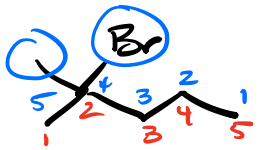
Chapter 7 - Alkyl Halide & Substitution/ Elimination Rxns

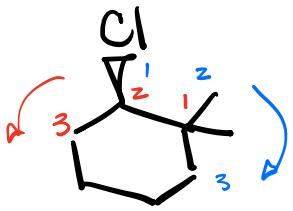
Nomenclature



→ 2, 2
4, 4

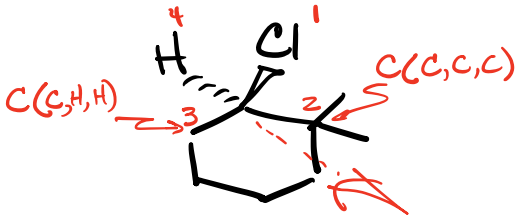
2-Bromo
2-methyl
pentane

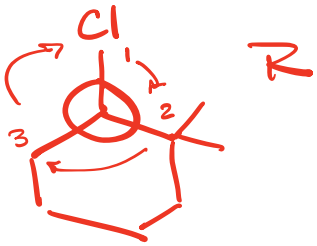
} 2-bromo-2-methylpentane



(R)
1,1-dimethyl
2-Chloro
Cyclohexane

1, 2, 2
1, II, 2

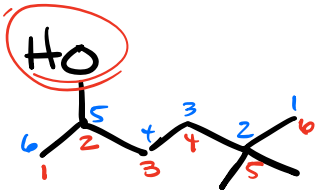




(R) - 2-Chloro-1,1-dimethylcyclohexane

Rules for Alcohols

Alcohol must be part of parent chain & have the lowest possible locant #.



