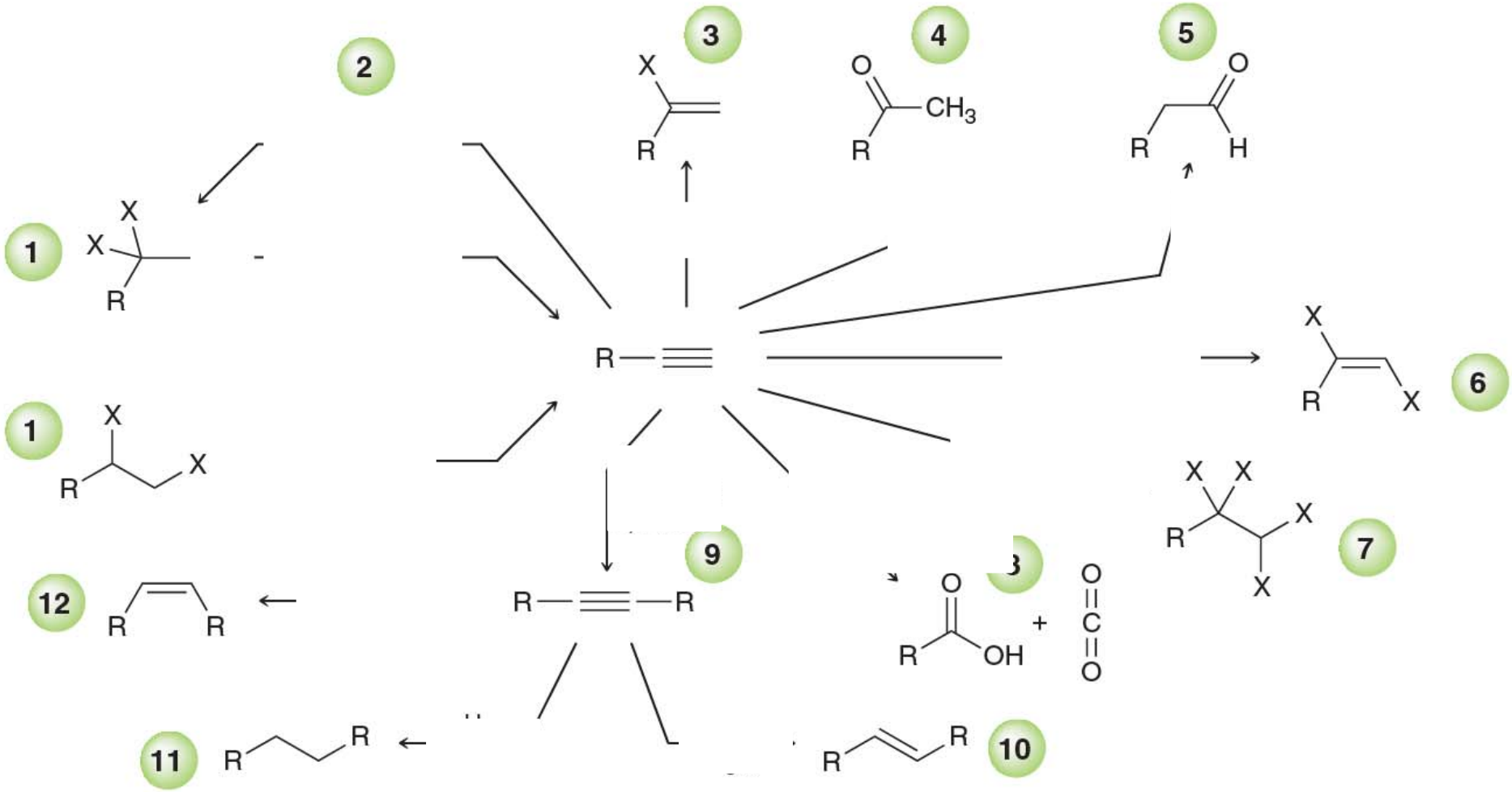
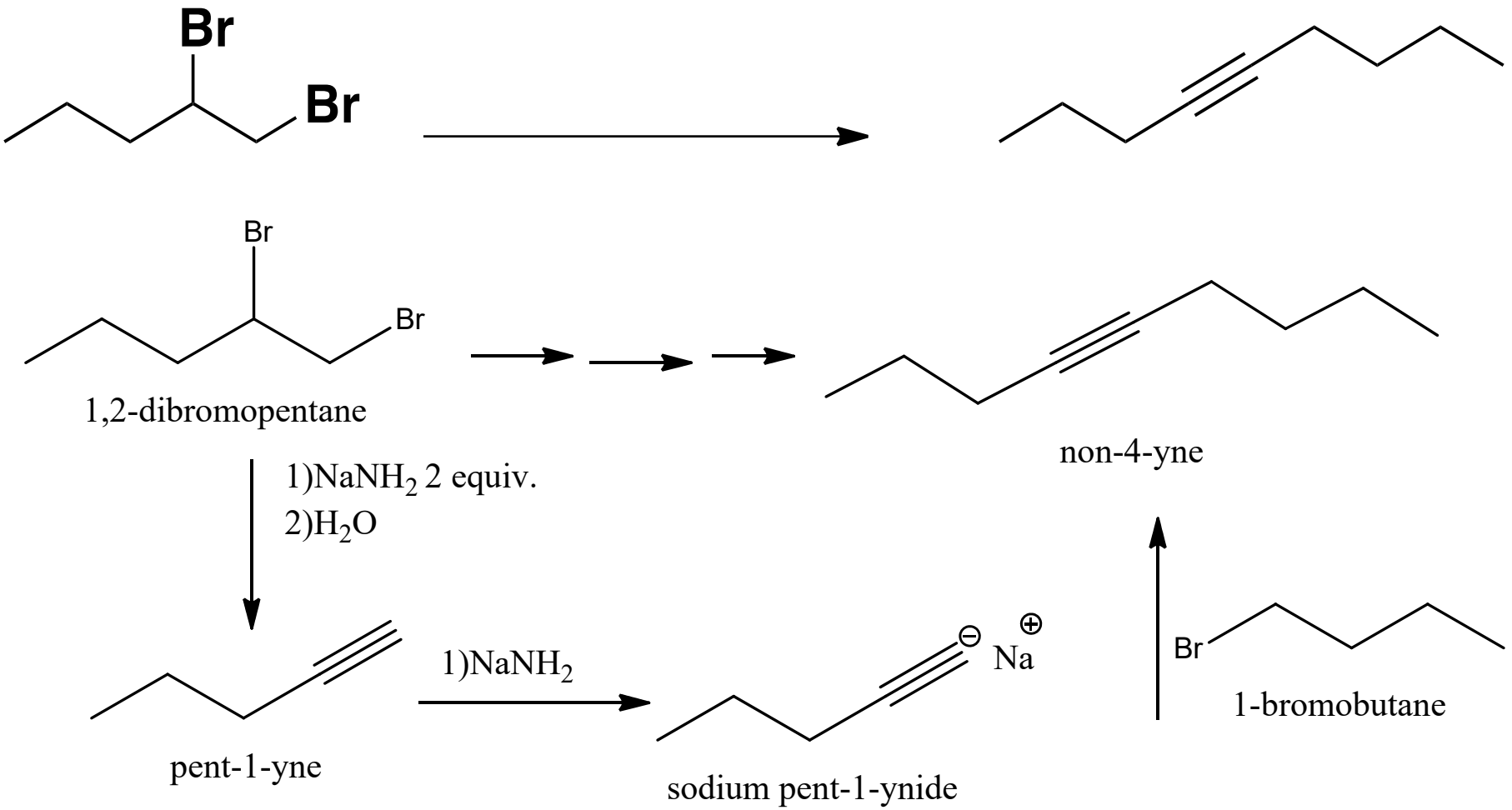
Chapter 10: Alkyl Halides Part 1: Preparing Alkyl Halides

