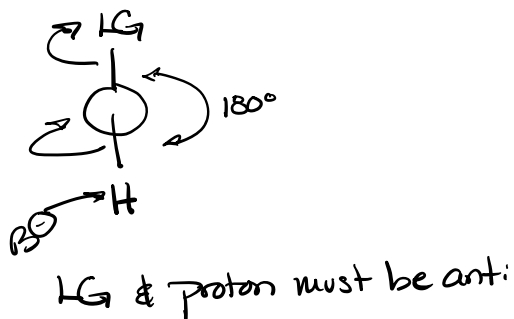
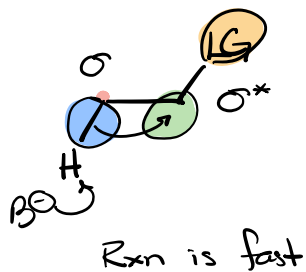
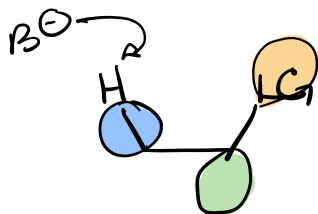


Stereoelectronic Effects E_2 Rxn

Anti periplanar

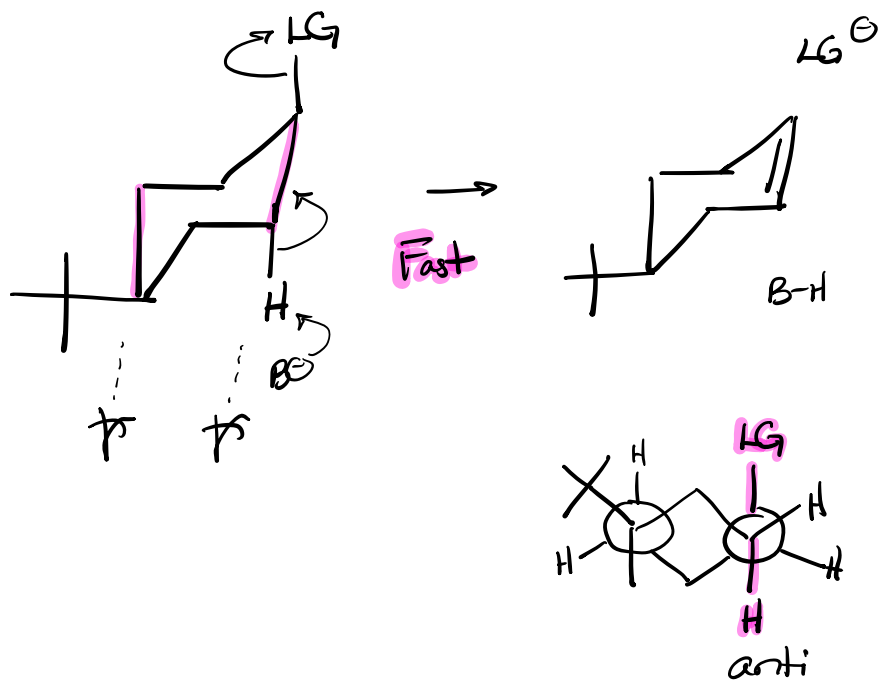
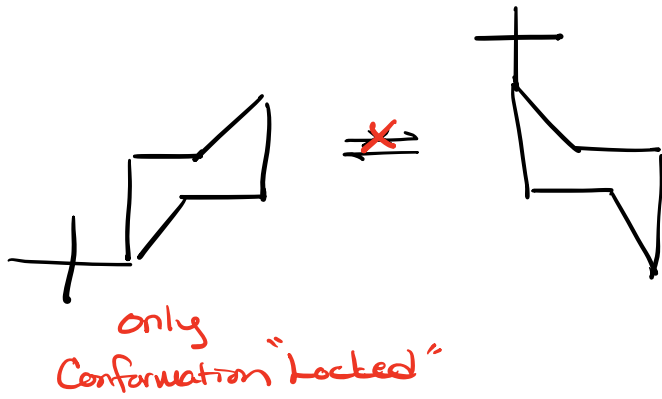