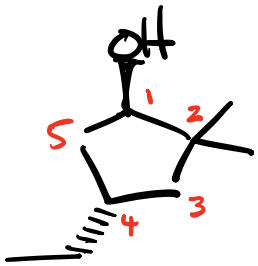
2,2,5

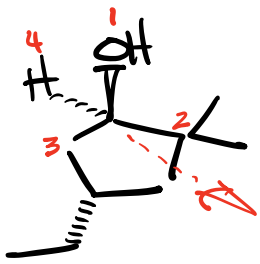
→ 2,5,5

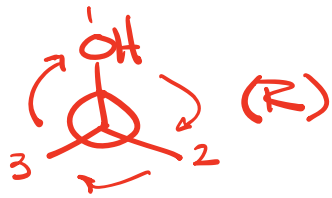
2-ol
5,5-dimethyl
hexanol

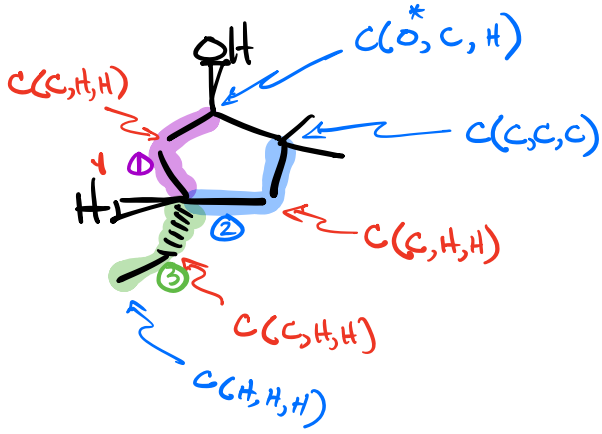
5,5-dimethylhexan-2-ol

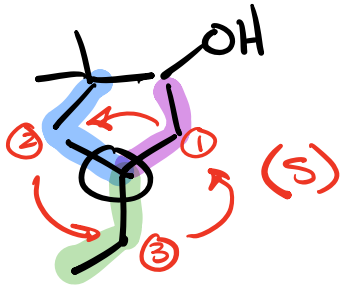
5,5-dimethyl-2-hexanol







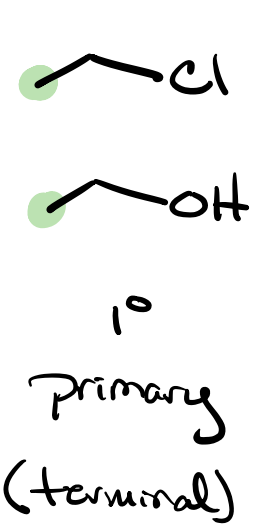




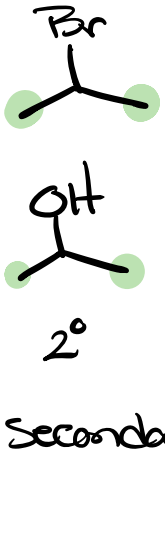
1-ol
2,2-dimethyl
4-ethyl
(1R,4S)
cyclopentane

(1R,4S)-4-ethyl-2,2-dimethylcyclopentan-1-ol

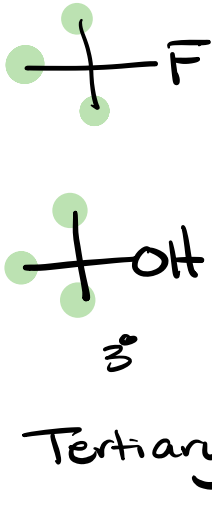
Types of positions



1°
Primary
(terminal)



