

Introduction to Alkenes and their Reactivity

1

From last time: Rxns of Alkanes

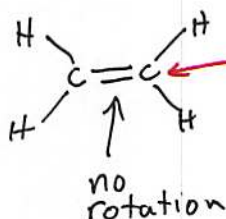
① Combustion

② Radical halogenation (Cl or Br) - know complete mechanism!

Alkenes \Rightarrow Unsaturated hydrocarbons

C_2H_4 :

Flat.



1 σ bond
1 π bond

Vinyl Carbon

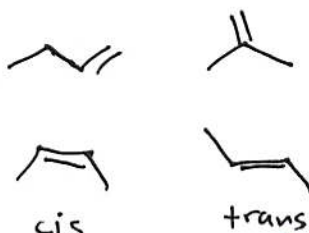
$C_3H_6 \Rightarrow$

allyl carbon (1°)

Constitutional Isomers



$C_4H_8 \Rightarrow$ 4 alkene const. isomers

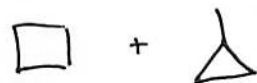


cis

trans

Geometric isomers
(Diastereomers)

2 alkane const. isomers



+

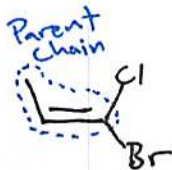


cis & trans refers to parent carbon chain

ex:



cis

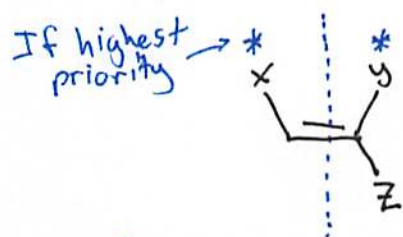


No cis/trans from Parent chain.

\Rightarrow Adopt E/Z system

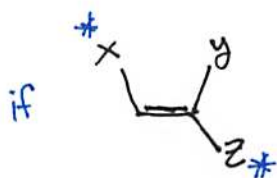
E/Z system - Based on Cahn-Ingold-Prelog sequence (2)

- Assign priority
- Refers to the relative position of the highest priority groups on the alkene



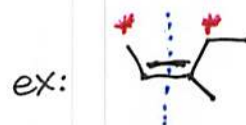
name starts with: (Z)-

~~zusammen~~
"ZU sammen"
together

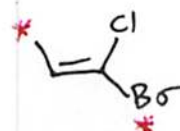


(E)-

"entgegen"
opposite

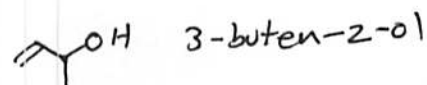
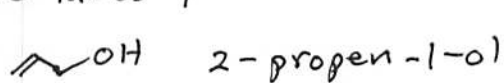


(Z)-3-methylpent-2-ene
"methyl-2-pentene"



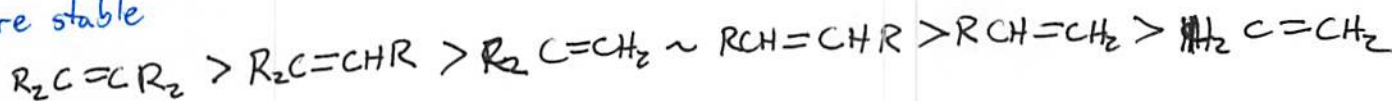
(E)-1-bromo-1-chloropropene

Note: -ol takes precedence over -ene



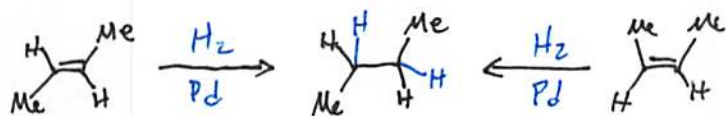
Alkene stability: Saytzeff Orientation

more stable



When comparing cis/trans, trans is more stable

-measure the ΔH° for the hydrogenation



$\Delta H^\circ = -27.7$
kcal/mol

$\Delta H^\circ = -28.7$ kcal/mol

more exothermic

-less stable ene

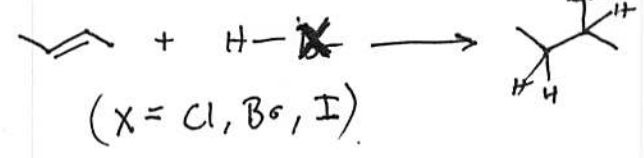
-higher E starting point.

