

# CHEM 322 Organic Chemistry II - Professor Kathleen Kilway

## "Organic Chemistry" by Maitland Jones, 3rd edition

Chapter 11 Homework - 7, 9, 12, 15, 17, 18, 20, 21, 25, 34, 35.

### CHAPTER 11: RADICAL REACTIONS

#### Section 11.1

##### I. Preview

###### A- Vocabulary

- 1- Radicals and chain reactions will be covered in this chapter.
- 2- There will be some selectivity of reactions depending on the halide.

###### B- Essential Skills

- 1- It is important to learn how the different steps of the chain (free radical) reaction.
- 2- These steps are important in order to understand the selectivity of the product formation.
- 3- *N*-Bromosuccinimide (NBS) is a standard reagent in bromination reactions. It delivers a small amount of Br<sub>2</sub> to the reaction mixture and brominates in the allylic position of alkenes.

#### Section 11.2

##### II. Formation and Simple Reactions of Radicals

A- Pyrolysis or thermolysis is heat supplied to induce a chemical reaction.

###### B- Bond Dissociation Energy

- 1- It is the energy required to break a bond homolytically.
- 2- Homolytic cleavage is bond breaking to yield the neutral species.



Fig 1

- 3- Heterolytic cleavage is bond breaking to yield charged species.

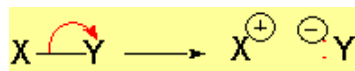


Fig 2

###### C- Possible Reactions of Radicals

- 1- Abstraction of a proton and selectivity of this process.

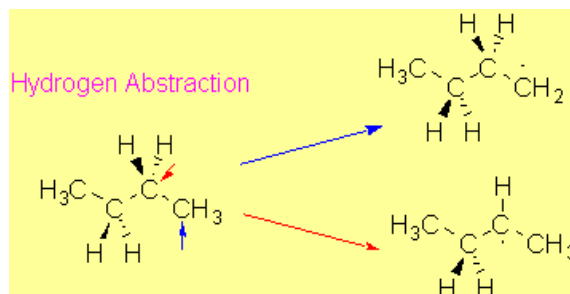


Fig 3

2- Abstraction of a proton forms a  $\beta$ -position of another radical disproportionation.

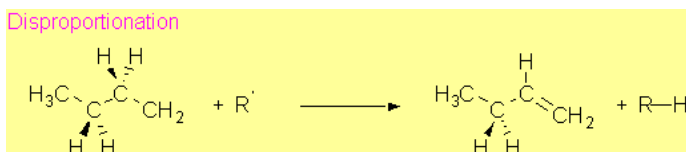


Fig 4

3-  $\beta$ -cleavage to give a new radical and an alkene.

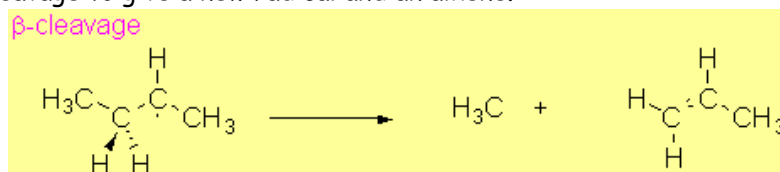


Fig 5

4- Two radicals can combine to form a dimer (dimerization).

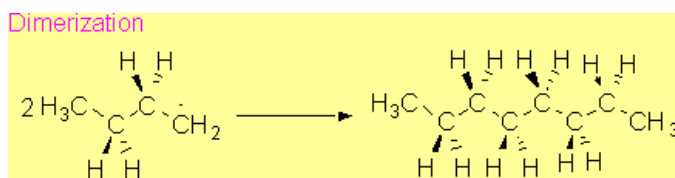


Fig 6

### D- Hydrogen Cracking

- 1- Process to convert high molecular weight hydrocarbons into lower-weight hydrocarbons.
- 2- This process is useful for the petroleum industry.

### E- Cyclic Compounds

- 1- Breaking a carbon-carbon bond in cyclopropane yields a 1,3-diradical.

### F- Stability of Radicals

- 1- One possible way is introduction of a vinyl group (decreases BDE by 10 kcal/mol).

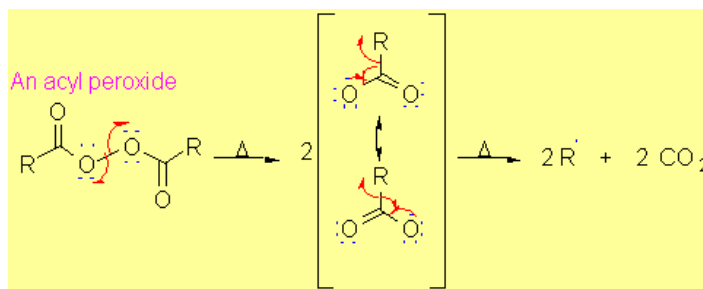


Fig 7

- 2- Another way to generate radicals is the introduction of a weak bond.
  - a- Peroxides contain a weak oxygen-oxygen bond (BDE 38 kcal/mol).

