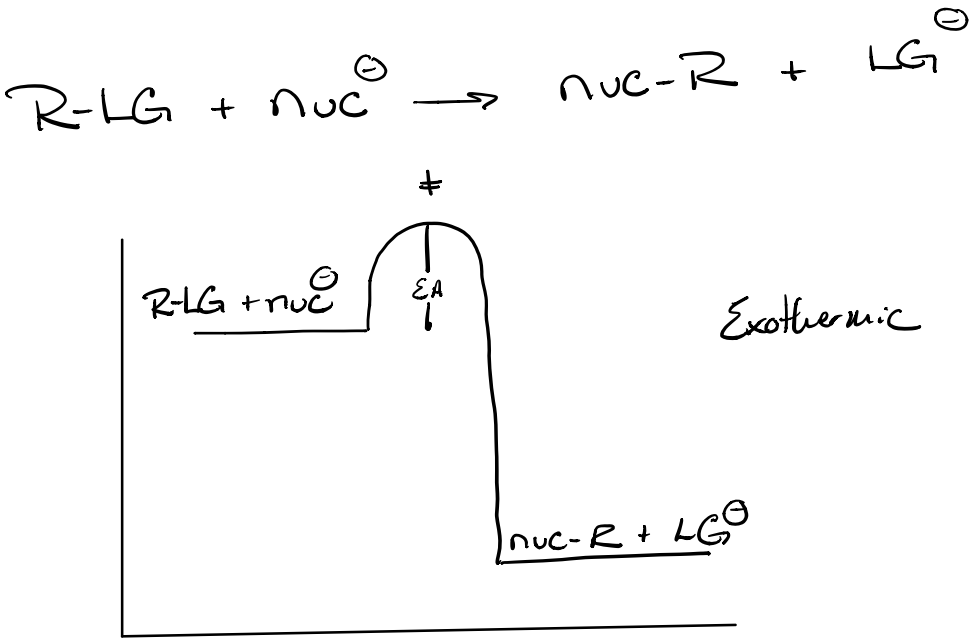
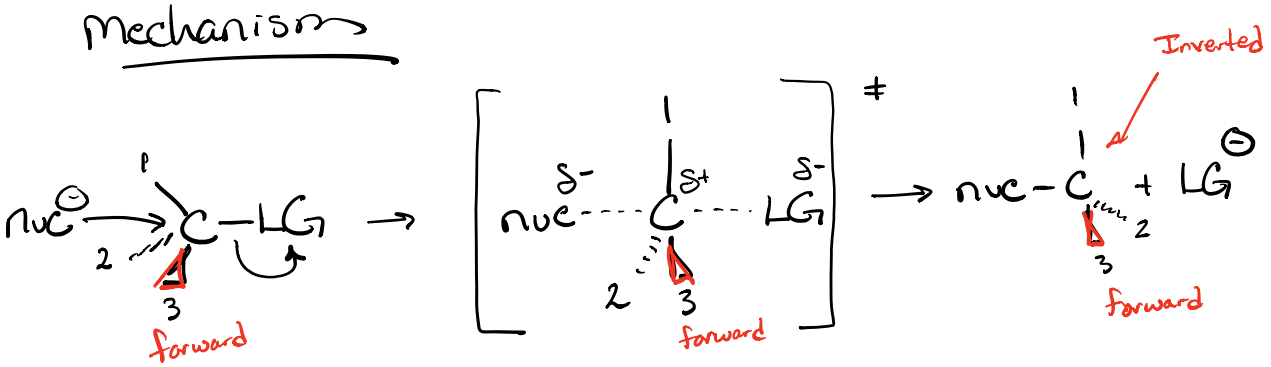
S_N2 Substitution Nucleophilic 2nd order