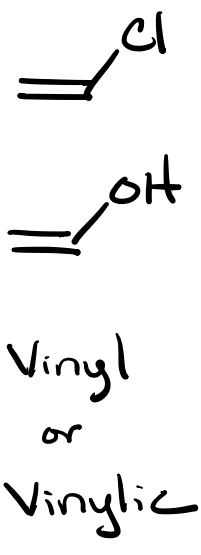
2°
Secondary



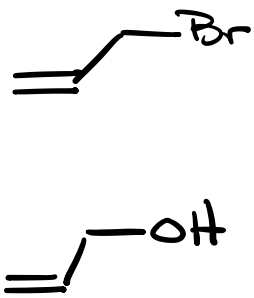
3°
Tertiary

Alkyl halide

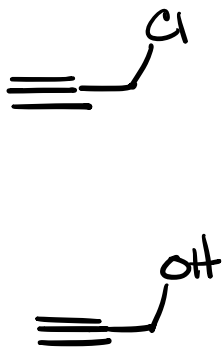
Alcohol



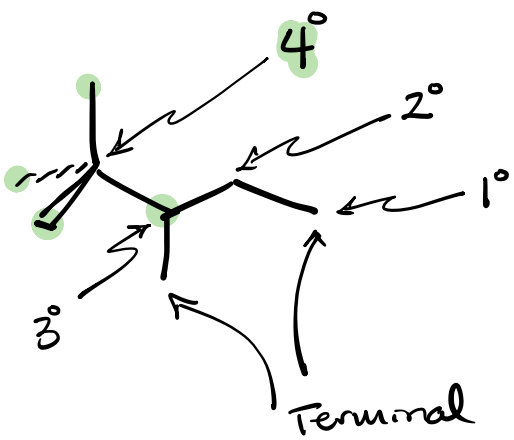
Vinyl
or
Vinylic



Allyl
or
Allylic



Propargyl
or
Propargylic



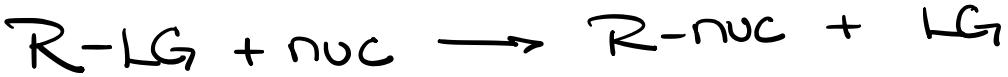
4° Quaternary

3° Tertiary

2° Secondary

1° Primary

Substitution Rxns



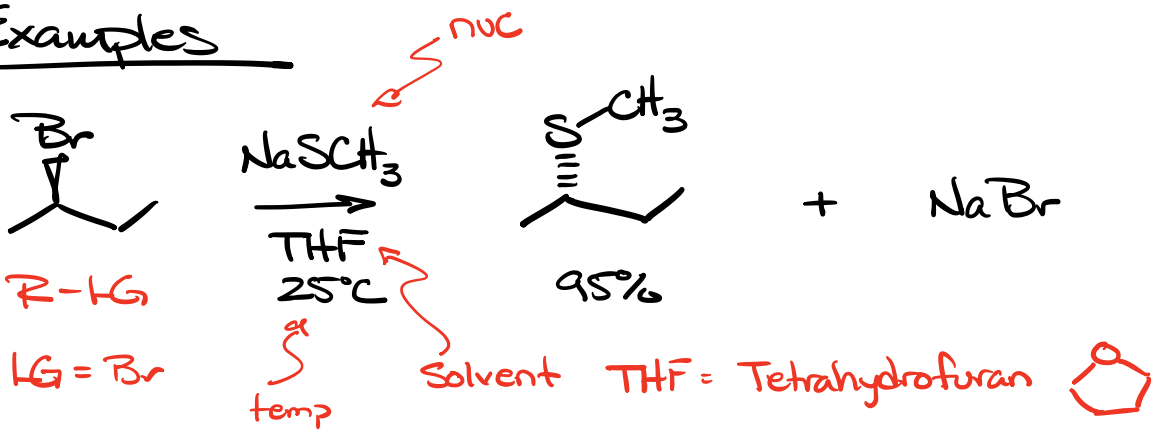
R = some molecule

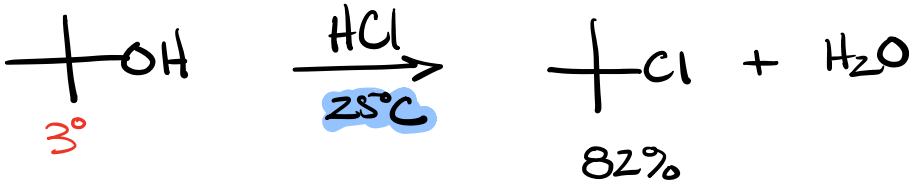
LG = Leaving group (often a halide)

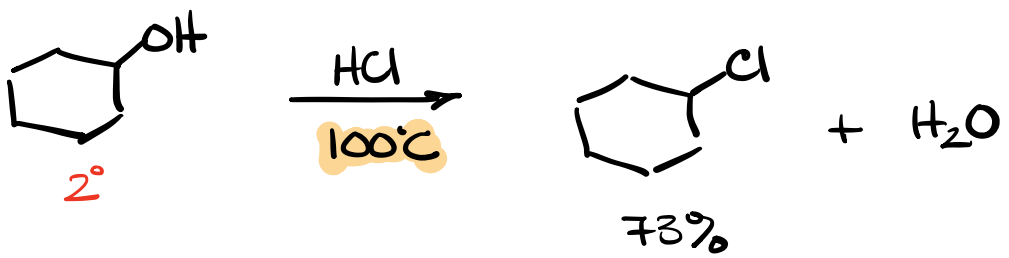
NUC = nucleophile

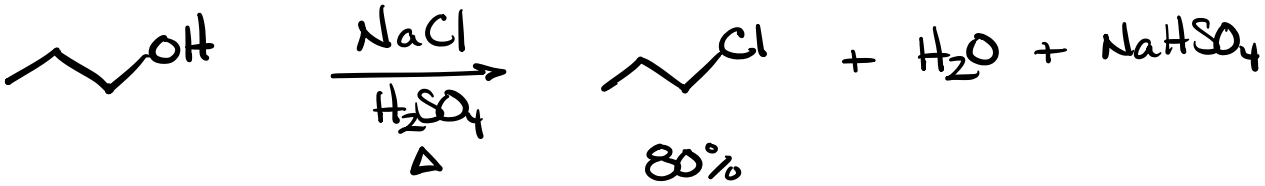
General Rate for all Substitution $3^\circ > 2^\circ > 1^\circ$ for R-LG in relation to the position of the LG.