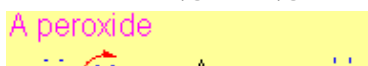


Fig 8

b- Acyl peroxides contain both carbonyl and oxygen-oxygen bonds (BDE = 29 kcal/mol). They generate  $\text{CO}_2$  molecules.

c- Azo compounds generate  $\text{N}_2$  gas and two alkyl radicals.

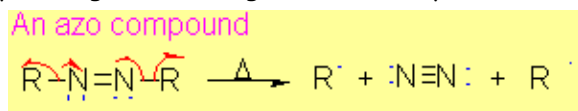


Fig 9

### Section 11.3

#### III. Structure of Radicals

A- Carbocation is planar ( $120^\circ$ ) and carbanion is pyramidal ( $99.8^\circ$ ). The radical is somewhere in between.

1- It is either a planar or a rapidly inverting pyramid.

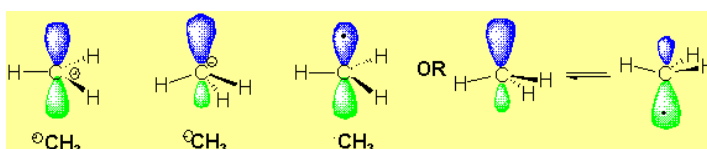


Fig 10

### Section 11.4

#### IV. Stability of Radicals

A- Stability of radicals follows the stability of carbocations.

B- Overlap of the radical involves overlap between a filled carbon-hydrogen bond and a half-filled  $2p$  orbital.

C- Resonance also stabilizes the radicals.

### Section 11.5

#### V. Radical Addition to Alkenes

A- The Radical Chain Mechanism of HBr Addition

1- **Step 1 is the Initiation step.** It is the first step in a radical chain reaction in which a free radical is produced but does not involve the hydrocarbon.

a- Initiators used are usually peroxides, which contain weak oxygen-oxygen bonds.

b- Light ( $\nu$ ) or heat ( $\Delta$ ) is used to initiate the reaction.

c- The second initiation step is abstraction of a proton of H-X.

2- **Step 2 is the Propagation step.**

a- These steps are the continuation of the chain reaction where the radicals react with alkenes and alkanes.

3- **Step 3 is the Termination step.**

a- It is any step where the radicals are combined by a combination step.

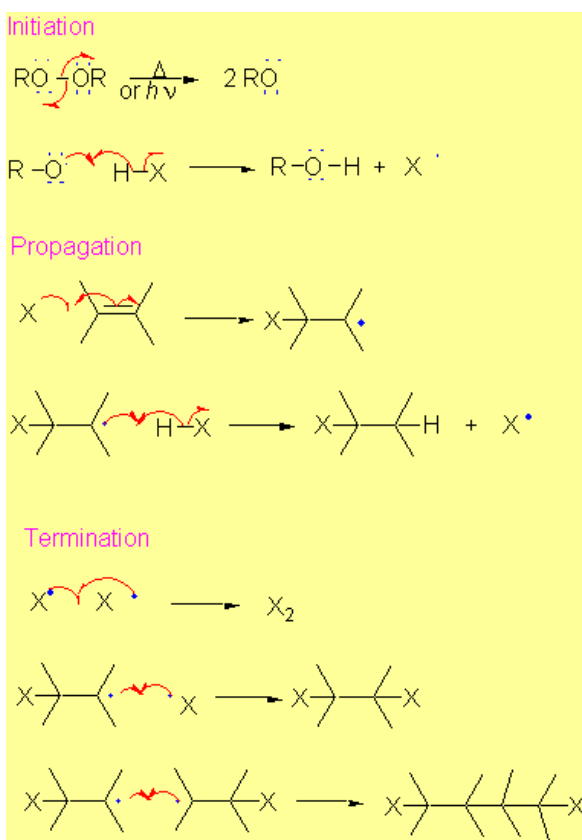


Fig 11

**B- Inhibitors**

- 1- These compounds are molecules, which stop the reaction.
- 2- Examples are hydroquinone, butylated hydroxy toluene (BHT) and butylated hydroxy-anisole (BHA).

