

# Chapter 10: Alkyl Halides Part 2: Radical Reactions

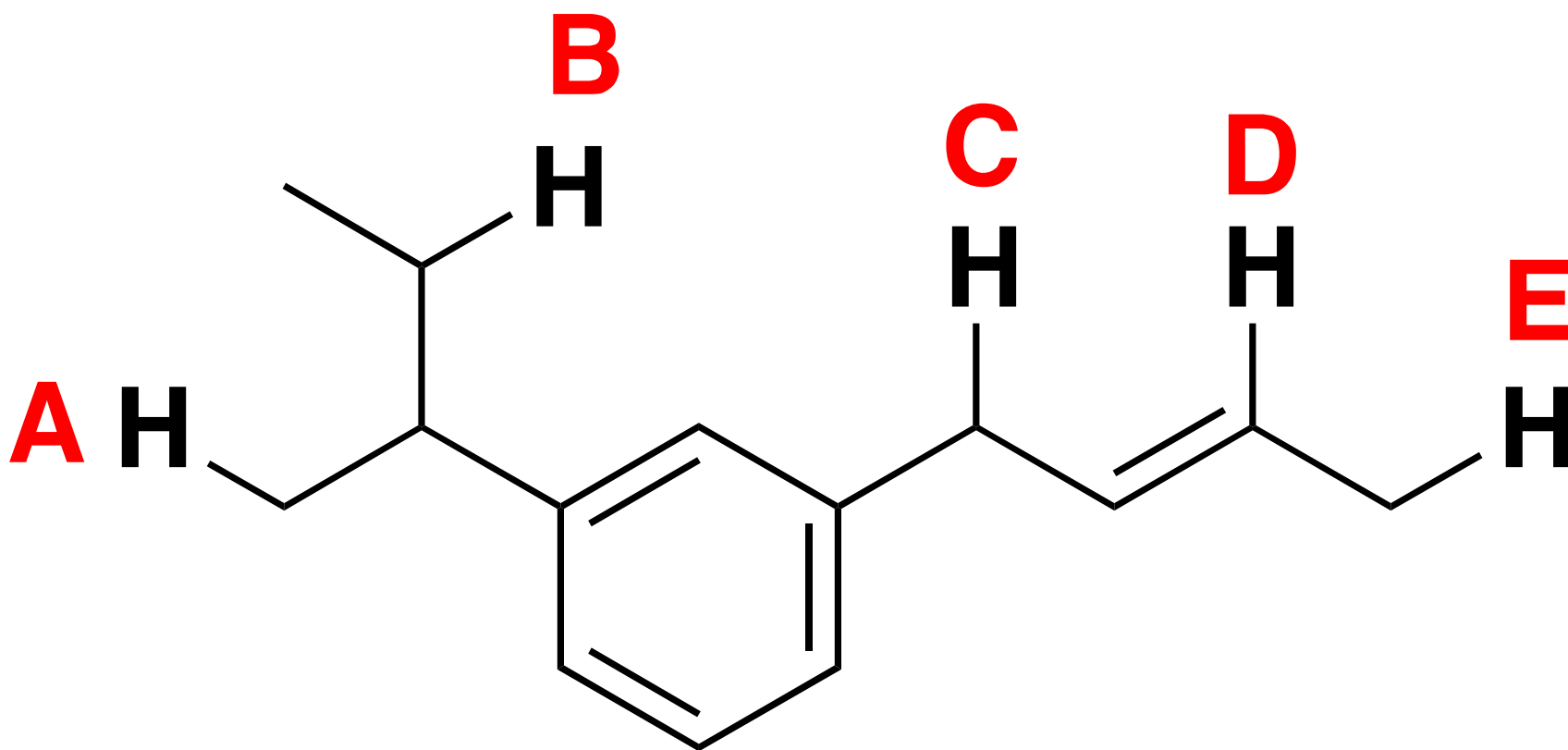
Today and Friday – 10.5-10.7, 10.10,10.11,  
10.13, and 10.9

We will not cover 10.8 or 10.12 in class, but  
they are interesting applications.

Rank the indicated carbon-hydrogen bonds from the STRONGEST to the WEAKEST.

