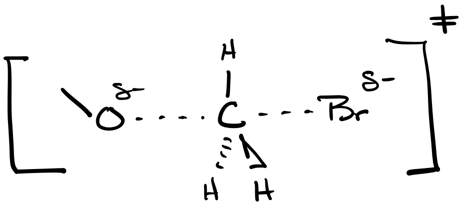
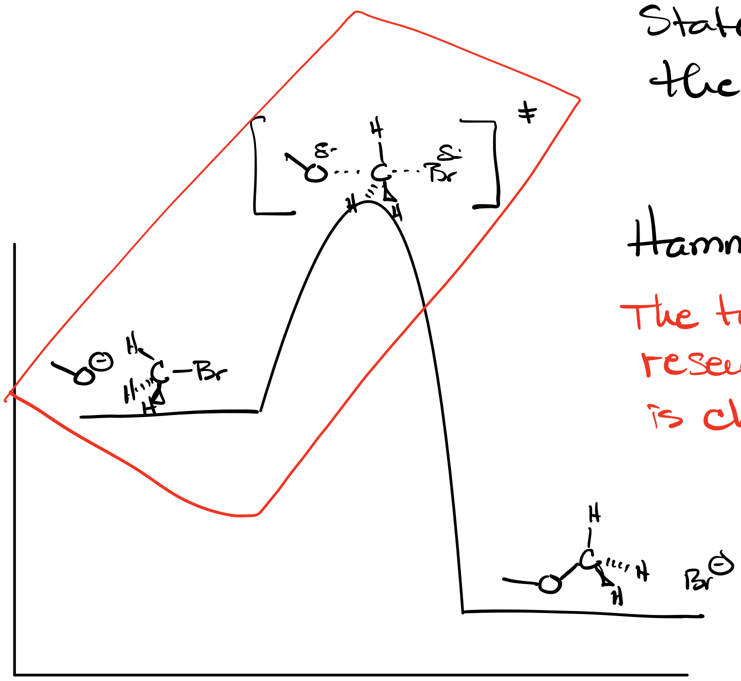
S_N2 Reaction



What does this transition state look like?

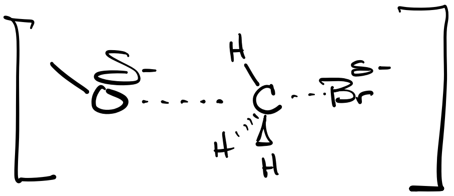
What can the transition state tell us about the rate?



Hammond Postulate

The transition state will resembol the side it is closest in energy to

⇒ ‡ is reactant Like

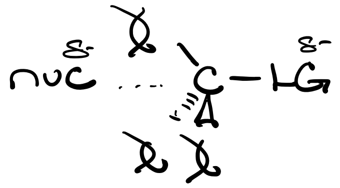


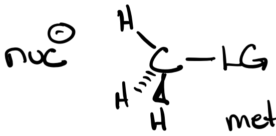
Reactant like

Early transition State

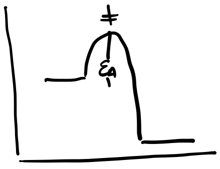
⇒ Anything that raises the energy of the reactants also raises the energy of the ‡ ⇒ Raises E_A for Rxn

