Reactions Of Alkenes Via Protonation

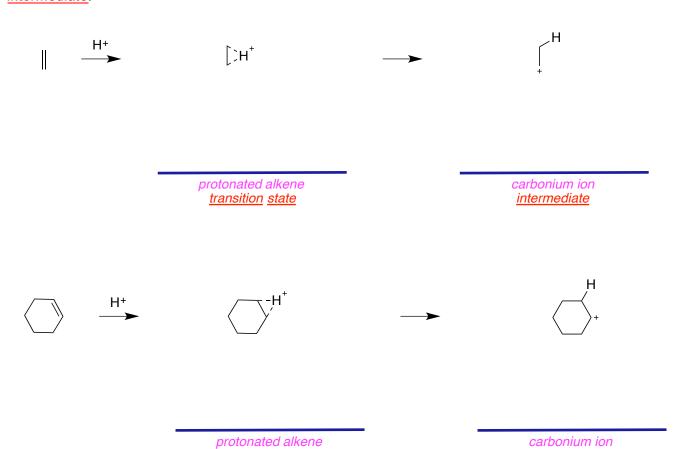
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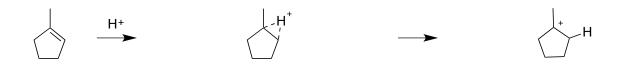
A. Introduction

B. Protonation Of Alkenes

Generation Of Carbocations Via Protonation

simplest sp^3 hybridized carbon and a sp^2 transition intermediate.





transition state

intermediate

 sp^3 hybridized carbon and sp^2

A Molecular Orbital Picture Of Alkene Protonation

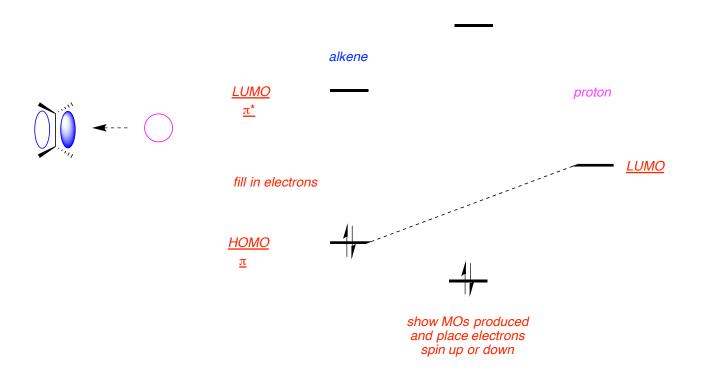
<u>more</u>

does not

<u>LUMO</u>

<u>LUMO</u>

<u>НОМО</u>

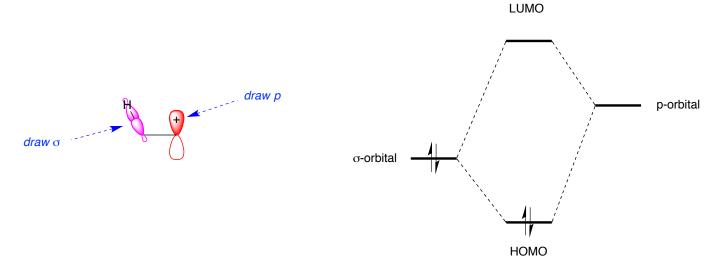


stabilizing.

C. Carbocation Stabilities

alternative theories to explain bonding in general. (LUMO)