$$Rate = k[R\text{-}LG][nuc]$$



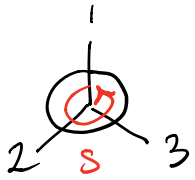
Mechanism

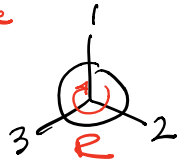


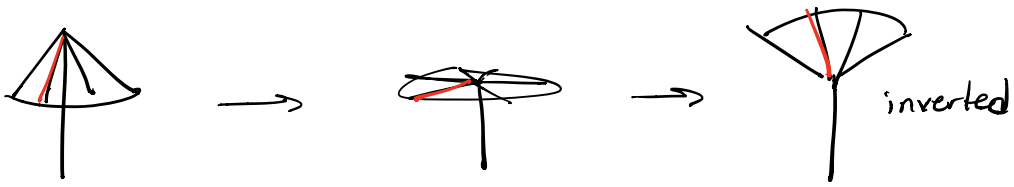
$Rate_{substrate} = 1^\circ > 2^\circ >> 3^\circ$

* Reverse of the general rate for substitution Rxns

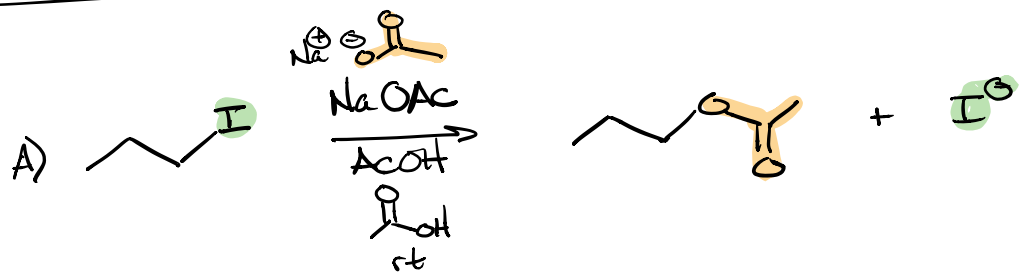
$R_{sub} = 3^\circ > 2^\circ >> 1^\circ$





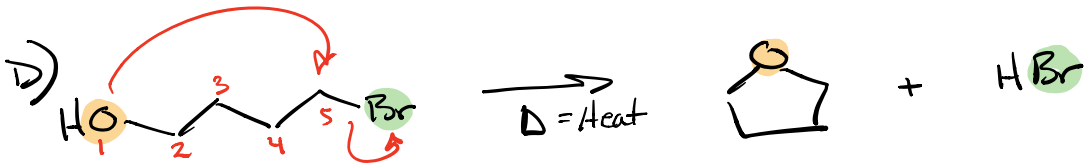


Examples of S_N2

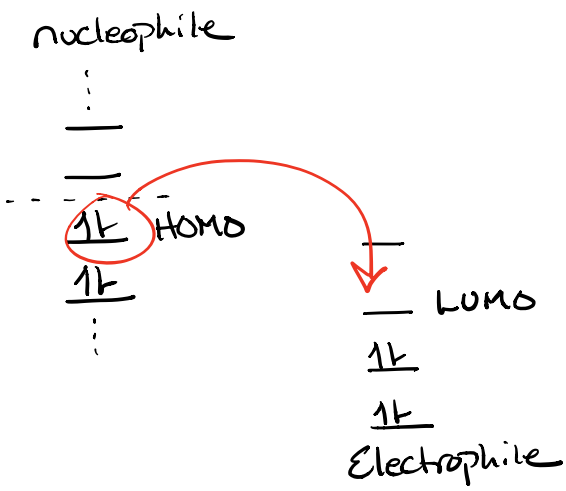
A) 

B) 

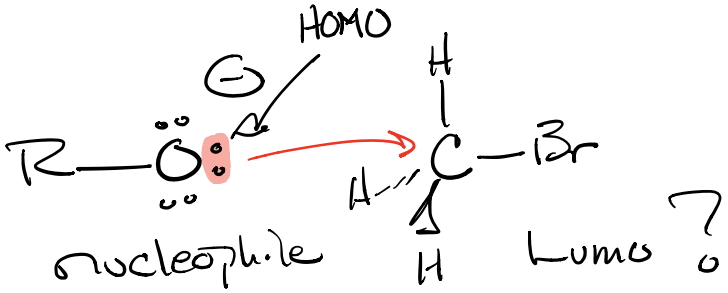
C) 

D) 