**C- Regiospecificity of Radical Additions: Anti-Markovnikov Addition**

- 1- The regiospecificity of radical addition to isobutenes is determined by the direction of radical attack on the alkene and thus by the stability of the initially formed radical, which tends to be on the tertiary carbon.
- 2- HBr can add either Markovnikov or anti-Markovnikov if radical initiators are present; HCl and HI only add Markovnikov.

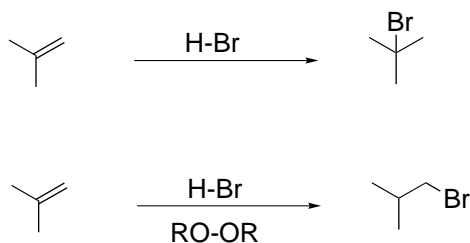


Fig 12

**D- Thermochemical Analysis of HX Additions to Alkenes**

- 1- The first propagation step is exothermic for Br and Cl, but endothermic for I, so the product will be disfavored and the reaction will be very slow; it does not compete

with the termination steps. (Tables 11.2 and 11.3 and Fig. 11.35)

2- The second propagation step is exothermic for Br and I, but endothermic for Cl, so this step of the reaction can succeed for Br and I, but fail for Cl. So it is only for H-Br addition that both steps are exothermic.

## Section 11.6

### VI. Other Radical Addition Reactions

A- Under certain conditions, alkenes can be polymerized by free radicals. See Table 10.2 for some common polymers and monomers from which they are built.

## Section 11.7

### VII. Radical-Initiated Addition of HBr to Alkynes

A- Hydrogen bromide adds to alkynes in the anti-Markovnikov sense when free radicals initiate the reaction, just as with alkenes.

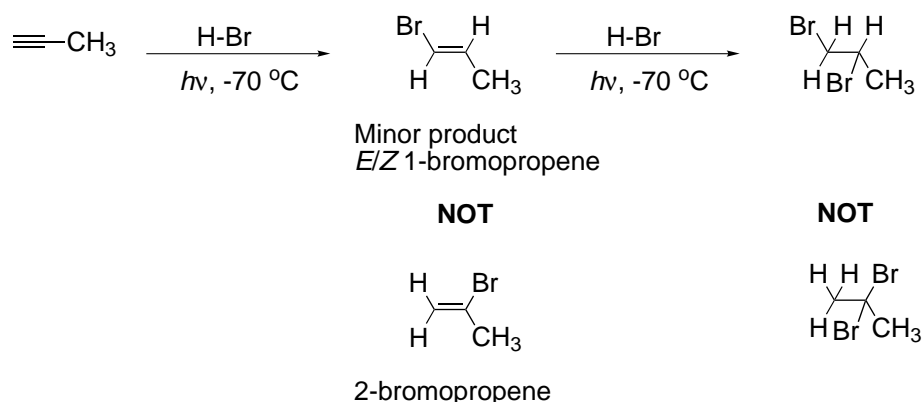


Fig 13

1- The free radical chain mechanism for addition to alkynes is similar to additions to alkenes, except that the formation of the more stable vinyl radical is favored over the less stable vinyl radical. (Fig. 11.38)

2- Although in principle, a second radical addition of HBr could form either a geminal (1,1) or vicinal (1,2) dihalide, the vicinal dibromide is preferred, unlike in ionic reactions. (Figs. 11.39 and 11.40)

## Section 11.8

### IIX. Photohalogenation

#### A- Methane

1- Photolysis of chlorine in methane produces a mixture of chlorinated methanes: methyl chloride, methylene chloride, chloroform and carbon tetrachloride.

2- Although methane can be photohalogenated with bromine, the overall reaction is much less exothermic than is chlorination, which has important consequences for selectivity.

#### B- Other Alkanes

1- Photochlorination of butane and isobutane gives mixed products.

2- Photobromination is much more selective because the abstraction reaction is very endothermic for bromine. Therefore the transition state is much closer to product for bromine, according to the Hammond postulate.

## Section 11.9

## IX. Allylic Halogenation

A- Alkenes with allylic hydrogens can sometimes be halogenated specifically at the allylic position.

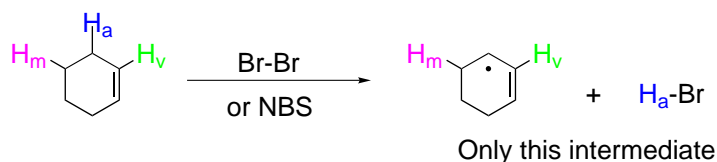


Fig 14

1- Because the allylic radical is resonance stabilized it will be more easily formed.

