

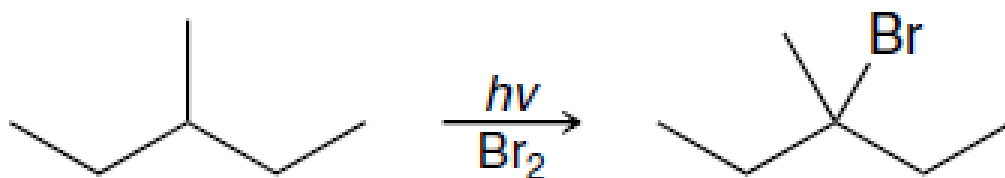
Chapter 10: Alkyl Halides Part 3: Radical Reactions

Today Finish up Chapter 10

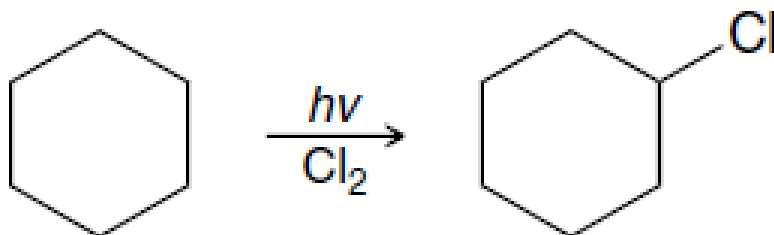
We will not cover 10.8 or 10.12.

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.

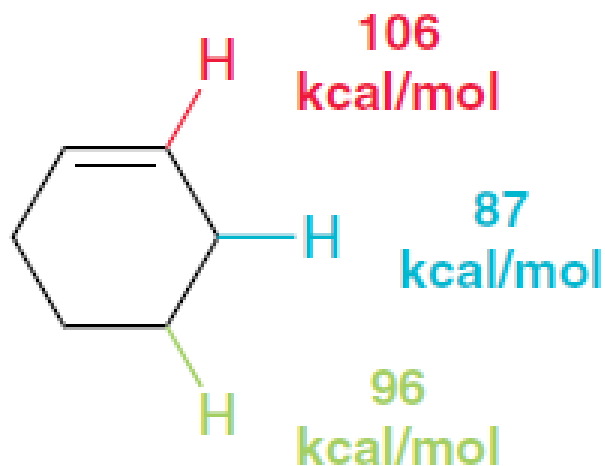


- ◆ The synthetic utility of halogenation is limited:

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

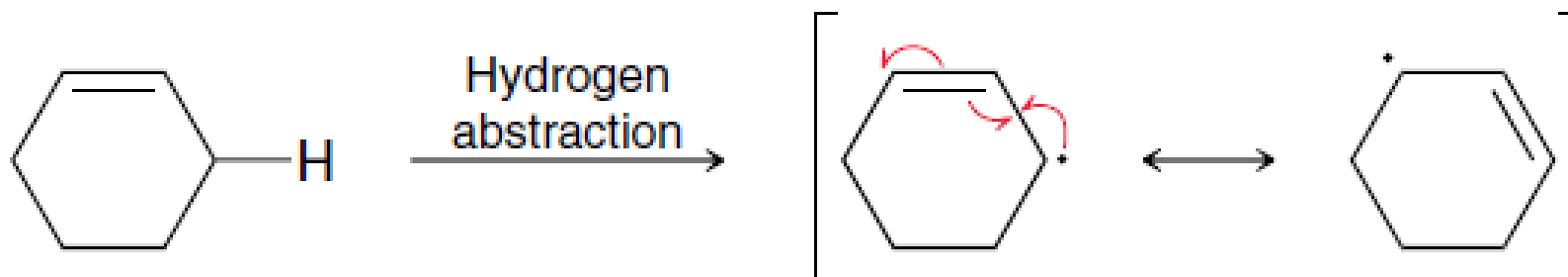
Allylic Halogenation

- ◆ When an C=C double bond is present, it affects the regioselectivity of the halogenation reaction.
- ◆ Given the bond dissociation energies below, which position of cyclohexene will be most reactive toward halogenation?