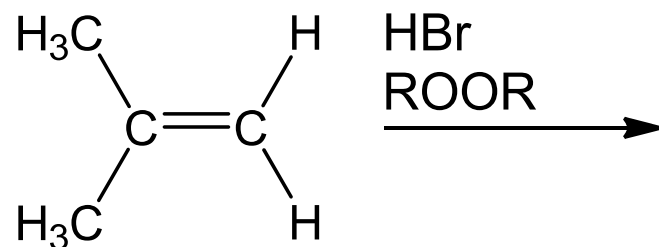
RESONANCE

Makes C and E easier to remove

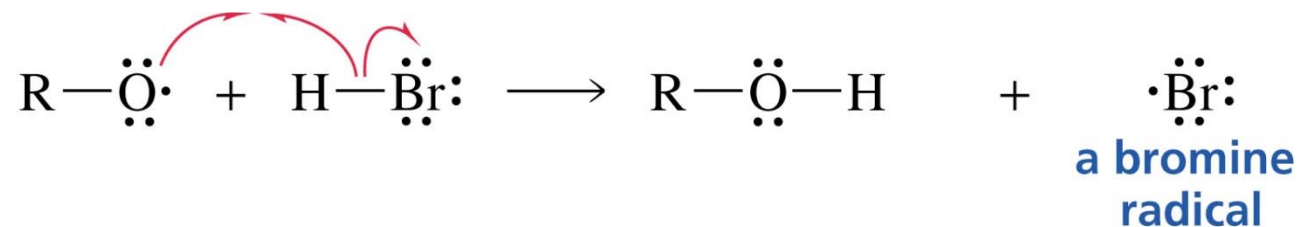
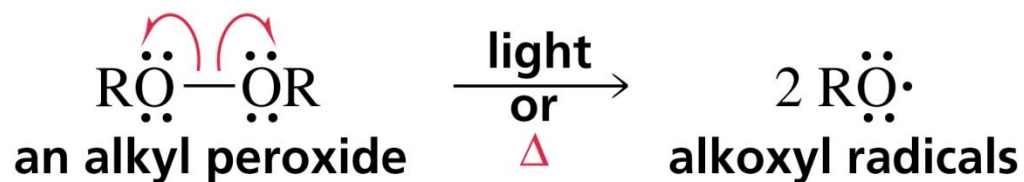


Answer: D, A, B, E, C.

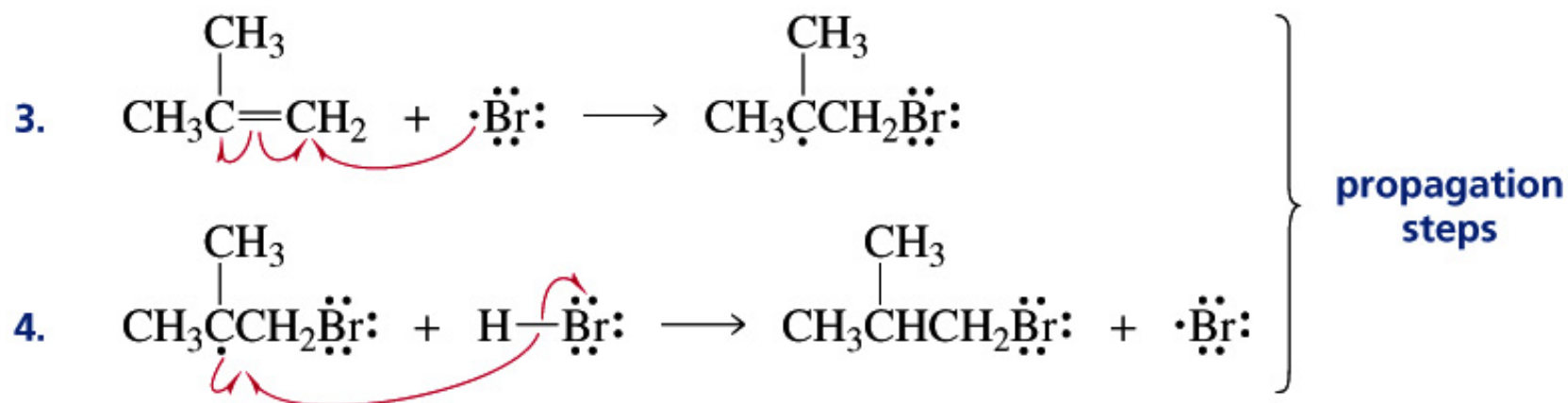
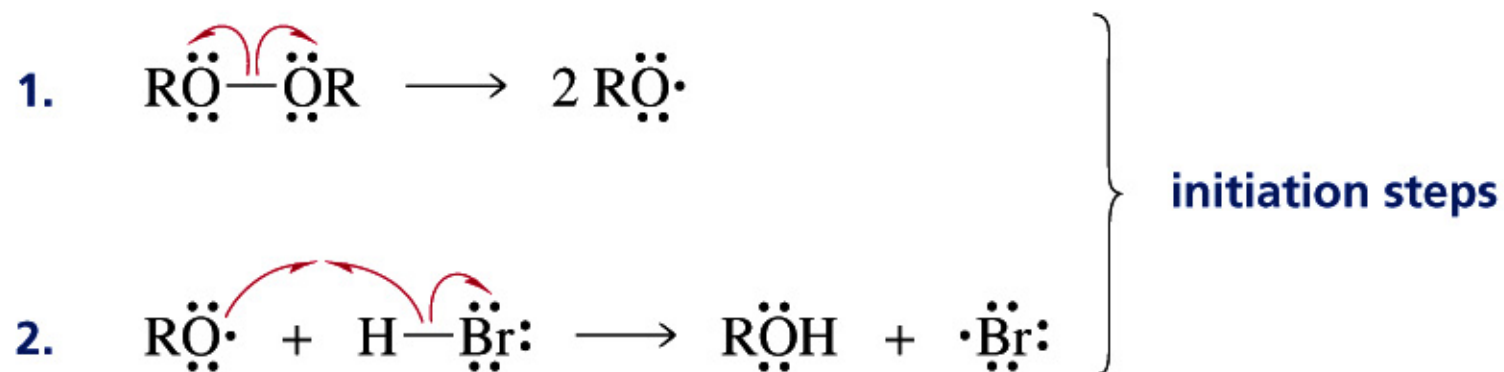
# Radical Reactions