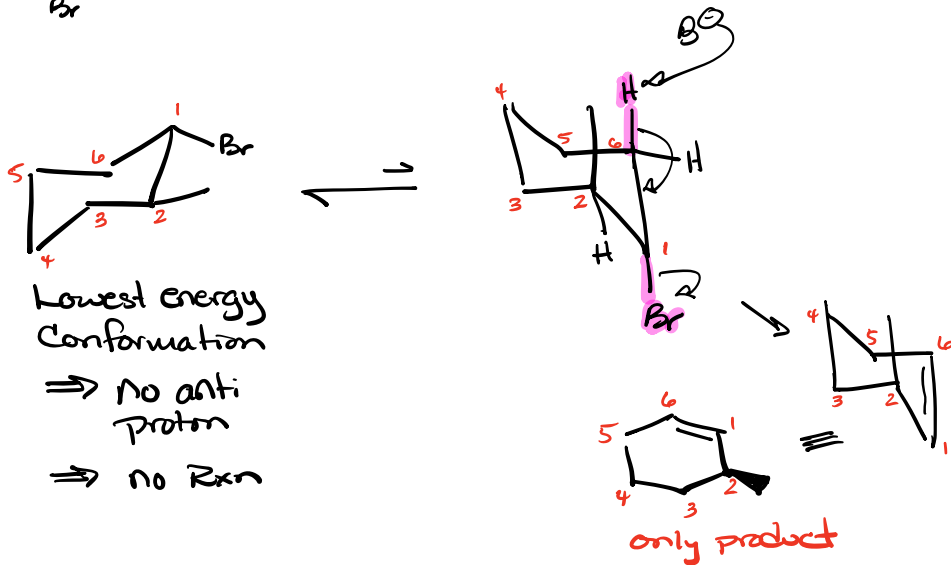
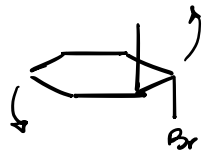
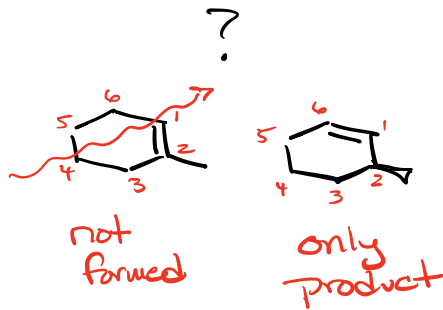
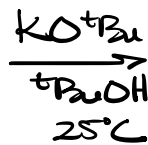
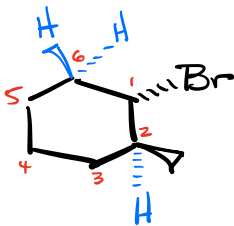
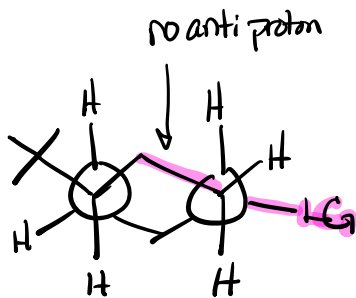
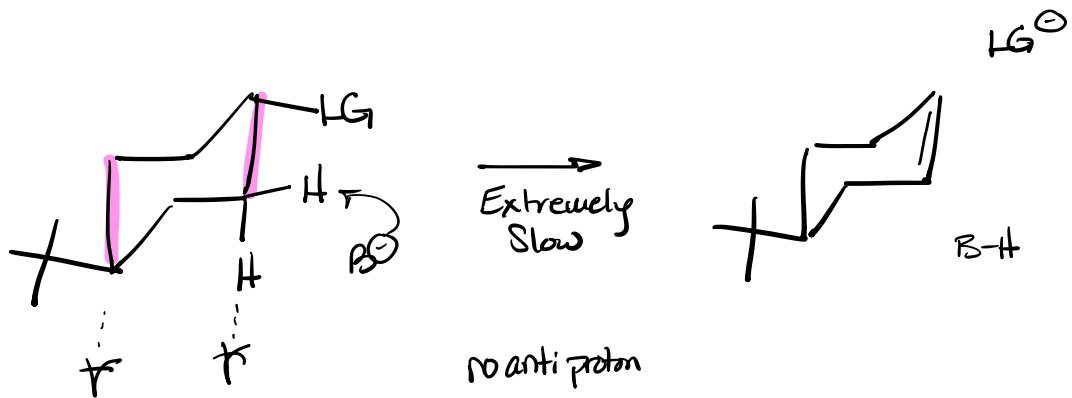
When Syn-Coplanar (dihedral = 0°)



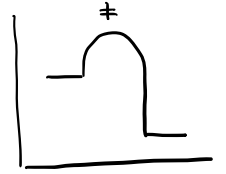
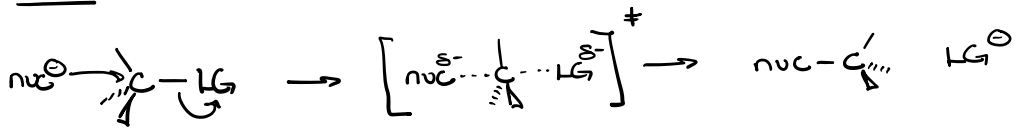
orbitals do not align
Makes Rxn extremely
Slow

How does this affect E_2 Rxn in
6 member ring systems?





