

S_N1 Mechanism

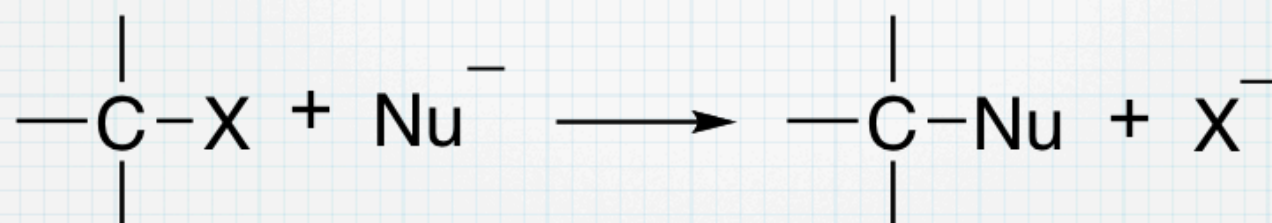
UCI Chem 51A
Dr. Link

Goals

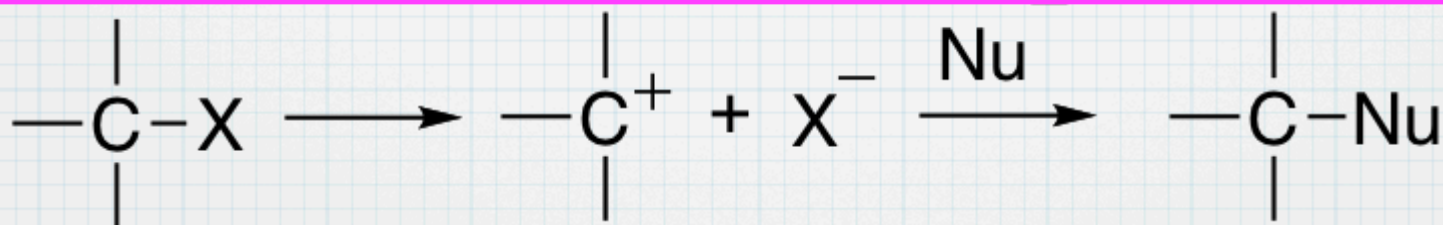
- * After this lesson you should be able to:
 - * Identify and draw an S_N1 mechanism
 - * Describe the experimental evidence that supports the S_N1 mechanism
 - * Identify electrophiles that are likely to undergo an S_N1 mechanism
 - * Rank and explain relative stabilities of carbocation intermediates
 - * Explain the importance of the leaving group in S_N1 reactions
 - * Explain the effect of the nucleophile on S_N1 reactions
 - * Explain the effect of the solvent on S_N1 reactions
 - * Predict and explain the stereochemical outcome of an S_N1 reaction at a stereocenter

Nucleophilic Substitution Mechanisms

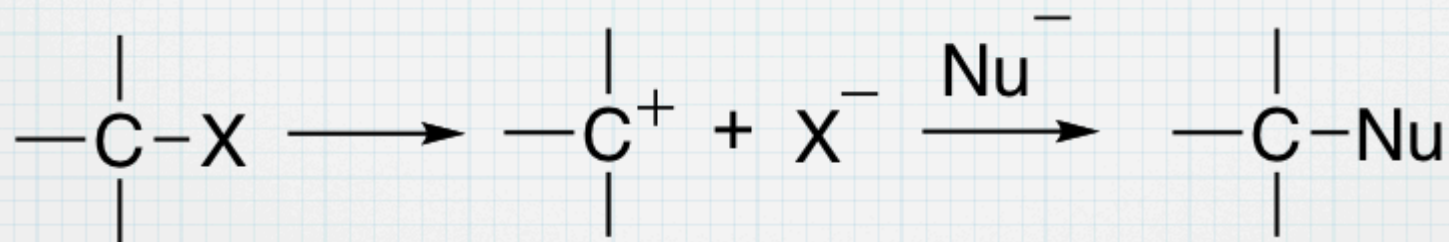
All at once:



Break, then form:



The S_N1 Mechanism



How Do We Know?

Rates $\text{rate} = k [E][I]$

Rate law derived experimentally.

Only electrophile both involved in RDS.

