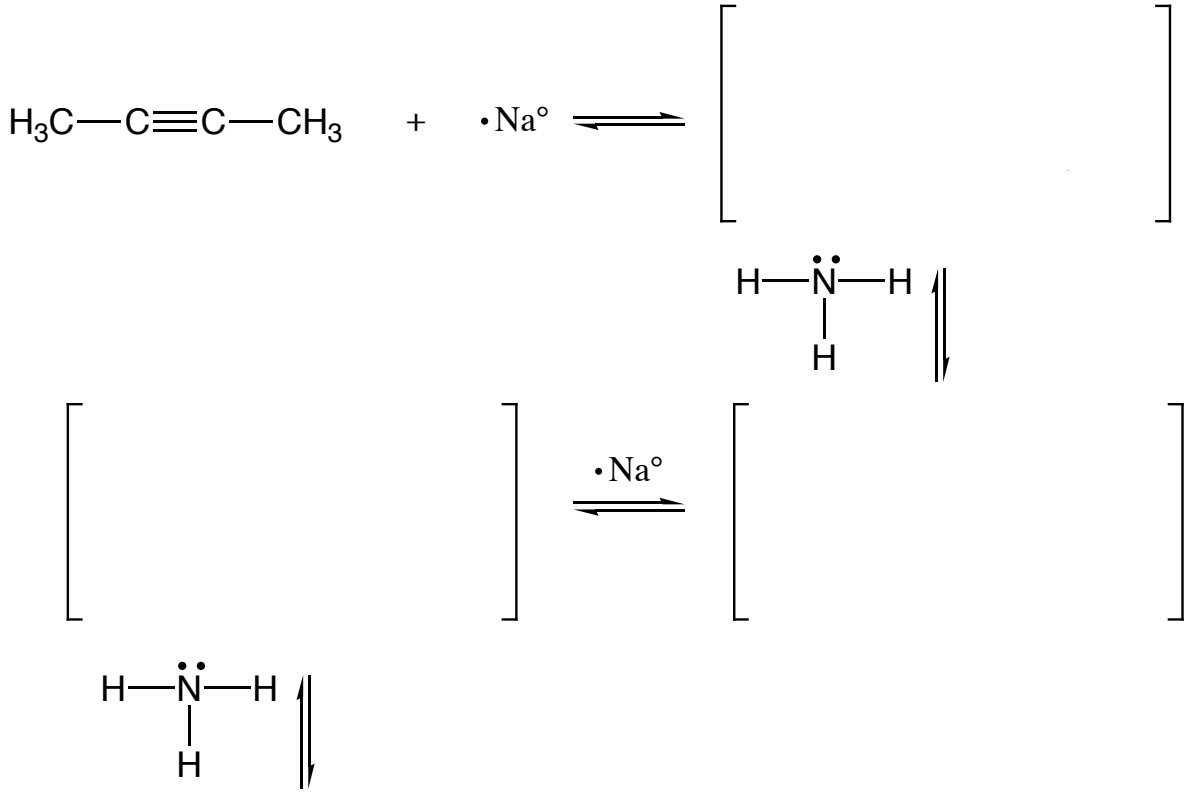
Sodium → (Na^0) is a very strong agent

because $Na^{\oplus}$ has a

in its valence shell

NH_3 → used as and the source of

Reduction of Alkynes Using Sodium and Ammonia



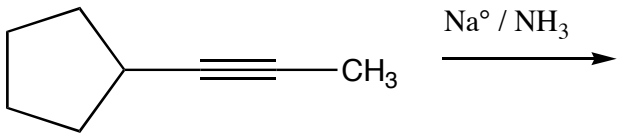
Products

Summary:

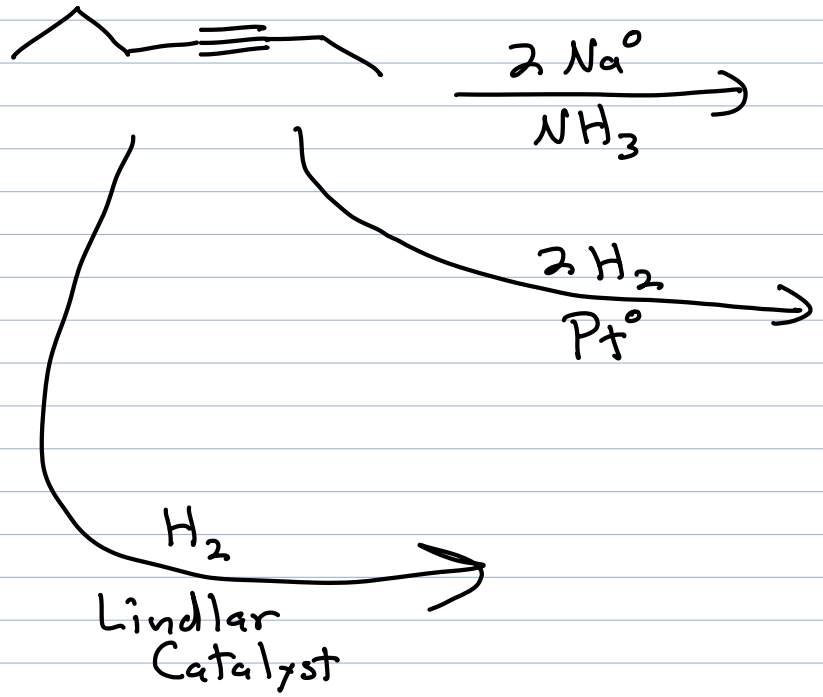
Regiochemistry:

Stereochemistry:

Example:

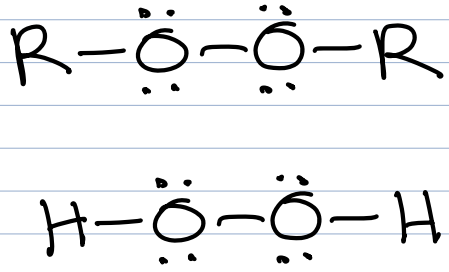


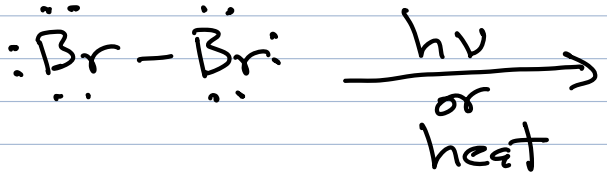
Reductions of alkynes → 3 choices



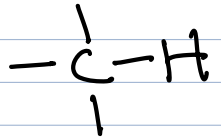

Energizer

Bonds between atoms with multiple lone pairs are generally weaker bonds

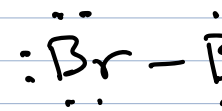




Reference Bond Strengths

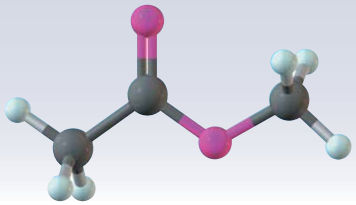


BDE ~100 kcal/mol



BDE ~46 kcal/mol

Appendix 3 Bond Dissociation Enthalpies



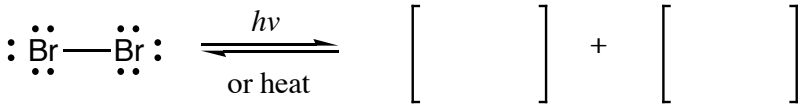
Bond dissociation enthalpy (BDE) is defined as the amount of energy required to break a bond homolytically into two radicals in the gas phase at 25°C.

$$A{-}B \rightarrow A\cdot + B\cdot \qquad \Delta H^0 \text{ [kJ (kcal)/mol]}$$

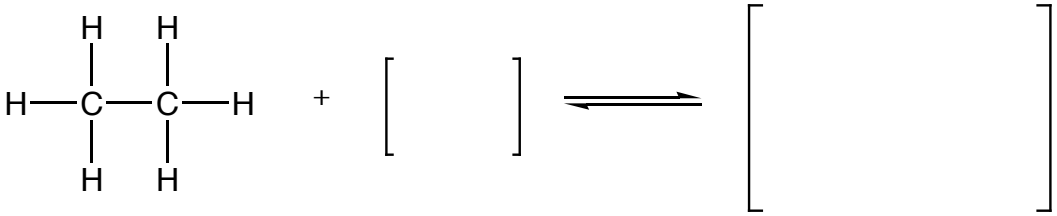
Bond	ΔH^0	Bond	ΔH^0	Bond	ΔH^0
H—H bonds		**C—C multiple bonds**		**C—Br bonds**	
H—H	435 (104)	$CH_2{=}CH_2$	727 (174)	CH_3—Br	301 (72)
D—D	444 (106)	HC≡CH	966 (231)	C_2H_5—Br	301 (72)
				$(CH_3)_2CH$—Br	309 (74)
X—X bonds		**C—H bonds**		$(CH_3)_3C$—Br	305 (73)
F—F	159 (38)	CH_3—H	439 (105)	$CH_2{=}CHCH_2$—Br	247 (59)
Cl—Cl	247 (59)	C_2H_5—H	422 (101)	C_6H_5—Br	351 (84)
Br—Br	192 (46)	$(CH_3)_2CH$—H	414 (99)	$C_6H_5CH_2$—Br	263 (63)
I—I	151 (36)	$(CH_3)_3C$—H	405 (97)		
		$CH_2{=}CH$—H	464 (111)	**C—I bonds**	
H—X bonds		$CH_2{=}CHCH_2$—H	372 (89)	CH_3—I	242 (58)
H—F	568 (136)	C_6H_5—H	472 (113)	C_2H_5—I	238 (57)
H—Cl	431 (103)	$C_6H_5CH_2$—H	376 (90)	$(CH_3)_2CH$—I	238 (57)
H—Br	368 (88)	HC≡C—H	556 (133)	$(CH_3)_3C$—I	234 (56)
H—I	297 (71)			$CH_2{=}CHCH_2$—I	192 (46)
		C—F bonds		C_6H_5—I	280 (67)
O—H bonds		CH_3—F	481 (115)	$C_6H_5CH_2$—I	213 (51)
HO—H	497 (119)	C_2H_5—F	472 (113)		
CH_3O—H	439 (105)	$(CH_3)_2CH$—F	464 (111)	**C—N single bonds**	
C_6H_5O—H	376 (90)	C_6H_5—F	531 (127)	CH_3—NH_2	355 (85)
				C_6H_5—NH_2	435 (104)
O—O bonds		**C—Cl bonds**			
HO—OH	213 (51)	CH_3—Cl	351 (84)	**C—O single bonds**	
CH_3O—OCH_3	159 (38)	C_2H_5—Cl	355 (85)	CH_3—OH	385 (92)
$(CH_3)_3CO$—$OC(CH_3)_3$	159 (38)	$(CH_3)_2CH$—Cl	355 (85)	C_6H_5—OH	468 (112)
		$(CH_3)_3$ C—Cl	355 (85)		
C—C single bonds		$CH_2{=}CHCH_2$—Cl	288 (69)		
CH_3—CH_3	376 (90)	C_6H_5—Cl	405 (97)		
C_2H_5—CH_3	372 (89)	$C_6H_5CH_2$—Cl	309 (74)		
$CH_2{=}CH$—CH_3	422 (101)				
$CH_2{=}CHCH_2$—CH_3	322 (77)				
C_6H_5—CH_3	435 (104)				
$C_6H_5CH_2$—CH_3	326 (78)				