Today – Chapter 10(10.1-10.4)

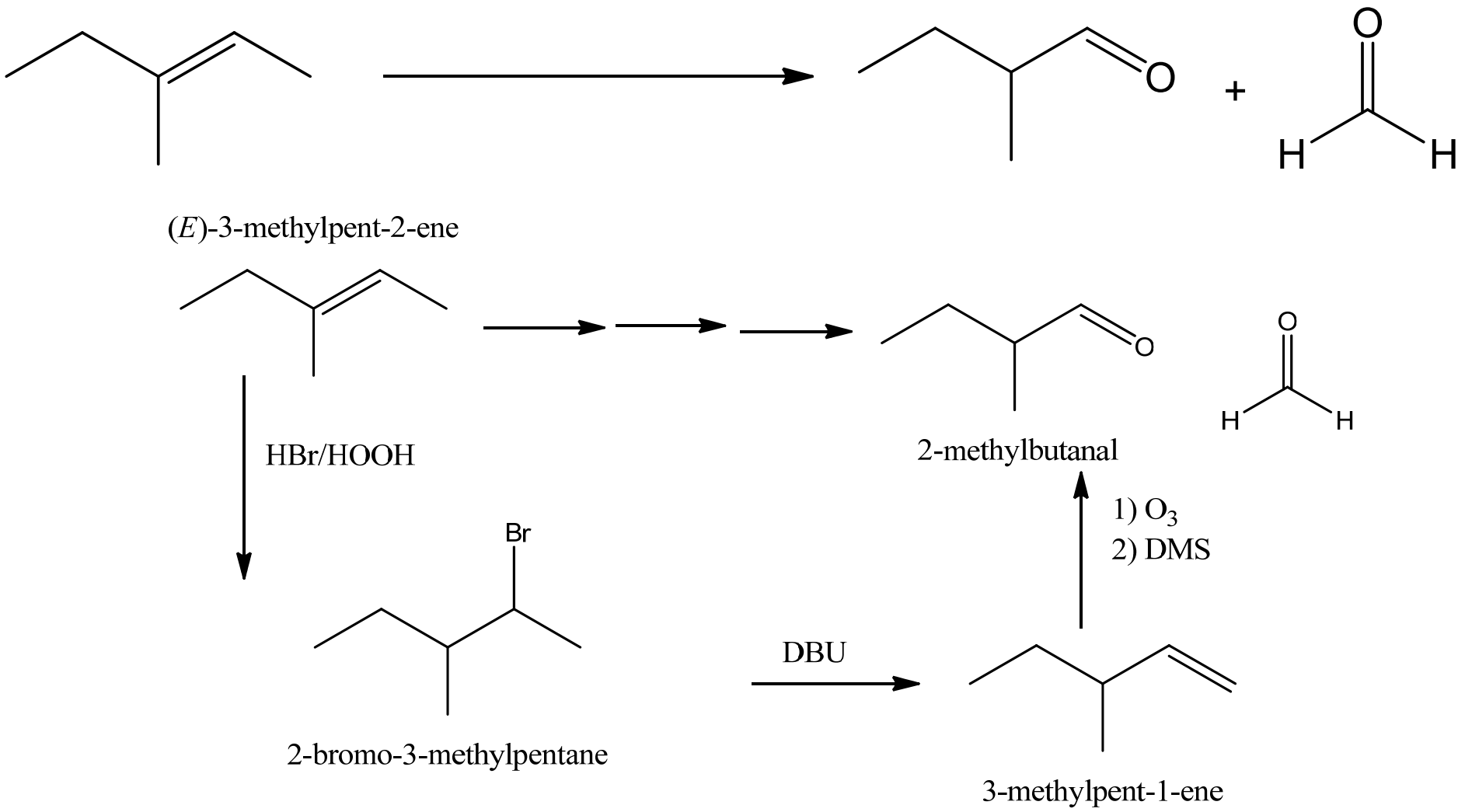
- **Making Aklyl Halides (Review)**
- **Radicals**
- **Patterns in Radical Mechanisms**
- **Anti-Markovnikov Hydrohalogenation**
- **Radical halogenation**