Polar Reactions of Alkenes

works with H⁺!

Example:

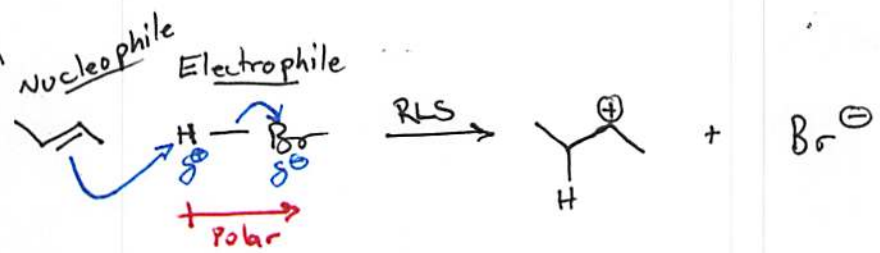
Net Rxn



An "addition" rxn
(H-Br "adds" across the double bond)

Mechanism

step ①

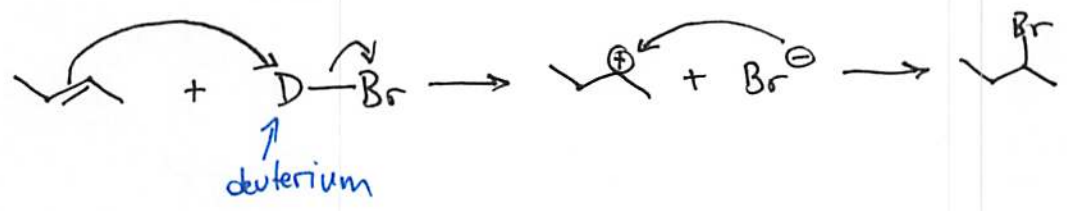


nucleophile attacks the e⁻-poor species

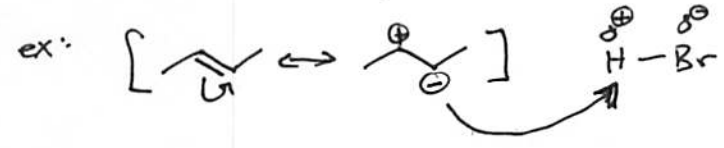
Step ②



Note: Another way to write the mechanism is in a single line



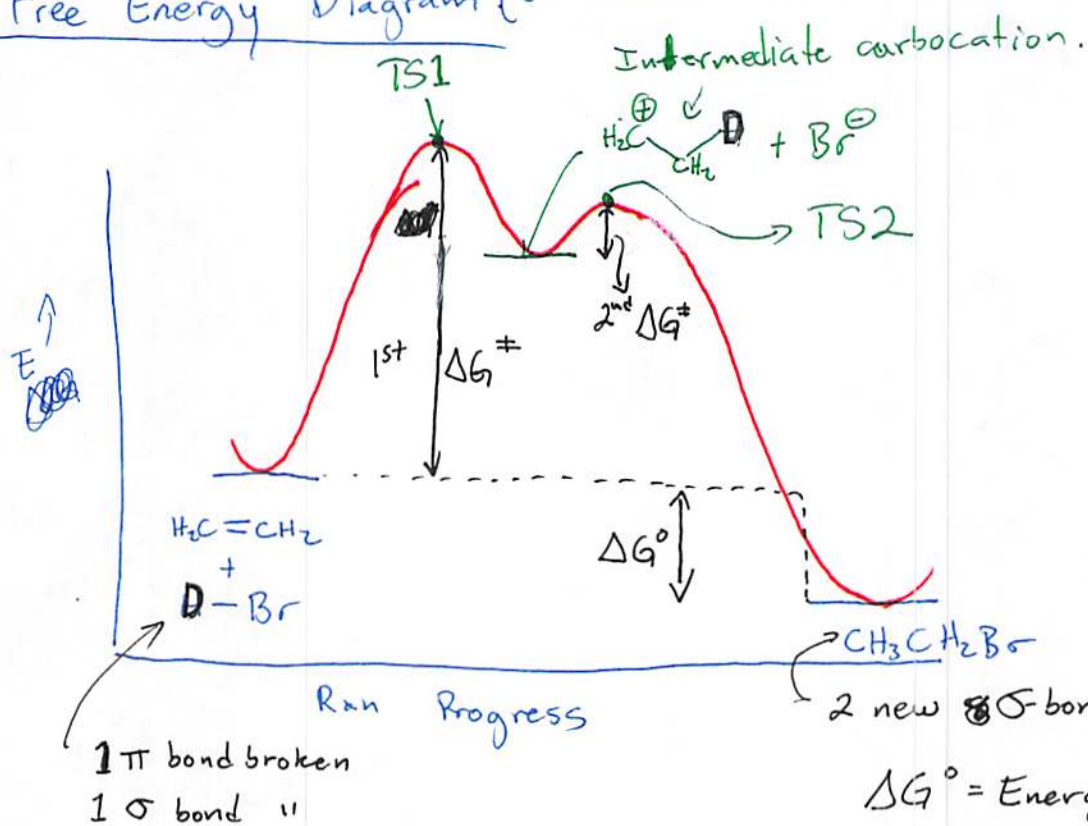
Resonance can "help" explain reactivity



-visualize nucleophilic attack.

(4)

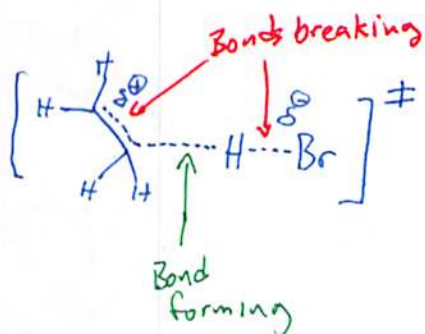
Free Energy Diagram (or Reaction Coordinate)



ΔG° = Energy of rxn.

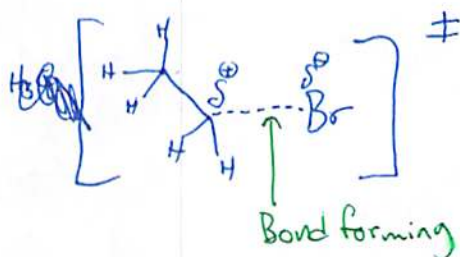
