
Energizer
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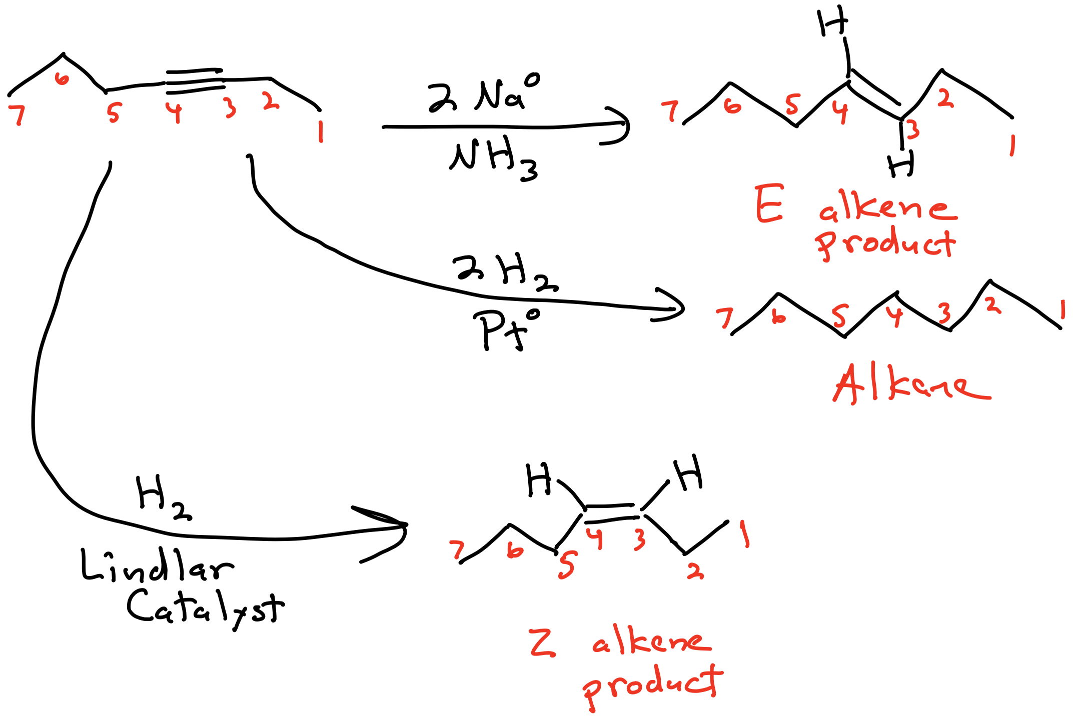
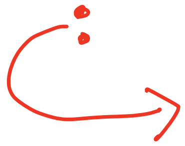
Reductions of alkynes → 3 choices



Time Out:

Regular Arrows



used to show movement of a pair of electrons

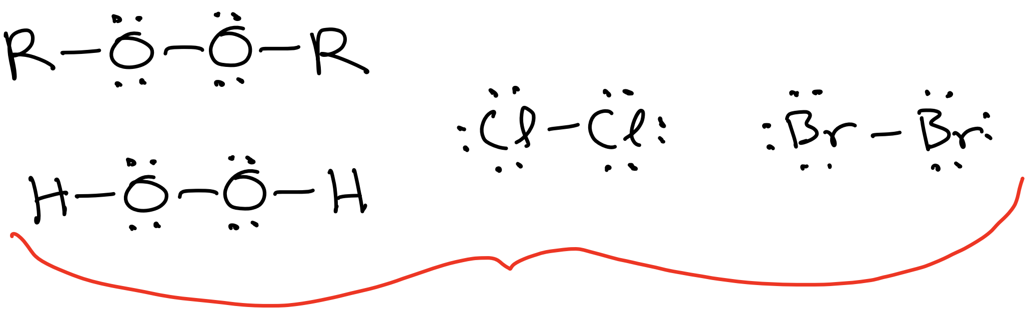
"Fish hook" Arrows

"fish hook" arrows are used to show movement of single electrons

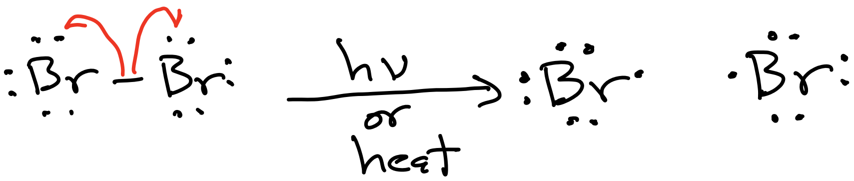
Radical → a species with an unpaired electron → unstable so we encounter radicals as reaction intermediates

