

CH 253 - Exam #3 Review Sheet

Chapter 6 - Nucleophilic Substitution and Elimination Reactions of Alkyl Halides

S_N1: mechanism, stereochemistry, cation stability, solvent effects

S_N2: mechanism, stereochemistry, steric effects, solvent effects

E1: mechanism, cation stability

E2: mechanism, stereochemistry (anti elimination)

Leaving group definition

Solvents: protic vs aprotic, polar vs nonpolar, solvation effects

Nucleophiles: strong vs weak, relative nucleophilicity, basicity vs nucleophilicity

Temperature effects

Competition between elimination and substitution

Functional group transformations (S_N2)

Chapter 7 - Alkenes and Alkynes I

Nomenclature of alkenes; E/Z system; dienes

Relative stability of alkenes; Zaitsev's Rule

Synthesis of alkenes - elimination reactions:

- Dehydration of alcohols
 - Ease of dehydration: 3° > 2° > 1°
 - Regioselective (follows Zaitsev's Rule); Stereoselective (prefers E isomer)
 - Mechanism: protonate oxygen, break C-O bond → cation, lose β proton - E1
 - Concerns: cation rearrangement
- Dehydrohalogenation of RX
 - Strong base (hydroxide or alkoxide) required
 - 2nd order kinetics; rate depends on identity of halogen (F < Cl < Br < I)
 - Mechanism: everything happens at once. E2
 - Regioselective (follows Zaitsev's Rule); Stereoselective (prefers E isomer)
 - Anti elimination (leaving group and β proton must be anti)
 - Note: if there's no strong base, this can go E1 (3° and 2° RX only)

- Anti elimination (leaving group and β proton must be anti)
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- Synthesis of alkynes - double dehydrohalogenation of vicinal or geminal dihalides
 - Acidity of terminal alkynes
 - Alkylation of terminal alkynes
 - Hydrogenation of alkenes and alkynes
 - syn addition
 - $\text{H}_2/\text{Ni}_2\text{B(P-2)}$ or Lindlar's Catalyst takes alkynes \rightarrow Z alkenes
 - $\text{Na}^\circ/\text{NH}_3$ takes alkynes \rightarrow E alkenes

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 B^\oplus 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)

Acid-Catalyzed Hydration of Alkenes

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

Oxymercuration-Demercuration

- Markovnikov's Rule
- no cations - cyclic mercurinium ion

Hydroboration-Oxidation

- anti-Markovnikov
- syn addition

****NOTE: We may or may not get this far for the exam. Whatever we do on Monday, November 17th, will be on the exam.****