ΔG^\ddagger = Energy of activation
(aka. E_a)

TS1 = Transition State 1



D-Br?

TS2 = Transition State 2



How About:



2 possible products.
which one do we get?

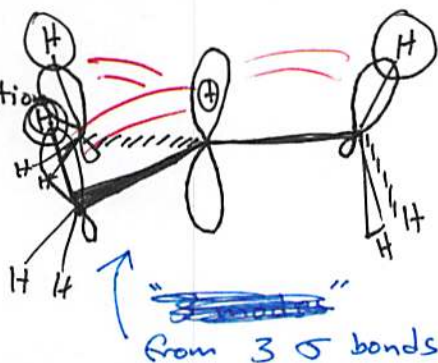
Consider the RLS



Which carbocation is more stable?

Carbocation stability: $3^\circ > 2^\circ > 1^\circ > \text{CH}_3^+$
why? Hyperconjugation.

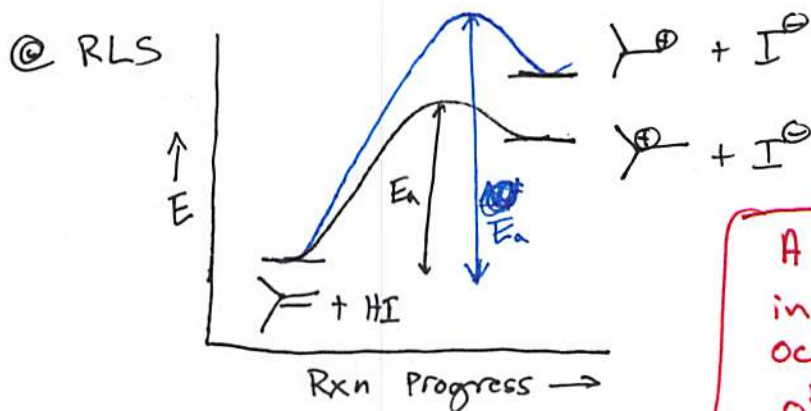
consider a 3° carbocation



Through-space e^- density donation from σ bonds to empty p-orbital



CH_3^+ is not stabilized by hyperconjugation.



A regioselective reaction is one in which bond-making or breaking occurs preferentially over all other possibilities.