Examples

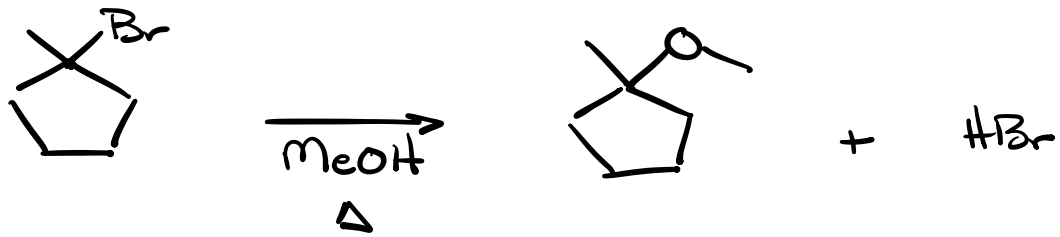


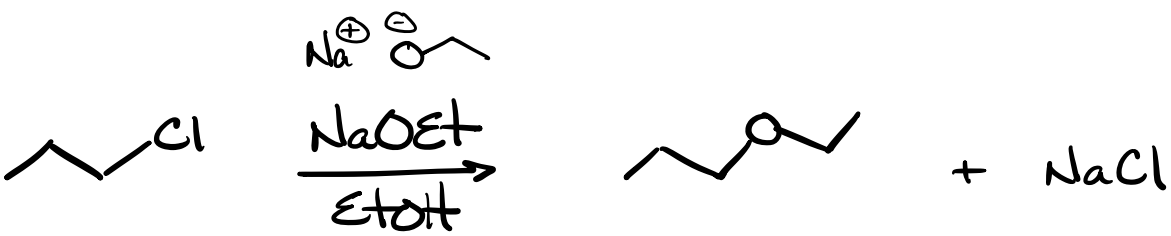


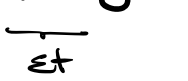




Δ = Capital Delta = Heat (usually Reflux)





EtOH = 

Two types of Substitution Rxns

S_N1 = Substitution Nucleophilic 1st Order Rate Law

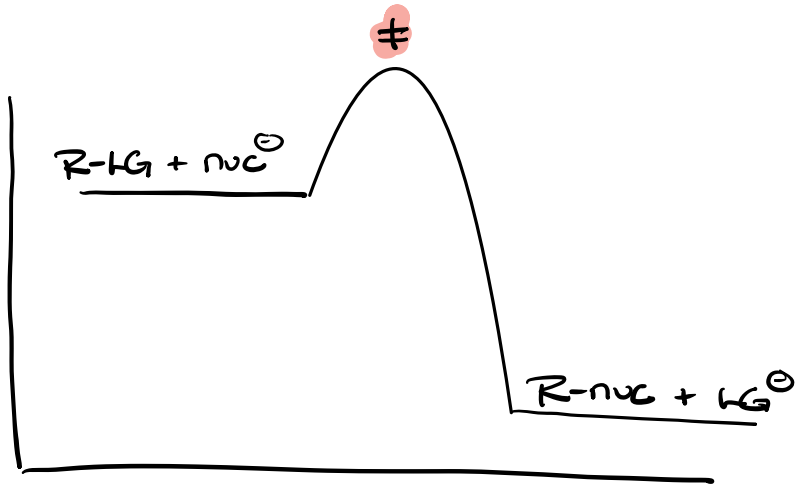
(Super / Sub)

S_N2 = Substitution Nucleophilic 2nd Order Rate Law

S_N2

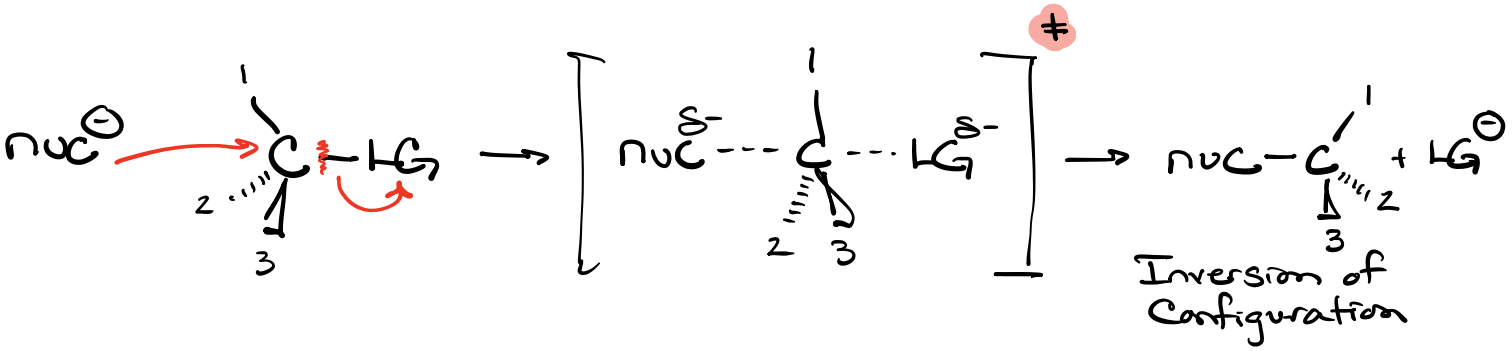
$$\text{Rate} = k[\text{R-LG}][\text{nuc}]$$