methyl (HOMO



2 elections into the interaction, whereas the p-orbital bears 2_

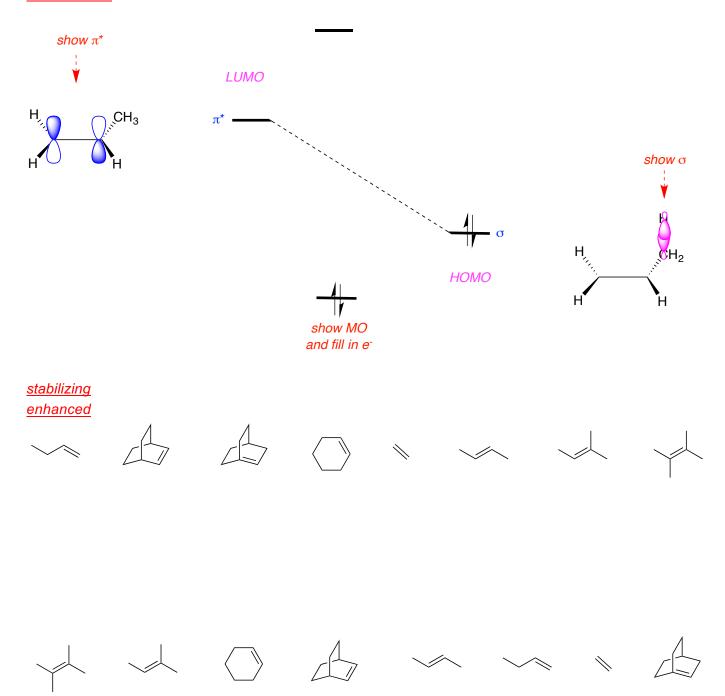
are in the same plane.

cannot achieve significant orbital overlap.

- 2 adjacent methyl groups, and therefore 2 more
- 2 adjacent methyl groups, and therefore 3 more

D. Alkenes Stabilities

increase with



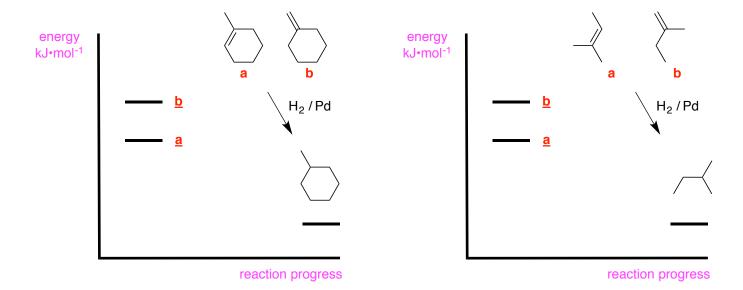
most stable least stable

Heats Of Hydrogenation

Energy is *liberated*

<u>lower</u> <u>can</u>

hydrogenation.



the right it is **b**.

E. Acid-mediated Alkene Isomerization

 $\underline{\emph{is}}$ an isomer of the first. thermodynamics.

Ph
$$K = \geq 1$$

Carbocation alkene

It is <u>conceivable</u>

F. Carbocation Rearrangements

Hydride Shifts

<u>hydride</u>

hydride anion.

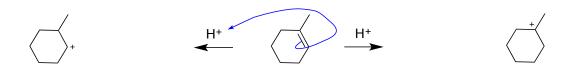
<u>true</u>

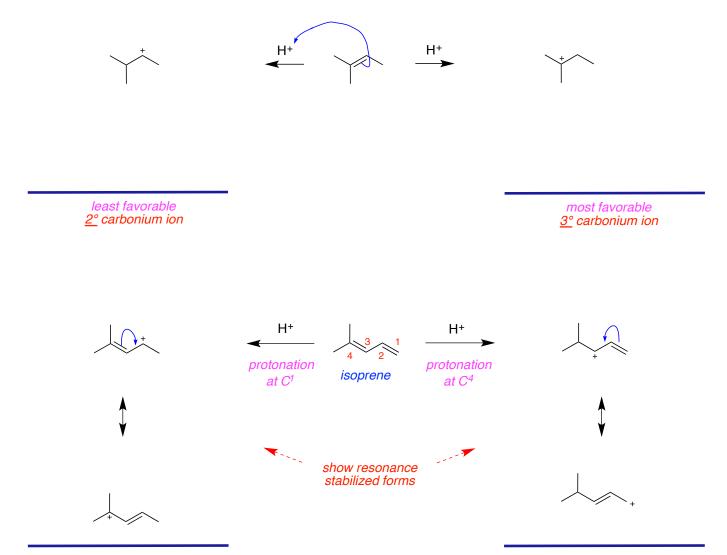
1,2-hydride



<u>may</u> <u>most</u>

intermediates





most favorable <u>3°</u> carbonium ion

least favorable
1° carbonium ion

gives does not.

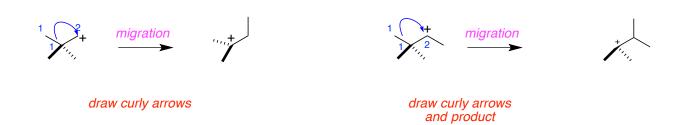
<u>small</u> <u>equals</u>

less than one.