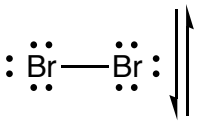
Alkane Free Radical Halogenation

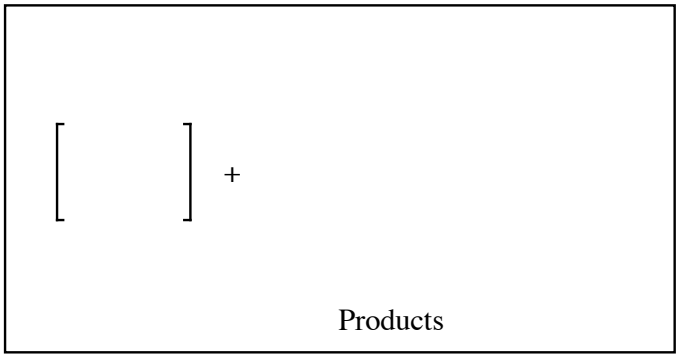
Initiation



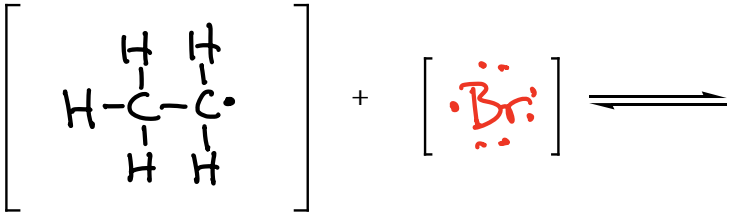
Propagation

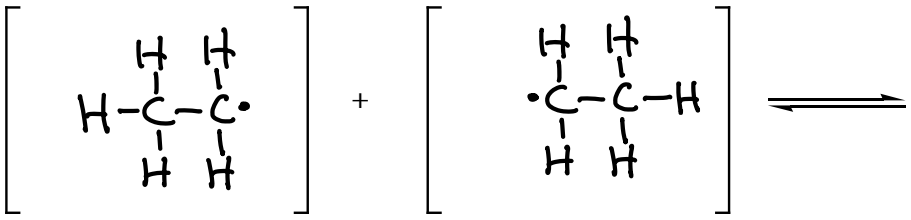




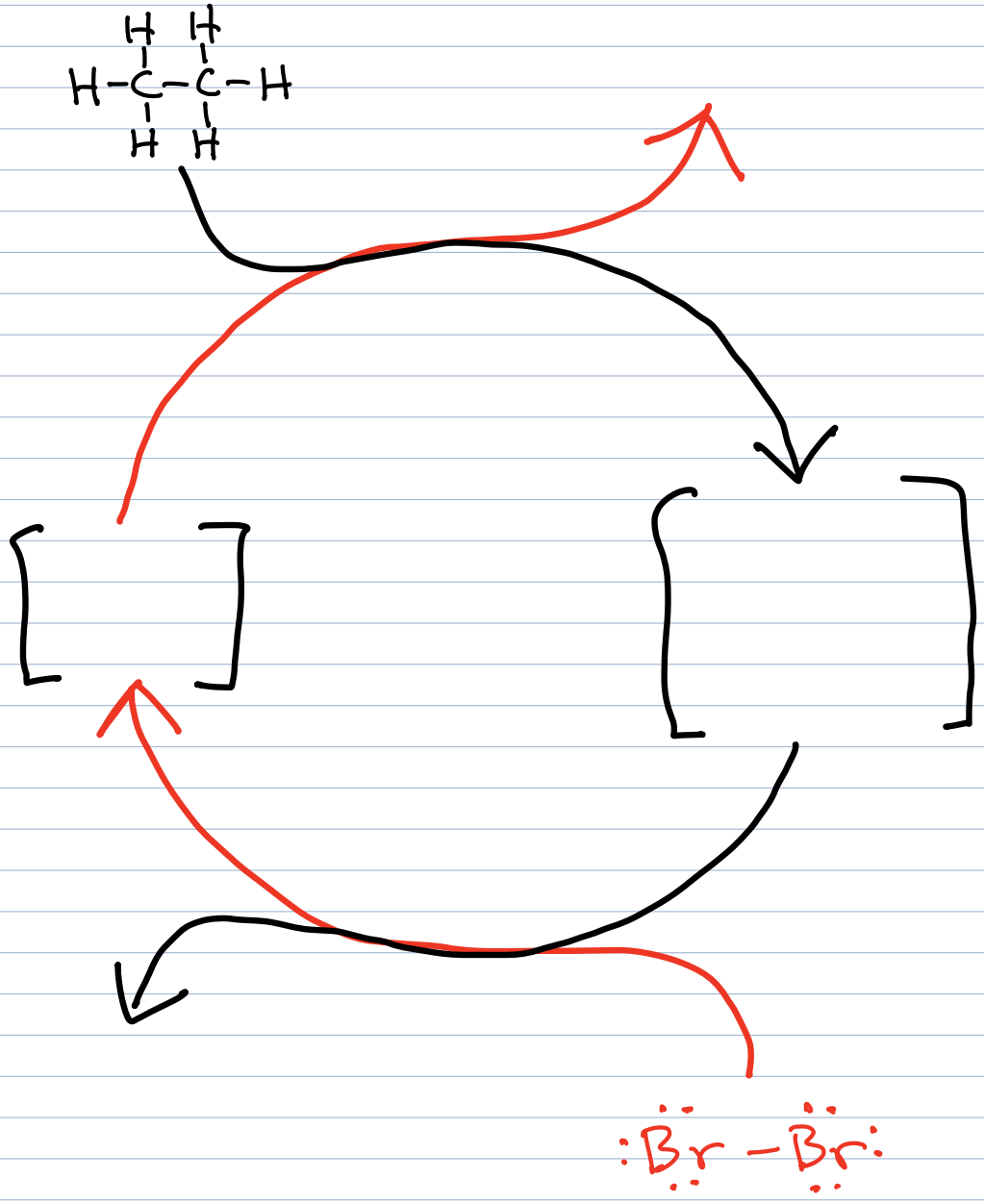


Termination

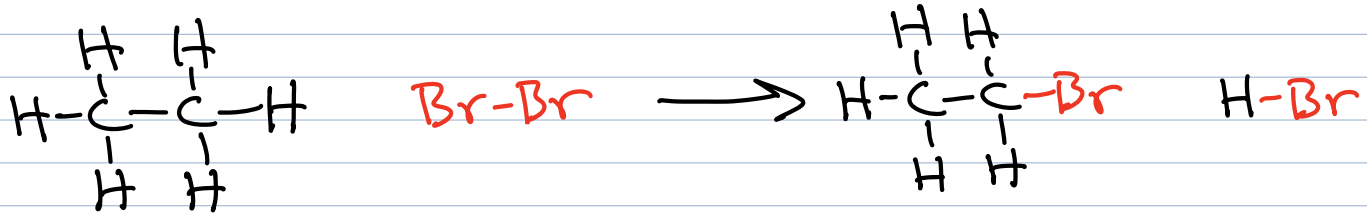




Propagation Process Diagram



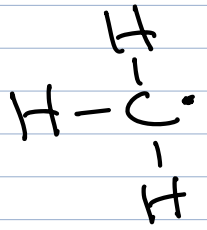
Motive for overall process



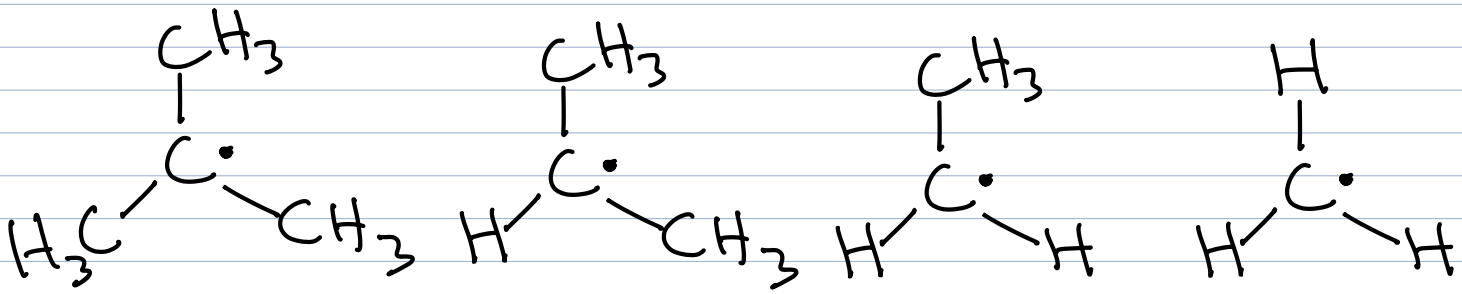
$$\text{Alkane} \xrightarrow[\substack{h\nu \\ \text{or} \\ \text{heat}}]{Br_2} \text{Haloalkane}$$

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

Radical → species with an unpaired electron → very reactive →



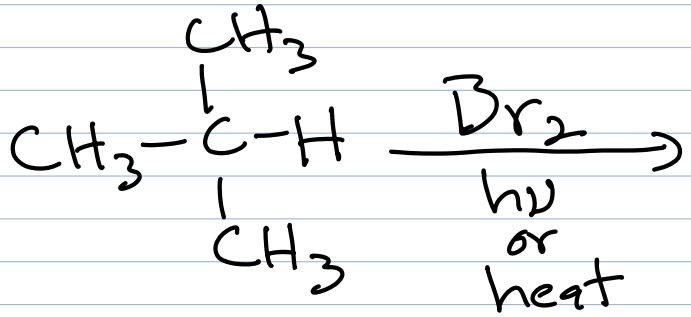
⇒ Think of a radical as being "analogous to a carbocation"



Radical Stability

$\bigstar \Rightarrow$ When there is a choice in a radical reaction with an alkane, the Br atom will end up on the most substituted C atom(s) in the molecule

