

Overheads: - Outline

Recap Friday: S_N2 vs S_N1 Reactions

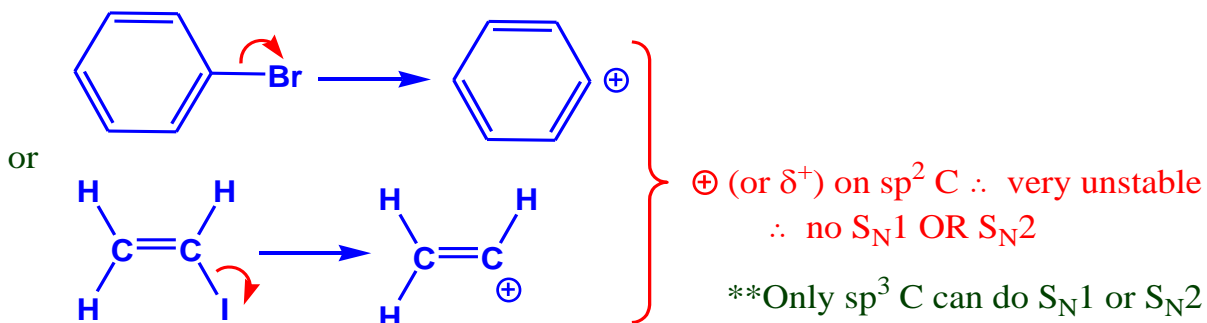
S_N2	vs	S_N1
- one step		- two steps
- no C^+		- C^+ intermediate (π can rearrange!)
- rate = $k[R-LG][Nu^-]$ (bimolecular)		- rate = $k[R-LG]$ (unimolecular)
- stereochem = inverted		- stereochem = racemic
- $1^\circ > 2^\circ$ (no 3°) {steric hinderance}		- $3^\circ > 2^\circ$ (no 1°) { C^+ stability}
- needs good LG		- needs good LG
- needs strong Nu^- (high conc. helps)		- weak Nu^- : ok

 1° R-Br 2° R-Br 3° R-Br S_N2 only

both reactions possible

 S_N1 only

2) Vinyl & Aryl Halides

Role of Equilibrium in S_N1 & S_N2  \rightarrow Whis is better LG? $I^- > Br^-$ \rightarrow Which is better Nu^- ? aprotic $\therefore Br^- > I^-$ General Rule: Stronger base kicks out weaker baseBUT – can shift eq'm by adding or removing reactants / products \Rightarrow LeChatellier \Rightarrow if $[I^-] \gg [Br^-]$ 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

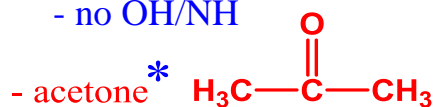
Two types of Polar Solvents:

Protic vs

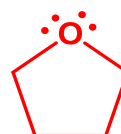
- OH/NH: can H-bond
- H_2O
- ROH
- RCO_2H
- R-NH_2 (less common)

Aprotic

- no OH/NH



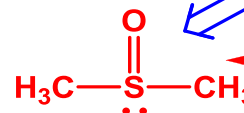
- THF* = tetrahydrofuran



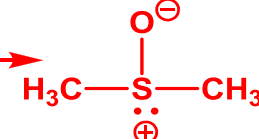
more polar than ether



- DMSO* = dimethylsulfoxide



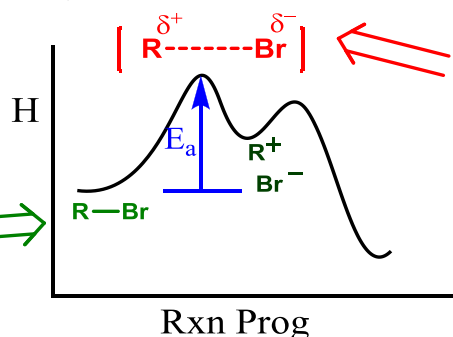
best, but stinky!



Effect of Solvent Polarity on Reactants & TS

$\text{S}_{\text{N}}1$:

uncharged, \therefore no big solvent effect

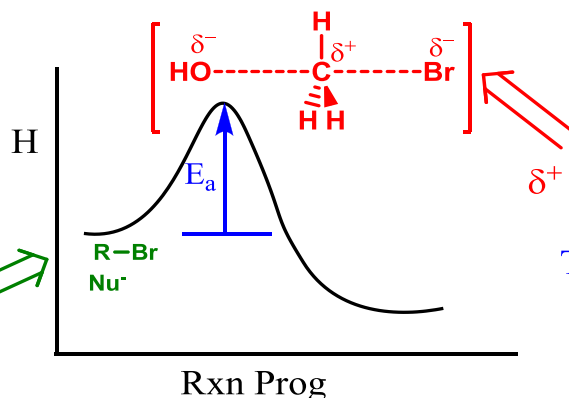


δ^+ / δ^- stabilized by all polar solvents
→ especially protic

TS ↓, E_a ↓, rate ↑
 \therefore protic = good

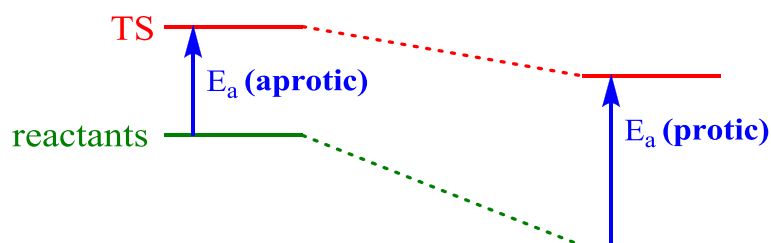
$\text{S}_{\text{N}}2$:

ionic Nu- stabilized more by polar, especially protic (H-bonds)



δ^+ / δ^- stabilized by polar solvents

TS ↓, reactants ↓ more



E_a ↑, rate ↓
 \therefore protic = bad

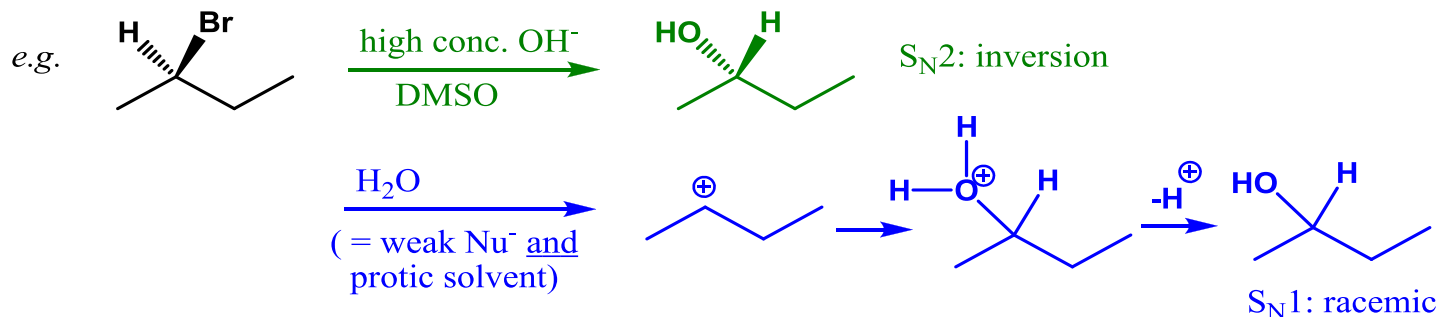
- ⇒ protic solvent favors S_N1
- ⇒ polar aprotic solvent favors S_N2

Predicting S_N1 vs S_N2



Depends on:

- 1) Nu^- strength (S_N2 needs strong Nu^-)
- 2) $[\text{Nu}^-]$ – higher conc. increases rate of S_N2 but not S_N1 !
- 3) Solvent: protic = S_N1 ; aprotic = S_N2



Q: Why do we care?

- ⇒ S_N2 generally better:
 - 1) control stereochemistry if chiral
 - 2) no rearrangements
 - 3) higher yields

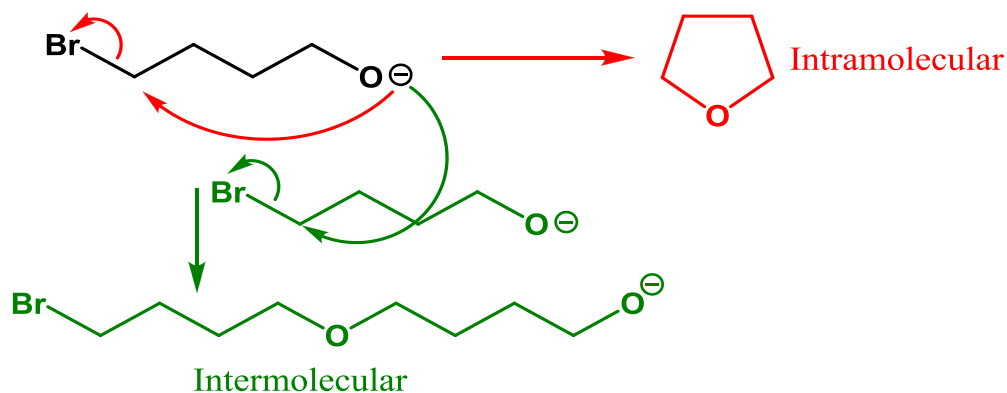
So why don't we always do S_N2 ?

- ⇒ S_N1 uses cheaper solvents and Nu^- (H_2O 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 \Rightarrow doesn't need to find 2nd molecule
(low conc. favors intra)

Ring size: 5-6 membered rings favor Intramolecular
3-4 membered rings \Rightarrow ring strain } favor Intermolecular
7+ rings \Rightarrow ends far apart }