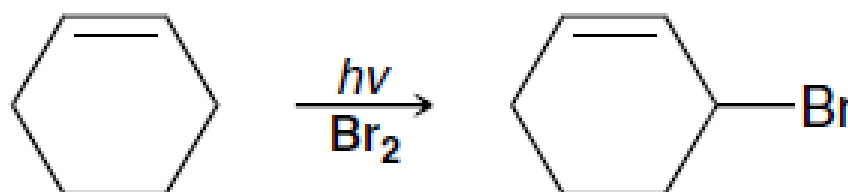


Allylic Halogenation

- ◆ When an allylic hydrogen is abstracted, it leaves behind an allylic free radical that is stabilized by resonance.



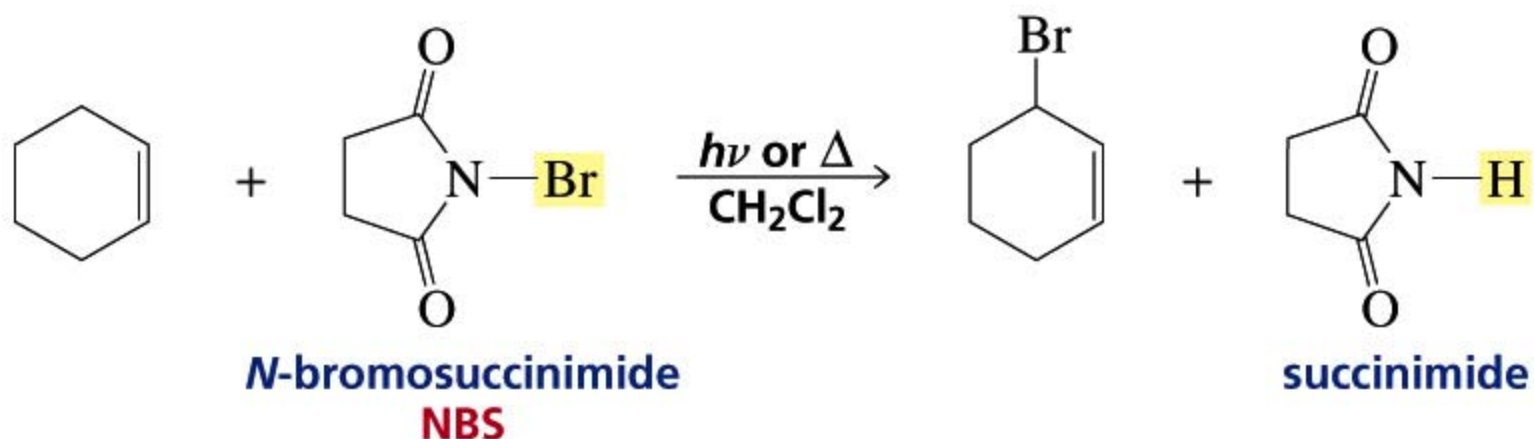
- ◆ Based on the high selectivity of bromination that we discussed, you might expect bromination to occur as shown:



- ◆ What other set of side-products is likely to form in this reaction?