Reason



Br_2 is more selective than Cl_2 so always use Br_2

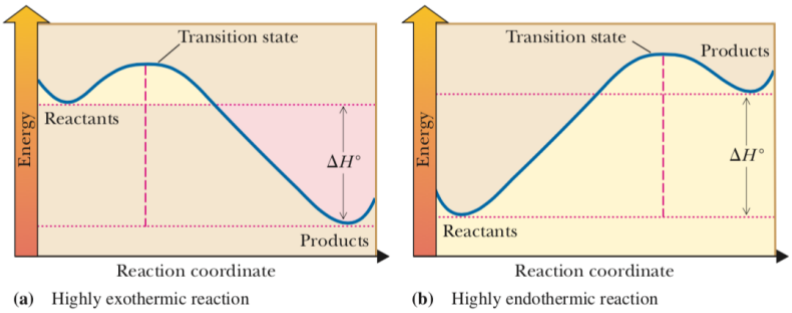
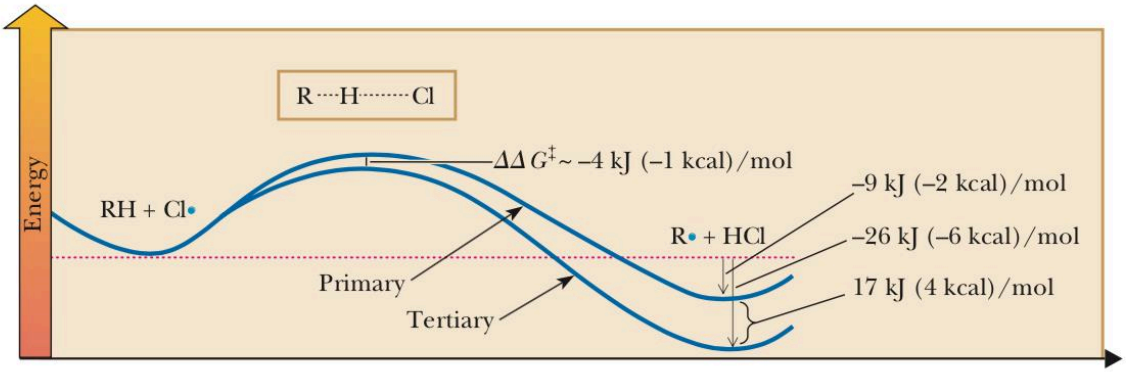
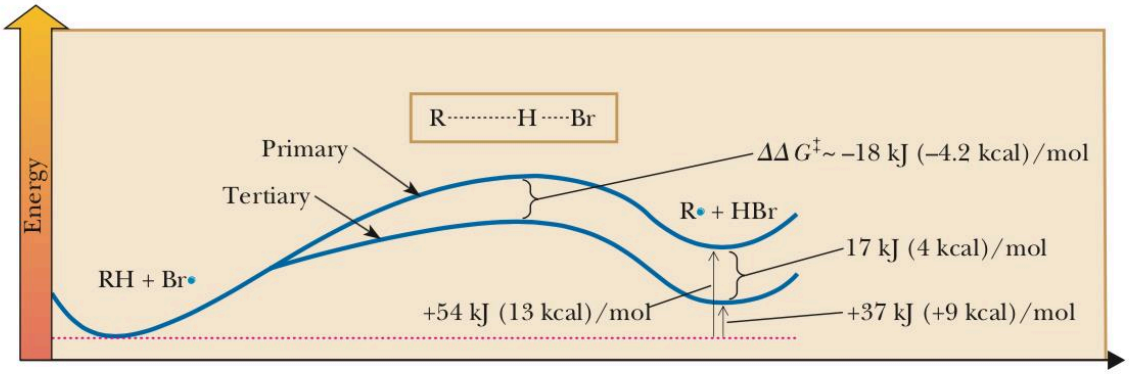


Figure 8.2
Hammond's postulate. Energy diagrams for two one-step reactions. In the exothermic reaction, the transition state occurs early, and its structure resembles that of the reactants. In the endothermic reaction, the transition state occurs late, and its structure resembles that of the products.



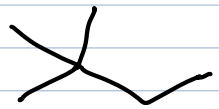
(a) Chlorination



(b) Bromination

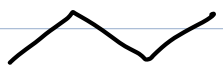
Figure 8.3
Transition states and energetics for hydrogen abstraction in the radical chlorination and bromination of 2-methylpropane (isobutane). The product is the intermediate radical, R·.

Examples



Br_2 → (hν or heat)

Br_2 → (hν or heat)



Br_2 → (hν or heat)

<u>Organic Chemistry</u> 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. 10/8/25

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.

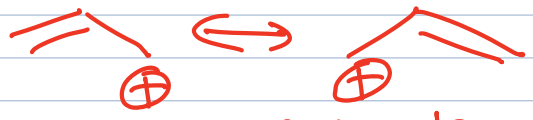
You will learn how to look at a molecule and accurately predict which atoms will react to make new bonds, and which bonds will break during reactions.

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

A)



Allylic Carbocation

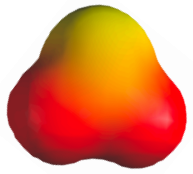
Allylic Radicals

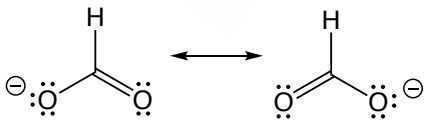
B) When given a choice in allylic halogenation reactions you always make

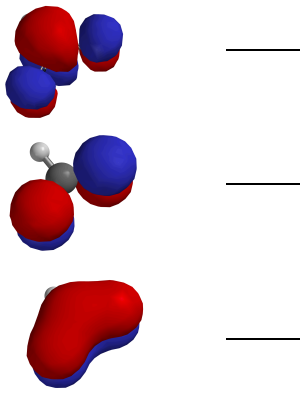
product

How to think about allyl radicals and allyl cations

Carboxylate anion





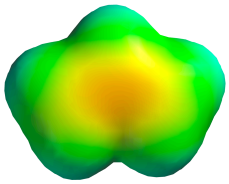


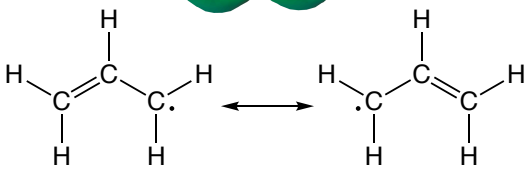
Total # of electrons in the π bond = ____

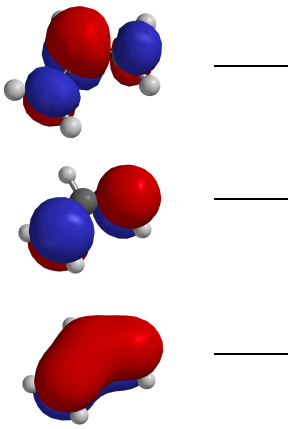
Total # of electrons in the 2p orbital of the other O atom = ____