Time In:

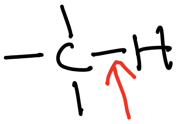
Bonds between atoms with multiple lone pairs are generally weaker bonds → Lone pairs repel each other

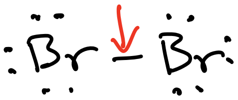


These bonds can be broken by $\underbrace{\text{light}}_{h\nu}$ or heat



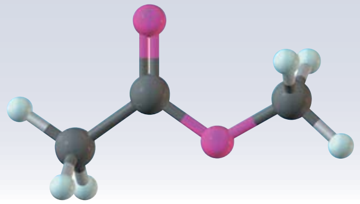
Reference Bond Strengths

 BDE ~100 kcal/mol

 BDE ~46 kcal/mol

Bond Dissociation Enthalpy → amount of energy required to break a bond and create two radicals

Appendix 3 Bond Dissociation Enthalpies



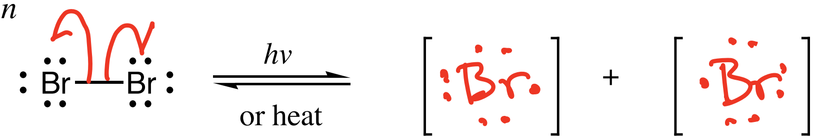
Bond dissociation enthalpy (BDE) is defined as the amount of energy required to break a bond homolytically into two radicals in the gas phase at 25°C.

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

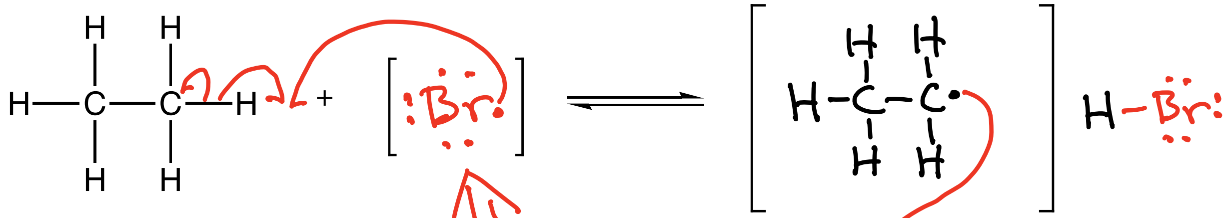
Bond	ΔH^0	Bond	ΔH^0	Bond	ΔH^0
H—H bonds		**C—C multiple bonds**		**C—Br bonds**	
H—H	435 (104)	$CH_2{=}CH_2$	727 (174)	CH_3—Br	301 (72)
D—D	444 (106)	$HC{\equiv}CH$	966 (231)	C_2H_5—Br	301 (72)
				$(CH_3)_2CH$—Br	309 (74)
X—X bonds		**C—H bonds**		$(CH_3)_3C$—Br	305 (73)
F—F	159 (38)	CH_3—H	439 (105)	$CH_2{=}CHCH_2$—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)	$HC{\equiv}C$—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)
		$(CH_3)_3C$—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)				