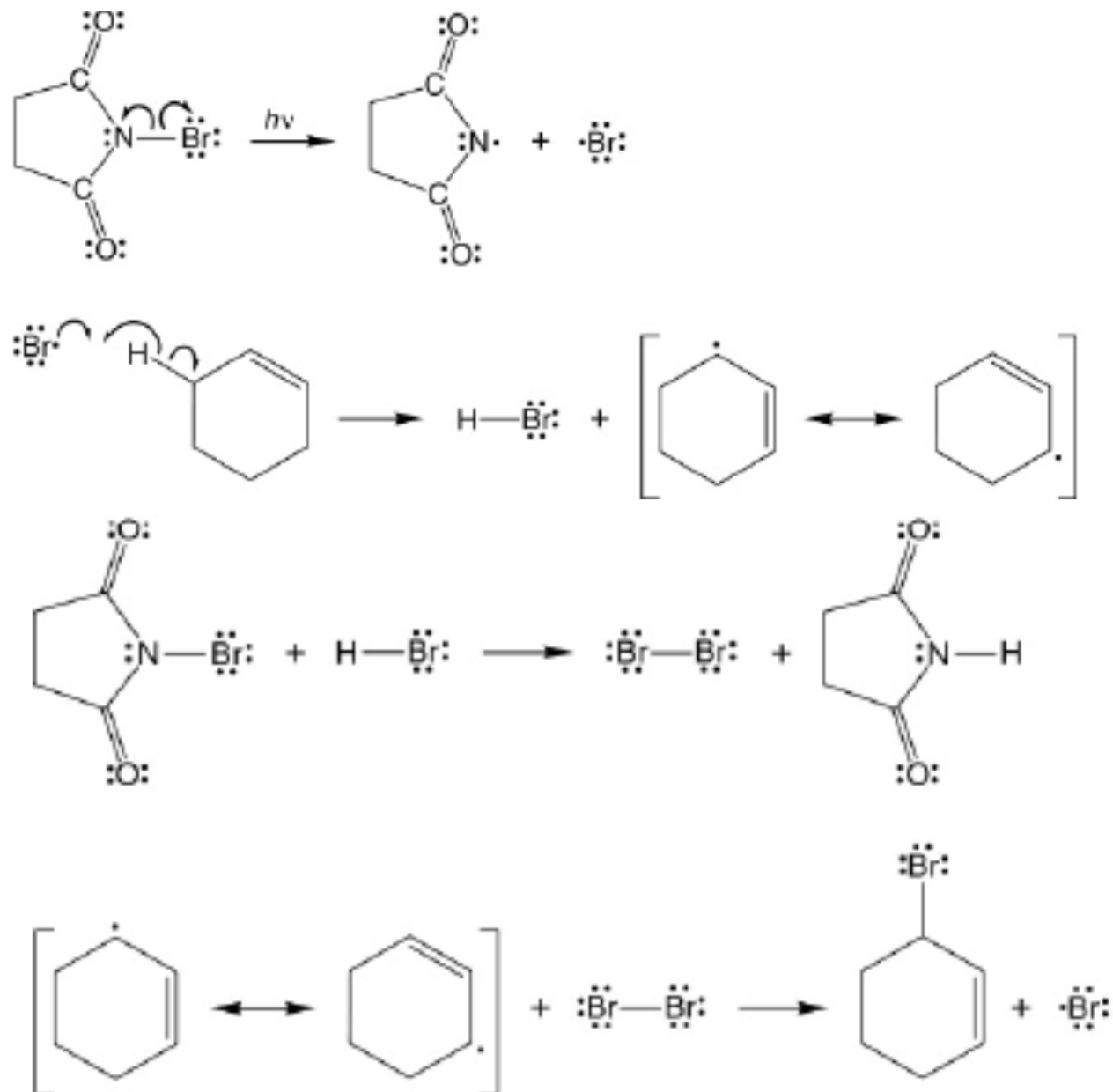
Allylic Halogenation with NBS

Because of the reactivity of allylic hydrogens, a milder brominating reagent can be used



- To avoid the competing halogen ADDITION reaction, NBS can be used to supply $\text{Br}\cdot$ radicals.
- N-bromosuccinimide (NBS) selectively brominates allylic positions
- Requires light for activation
- Can be a source of dilute bromine atoms