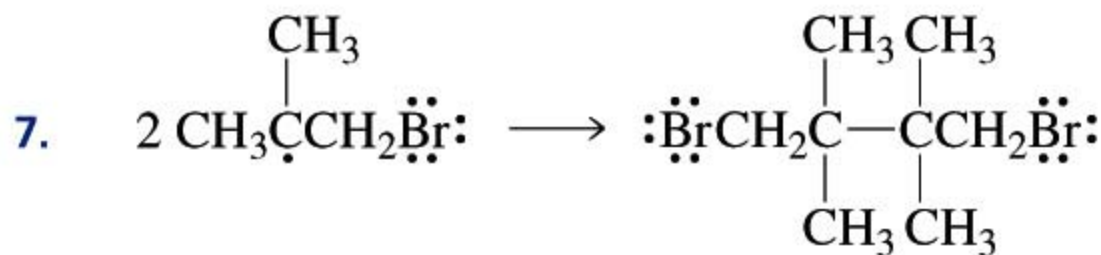
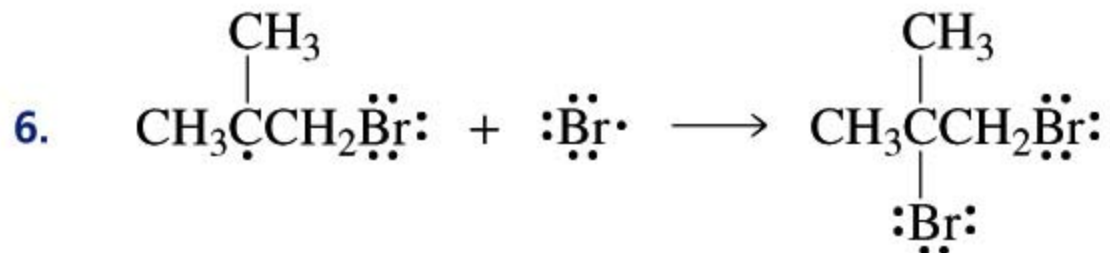
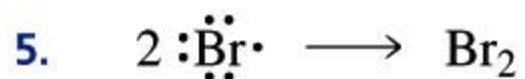
Free radicals form when bonds break HOMOLYTICALLY