Reaction Theory

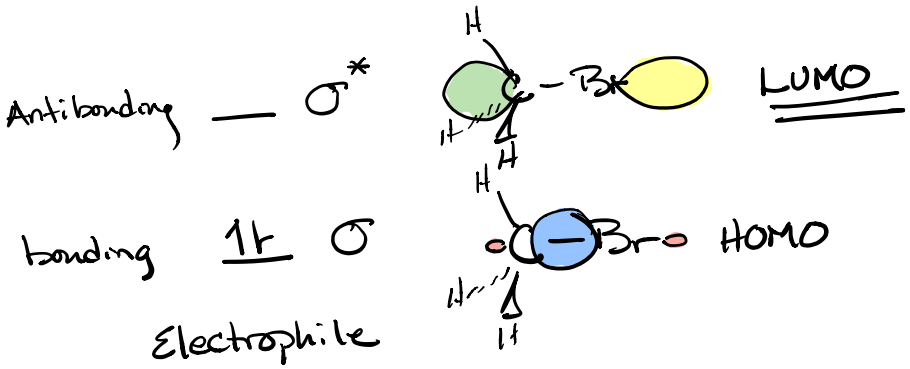


from HOMO of nucleophile → into LUMO of electrophile



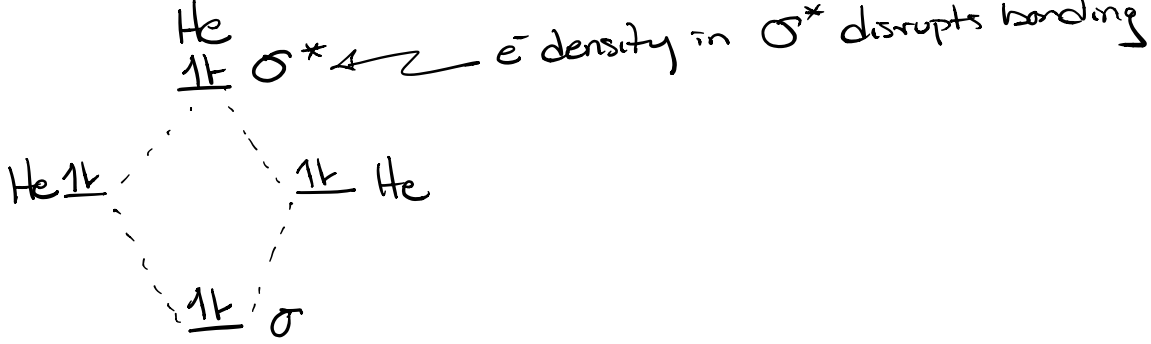
Two ways to look at LUMO

Valence bonding theory - Localized σ bond w/ σ*

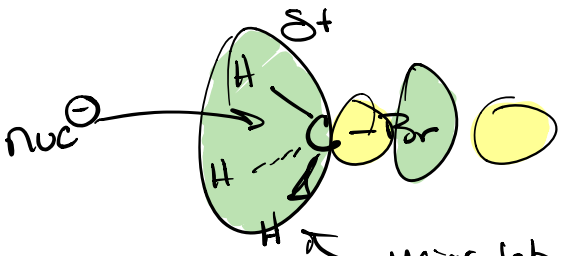


e^- from nuc$^-$ must be placed into σ to disrupt the σ bond and push out the LG

Why isn't He diatomic? (like H_2)