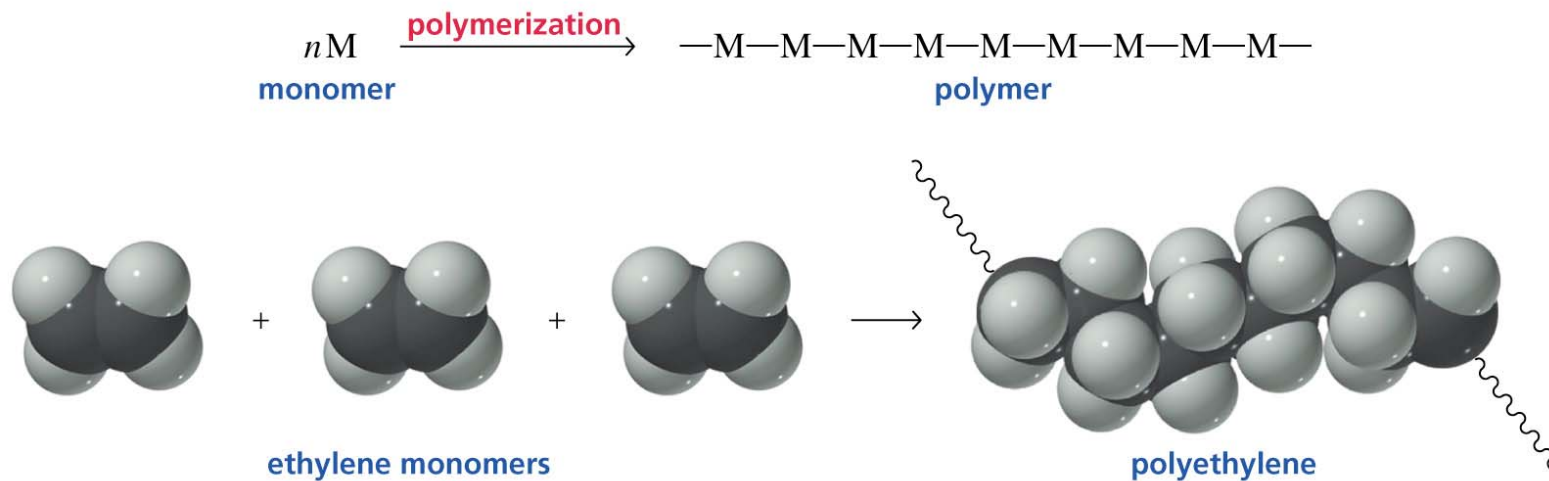
NBS mechanism:



Advantage: the low concentration of Br_2 and HBr present cannot be added to the double bond

Radical Polymerization

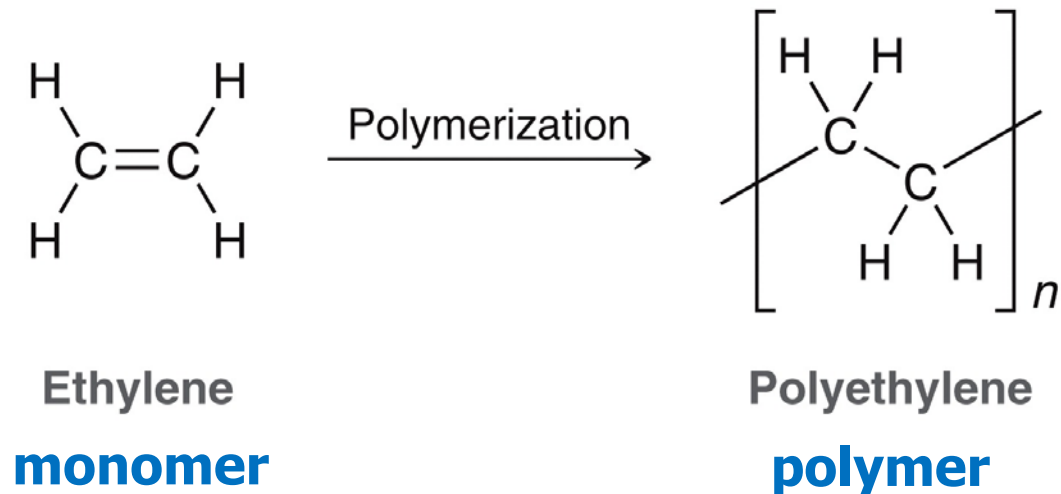
- ❖ Free radical conditions can also be used to form polymers.
- ❖ A polymer is a large molecule made by linking together repeating units of small molecules called monomers



- ◆ Radical polymerizations generally proceed through a chain reaction mechanism.