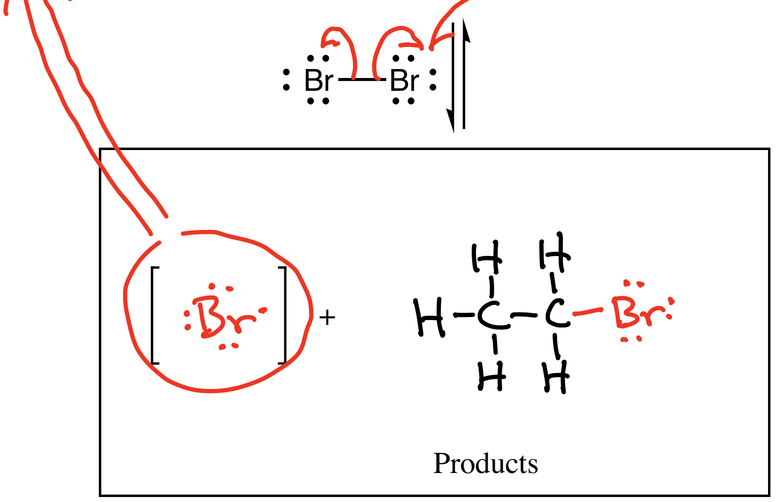
Alkane Free Radical Halogenation

Initiation



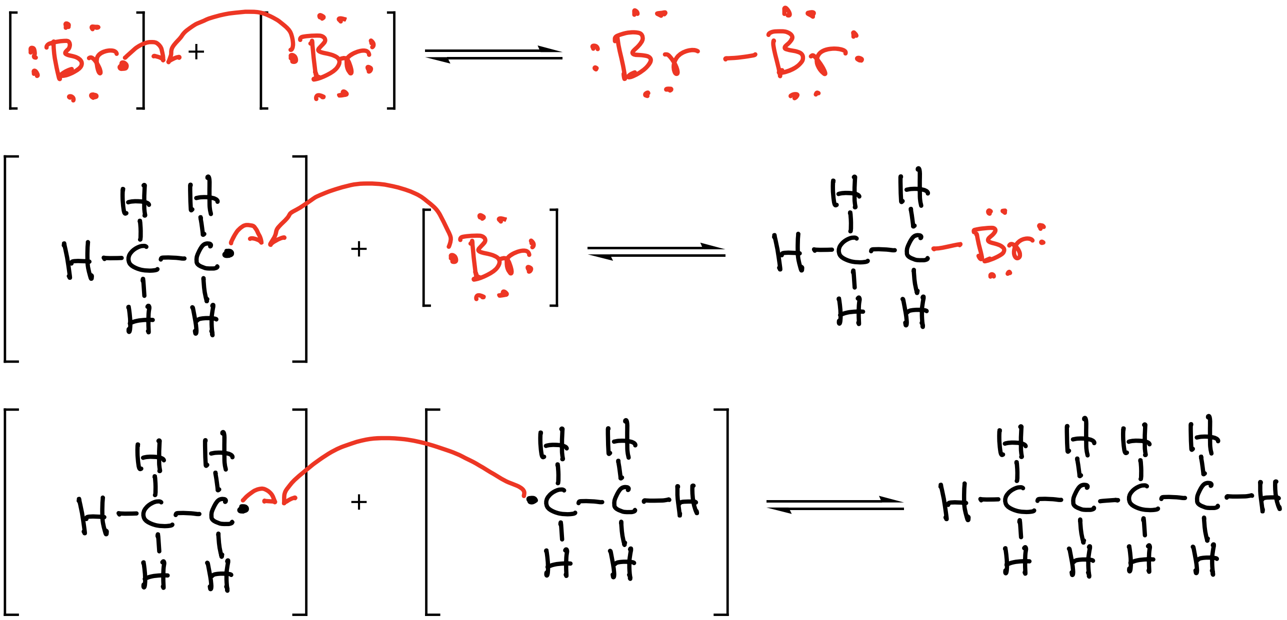
Propagation



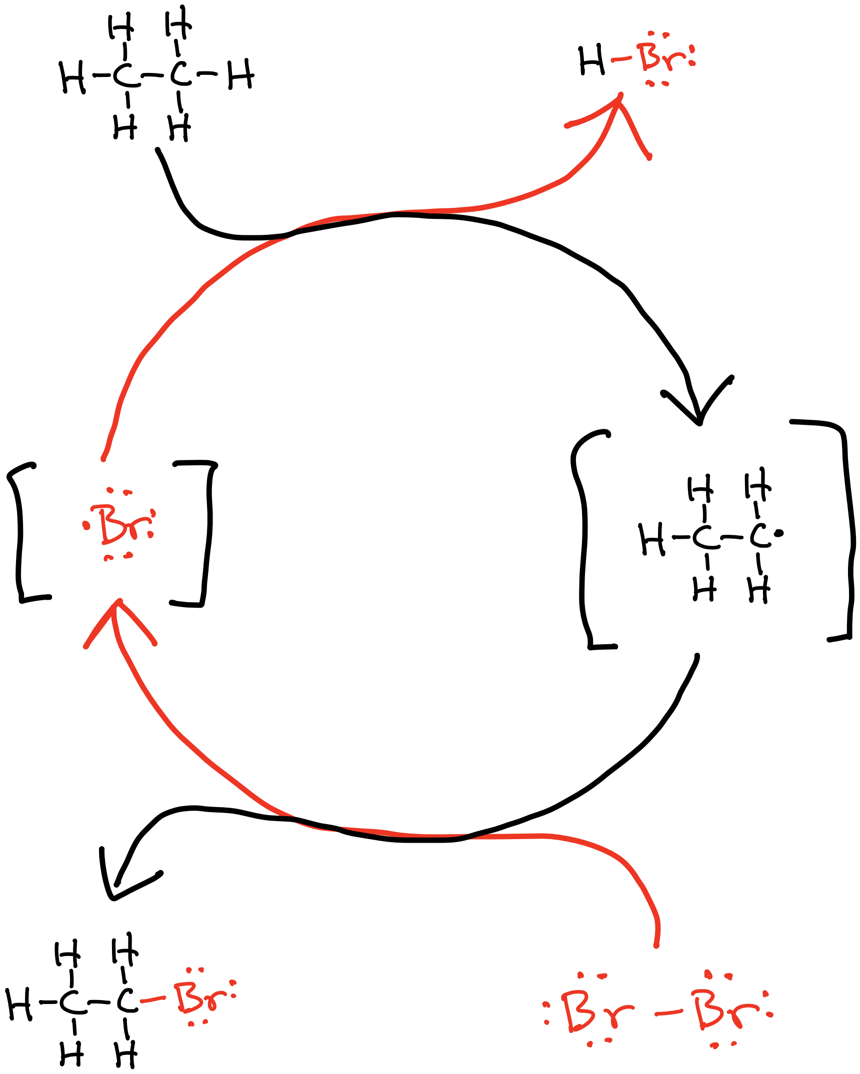


This process keeps going and going and going....