Total # of electrons in the π-way = ☐

Allyl radical





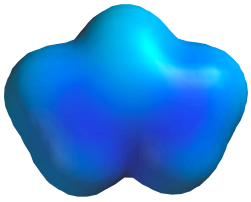


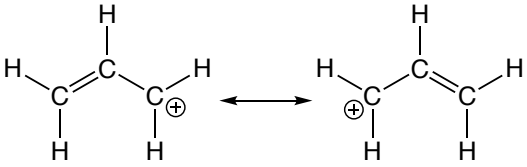
Total # of electrons in the π bond = ____

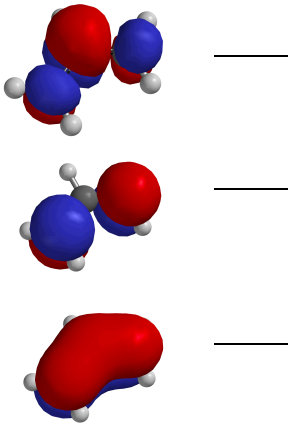
Total # of electrons in the 2p orbital of the other C atom = ____

Total # of electrons in the π-way = ☐

Allyl cation







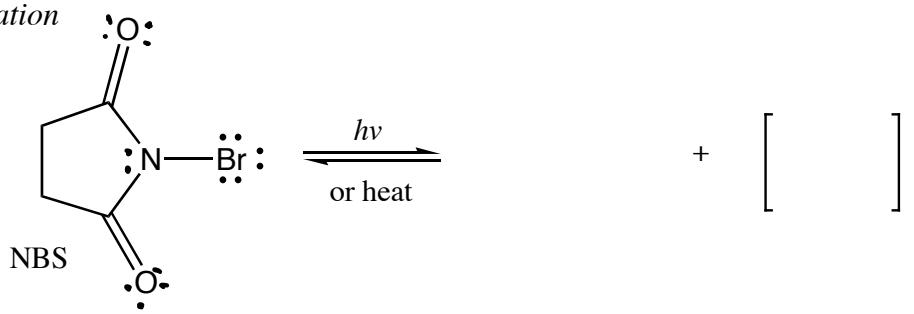
Total # of electrons in the π bond = ____