# Addition of Radicals to Alkene



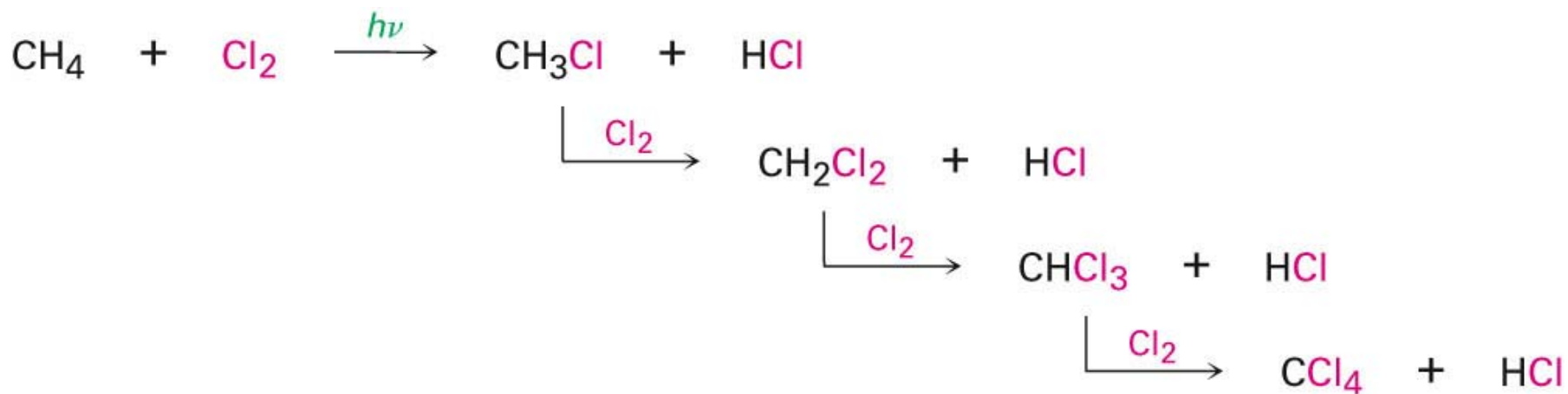
# Addition of Radicals to Alkene



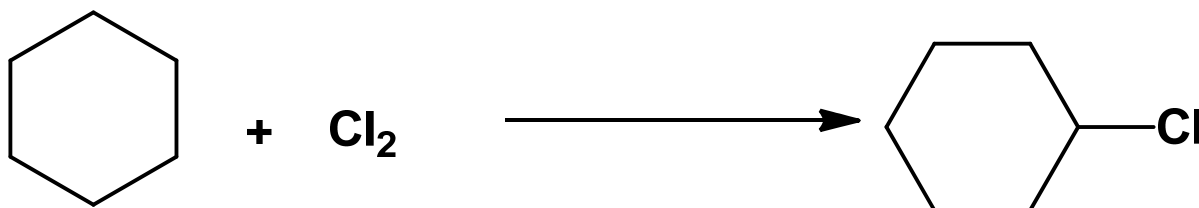
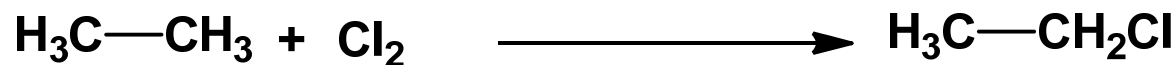
} **termination steps**

# Preparing Alkyl Halides from Alkanes: Radical Halogenation

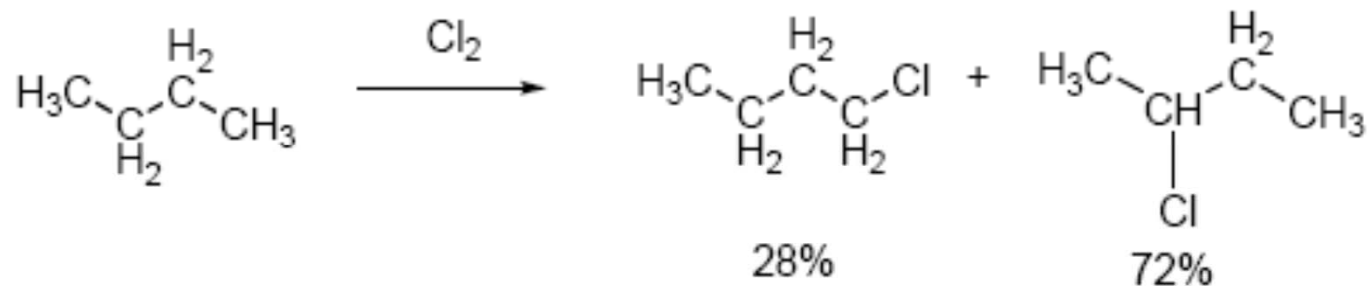
- ◆ Alkane + Cl<sub>2</sub> or Br<sub>2</sub>, heat or light replaces C-H with C-X but gives mixtures
  - Hard to control
  - free radical mechanism
- ◆ It is usually **not** a good idea to plan a synthesis that uses this method



# Chlorination of Higher Alkanes



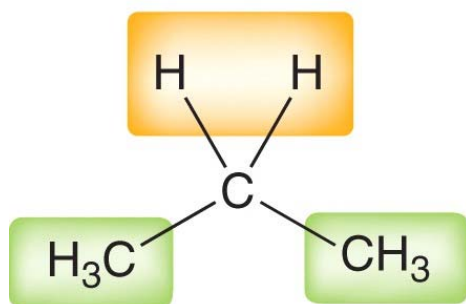
This becomes interesting when choices exist. We'll do butane as an example:



more stable by only 1 kJ/mole

# Halogenation Regioselectivity

- ◆ With substrates more complex than ethane, multiple monohalogenation products are possible