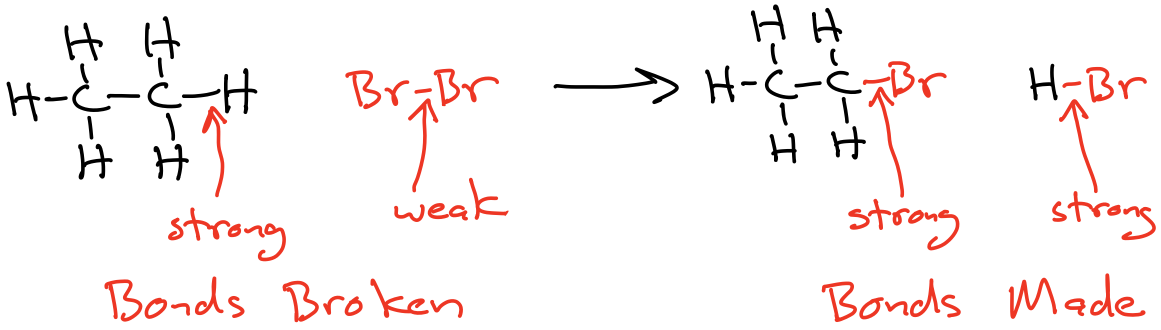
Termination



Propagation Process Diagram



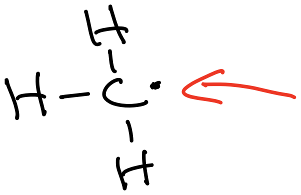
Motive for overall process



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

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

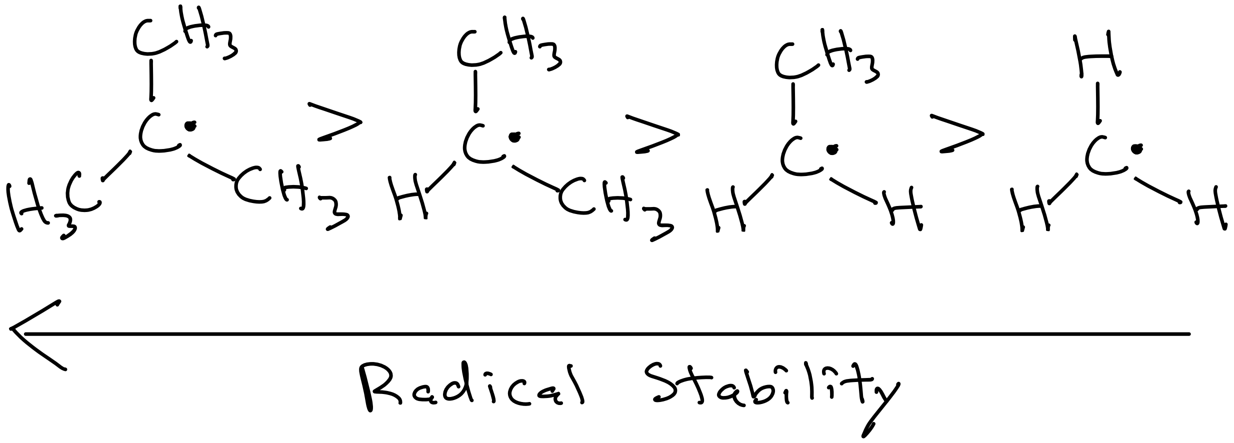
Radical → species with an unpaired electron → very reactive → we only see these as a reaction intermediate



Neutral (no charge!)

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

- → sp^2 hybridized with the unpaired electron in the 2p orbital
- → Alkyl groups stabilize radicals through hyperconjugation



<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. 8/28/24

You will learn the secret structural reason proteins, the most important molecular machines in our bodies, can support the chemistry of life. 9/11/24

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

You will learn how toothpaste works. 10/7/24

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. 10/30/24

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. 10/9/24

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. 10/30/24

You will learn reactions that can make antifreeze from vodka.

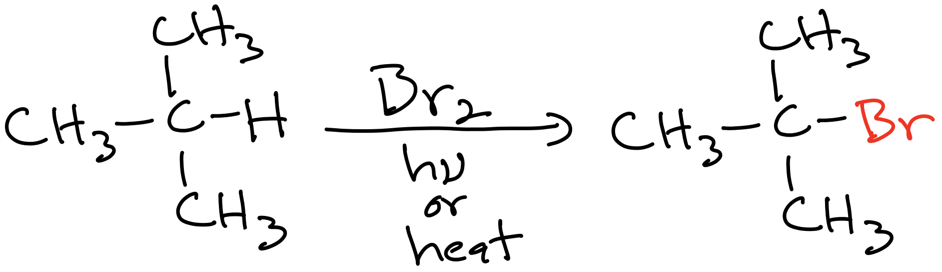
You will learn a reaction that can make nail polish remover from rubbing alcohol.

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.

☆ ⟹ 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

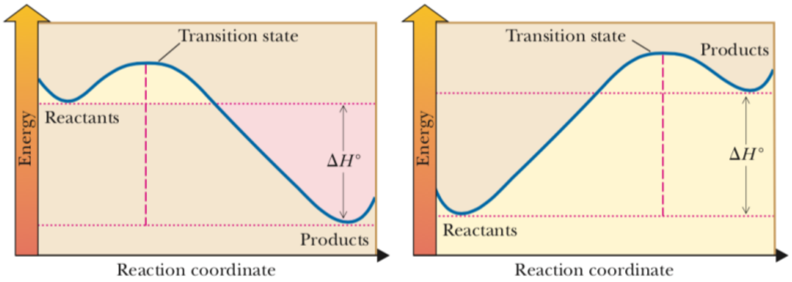
<u>Reason</u> ⟹ More stable radicals form more easily



$$CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-H \xrightarrow[h\nu \text{ or heat}]{Br_2} CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-Br$$

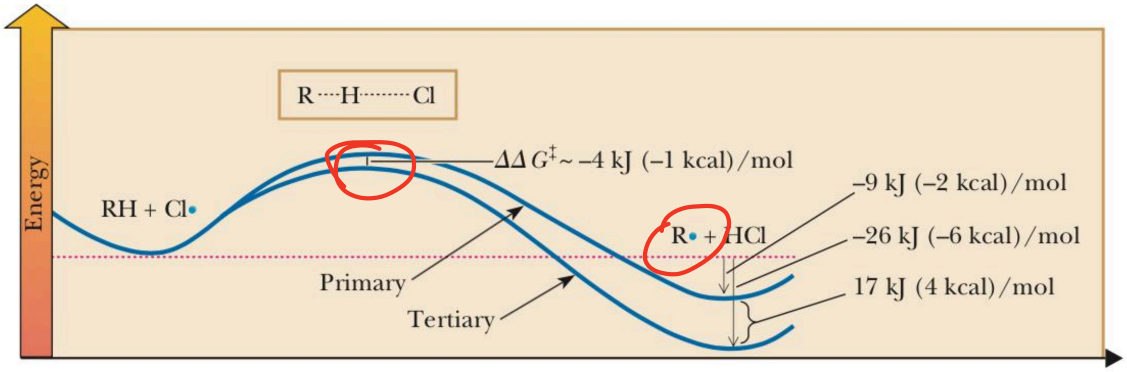
Br_2 is more selective than Cl_2 so always use Br_2