Intermediates

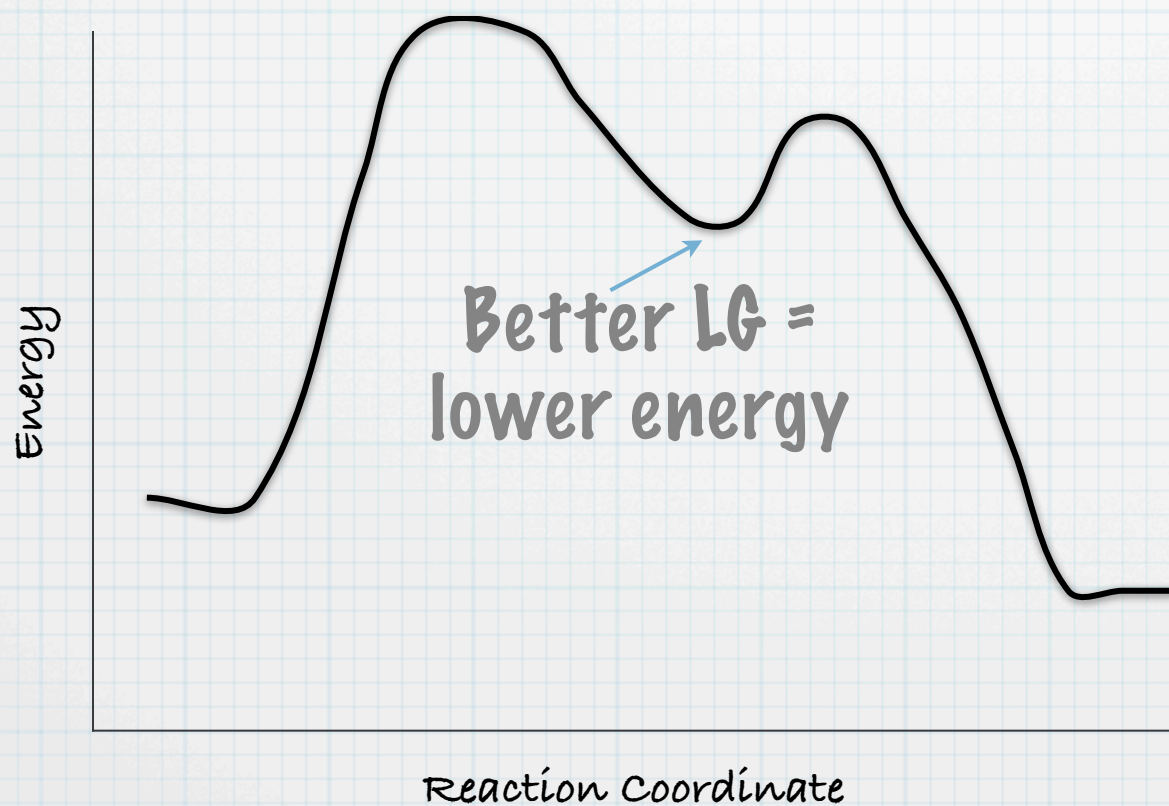
Carbocation intermediates identified experimentally.

Stereochemistry

Effects on stereocenters support S_N1

The Leaving Group

- * **All** nucleophilic substitution reactions require a good leaving group.



increases
amount that
intermediate
formation
favored

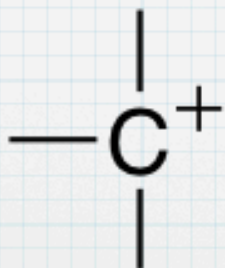
The Electrophilic Carbon

Type of C matters

$3^\circ > 2^\circ > 1^\circ > \text{methyl}$

Why? Carbocation stability!

No RXN!

