

Reactions Of Alkenes Via Protonation

from chapter(s) _____ in the recommended text

A. Introduction

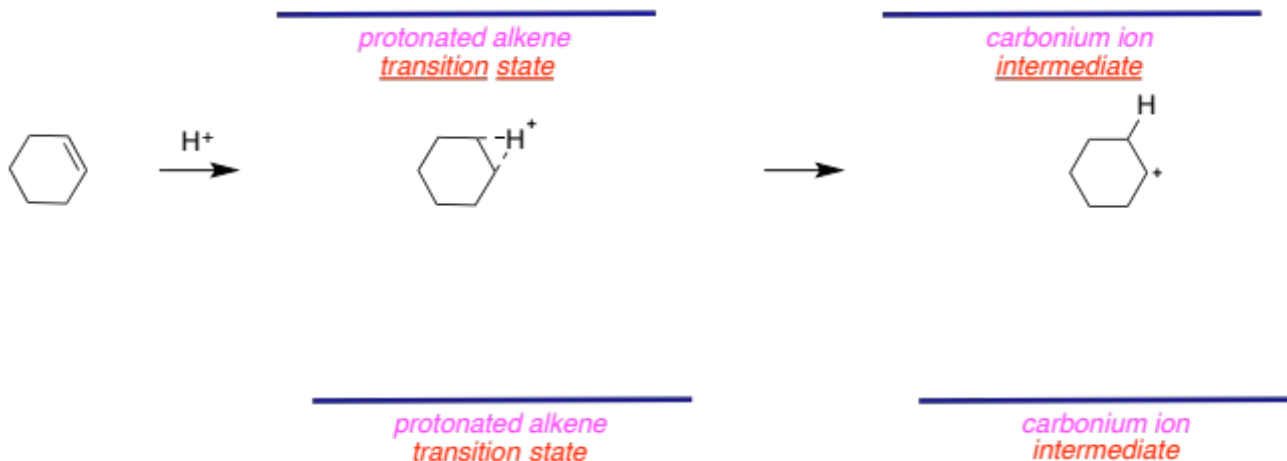
B. Protonation Of Alkenes

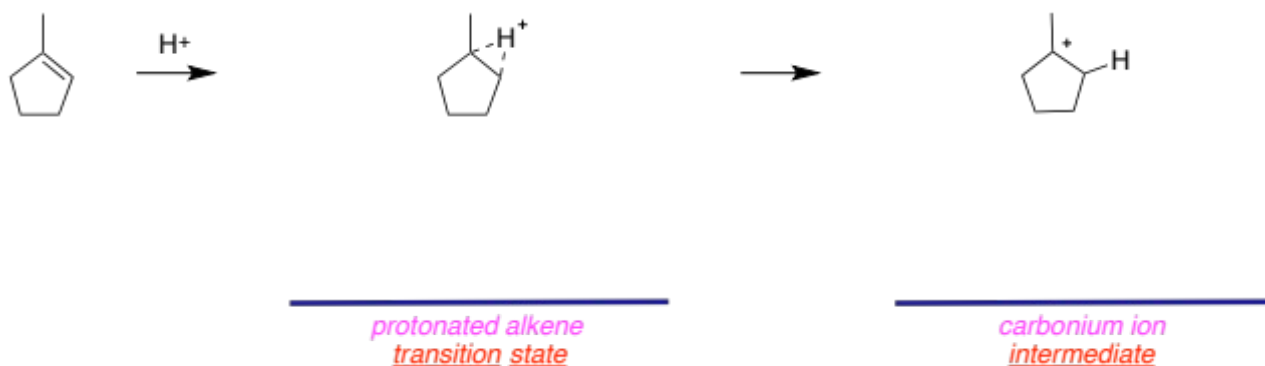
Generation Of Carbocations Via Protonation

Protons are the *simplest* of all electrophiles.

Alkenes react with protons at either end of the alkene or the other, giving one neutral *sp³-hybridized* carbon and a *sp²-hybridized*

Alkenes oriented perpendicular to a proton represent a *transition* while the carbonium ion is an *intermediate*.