Hammond's Postulate

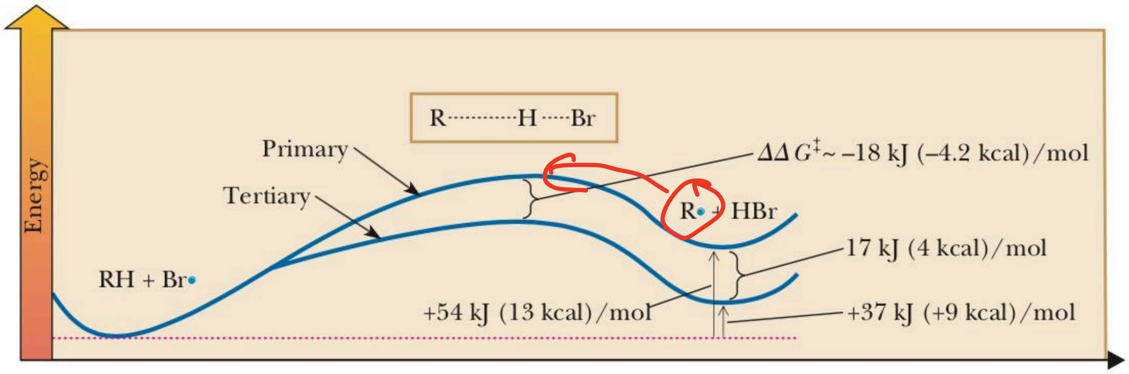


(a) Highly exothermic reaction **(b)** Highly endothermic reaction

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.