$$\text{R-LG} + \text{nuc}^{\ominus} \longrightarrow \text{R-nuc} + \text{LG}^{\ominus}$$



Single Step Rxn mechanism
Usually Exothermic

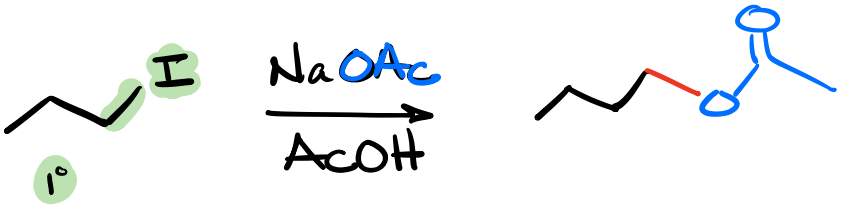
mechanism

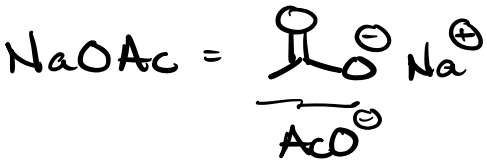


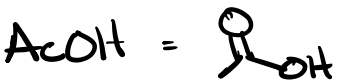
$$\text{Rate } S_N2_{\text{substrate}} = 1^{\circ} > 2^{\circ} >> 3^{\circ}$$