Steric Impact

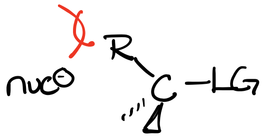




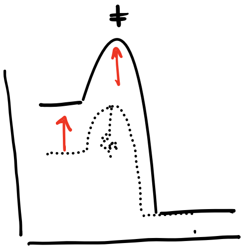
methyl substrate



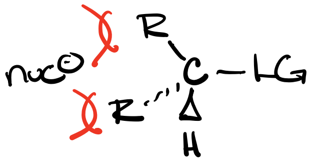
Base Line



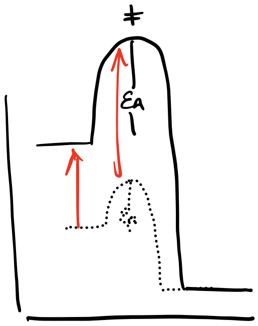
1° substrate



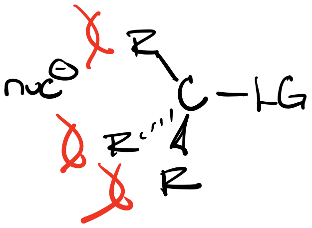
Larger E_A
slower reaction



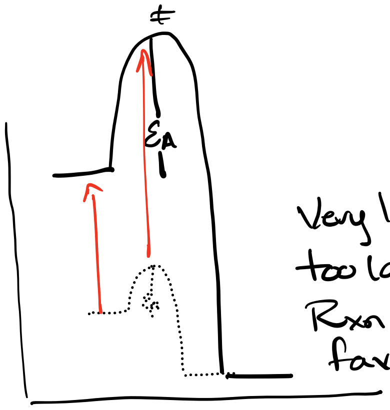
2° substrate



Larger E_A



3° substrate



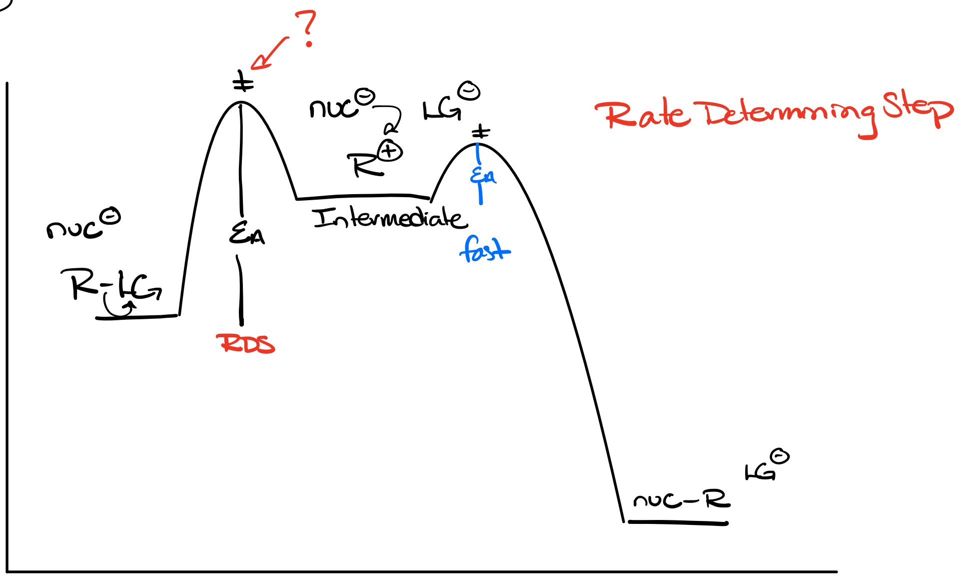
Very large E_A
too large for
Rxn to be
favorable

Rate based on Substrate

1° >> 2° > 3°

S_N1 Substitution Nucleophilic 1st Order

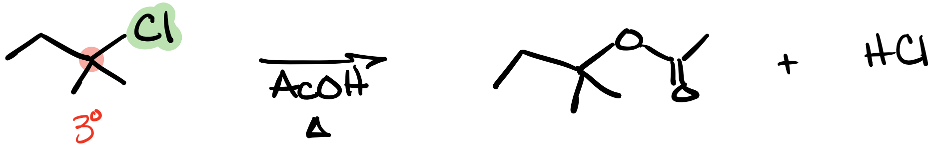
$$R\text{-}LG \longrightarrow R^{\oplus}\ {}^{\ominus}nuc \longrightarrow R\text{-}nuc + LG^{\ominus}$$