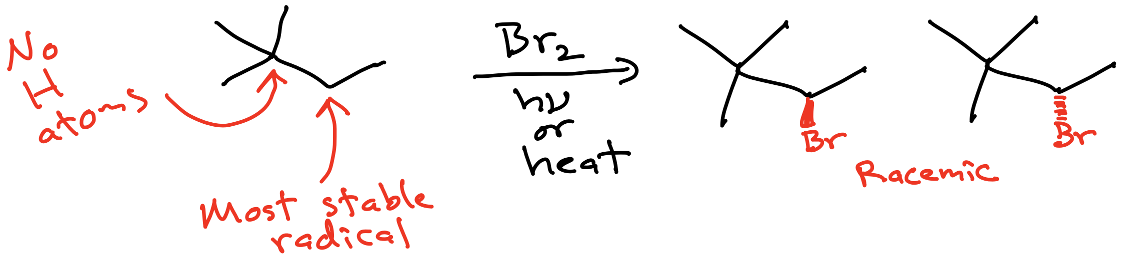
(a) Chlorination

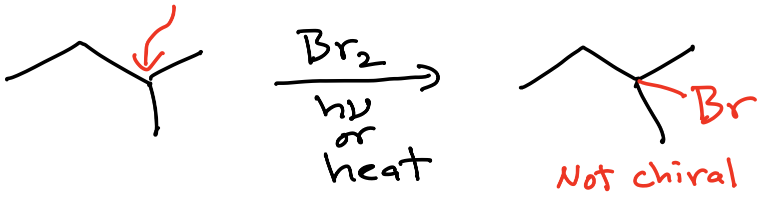


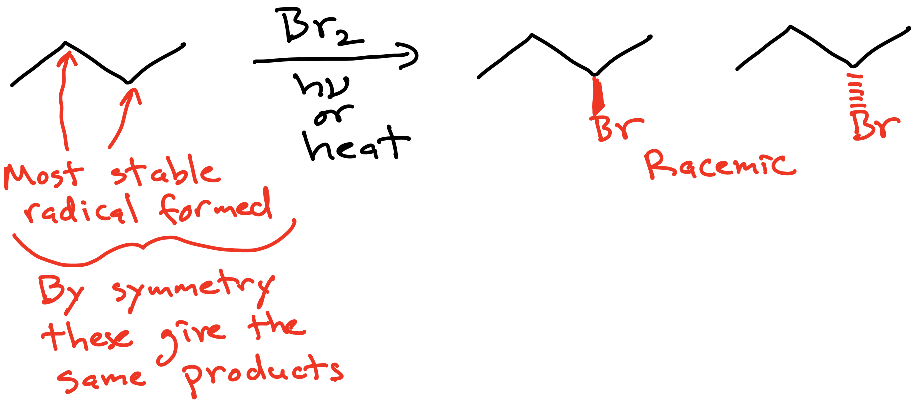
(b) Bromination

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


No H atoms
Br2
hν or heat
Br
Br
Racemic
Most stable radical


Br2
hν or heat
Br
Not chiral


Br2
hν or heat
Br
Br
Racemic
Most stable radical formed
By symmetry these give the same products