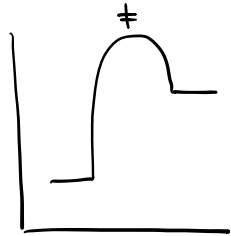
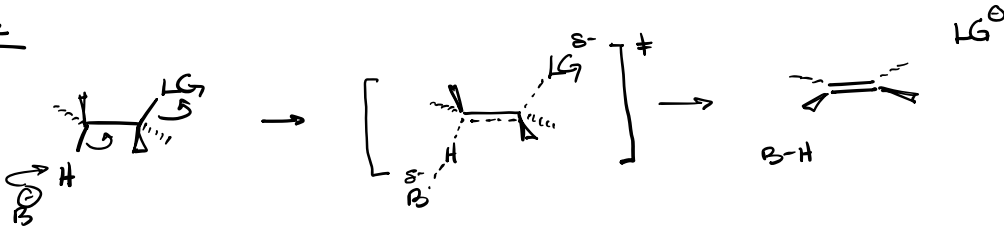
S_N²



Exothermic

Rate = k [Nuc] [R-LG] 1° >> 2° > 3°

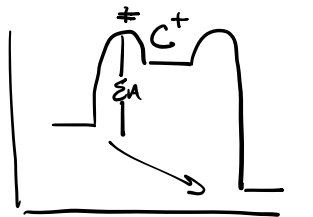
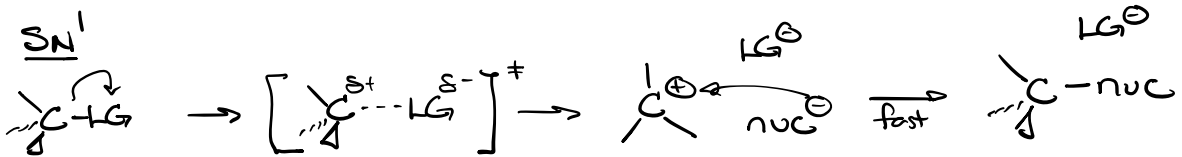
E₂



Endothermic

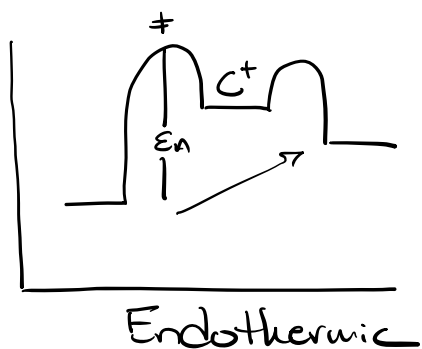
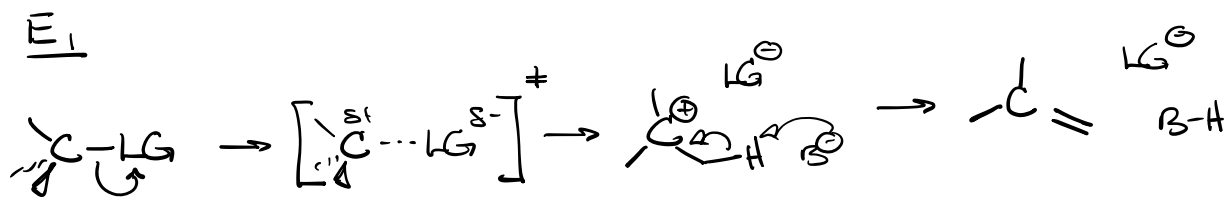
Rate = k [Base] [R-LG] 3° >> 2° > 1°

S_N¹



Exothermic

Rate = k [R-LG] 3° >> 2° > 1°

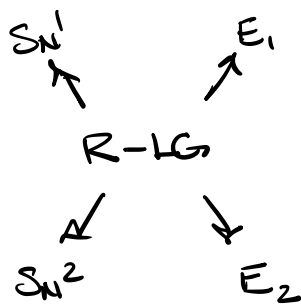


$$\text{Rate} = k[\text{R-LG}] \quad 3^\circ >> 2^\circ > 1^\circ$$

SN^2 vs E_2 Reactions Compete
 Similar rate laws
 nuc^- vs. base^-
 SN^2 E_2

SN^1 vs E_1 Reactions Compete
 Identical Rate laws
 Temperature
Anion present?
 No | yes
 SN^1 E_1

