



Mechanism 101

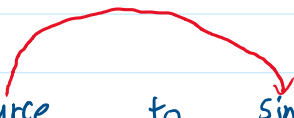
- Agenda:
- mechanism 101
 - Arrow "Pushing"
 - Nucleophiles vs. Electrophiles
 - Alkene: structures and Arrow pushing
 - Regiochemistry
 - mechanism 102
 - motive and opportunity
 - Carbocations: stability, reactivity, and geometry
 - Stereochemistry:

Pushing Arrows in Mechanisms




Arrows represent the movement of e⁻s as they "move" in a reaction.

Double Headed arrows  represent 2 e⁻s
 Single Headed arrows (Fish hooks)  represent 1 e⁻s

Arrows move from source to sink



side note:

Equilibrium arrow 	Resonance arrow 	retrosynthesis arrow 
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source : to sink

⇓
mostly π-bonds,
and Lone Pairs (LP)

⇓
Nucleophiles
↳ e⁻ rich

- ① Formal ⊖ (:Br:[⊖], :Cl:[⊖])
- ② Area of increased e⁻ density

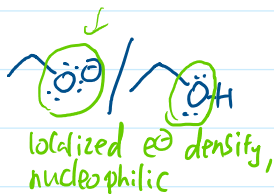
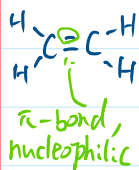
⇓
Atoms that can
accept e⁻s

⇓
Can make a new bond,
or a new L.P.

⇓
Electrophile
↳ e⁻ deficient

① Formal \ominus ($:\ddot{\text{Br}}:\ominus$, $:\ddot{\text{Cl}}:\ominus$)

② Area of localized \ominus density
(mostly π -bonds, LP)



Electrophile

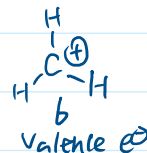
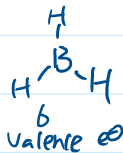
$\hookrightarrow e^-$ deficiency

① Region of low e^- density:

Partial or full \oplus



② Lack a filled valence/octet



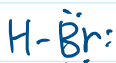
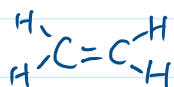
③ molecule w/ a weak bond that can break to make a stable molecule or ions.



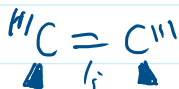
Clarifying: when an H-atom is being "moved" — functions as an electrophile (e.g. $\text{H}-\text{Cl}$) — we usually call it an acid.

when something picks up an H^+ (e.g. H_2O), a base

Pushing Arrows?



First, Alkene \rightarrow $:\text{C}=\text{C}:$ flat/planar



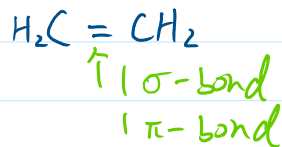
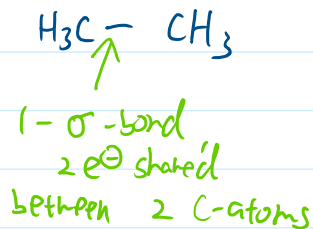
1 σ -bond, formed by the sp^2
1 π -bond, formed by the $2p$

think about the "Hot Dog and Diet Coke":

\hookrightarrow the Bun = π -bond, above and below
 \hookrightarrow the meat = σ -bond, between C-atoms

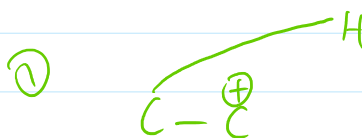
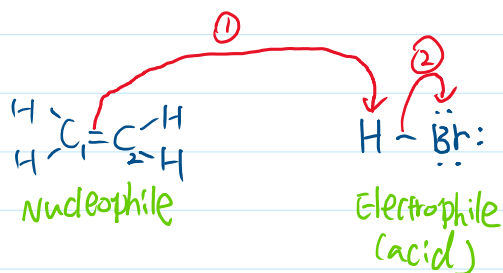
↳ the Bun = π -bond, above and below
 ↳ the meat = σ -bond, between C-atoms
 π -bonds "cover" σ -bonds, and react first.

