*CHEM 242 – Lecture 7 20/01/2014*

Overheads: - Outline

Recap Friday: SN2 *vs* SN1 Reactions

SN2 *vs* SN1

- one step - two steps

- no C+ - C+ intermediate (⮳ can rearrange!)

- rate = k[R-LG][Nu-] - rate = k[R-LG]

(bimolecular) (unimolecular)

- stereochem = inverted - stereochem = racemic

- 1° > 2° (no 3°) {steric hinderance} - 3° > 2° (no 1°) {C+ stability}

- needs good LG - needs good LG

- needs strong Nu- (high conc. helps) - weak Nu**:**ok



2) Vinyl & Aryl Halides



Role of Equilibrium in SN1 & SN2



General Rule: Stronger base kicks out weaker base

BUT – can shift eq’m by adding or removing reactants / products ⇨ LeChatellier

⇨if [I-] >> [Br-] can “force” reaction to go forward

(as long as I- & Br- have similar LG ability)

Solvents for Substitution Reactions:

⇨ need polar solvent

⇨ to dissolve charged species (Nu- etc)

⇨ to stabilize charged species

⮱ solvation / H-bonding / dipole-dipole interactions

Two types of Polar Solvents:

Protic *vs* Aprotic

- OH/NH: can H-bond - no OH/NH



Effect of Solvent Polarity on Reactants & TS



⇨ protic solvent favors SN1

⇨ polar aprotic solvent favors SN2

Predicting SN1 *vs* SN2



⮱3° ⮱1°

Depends on:

1. Nu- strength (SN2 needs strong Nu-)
2. [Nu-] – higher conc. increases rate of SN2 but not SN1!
3. Solvent: protic = SN1; aprotic = SN2



Q: Why do we care?

⇨ SN2 generally better:

1. control stereochemistry if chiral
2. no rearrangements
3. higher yields

So why don’t we always do SN2?

⇨ SN1 uses cheaper solvents and Nu-  (H2O vs NaOH/DMSO

⇨ easier to do

Intermolecular & Intramolecular Reactions

⮱ between 2 molecules ⮱ within one molecule

⇨ compare to intermural *vs* intramural sports

* If Nu- and LG are in the same molecule:



Intramolecular usually favored ⇨ doesn’t need to find 2nd molecule

(low conc. favors intra)

Ring size: 5-6 membered rings favor Intramolecular



3-4 membered rings ⇨ ring strain favor Intermolecular

7+ rings ⇨ ends far apart