Anion = Base

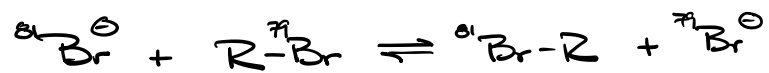


Factors

- ① Substrate 3° 2° 1° ?
- ② { Leaving Group
Base / Nucleophile
- ③ Solvent
- ④ Temperature

Loose Ranking \Rightarrow not Hard Ranking

S_N² Rates by Substrate



R	CH ₃ -	CH ₃ CH ₂ -	CH ₃ CH ₂ CH ₂ -	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}-\text{C}- \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}- \\ \\ \text{CH}_3 \end{array}$
	Me	Et	Prop	i-prop	t-Bu
Rate	100	1.31	0.89	0.015	0.004*
	fast	→			Super Slow
	No Sterics	→			Huge Sterics

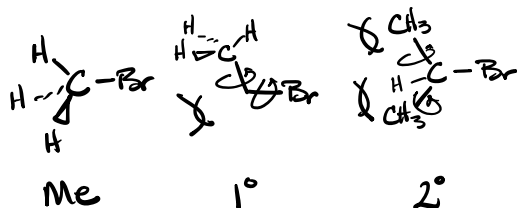
* Requires protic Solvent



R Me Et iPr tBu

Relative Rate	$\frac{k_{iPr}}{k}$	221,000	1,350	1	—
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Low Sterics



What happens if all 1°, but increased sterics (S_N2)?



R Et- pr- iBu- n-pent-



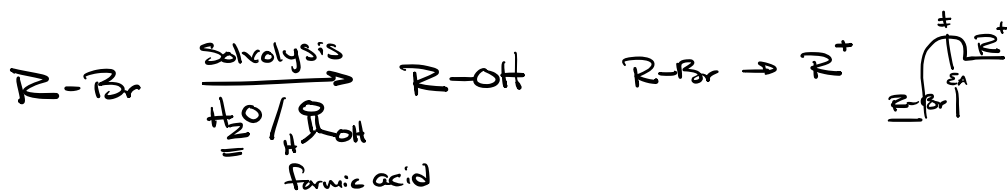
$\frac{k}{k_{Et}} =$	1	0.8	0.036	0.00002
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Not all 1° substrates are the same!

Cannot just look at 1° vs. 2° vs. 3°

must look at whole molecule

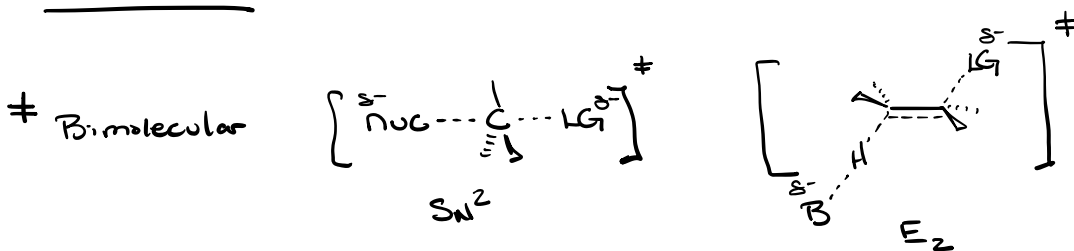
SN¹ Rates by Substrate



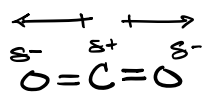
R	Me-	Et-	iPr-	tBu-
$\frac{k}{k_{Et}}$	0.6	1.0	26	10 ⁸ !
	$\begin{array}{c} H \\ \\ H-C^{\oplus} \\ \\ H \end{array}$	$\begin{array}{c} H \\ \\ CH_3-C^{\oplus} \\ \\ H \end{array}$	$\begin{array}{c} H \\ \\ CH_3-C^{\oplus} \\ \\ CH_3 \end{array}$	$\begin{array}{c} CH_3 \\ \\ CH_3-C^{\oplus} \\ \\ CH_3 \end{array}$
		1°	2°	3°