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

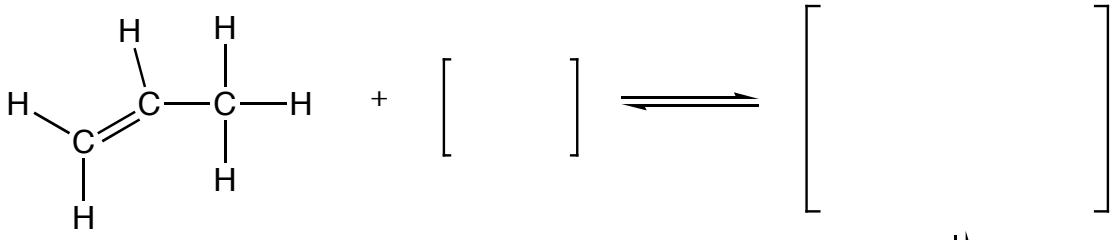
Total # of electrons in the π-way = ☐

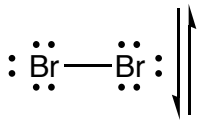
Allylic Halogenation

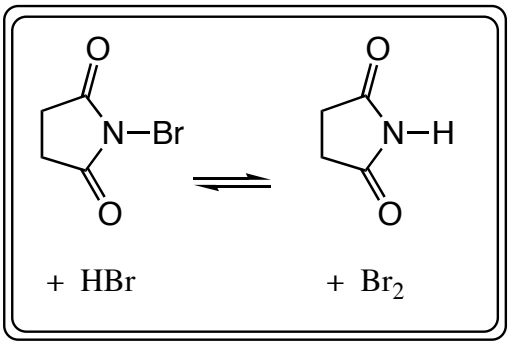
Initiation

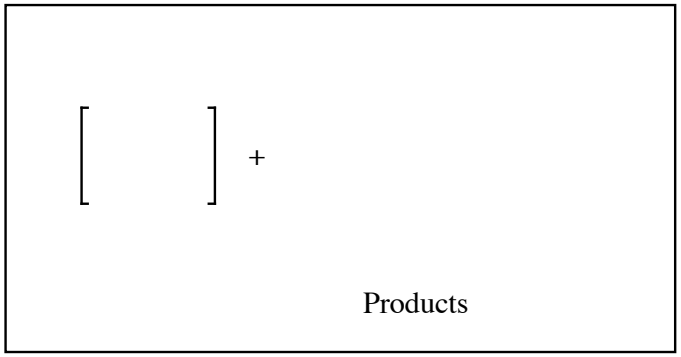


Propagation

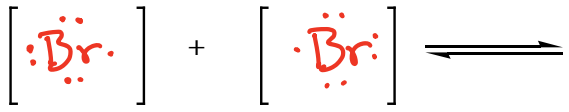


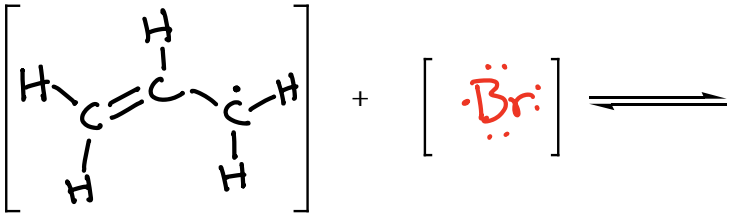


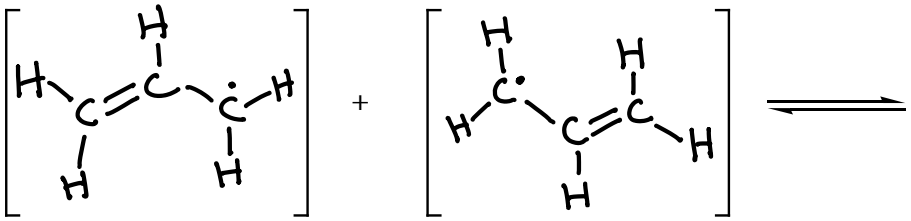




Termination

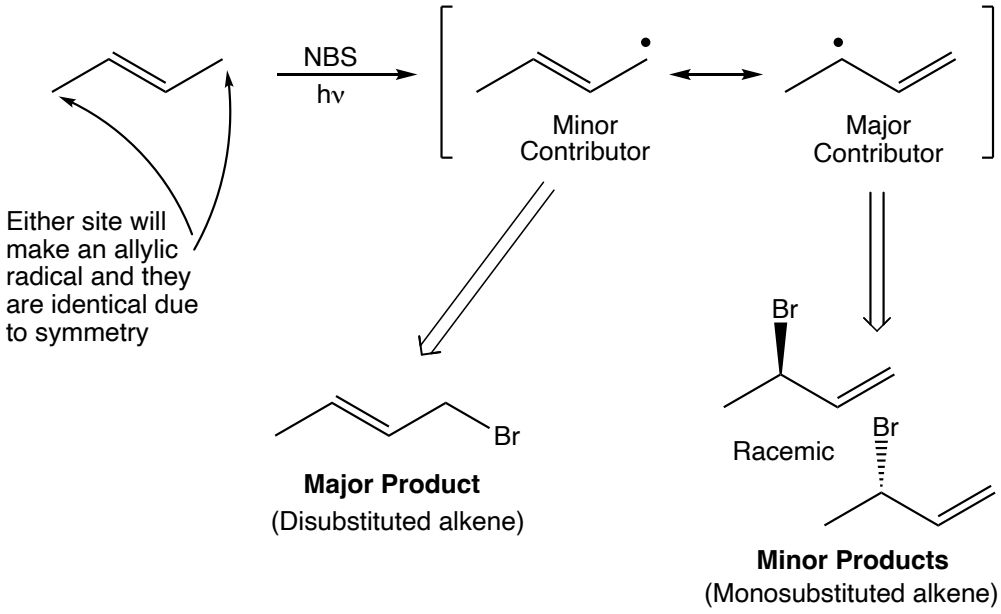


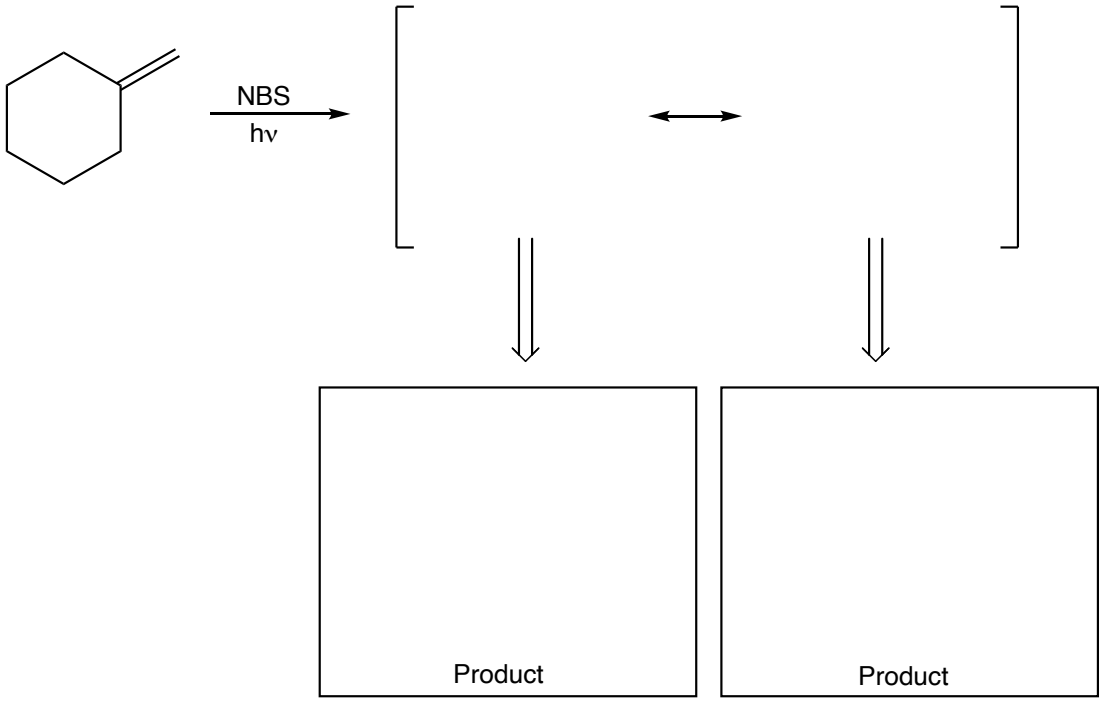




When analyzing allylic halogenation reactions (NBS and hν)

1. **Consider <u>all</u> possible allylic radicals that can be formed.**
2. **Analyze <u>all</u> contributing structures for <u>all</u> of the allylic radicals.**
3. **Add a Br atom at the site of the unpaired electron for <u>all</u> contributing structures for <u>all</u> of the allylic radicals.**
4. **From <u>all</u> of the possible products, the predominant product is the one THAT IS THE MOST STABLE ALKENE – the most substitued 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.**

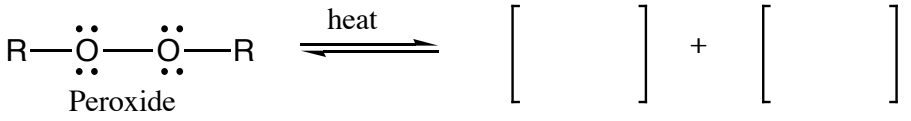


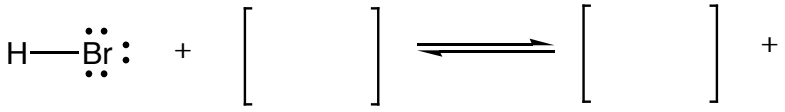


Big Change — For this reaction you need to choose the most stable , NOT worrying about the most stable of an allylic radical intermediate.