Alkyl Shifts

<u>opposite</u> <u>more</u> secondary / tertiary <u>tertiary</u>

<u>1,2</u>-

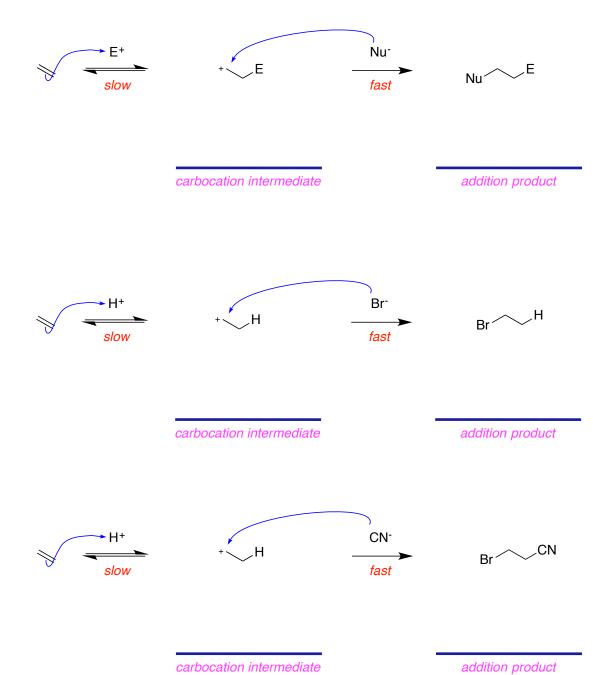


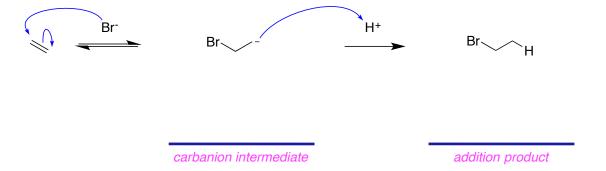


alkyl shift most able less stable than Et⁺.

G. Electrophilic Addition Mechanisms

<u>slow</u>

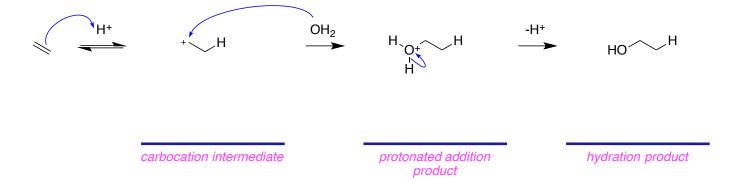




<u>does not</u> proceed

• bromide, being negatively charged, is repelled by electrons in the alkene π -bond

proton,



H. Acid-mediated Hydration Of Alkenes

1°.

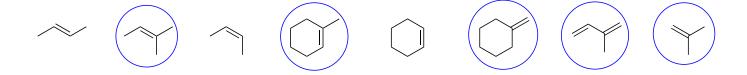
two

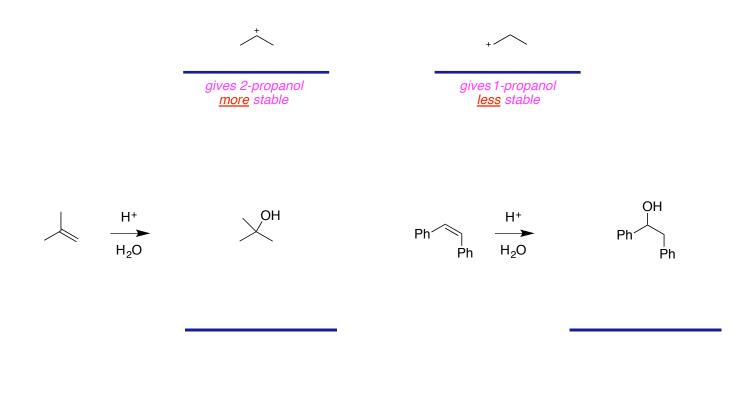
ie <u>regioisomers</u>;

regioselective.

, reactions that involve reaction of one chemical functional group in preference to others are called chemoselective.

enantioselective and diastereoselective





 H_2O

<u>E1</u> pathway.

ethers.

ОМе

are not

$$\nearrow^{\mathsf{OH}} \implies \qquad \downarrow$$