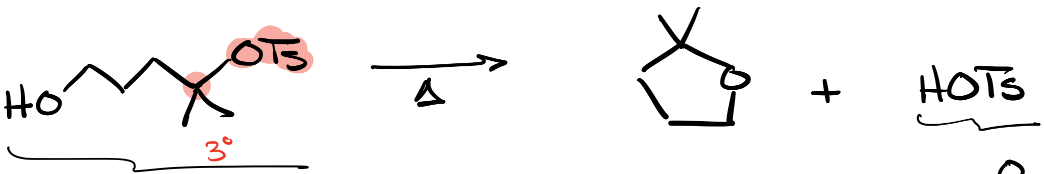


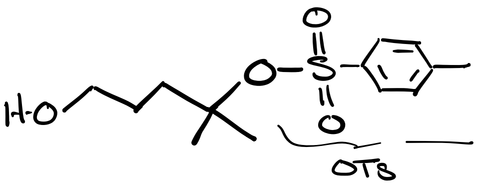
$$Rate = k[R\text{-}LG]$$

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

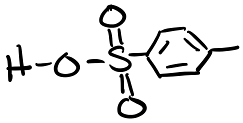
Examples



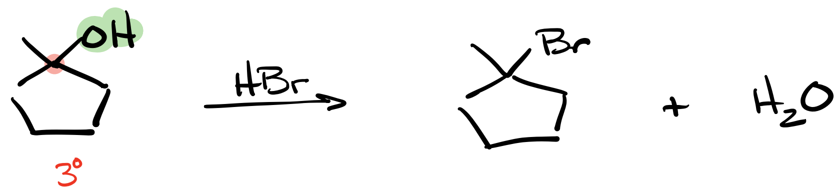




Tosylate

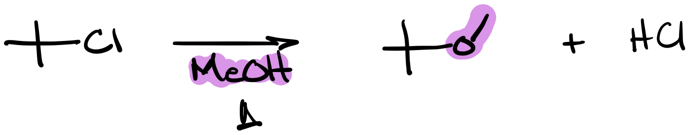


Paratolyl sulfonic acid
PTSA

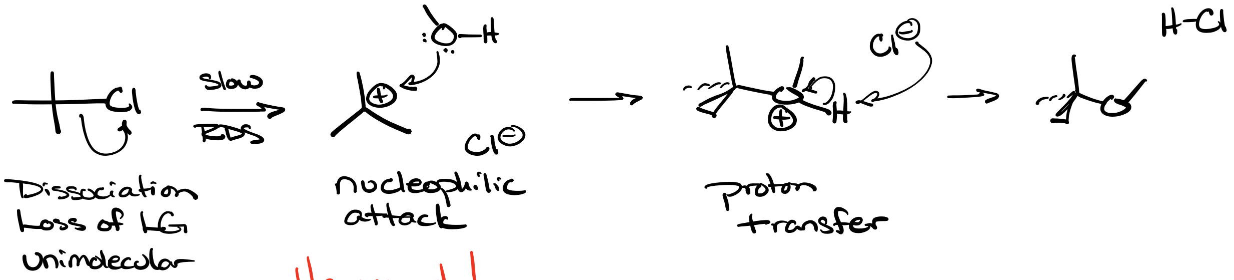


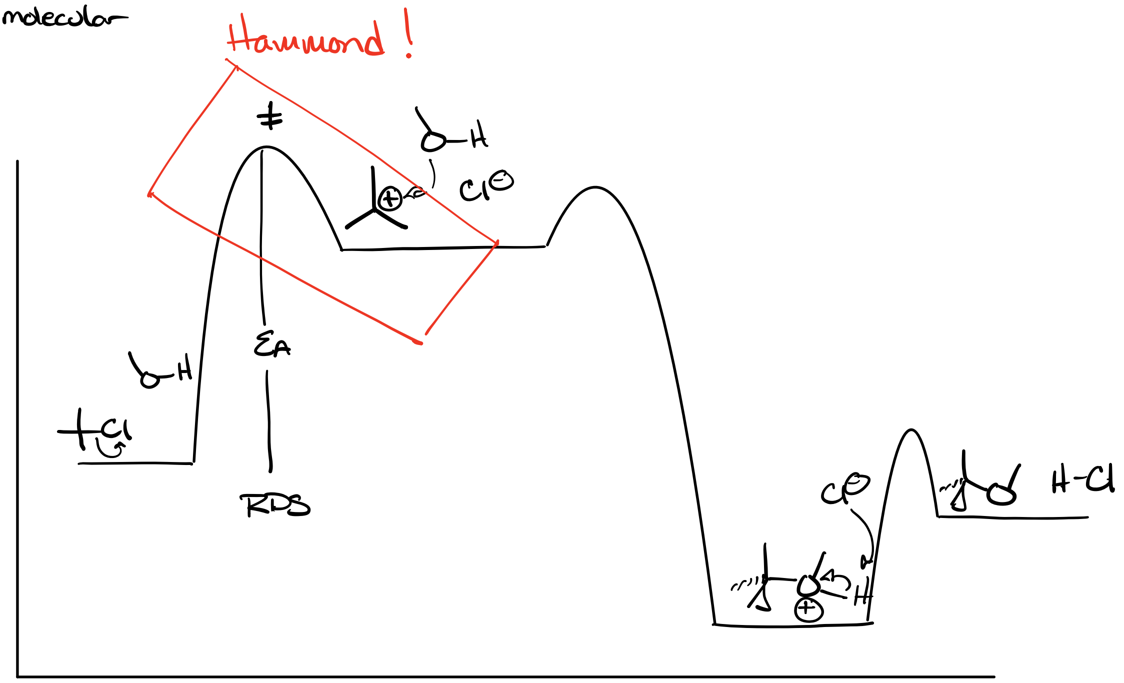
Solvolysis Replacement by Solvent (S_N1)