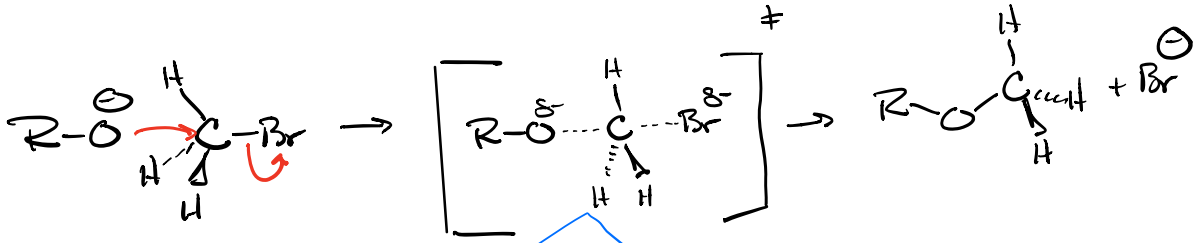


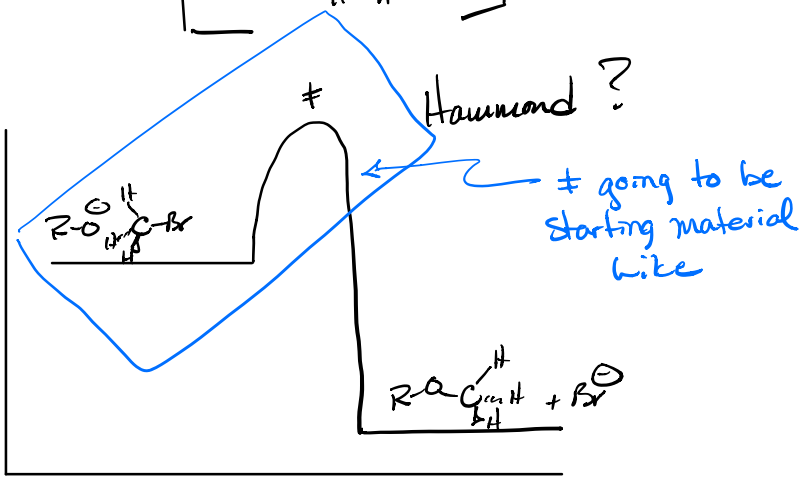
Molecular Orbital Theory

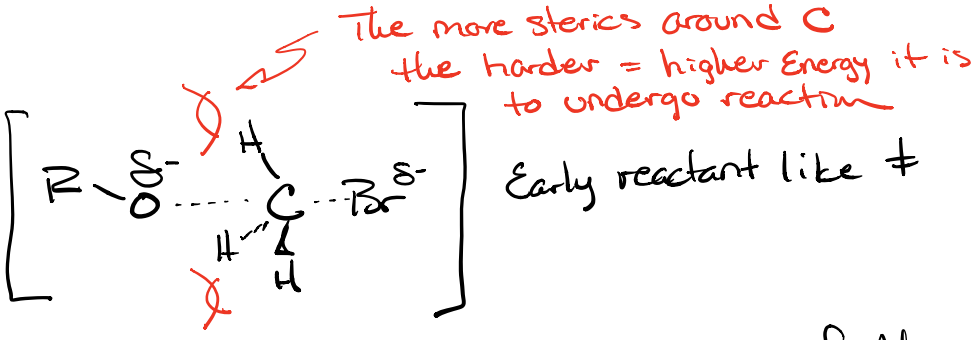


↖ major lob of the σ* molecular orbital
LUMO orbital
Large Coefficient = δ+

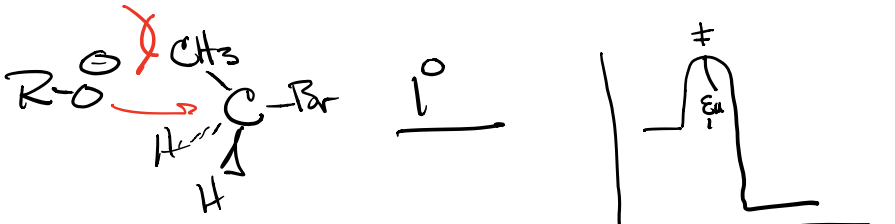
Both models show need for "backside" attack of the nucleophile on the substrate.