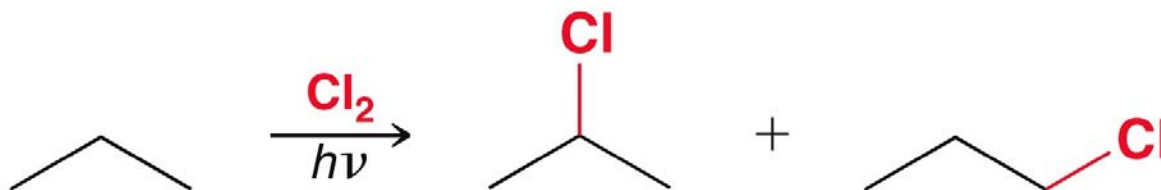


Two hydrogen atoms

Six hydrogen atoms

Two monohalogenation products are possible for propane

- ◆ Chlorine is indiscriminant; significant amount of each product is formed



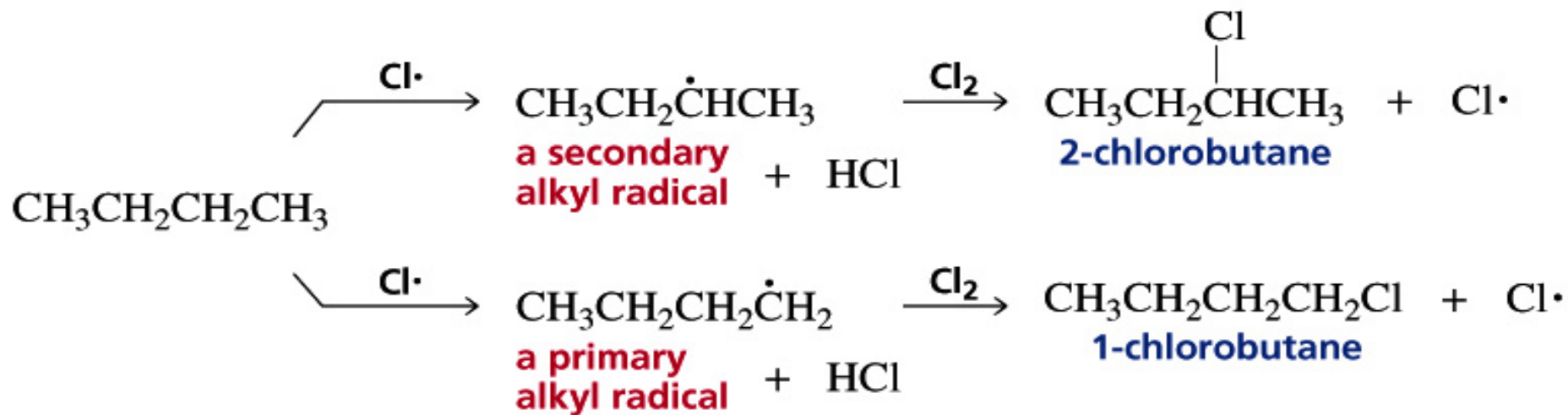
- ◆ Since  $2^\circ$  radicals are more stable than  $1^\circ$ , the secondary halide is the major product



In determining the relative amounts of products obtained, both probability and reactivity should be considered

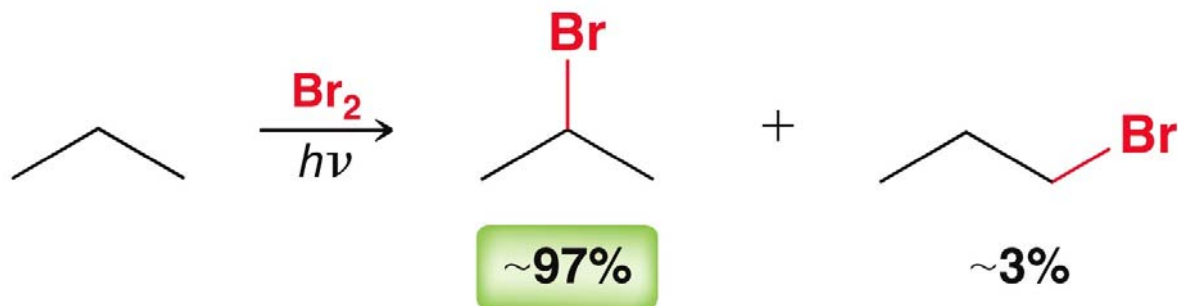
probability: the number of hydrogens that can be abstracted that will lead to the formation of the particular product