Allylic Halogenation

2 New Ideas

A)

Allylic Carbocation

Allylic Radicals

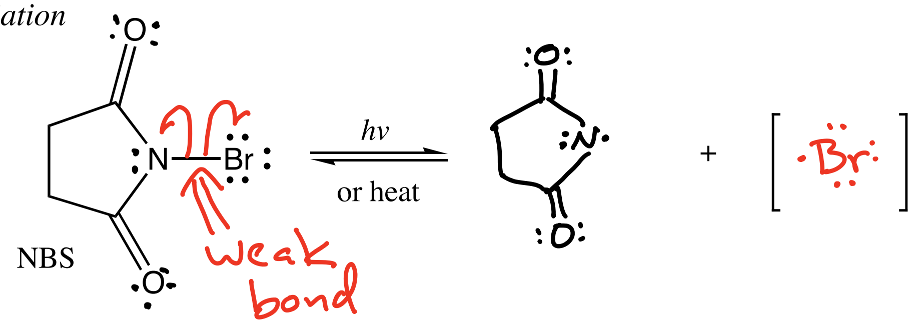
Resonance
delocalization
stabilized -
π-way

⟹ Radicals easily form on the carbons adjacent to a pi bond (C=C)

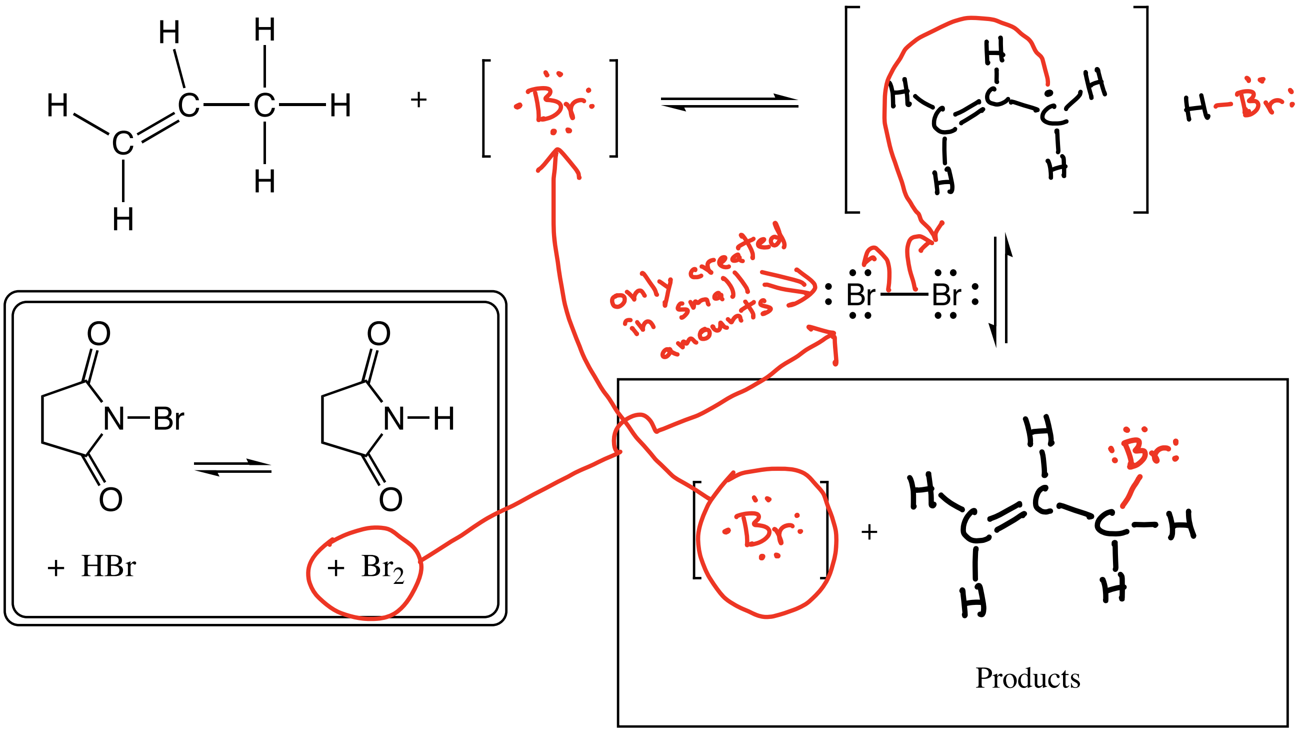
B) When given a choice in allylic halogenation reactions you always make the most stable alkene product