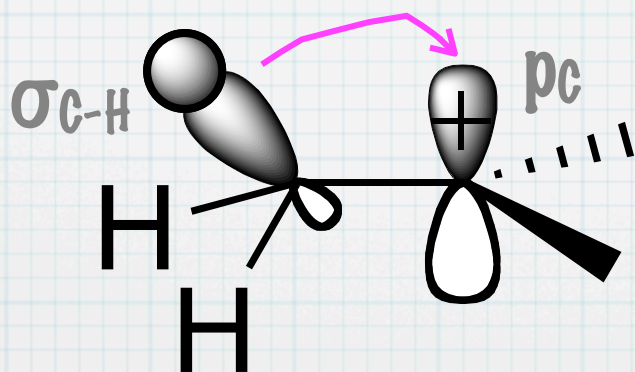


Carbocation Stability



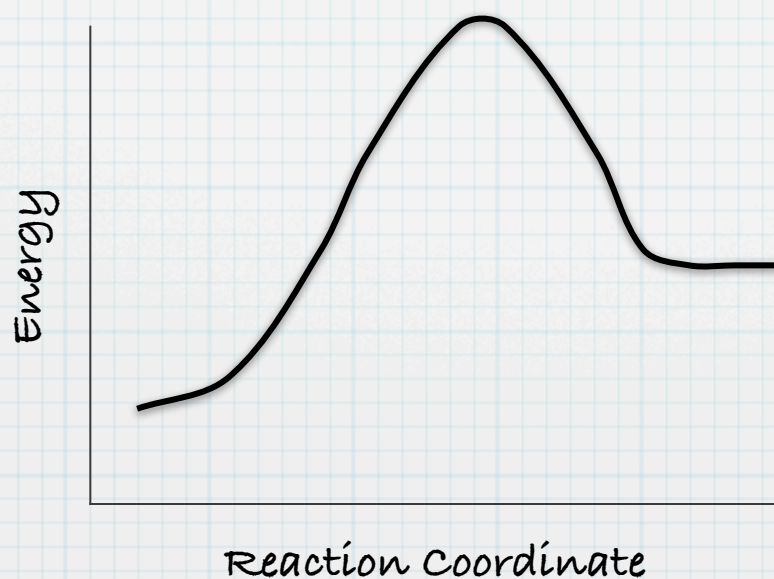
Hyperconjugation

Neighboring $\sigma_{\text{C-H}}$ bonds can donate small amount of e^- density
More neighboring bonds = more donation = lower energy



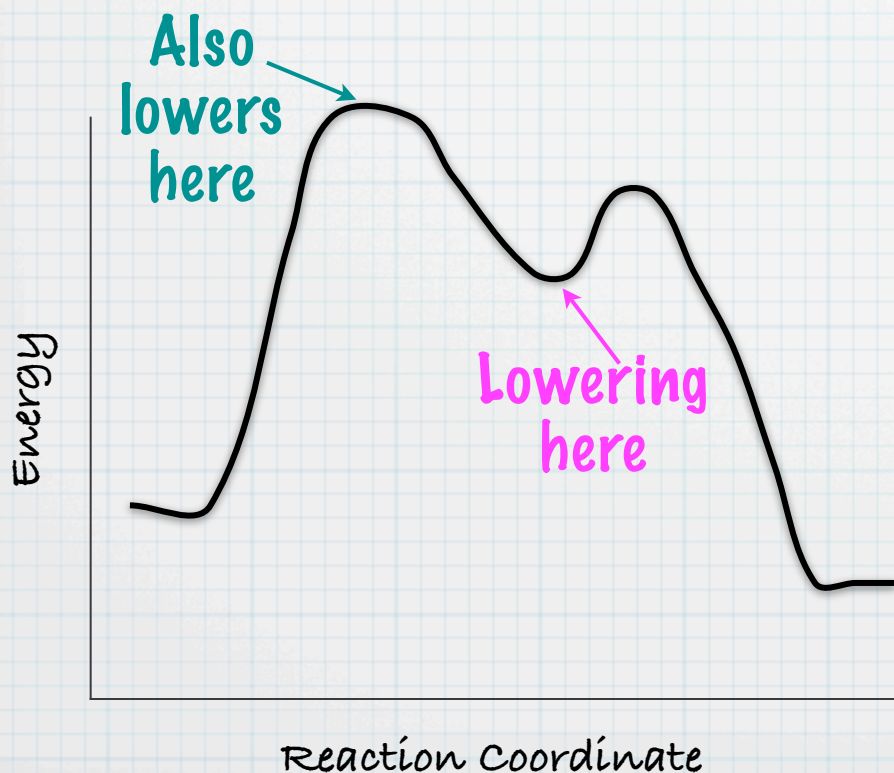
The Hammond Postulate

- * TS^\ddagger resembles structure that is closest to it in energy
- * For an endothermic process, TS^\ddagger is more similar to product than reactant
 - * Anything that lowers energy of product also lowers energy of TS^\ddagger



Applying Hammond Postulate to S_N1 Mechanism

- * Whatever stabilizes carbocation stabilizes TS[‡]
- * Stabilizes TS[‡] = lower E_a = faster rxn!



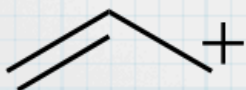
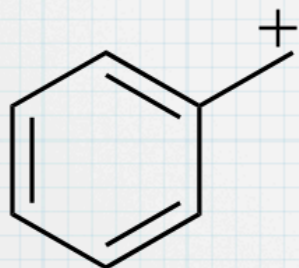
So...