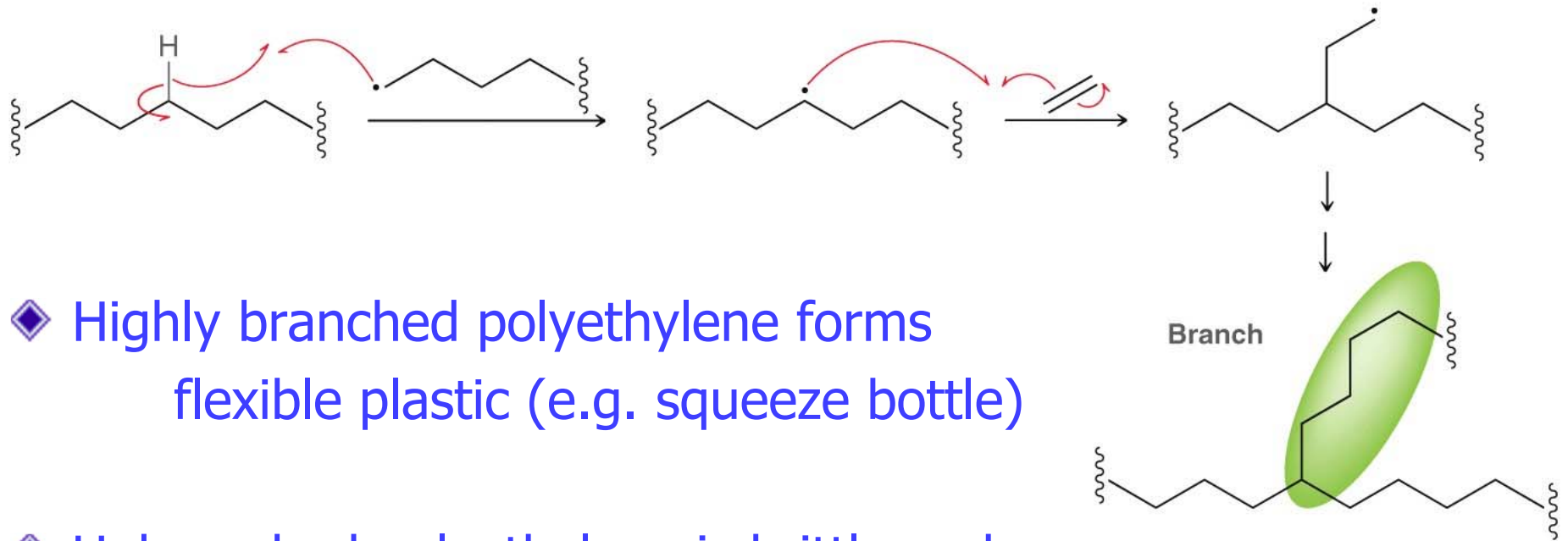
Radical Polymerization

- ◆ Free radical conditions are also frequently used to form polymers
- ◆ Recall that a **polymerization process joins together many small units called monomers** in a long chain



Radical Polymerization

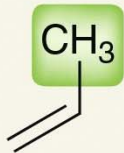
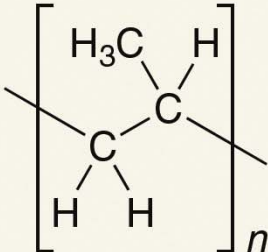
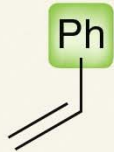
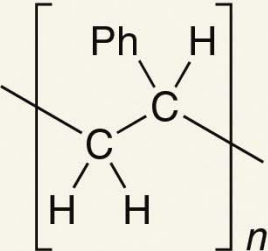
- ◆ **Chain Branching** is inevitable in this process, and occurs by the following mechanism



- ◆ Highly branched polyethylene forms flexible plastic (e.g. squeeze bottle)
- ◆ Unbranched polyethylene is brittle and rigid (like a plastic bottle cap)

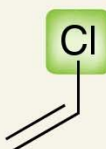
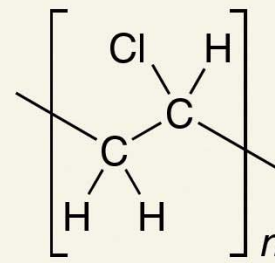
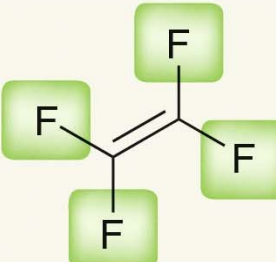
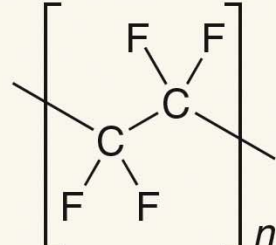
Radical Polymerization

- ◆ Polymers with varying properties are obtained by polymerizing substituted ethylene derivatives:

MONOMER	POLYMER	APPLICATION
 Propylene	 Polypropylene	Carpet fibers, appliances, car tires
 Styrene	 Polystyrene	Televisions, radios, Styrofoam

Radical Polymerization

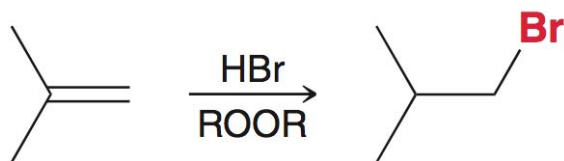
- ◆ Polymers with varying properties are obtained by polymerizing substituted ethylene derivatives:

MONOMER	POLYMER	APPLICATION
 Vinyl chloride	 Poly(vinyl chloride)	PVC piping for plumbing, CDs, garden hoses, raincoats, shower curtains
 Tetrafluoroethylene	 Teflon	Nonstick coating for frying pans

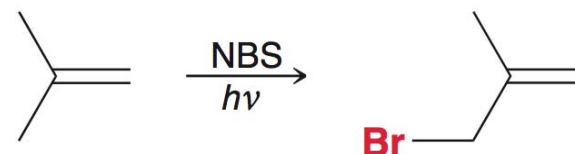
Review of Chapter 10 Reactions

- ◆ Radical reactions are synthetically useful, and will be applied to multistep syntheses throughout this course:

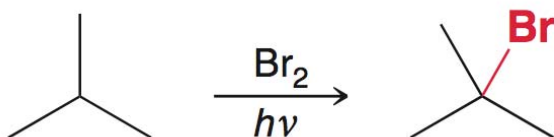
Anti-Markovnikov Addition of HBr to Alkenes



Allylic Bromination

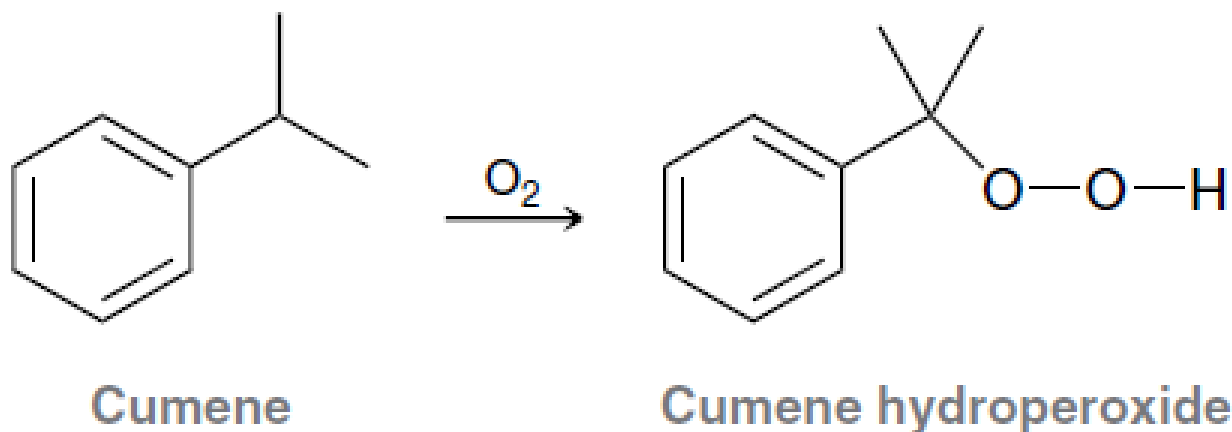


Bromination of Alkanes



Autooxidation vs. Antioxidation – Autooxidation

- ◆ Autooxidation is the process by which compounds react with molecular oxygen.



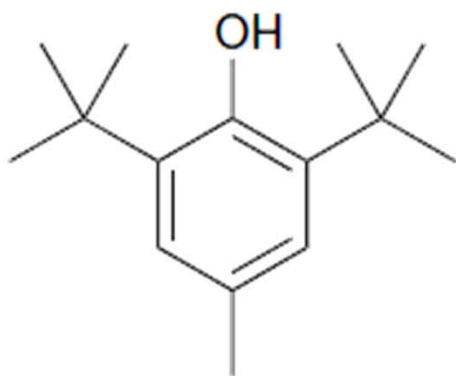
- ◆ The process is generally very slow.