1
X
X
R
1
X
R
X
2
3
X
R
4
O
CH3
R
5
O
R
H
6
X
R
X
7
X
X
R
X
X
8
O
R
OH
+
O=C=O
9
R
R
10
R
R
11
R
R
12
R
R

Designing a Synthesis



Designing a Synthesis

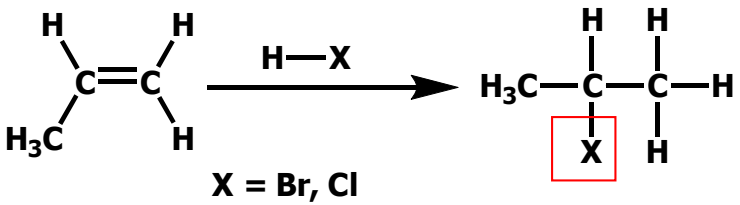


How do we Synthesize 1-Bromobutane?

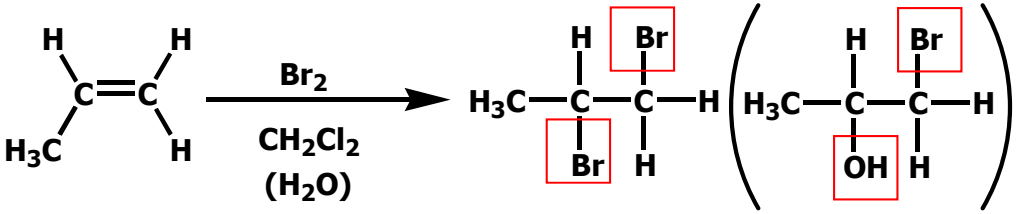
Markovnikov

Anti- Markovnikov?

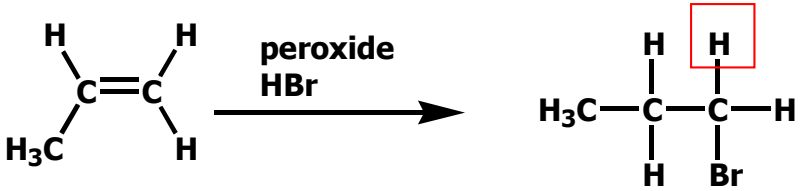
Preparing Alkyl Halides



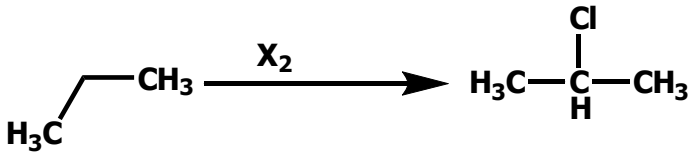
Hydrohalogenation



Bromination (Halogenation)