Other ways to stabilize carbocation?

Benzyl and Allyl Carbocations

* Resonance!



Carbocation Summary

- * Stabilized by hyperconjugation
 - * 1° & methyl too high energy to form
- * Stabilized by resonance
- * Can be stabilized by both simultaneously! Even better!

The Nucleophile

- * S_N1 reactions are favored by **WEAK** nucleophiles

S_N1 reactions in competition with S_N2 reactions

Strong Nu means faster rate for S_N2

No time for S_N1 !

Common S_N1 Nu

The Solvent

* S_N1 reactions are favored by **POLAR PROTIC** solvents

H_2O

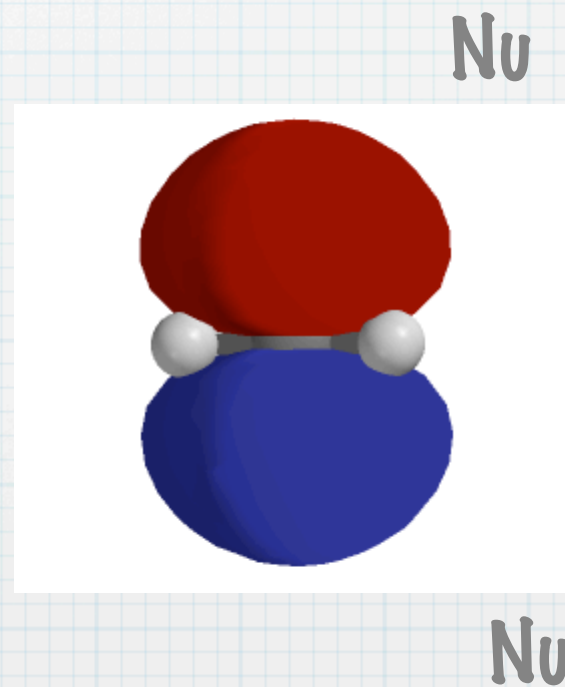
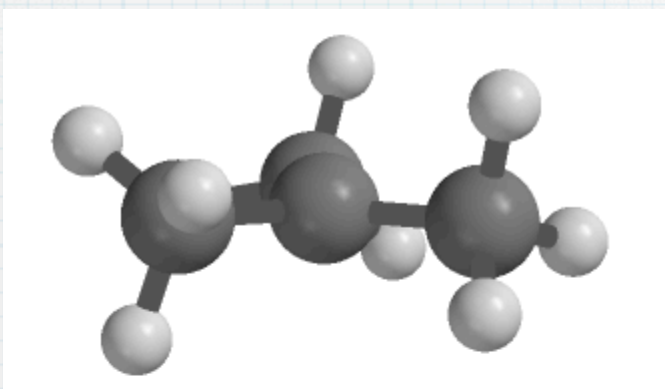
$EtOH$

$MeOH$

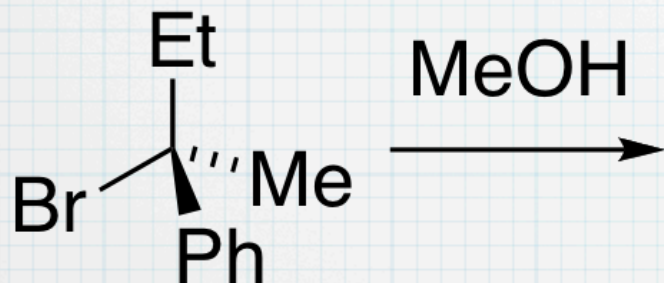
Why?

Stereochemistry and The S_N1 Mechanism

* Carbocations = trigonal planar



S_N1 at Stereocenter Example



S_N1 Summary

- * Rate = 1st order
- * Mechanism = 2 steps
- * Electrophile: benzyl, ally, 3° > 2°...
 - * no 1°, no methyl
- * LG = good LG required
- * Nu = weak Nu favors S_N1
- * Solvent = polar protic solvent favors S_N1
- * Stereochemistry = racemization of stereocenter

University of Surrey summary video

<http://www.youtube.com/watch?v=JmcVgE2WKBE>

Wrapping Up

- * Practice drawing mechanisms for S_N1 reactions
- * Practice predicting which electrophiles are most likely to undergo S_N1 reactions
- * Practice comparing carbocation stabilities
- * Practice drawing the products for an S_N1 reaction at a stereocenter