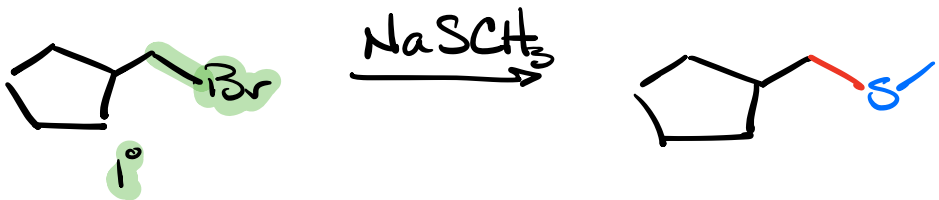
fastest ... Slowest

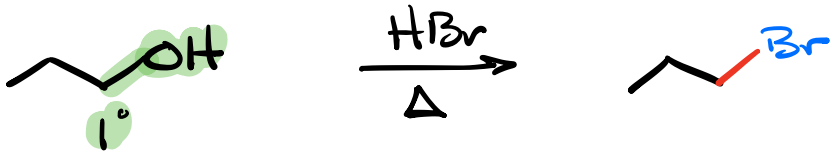
Examples of S_N2

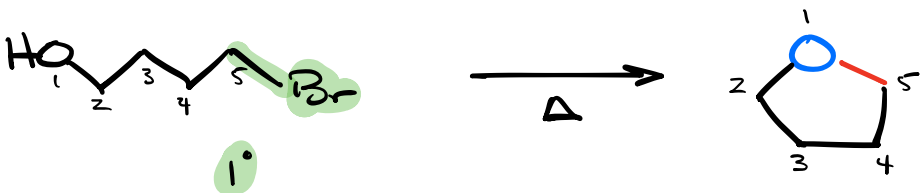




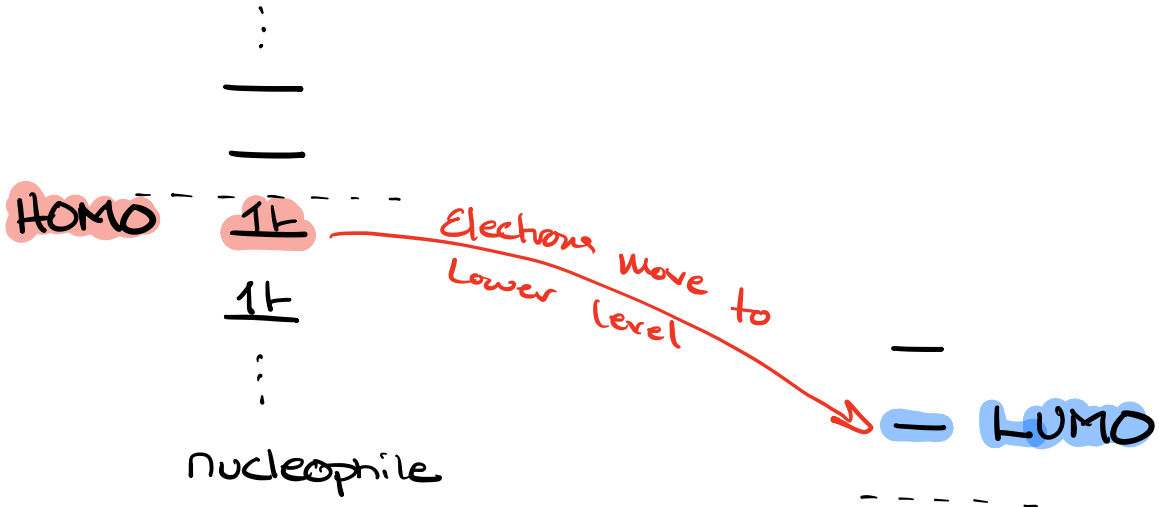








Reaction Theory



Nucleophile

Highest Occupied Molecular Orbital

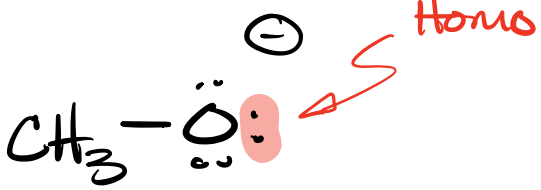
Electron Rich Nucleophile

Electrophile

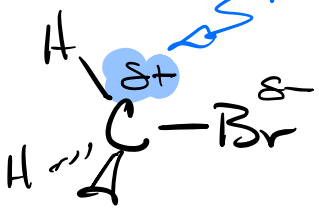
Lowest Unoccupied Molecular orbital

Electron Poor Species

Electrophile



Nucleophile



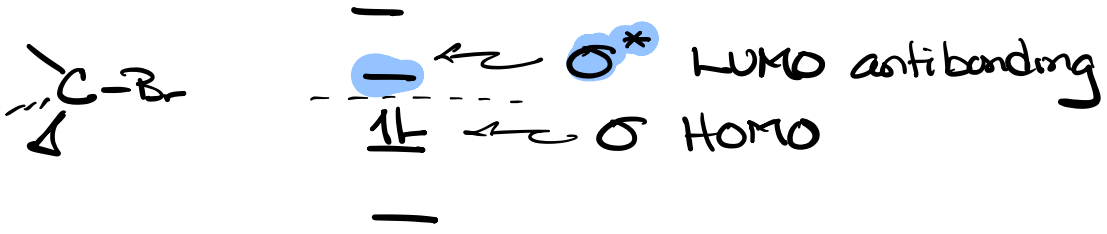
Electrophile

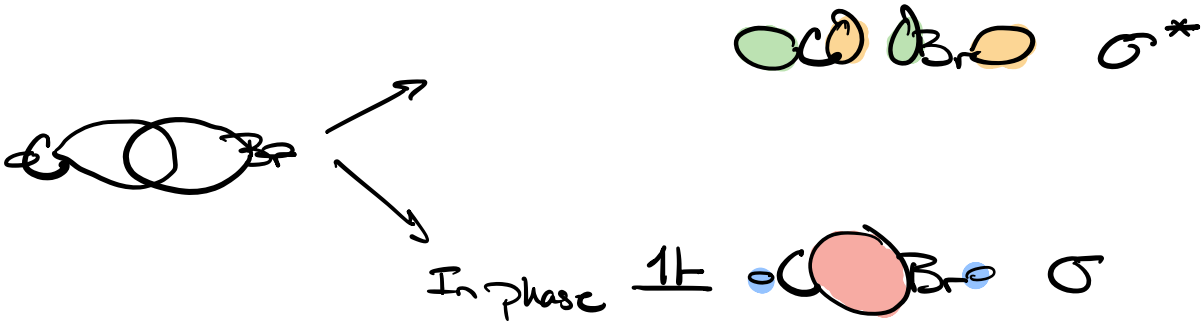
What does LUMO look like?