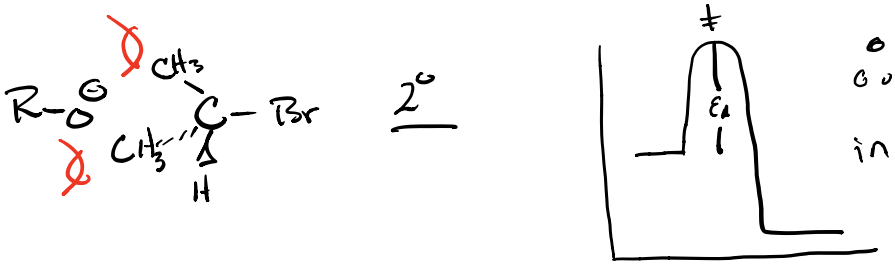


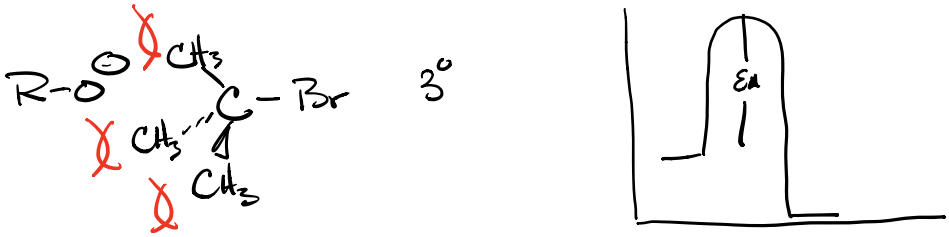




This implies that the structure of the reactant will most influence the E_A of the reaction







