

MTW 10.10.24

①

Mechanism 101

{ Arrow pushing
Nucleophiles vs Electrophiles
Alkene: structures and arrow pushing

Pushing arrows in mechanism

arrows represent the movement of e^- s as they "move" in a reaction.

Double headed arrows " \curvearrowright " represent $2e^-$ s

single headed arrows " \curvearrowleft " represent $1e^-$

Arrows move from source to sink

side notes:

{ Equilibrium arrow " \rightleftharpoons "
resonance arrow " \longleftrightarrow "
retrosynthesis arrow " \Rightarrow "

Source
 \Downarrow
mostly π bonds,
lone pairs (LP)

\Downarrow
Nucleophiles
 e^- rich

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

② Area of localized e^- density

to Sink
 \Downarrow

Atoms that can accept e^- s

\Downarrow
Can make a new bond or a
new L.P.

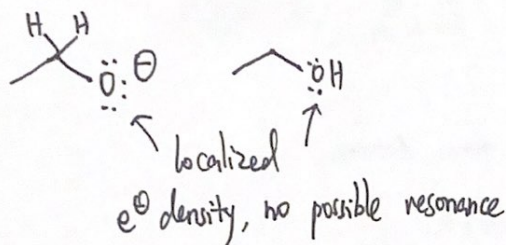
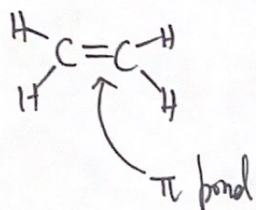
\Downarrow
Electrophile, e^- deficient

Source
Nucleophile

to

sink:
Electrophile.

②

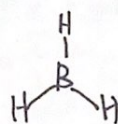
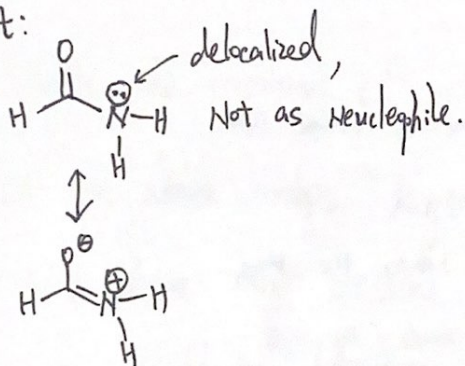


① region of low e^- density
partial or full " \oplus "

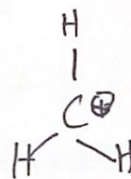


② lack a filled valence / octet

Contrast:



B: 6 valence e^- s



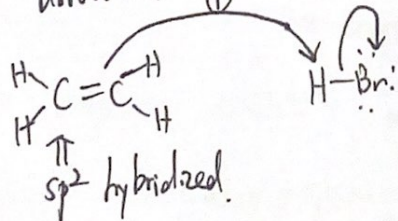
C: 6 valence e^- s

③ molecules with a weak bond
that can break to make stable
molecules or ions.

eg. Br-Br Cl-Cl I-I

pushing

arrows:



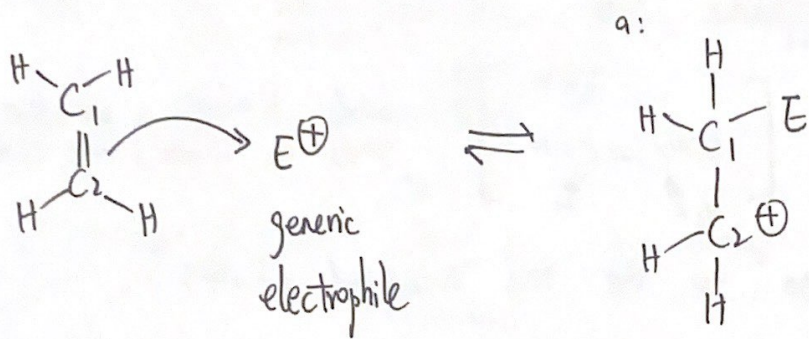
1 σ bond, 1 π bond
4 e^- btw 2 C-atoms
lots of e^- density,
Nucleophile!

① source: π bond
sink: H^+ , electrophile

② source: σ bond btw H and Br atom
sink: Br atom

Two scenarios:

③



where does the incoming E^+ go? $\left\{ \begin{array}{l} \text{which C makes } \sigma \text{ bond?} \\ \text{which C gets the carbocation?} \end{array} \right.$

We call the above analysis "Regiochemistry".

Regio = site where rxn occurs.

Regiochemistry reflects difference in reactivity of two sites (C_1 vs C_2)

In above example, ① and ② equally likely to form.

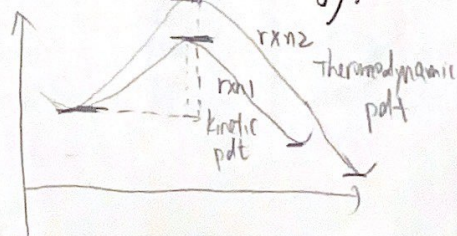
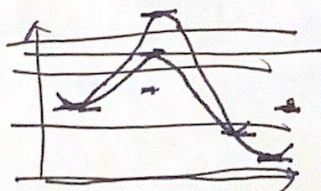
↳ same energy for reaction pathway

↳ same energy ~~for~~ intermediate.

Two factors influence reactivity

Kinetics: low energy pathway, more stable intermediate, lead to products "faster"

Thermodynamics: more stable products are lower in energy.

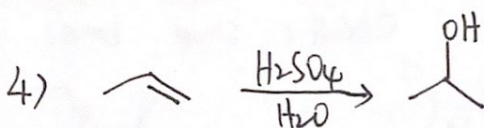
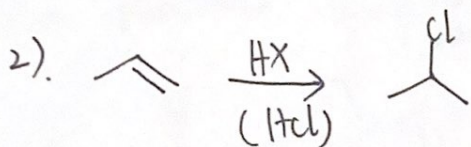
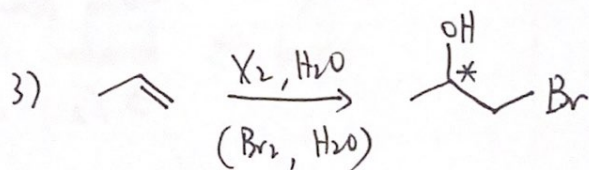
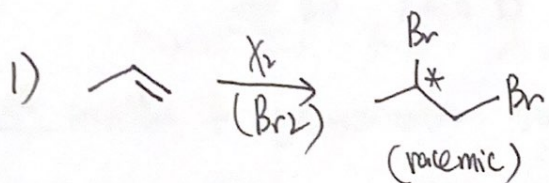


(do ③ first)

For the four reactions that create intermediates

④

with carbocation character:



The major product results from reaction with the more stable carbocation \rightarrow the carbon that can best stabilize the \oplus charge.
 \downarrow
lower in energy

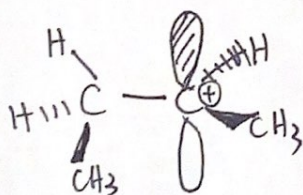
Recall carbocation:



sp^2 hybridized, planar flat,
empty p orbital, 6 valence e^- ,
electrophile (want 2 more e^-)
 \downarrow
very electronegative.

what stabilize carbocation?

① hyperconjugation: adjacent σ -bonds overlap with empty $2p$ orbital



How many bonds hyperconjugate with empty $2p$ orbital? 6

① Inductive effect :

(5)

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

More substituted carbocations are more stable.