Two ways to look at the electrophile LUMO

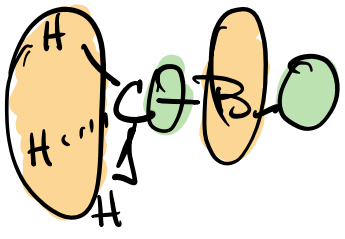
① Valence Bonding Theory (Natural Bonding Theory)

σ^* anti bonding for R-LG





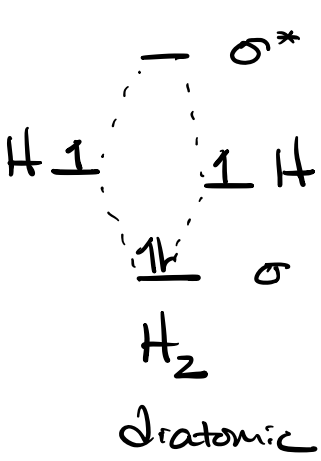
Molecular Orbital Theory

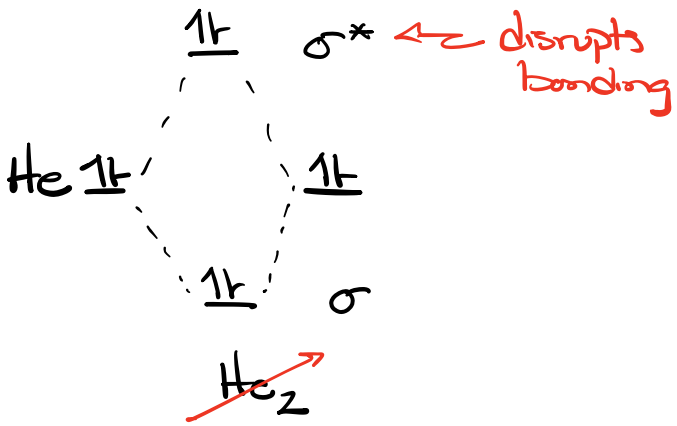


MO LUMO

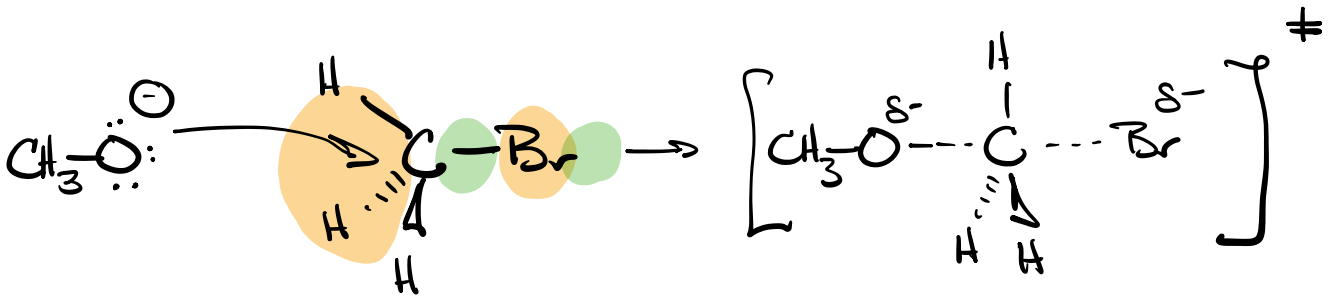
largest Coefficient

* Electrons from nucleophile must be placed into σ^* to disrupt and break the σ bond





For S_N2 Rxn both models show that the nucleophile must attack the "backside" of the carbon with the LG to reach the σ^*.



must attack "backside"