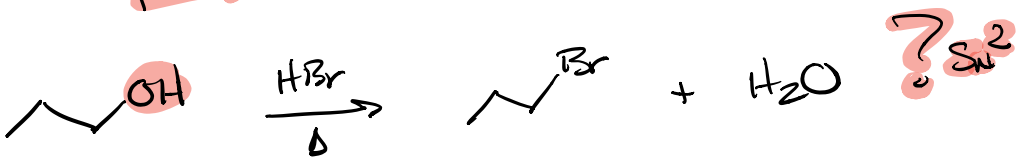
S_N2 Rxns w/ Alcohols as LG

Good LG = weak base

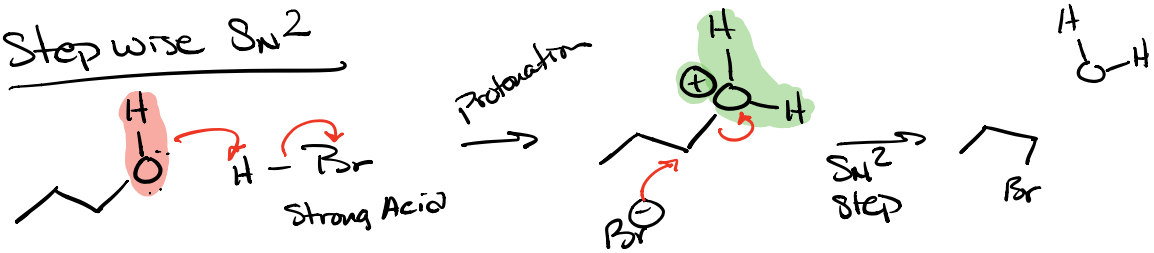
$^{\ominus}OH$ strong base
poor LG

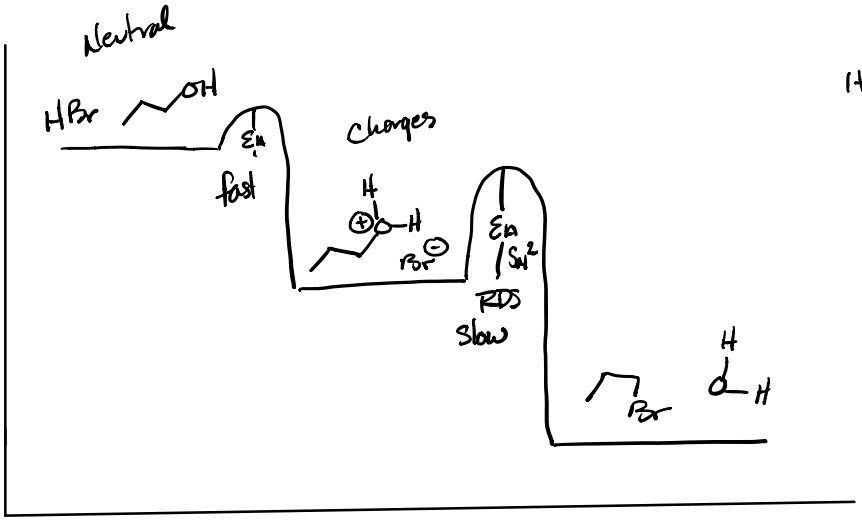
$Br^{\ominus}$ weak base
good LG

S_N2 requires a good LG



Stepwise S_N2

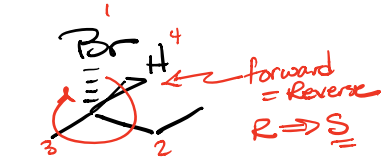


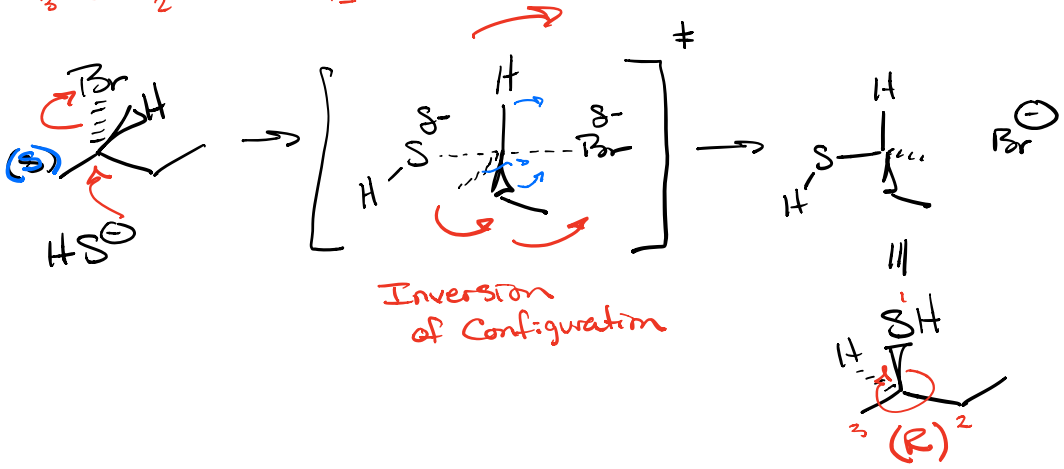


HBr pka = -3

pka = -1

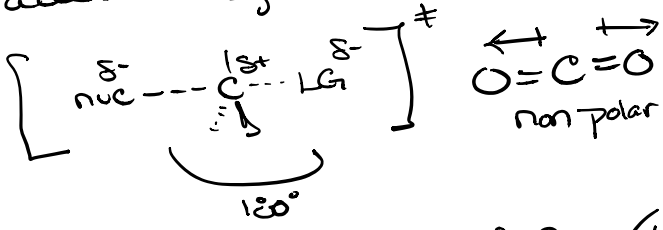
Inversion of Configuration



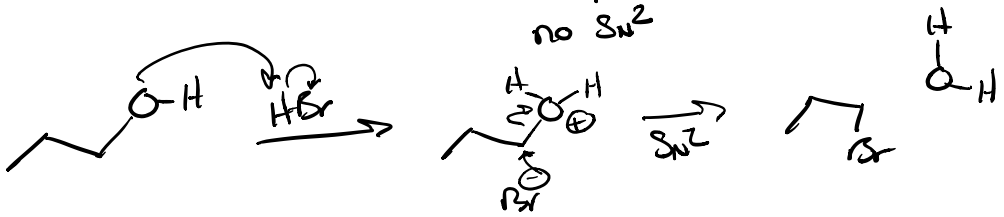


S_N2

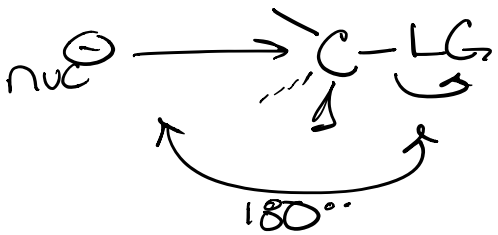
- Concerted mechanism (Single Step ≠)
- nucleophile must attack backside of substrate in σ*
- Reaction proceeds via symmetrical ≠ (non-polar)