Example

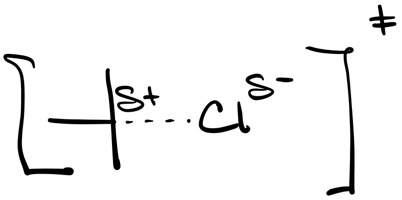


mechanism



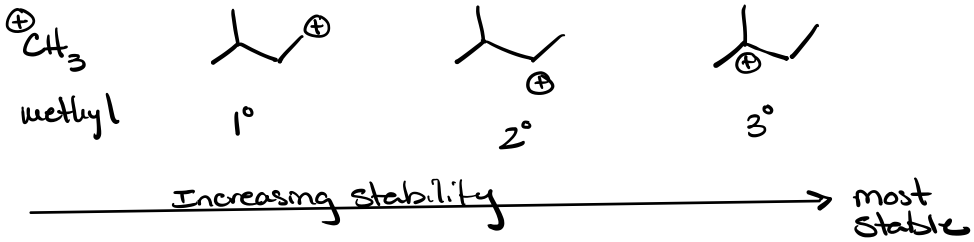


Rate Determining Step transition state

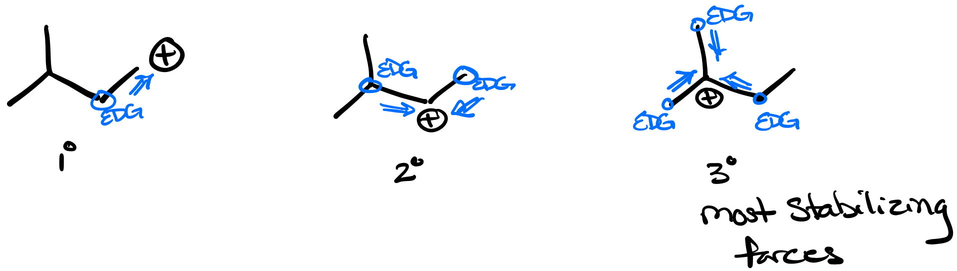


must look at C^+ stability to understand S_N1 Rxn.

Carbocation Stability

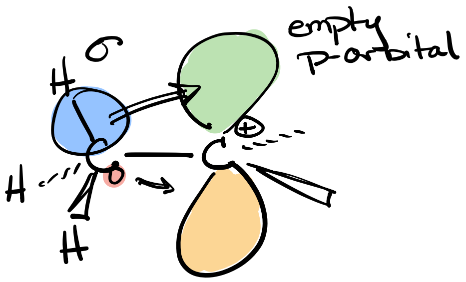


Why? ⇒ Remember that alkyl group is an EDG!



How is alkyl group EDG?

