*CHEM 242 – Lecture 4 13/01/2014*

Overheads: - Outline

Recap Friday:

I) Radical Halogenation

Selectivity: Ratios result from:

1. # of each type of H
2. Halogen radical being used

Br• is more stable than Cl• it is more selective

get more 3° for Br than Cl

1. Relative stabilities of carbon radicals

Resonance > 3° > 2° > 1°

\*\* for allylic halogenations of alkenes use NBS to avoid EA

NOTE: Only C+ can rearrange, so once formed radical does NOT rearrange

Stereochemistry of Radical Halogenation (and all radical reactions)



reaction is not stereoselective!

🢡 if a chiral center is formed, usually get racemic product (50:50 R:S)

II) Radical Addition of H-Br to Alkenes: second radical reaction



🢡 What if we want the Br to go to the end with the most H’s?

🢡 we need the Br to be the E+!

How? Radicals! Br• = E+ (only has 7 e-)



🢡 Need to add radical initiator (such as HOOH or ROOR) to make Br• from H-Br



Mechanism:









Now know 3 ways to make R-Br (or R-Cl etc.)

1. R-H + Br2/h or Cl2/h
2. R2C=CR2 + H-Br (or HCl, HI, HF) - Markov
3. R2C=CR2 + H-Br/H2O2/h - Anti-Markov

🢡 Can use these alkyl halides to make all kinds of other groups 🢡 next 2 chapters

Two Main Reactions:



Nucleophilic Substitution Reactions





SN2 Reaction

S: substitution

N: nucleophilic

2: bimolecular 🢡 2 molecules in RDStep

(SN1 = unimolecular)