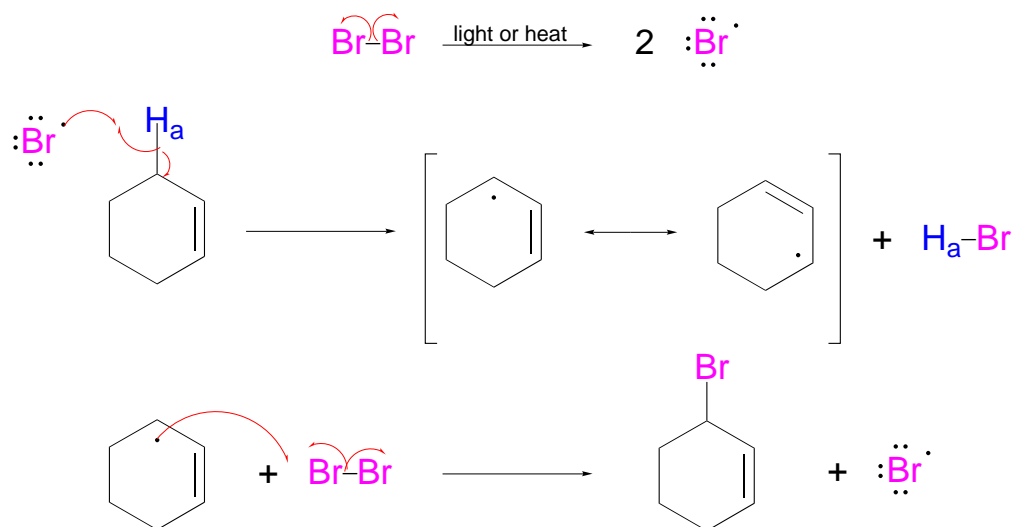


Fig 15

2- *N*-bromosuccinimide (NBS) in the solvent carbon tetrachloride ( $\text{CCl}_4$ ) selectively adds bromine to the allylic carbon of cyclohexene.

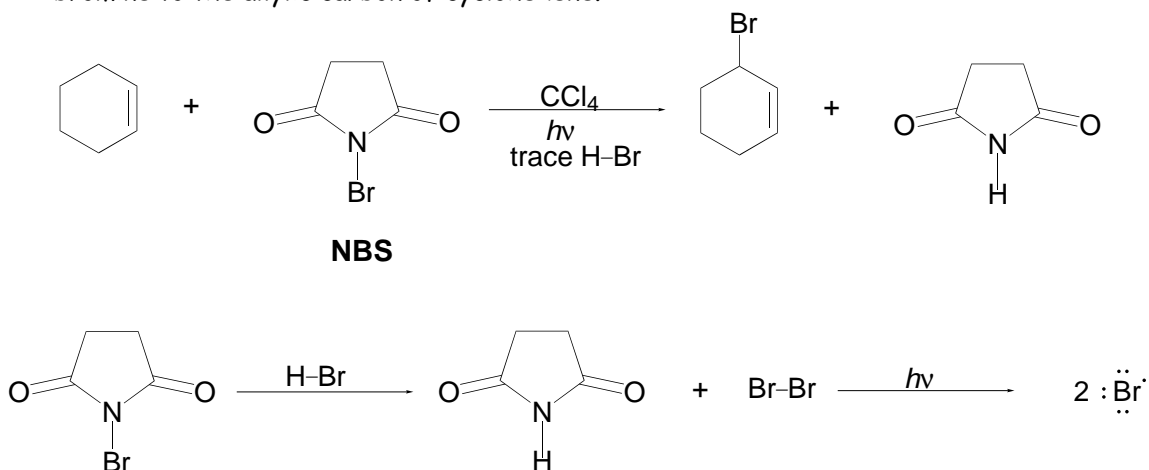


Fig 16

## Section 11.10

## X. Rearrangements (and Nonrearrangements) of Radicals

A- Unlike 1,2-hydride shifts, which are very common the 1,2-shift of a hydrogen atom (or an alkyl

group) is unknown.

1- An analysis of the molecular orbitals during the transition state shows why the high-energy electron of a radical is destabilizing enough to stop, the 1,2-shift. (Figs. 11.64-68)

### Section 11.11

#### XI. Radicals in Your Body: Do Free Radicals Age Us?

A- Vitamin E is an antioxidant and a free radical scavenger; it may be effective in delaying aging.

The long hydrocarbon chain makes it soluble in fatty acids, like those that cell membranes.

### Section 11.12

#### XII. Summary

A- Radical reactions select for the most stable configuration, very similar to carbocation stability.

B- Radical chain reactions can have an impact far out of proportion to the numbers of chain-initiating radicals involved.