reactivity: the relative rate at which a particular hydrogen is abstracted



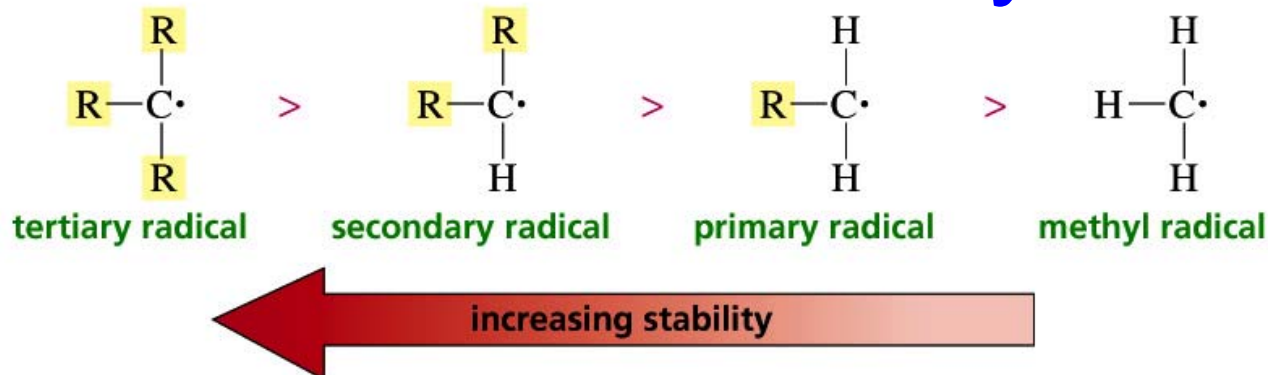
# Halogenation Regioselectivity

- ◆ **Bromination is much slower**, and so it is much more selective for the the more reactive 2° carbon:



- ◆ The fact **bromination is more regioselective** than chlorination can be explained by the Hammond Postulate

# Relative Stabilities of Alkyl Radicals



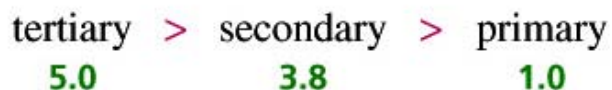
Groups that can push (donate) electrons toward the free radical will help to stabilize it.

relative rates of radical formation by a bromine radical at 125 °C



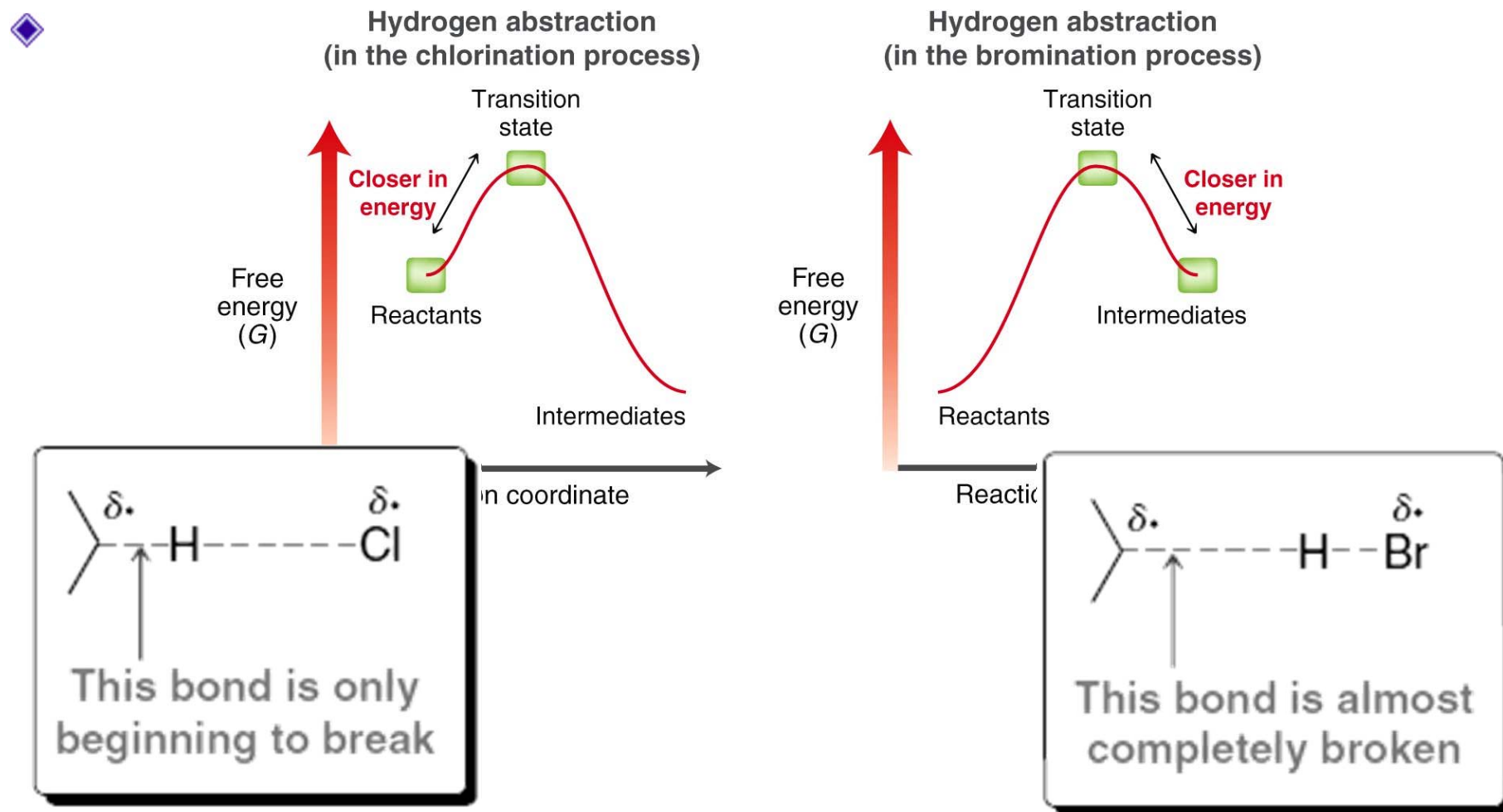
A bromine radical is less reactive and more selective than a chlorine radical

relative rates of alkyl radical formation by a chlorine radical at room temperature