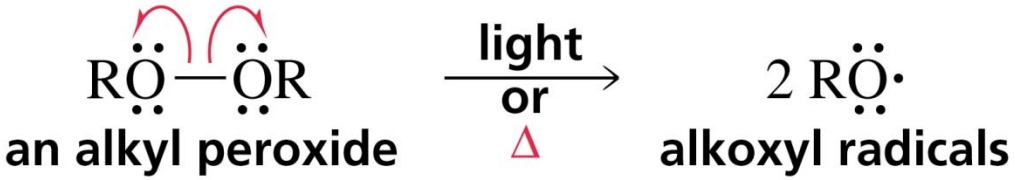
Radical Addition – to an alkene



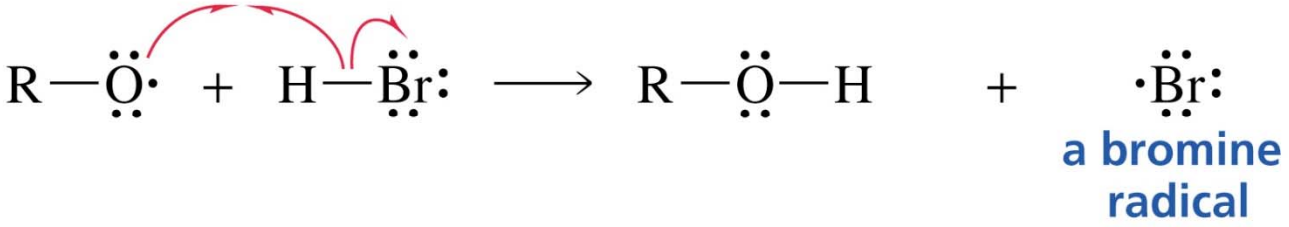
Radical Addition – to an alkane

Generation of Radicals

Free radicals form when bonds break HOMOLYTICALLY



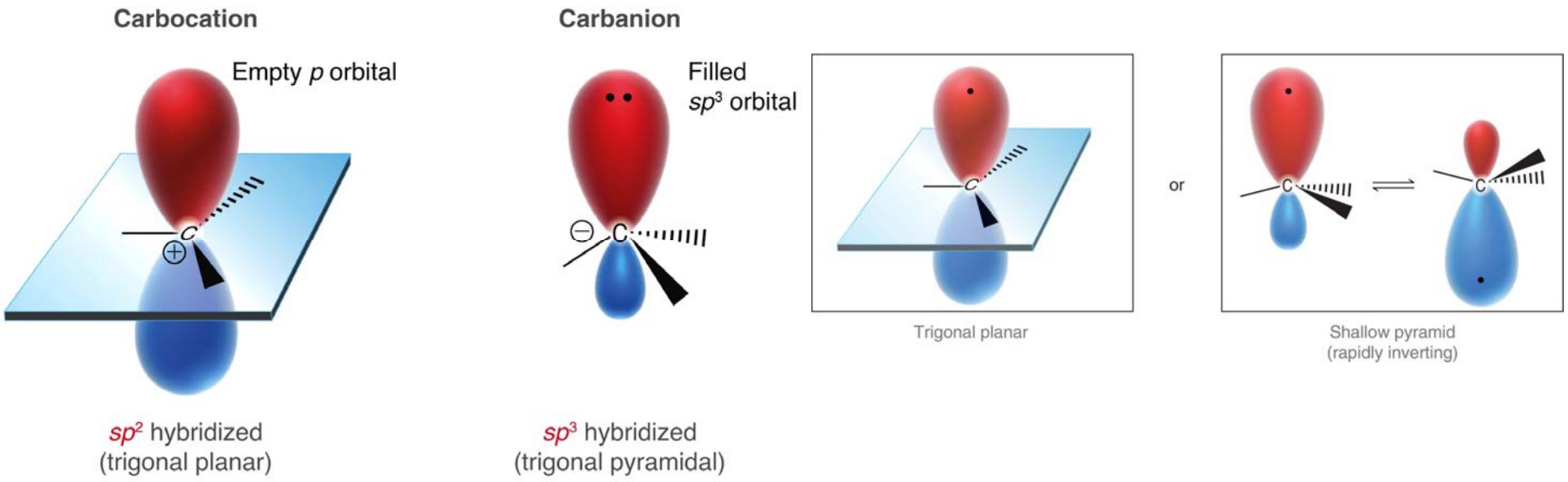
Note the single-barbed or fishhook arrow used to show the electron movement.