Autooxidation vs. Antioxidation – Autooxidation

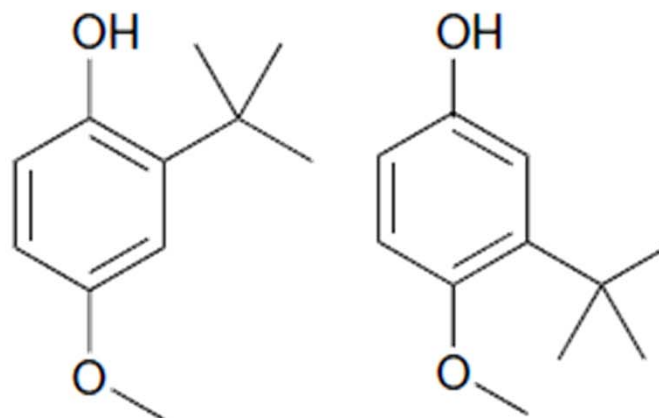
- ◆ Light accelerates the autooxidation process.
- ◆ Dark containers are often used to store many chemicals such as vitamins.
- ◆ In the absence of light, autooxidation is usually a slow process.
- ◆ Compounds that can form a relatively stable $C\bullet$ radical upon H abstraction are especially susceptible to autooxidation.



Autooxidation vs. Antioxidation – Antioxidants



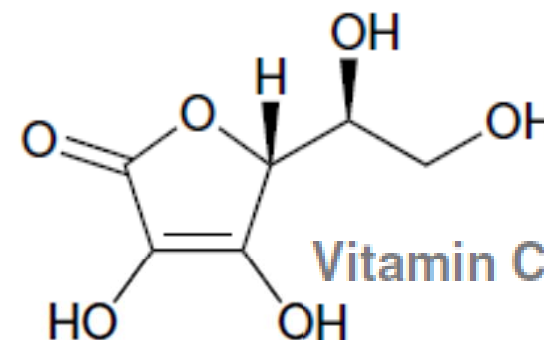
Butylated hydroxytoluene
(BHT)



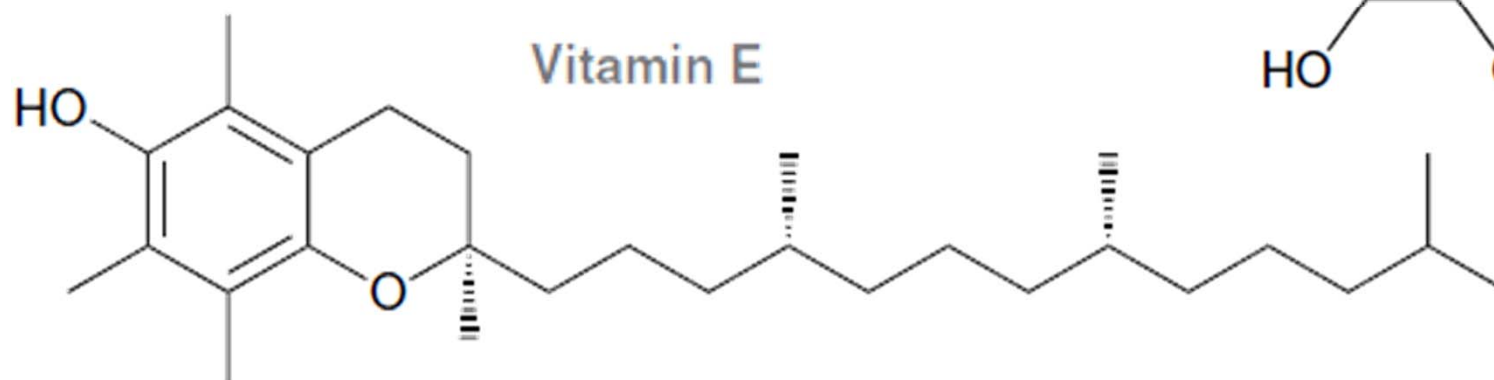
Butylated hydroxyanisole
(BHA)

Natural Antioxidants

- ❖ Vitamins C is hydrophilic.
- ❖ Vitamin E is hydrophobic.



Vitamin C



Vitamin E

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!