Hyperconjugation

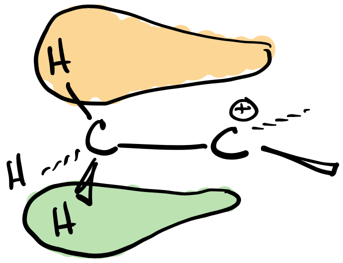


σ – p-orbital overlap

Donation

Valence Bonding Theory

Molecular Orbital Theory

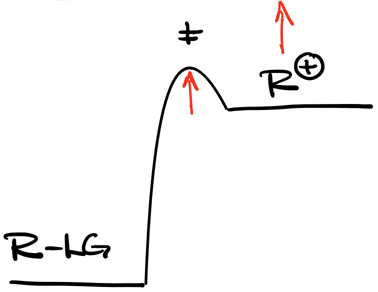


LUMO

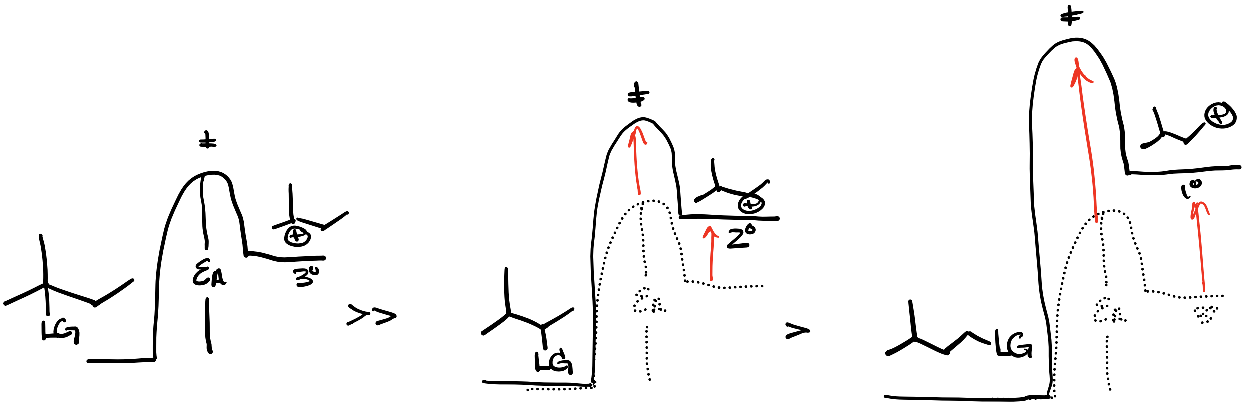
π-bond like

e^- donation to C^+ from adjacent alkyl group

Hammond



Transition State energy is linked to Carbocation Stability



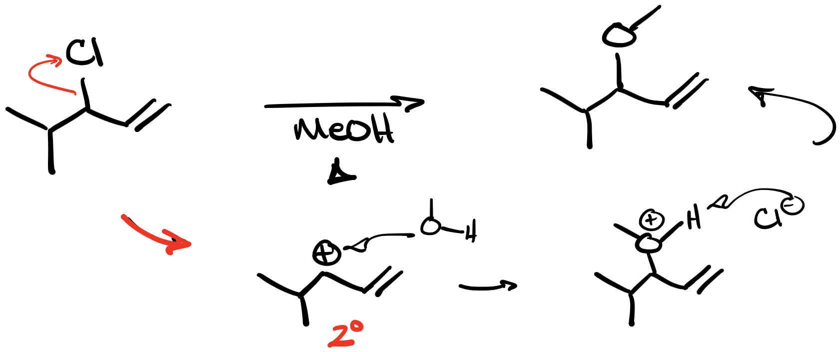
$$\text{Rate} = k[\text{R-LG}]$$

$$k \propto E_A$$

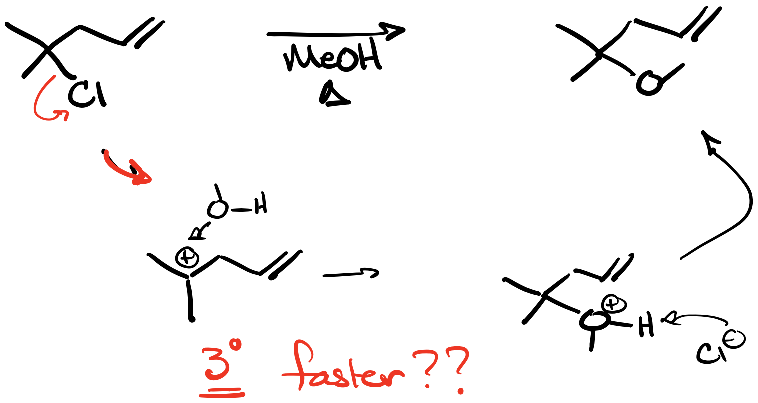
$$k = k_0 e^{-(\Delta G^{\ddagger}/RT)} = k_0 e^{-(E_A/RT)}$$

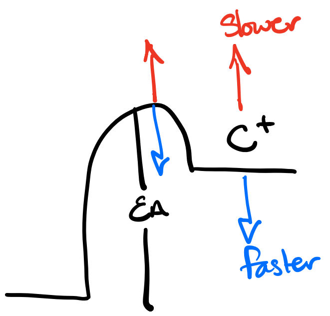
Which Rxn is faster?

S_N1

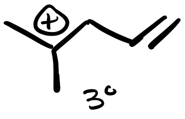


S_N1

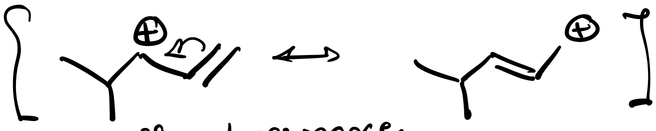




Which C+ is more stable?