Contrast:



↳ 4 e^- s in total
 ↳ lots of e^- density between C-atoms
 ↓
 makes alkene nucleophilic
 ↓

Alkene reacts w/ Electrophiles



① source: π -bond / Alkene \rightarrow nuc.
 sink: H-atom / Electrophile

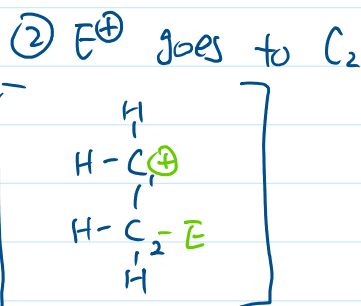
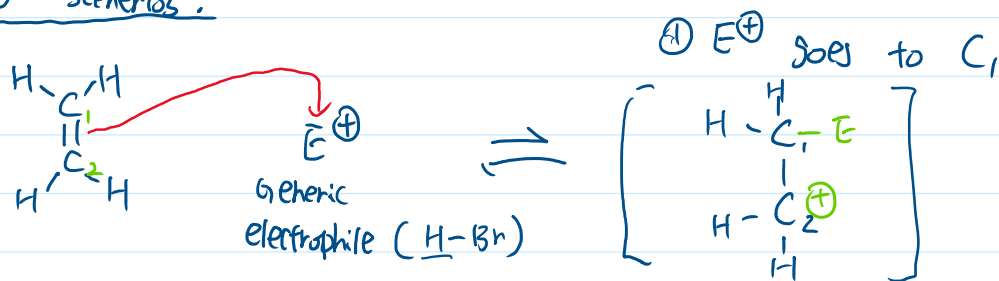
② source: σ -bond (H-Br) } we need this arrow to
 sink: Br-atom } avoid over-filling the H-atom valence

The 2 e^- s of the π -bond are shared, when the 2 e^- s attack the Electrophile (E^+), the π -bond breaks, and forms a new σ -bond and creates a Carbocation

The new σ -bond can be between either Carbon (C_1 , or C_2)
 The Carbocation forms on the other Carbon.

Two Scenarios:

Two Scenarios:



So where does incoming E^+ go?

↳ which C-atom get the new σ -bond?

↳ which C-atom get the " \oplus "

We call the above analysis Regiochemistry

Regio = site where rxn takes place

↳ which isomer is favored

↳ where new bond and carbocation are located

Regiochemistry reflects the reactivity difference.

In above example, ① and ② equally likely to form

↳ same energy for reaction pathway

↳ same energy intermediate

What about different molecules/substrates?

↳ we must analyze difference in "sites" reactivity

Two Factors Influence Reactivity

- opportunity (kinetics)

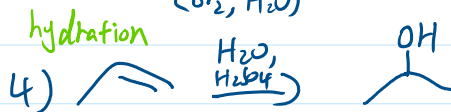
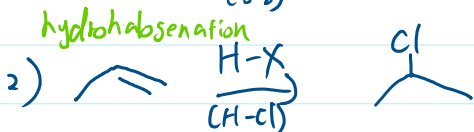
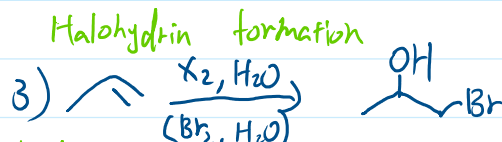
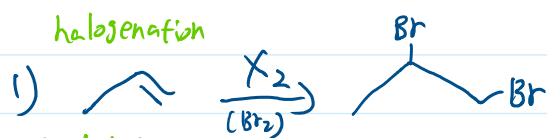
- motive (thermodynamics)

↳ lowest energy pathway, more stable intermediate, leads to prod. faster than higher E. intermediate

— motive (thermodynamics)

↳ more stable p.d.t. are lower in energy

For the four rxns that create intermediate w/ Carbocation Character:



The major p.d.t. results from the more stable Carbocation

↳ the Carbon that can better stabilize "⊕"

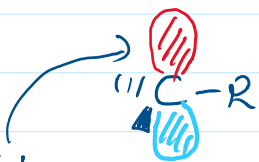
Recall: Carbocation

— sp² hybridized

— Planar / flat

— Empty 2p orbital

— Unstable intermediate



6 valence e⁻s

want 2 more e⁻s
↓
Electrophile
↓
very Electronegative

What stabilizes the Carbocation? 2 main factors:

↳ Hyperconjugation: adjacent σ-bonds overlap w/

Empty 2p orbital → delocalizes ⊕

"adjacent?"

σ_{C-H} overlap w/ empty 2p orbital

↳ Favorable, stabilizing



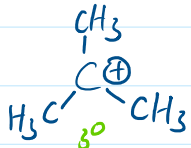
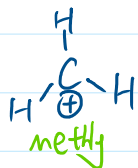
How many bonds hyperconjugate w/ empty 2p?