Allylic Halogenation

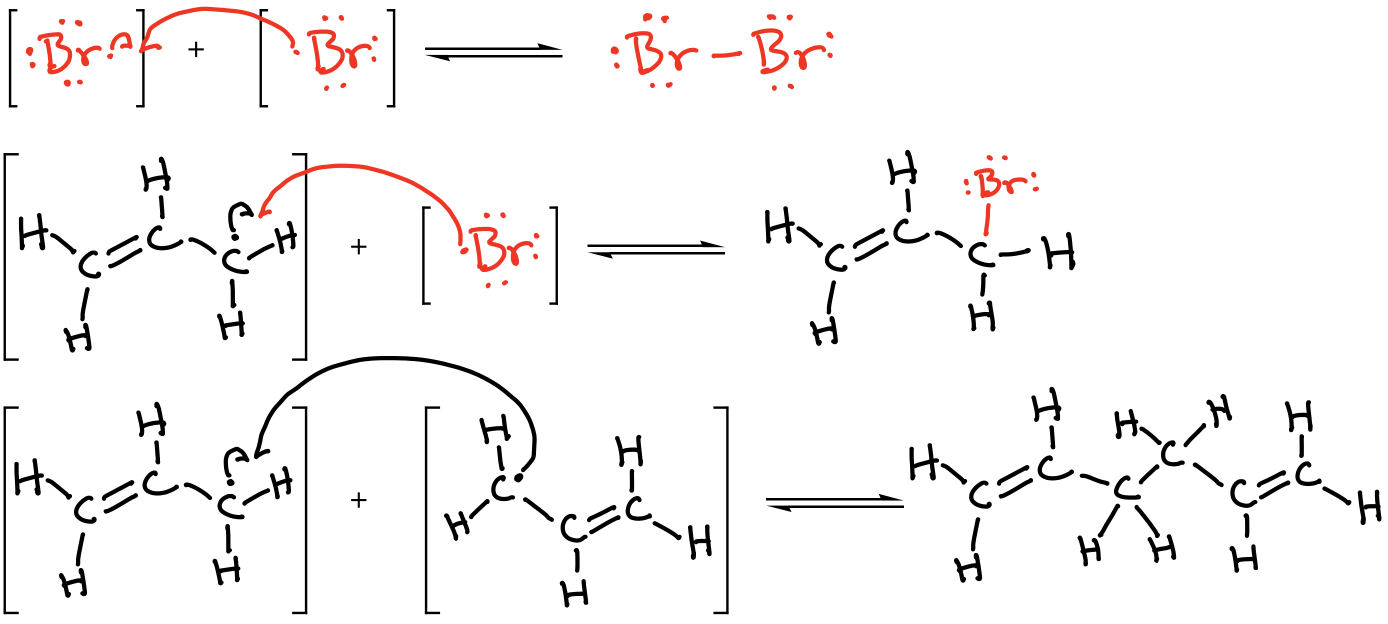
Initiation



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.

When analyzing allylic halogenation reactions (NBS and hν)

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 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.**