

# CH 251 - Exam #4 Review Sheet

---

## Chapter 8 - Alkenes & Alkynes II - Addition Reactions

**Skip 8.4**

### Electrophilic Addition of HX to Alkenes

- reverse of E1
- regioselective (Markovnikov's Rule)
- not stereoselective (cation intermediate  $\rightarrow$  racemic products)

### Free-Radical Addition of HBr to Alkenes

- in the presence of peroxides (ROOR) get anti-Markovnikov addition
- mechanism changes (free radicals - see Chapter 10)
- only works with HBr; not HCl, HI, HF

### Acid-Catalyzed Hydration of Alkenes

- reverse of dehydration (know mechanisms for both)
- cation intermediates (watch out for rearrangement)
- regioselective (Markovnikov's Rule)

### Oxymercuration-Demercuration

- regioselective (Markovnikov's Rule)
- no cations - cyclic mercurinium ion

### Hydroboration-Oxidation

- regioselective (anti-Markovnikov)
- syn addition

### Addition of Halogens to Alkenes

- anti addition (stereoselective - goes through cyclic halonium ion intermediate)
- in the presence of water (rather than  $\text{CCl}_4$ ) get halohydrins (add X and OH)
- both stereoselective and regioselective
- nucleophile (water) attacks more substituted carbon

### Carbenes (neutral divalent carbon)

- decomposition of diazomethane ( $\text{CH}_2\text{N}_2 + \text{heat or light} \rightarrow \text{:CH}_2$ )
- alpha elimination of HCl from  $\text{CHCl}_3$  using tBuOK  $\rightarrow \text{:CCl}_2$

- Simmons-Smith cyclopropanation ( $\text{CH}_2\text{I}_2 + \text{Zn}/\text{Cu}$ )
- All of these add to alkenes in a syn addition (stereoselective)
- stereochemistry of alkene is retained

#### Oxidation of Alkenes

- $\text{KMnO}_4/\text{NaOH}/\text{cold} \rightarrow$  vicinal diol
- $\text{OsO}_4$  followed by  $\text{NaHSO}_3/\text{H}_2\text{O} \rightarrow$  vicinal diol
- both are syn additions

#### Oxidative Cleavage of Alkenes

- $\text{KMnO}_4/\text{NaOH}/\text{heat} \rightarrow$  carboxylic acids and ketones
- $\text{O}_3$  followed by  $\text{Zn}/\text{HOAc} \rightarrow$  aldehydes and ketones

#### Additions to Alkynes

- $\text{Br}_2$  or  $\text{Cl}_2 \rightarrow$  dihaloalkene (E isomer) if use one equivalent; get a tetrahaloalkane if use two equivalents
- $\text{HX}$  - add once or twice depending on number of equivalents used. Once: anti addition, Markovnikov's Rule. Twice: gem-dihalide, Markovnikov's Rule.
- $\text{HBr}/\text{ROOR}$  - anti-Markovnikov addition

#### Oxidative Cleavage of Alkynes

- either method (ozone or  $\text{KMnO}_4$ ) gives carboxylic acids

### Chapter 9 - Nuclear Magnetic Resonance and Mass Spectroscopy

**Skip: 9.10, 9.12-9.18**

#### 9.1 - Introduction

#### 9.2 - Electromagnetic Spectrum

#### 9.3 - NMR (CW vs. FT)

#### 9.4 - Nuclear Spin, 9.5 - Shielding and Deshielding, 9.6 - Chemical Shift

#### 9.7 - Chemical Shift Equivalent and Nonequivalent Protons

- homotopic - chemically equivalent and chemical-shift equivalent (show up at the same place in the NMR). Example: the  $\text{CH}_3$  protons in  $\text{CH}_3\text{CH}_2\text{OH}$
- enantiotopic - replacing each of the two protons generates a pair of enantiomers. They are not chemically equivalent, but they are chemical-shift equivalent (except in specialized chiral experiments). Example: the  $\text{CH}_2$  protons in  $\text{CH}_3\text{CH}_2\text{OH}$
- diastereotopic - replacing each of the protons generates a pair of diastereomers. They are not chemical-shift equivalent, so they show up in different places in the NMR spectrum and could conceivably split each other. Example: the  $\text{CH}_2$  protons in  $\text{CHCl}=\text{CH}_2$

## 9.8 - Spin-Spin Coupling

- remember the n+1 rule (holds when all of the coupling constants are approximately the same - note that J values for H's on adjacent sp<sup>3</sup> carbons all tend to be about 7 Hz and therefore the n+1 rule works in most cases)
- use Pascal's Triangle to figure out theoretical peak heights in multiplets: start with 1, then always bring down a 1 on the outside of the triangle, and add the diagonals to get the inside numbers.

### Pascal's Triangle

1						
1	1					
1	2	1				
1	3	3	1			
1	4	6	4	1		
1	5	10	10	5	1	
1	6	15	20	15	6	1

### Problems with spin-spin coupling:

- overlapping signals can make things complex
- long-range coupling (coupling between non-adjacent H=s) is sometimes seen
- aromatic splitting is difficult to analyze (recognize 1,4-disubstituted aromatics)

## 9.10 - <sup>13</sup>C NMR (see separate handout on web page for details)