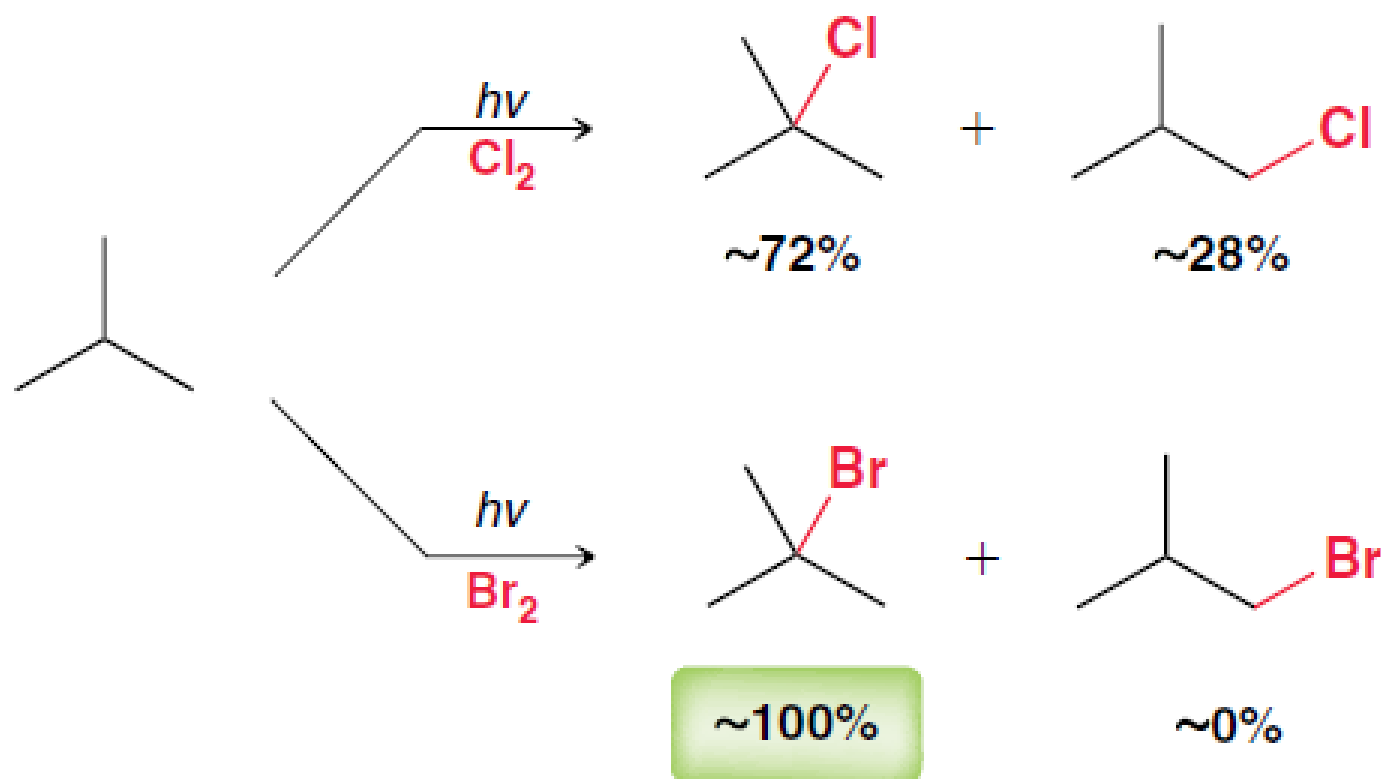


# Halogenation Regioselectivity

- ◆ Think about the H abstraction step, and consider the Hammond postulate—species on the energy diagram that are similar in energy are similar in structure.