- Sterics of Substrate increase E_A of Rxn (Hammond)
- Rate = $k[R\text{-}LG][nuc^-]$ Substrate 1° >> 2° > 3°
  - $k \propto E_A$ ⇒ Sterics on rxn
- Alcohols as LG need to be protonated or no Rxn



"Backside attack" 180° to LG



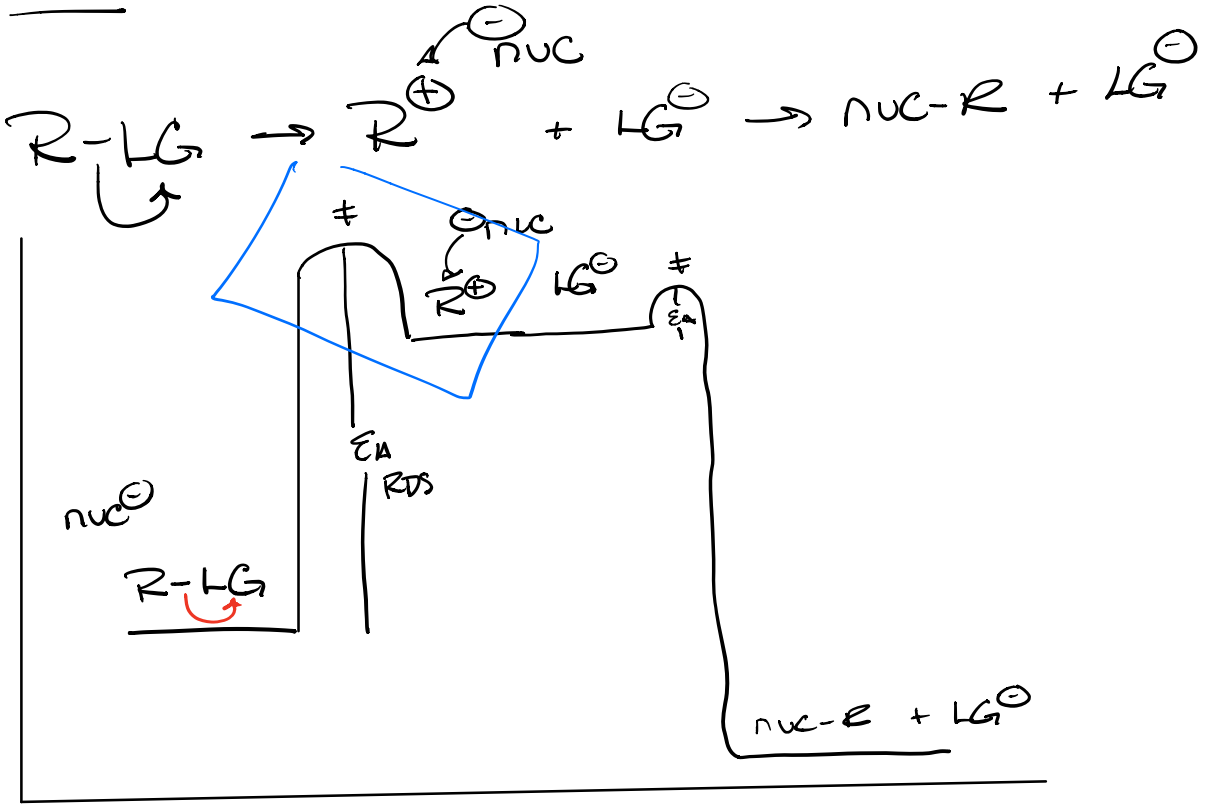
S_N1 Substitution nucleophilic 1° order Rate = k[R-LG]

S_N2 2° order Rate = k[R-LG][nuc]

E_1 Elimination Rxn 1° order Rate = k[R-LG]

E_2 Elimination 2° order Rate = k[R-LG][base]

S_N1 Substitution Nucleophilic 1st Order



$$\text{Rate} = k[\text{R-LG}]$$

Examples

Rate S_N1 $3^\circ > 2^\circ >> 1^\circ$