Free Radicals

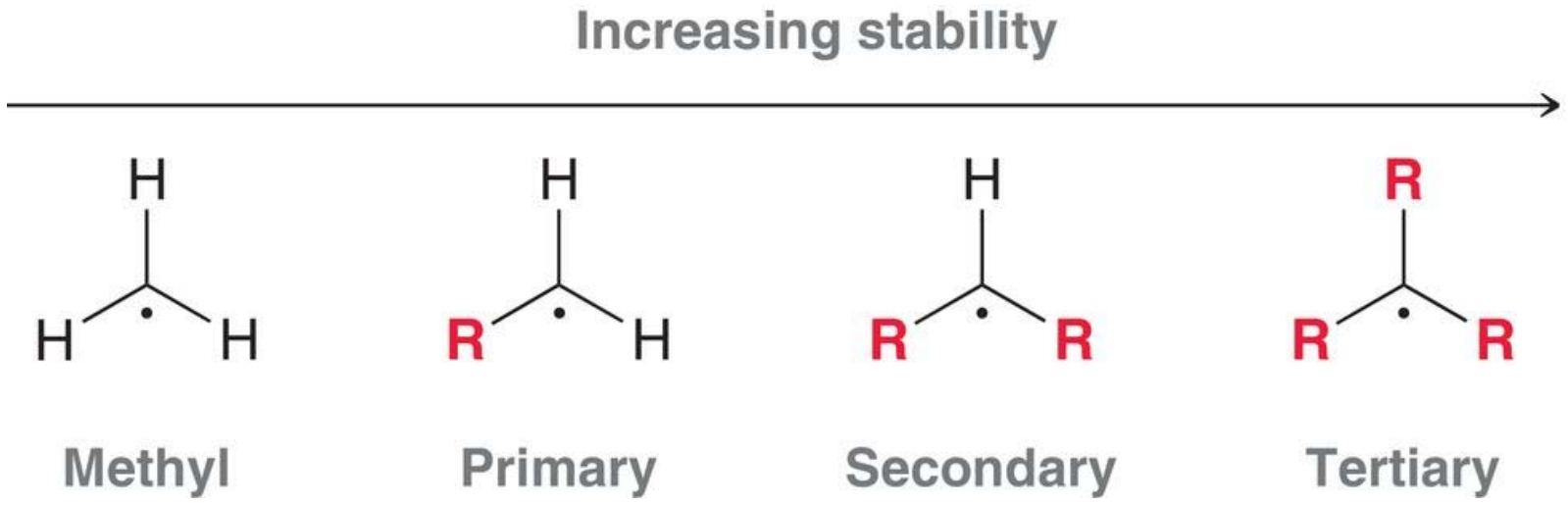
- Recall the orbital hybridization in carbocations and carbanions.

- Radicals appear to be trigonal planar (sp^2 hybridized) or shallow trigonal planar (sp^3 hybridized)



Free Radical Stability

- Radicals are neutral (**no formal charge**) but still electron deficient (**incomplete octet**)
- Radicals follow the same stability trend as carbocations, as they are both electron deficient species

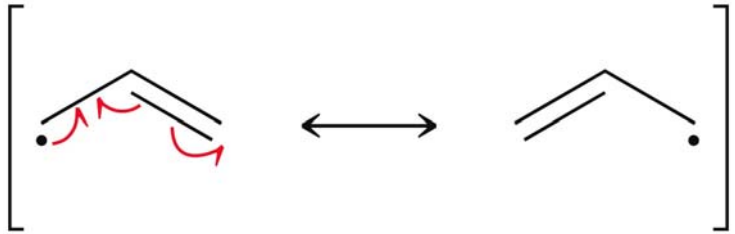


- The more stable the resulting radical(s), the weaker the bond

Free Radical Resonance

- Radicals, like carbocations, can be **stabilized by resonance delocalization.**

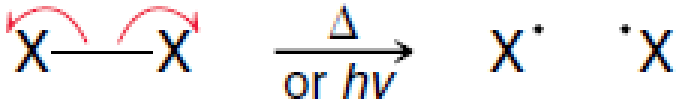
- Fishhook arrows are used to present possible resonance forms



- The more resonance delocalized a radical is, the more stable it is

Radical Electron Movement

1. Homolytic cleavage, initiated by light or heat:



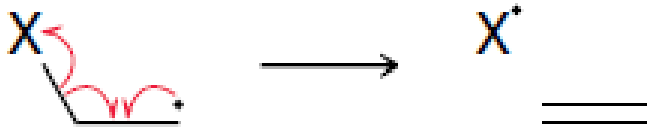
2. Addition to a pi bond:

3. Hydrogen abstraction (NOT the same as proton transfer):

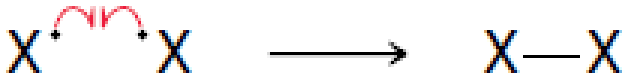
4. Halogen abstraction:

Radical Electron Movement

5. Elimination: the radical from the α carbon is pushed toward the β carbon to eliminate a group on the β carbon (reverse of addition to a pi bond):

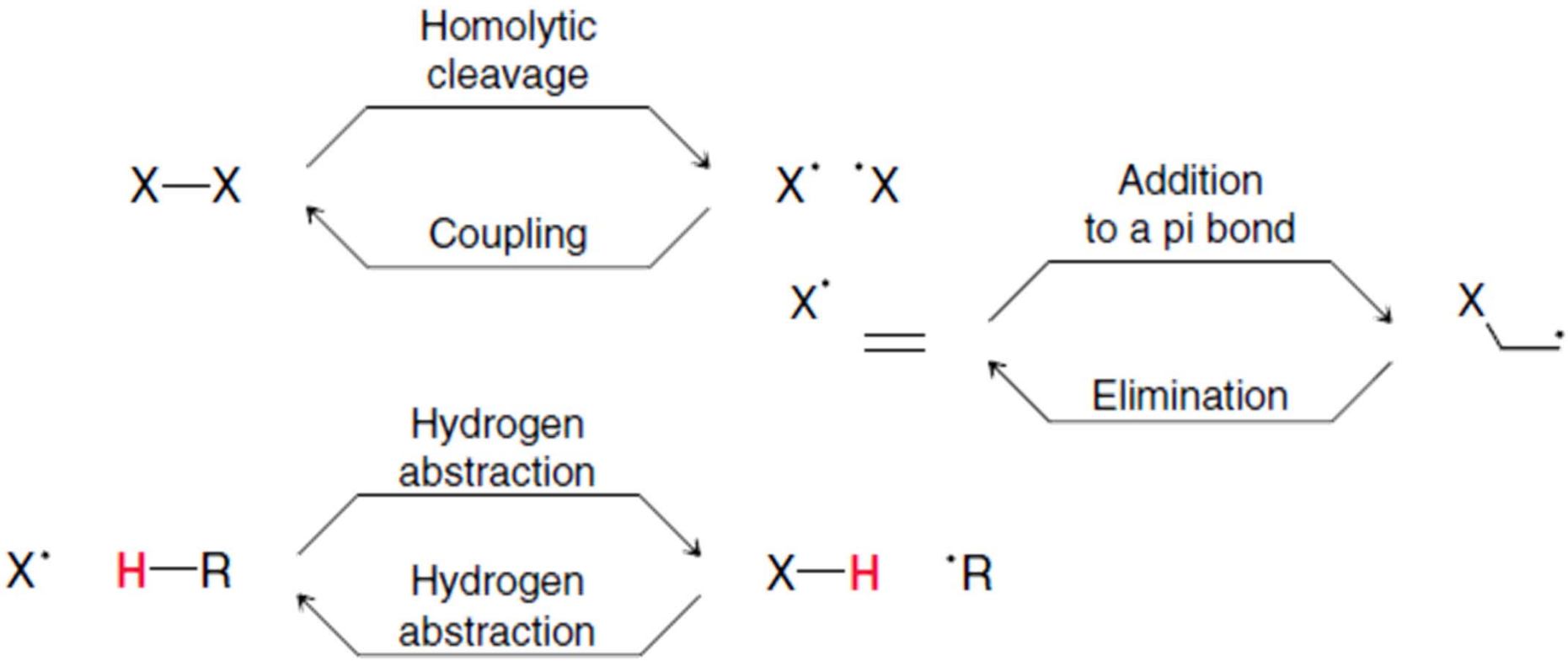


6. Coupling, the reverse of homolytic cleavage:



Radical Electron Movement

- Note the reversibility of radical processes:



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