⇒ SN¹ Rate 3° >> 2° > 1°

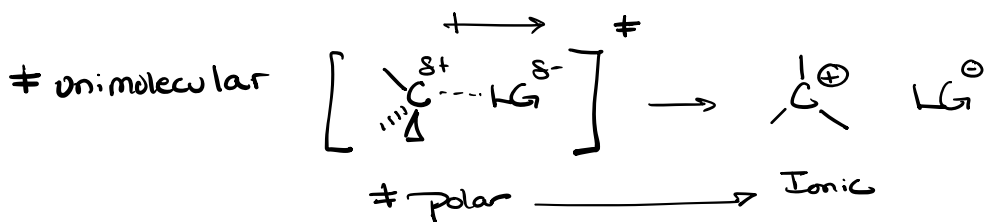
Solvent





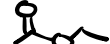


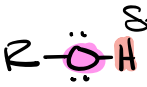
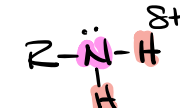

≠ non-polar similar to CO₂



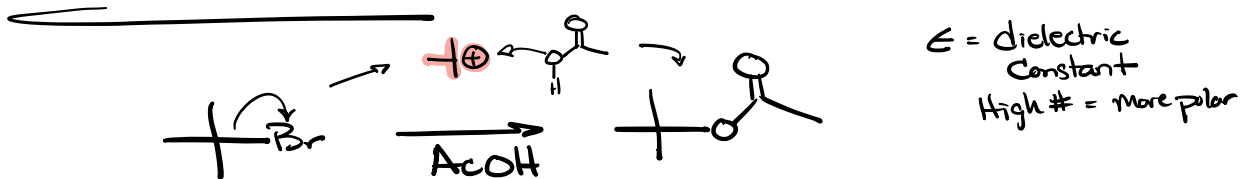
Has polar bonds
due to symmetry
is non-polar





Solvent types

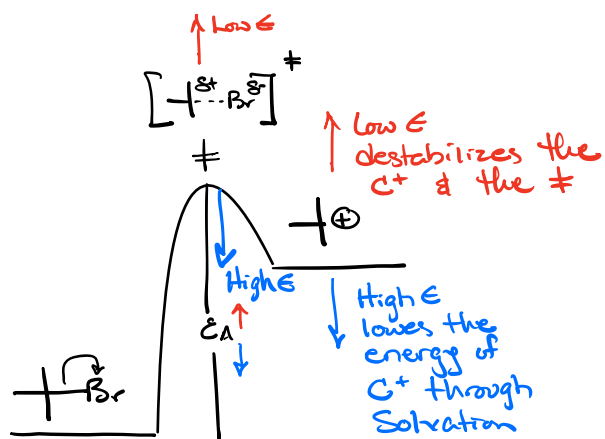
<u>Nonpolar</u>	<u>Polar aprotic</u>	<u>Polar protic</u>
Hydrocarbon hexane Cyclohexane heptane petroleum ether	 Methylene Chloride (CH ₂ Cl ₂) acetone  ethyl acetate  diethyl ether  THF 	 or  Alcohols MeOH EtOH H ₂ O Acids AcOH 
Aromatic Benzene toluene		

Unimolecular ≠ strongly affected by Solvation E_s & S_N1



ε Solvent	6 AcOH	33 MeOH	58 Formic Acid	78 H ₂ O
		-OH		
$\frac{K}{K_{AcOH}}$	1	4	5,000	150,000

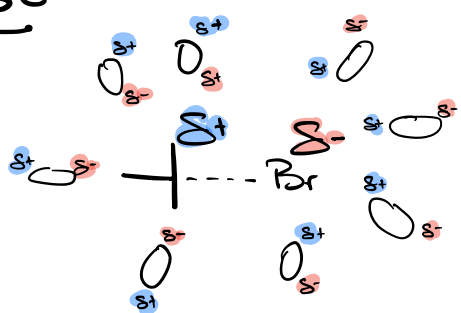
The more polar the solvent
the faster the R₁an



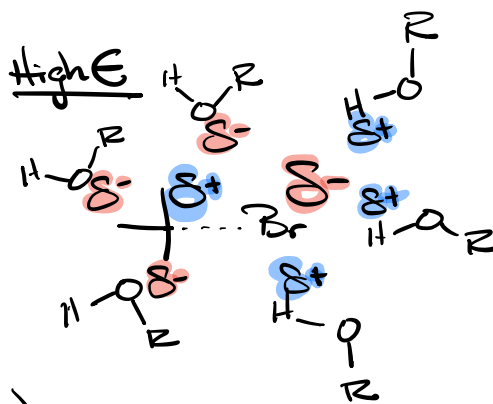
Hammond

High ϵ stabilizes the \ddagger and lowers E_A
 Speeding Rxn up.

Low ϵ



Low ϵ solvent (non-polar)
 not able to solvent \ddagger well
 \uparrow energy \ddagger



High ϵ solvent
 Highly stabilizes
 the \ddagger
 \downarrow Energy of \ddagger