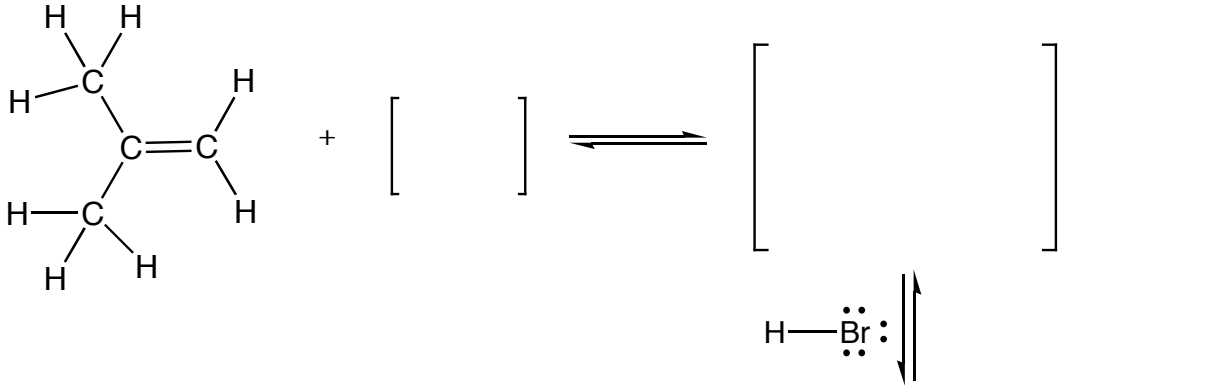
Non-Markovnikov Addition of HBr to an Alkene

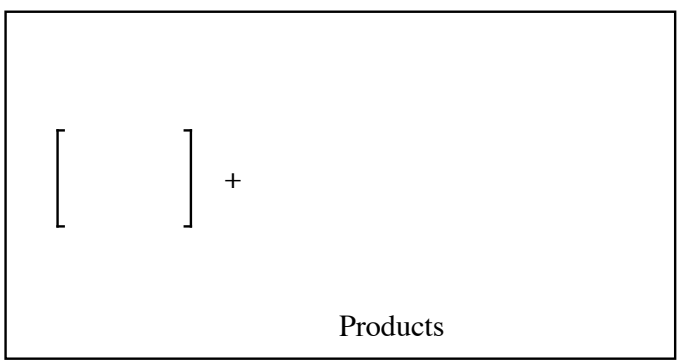
Initiation



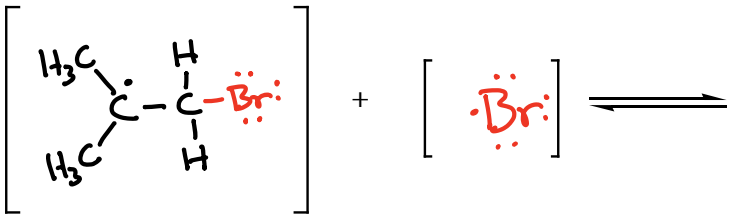


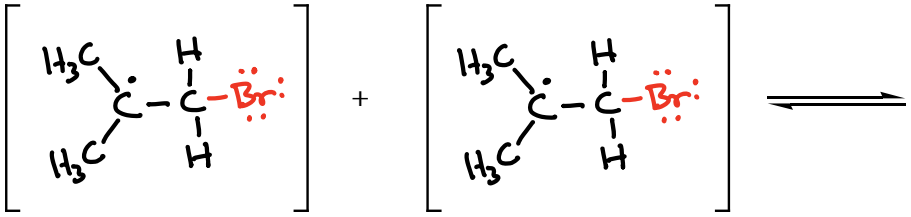
Propagation





Termination



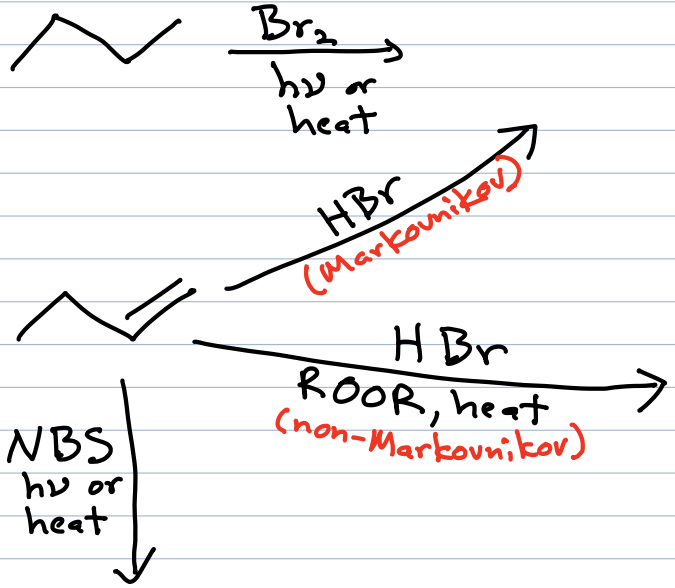


For subtle reasons (not discussed) H-Br, ROOR and heat gives very little allylic halogenation, and NBS/hν or heat gives very little alkene addition even though they both involve $[\cdot\ddot{\underset{\cdot\cdot}{Br}}:]$ and an alkene starting material.

Please accept this

HBr
ROOR
heat
→ Non-Markovnikov Regiochemistry

Making Haloalkanes




Never use Br_2 and hν or heat with an alkene
Br_2
hν or heat