No Resonance



2° w/ resonance
Allylic C+

Stability

More Important ↑

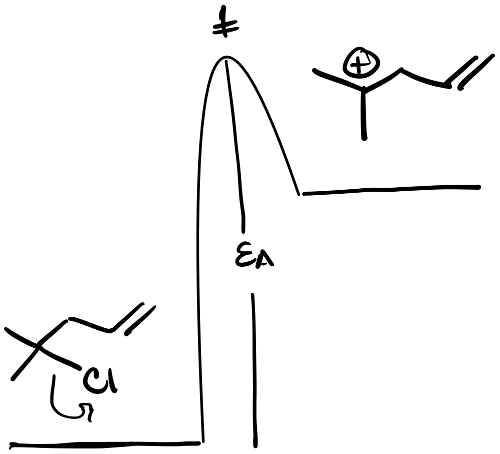
EN / Hybridization

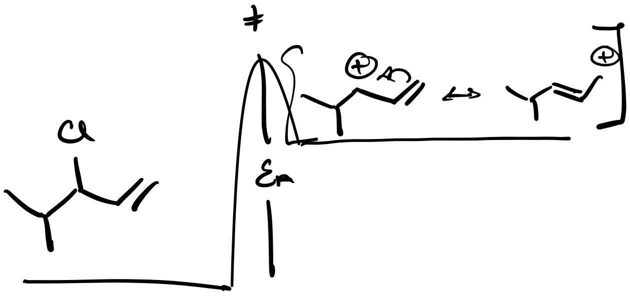
Resonance

Size

Induction

Resonce > Induction



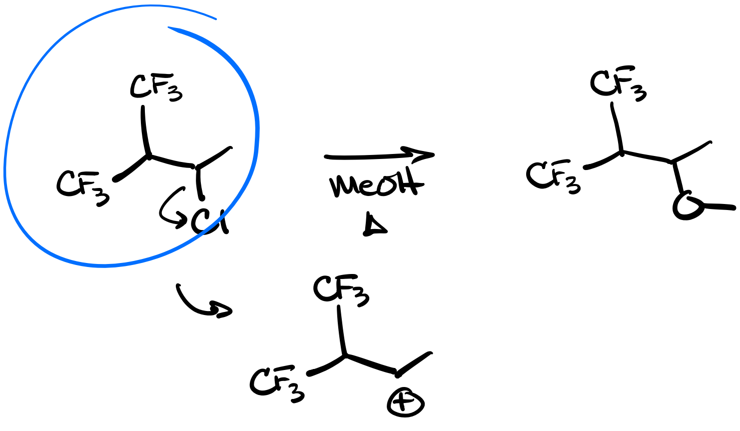


Faster Reaction!

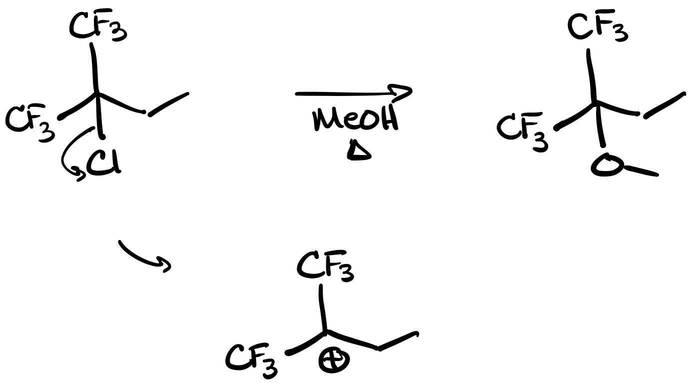
Lower E_A

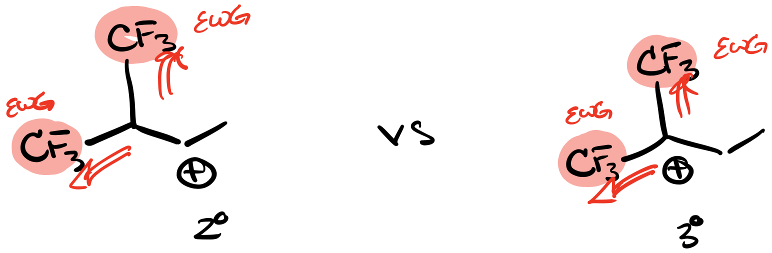
Which reaction is faster?

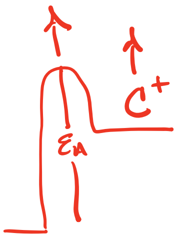
Both S_N1



Faster
Lower
E_A
more stable
C⊕







EwG farther from
C^+ ⇒ less of an effect

Lower E_A
faster Rxn

EwG Closer
less stable
Higher E_A
Slow Rxn