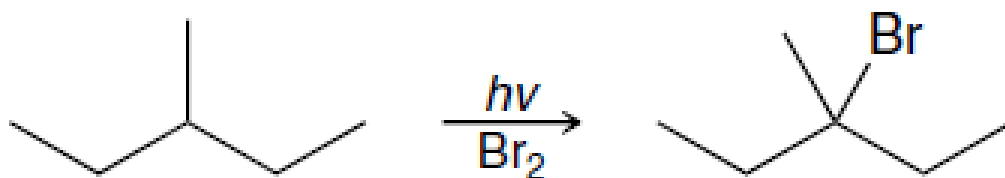
# Halogenation Regioselectivity



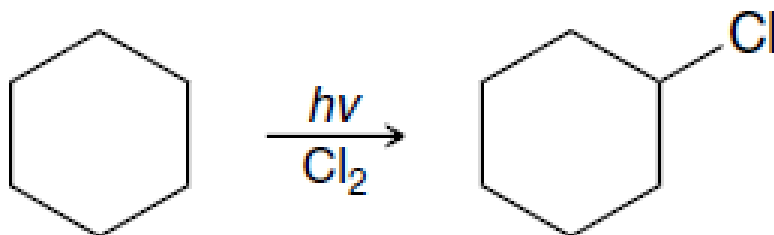
- ◆ Bromination at the  $3^\circ$  position happens 1600 times more often than at the  $1^\circ$  position

# Synthetic Utility of Halogenation

- Radical chlorination and bromination are both useful.
- Recall that bromination is more selective.



- ◆ Chlorination can be useful with highly symmetrical substrates.

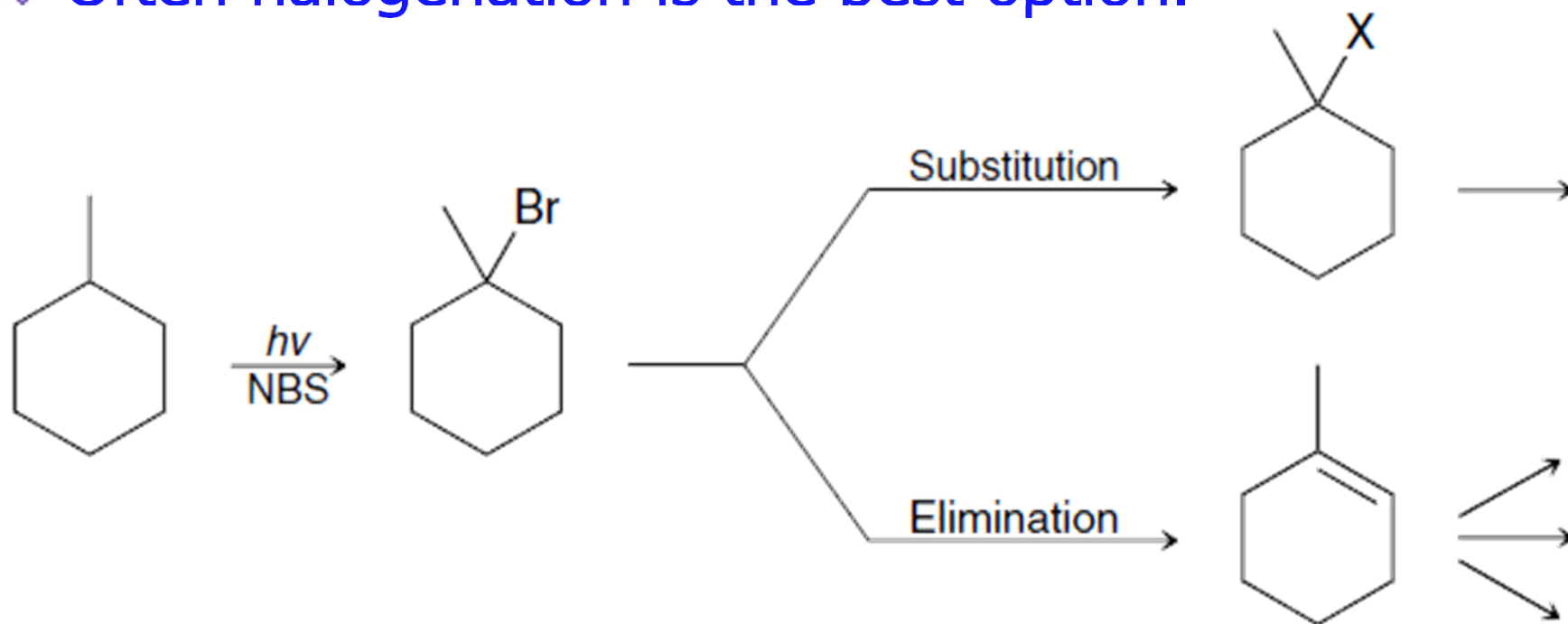


- ◆ The synthetic utility of halogenation is limited:

- Chlorination is difficult to control.
- Bromination requires a substrate with one site that is significantly more reactive than all others.

# Synthetic Utility of Halogenation

- ◆ Synthesizing a target molecule from an alkane is challenging because of its limited reactivity.
- ◆ Often halogenation is the best option.



# For Next Time....

Suggested Homework Problems Chapter 9

# 1,7,9,13,18,20,32-37, 41,44,52,57

Suggested Homework Problems Chapter 10

# 1, 2, 12, 16, 23,24, 33, 42

Next Up Chapter 12 on Monday!