6

↳ Inductive Effect:

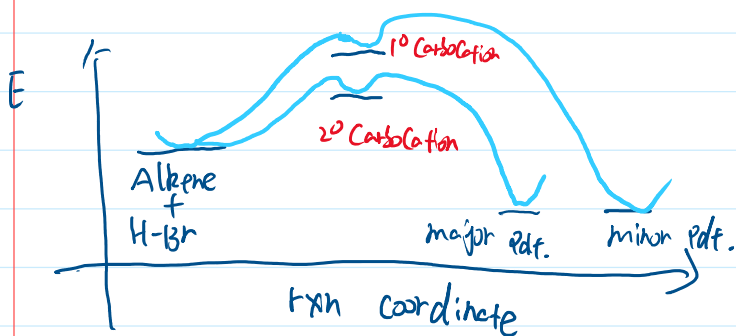
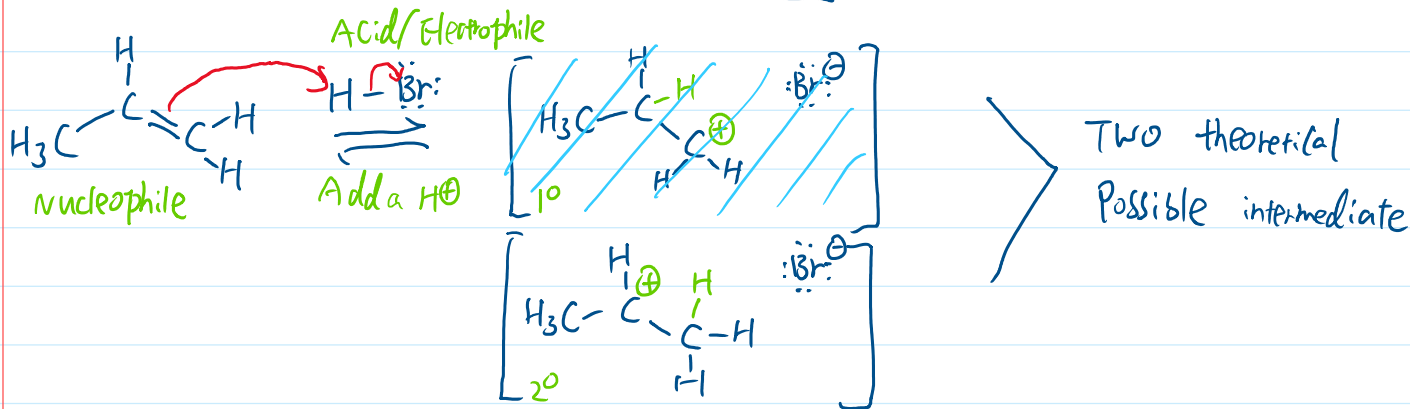
↳ Adjacent E.N. elements "take" e⁻ density from nearby less E.N. through σ-bonds

→ Major E.N. elements take e density from nearby less E.N. through σ -bonds
 ↳ favored, stabilizing



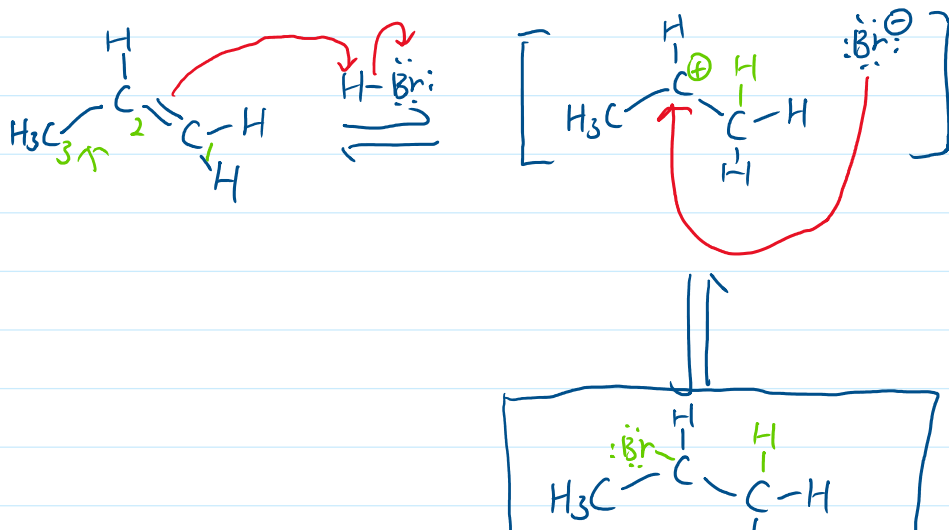
Inductive effect stabilizes both, while hyperconjugation only stabilizes 3° carbocation.

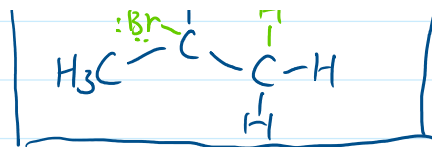
More substituted carbocations are more stable.



Intermediates: high energy species formed between two rxn steps.

Real mech!





which C-atom of the alkene does H of HX add to?

↳

The C-atom of alkene w/ most H-atoms

↳ It adds to the C-atom to make more stable Carbon Cation

↳ Markovnikov's Rule \Rightarrow Regiochemistry