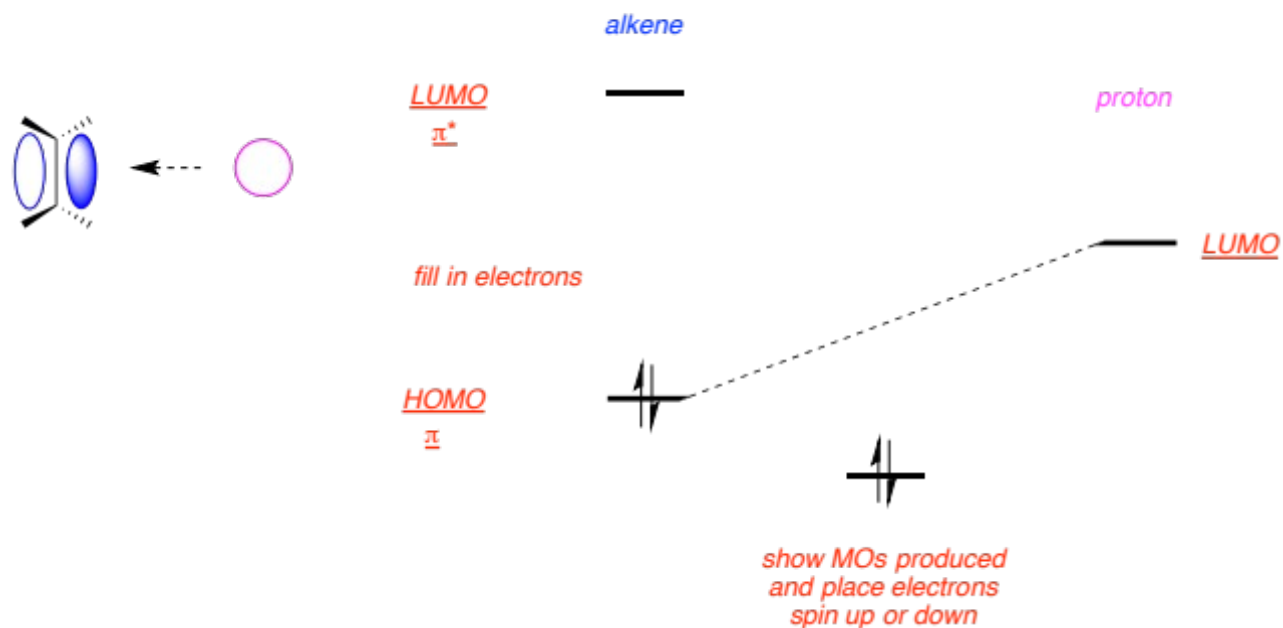


while other trajectories give more stabilization of the developing sp^3 -hybridized carbon.

A Molecular Orbital Picture Of Alkene Protonation

and when that lower-energy orbital is *more* populated with electron density

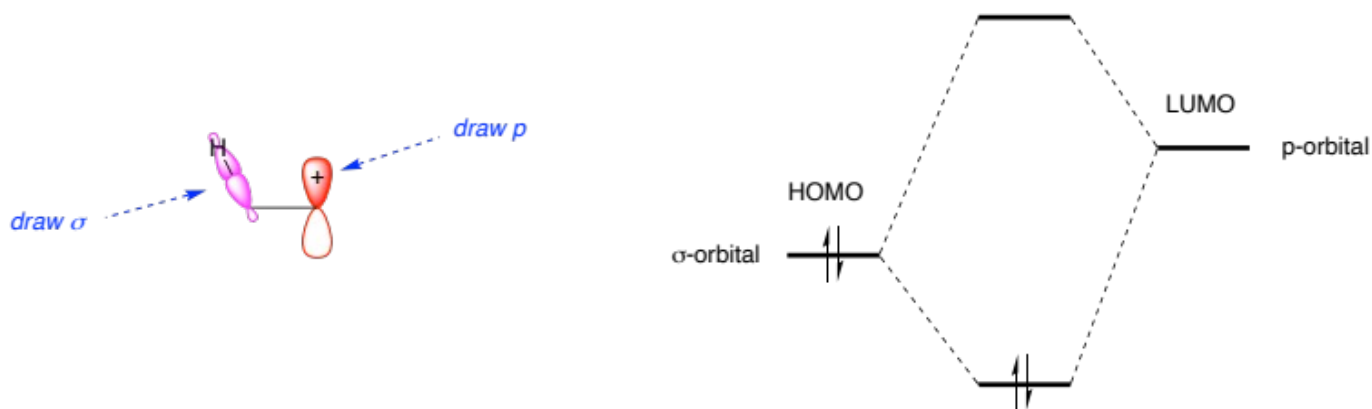
A proton *does not* have a highest occupied molecular orbital (HOMO), so only the **LUMO**. Thus the **LUMO** of a proton and the **HOMO** of an alkene should be considered when a proton



Perpendicular approach of a proton to a symmetrical π -cloud is net *stabilizing*.

C. Carbocation Stabilities

Valence bond and molecular orbital approaches are *alternative theories to explain bonding in general*.
 methyl cation due to mixing of the empty p-orbital (*LUMO*)
 the filled σ -bonding orbital of a C-H bond on the adjacent methyl (*HOMO*).



The σ -orbital brings **2** electrons into the interaction, whereas the p-orbital bears **0** e⁻; thus the total number of electrons to place in the new molecular orbitals is **2**;

C-H bond on the adjacent methyl can only occur when the orbitals *are in the same plane*.

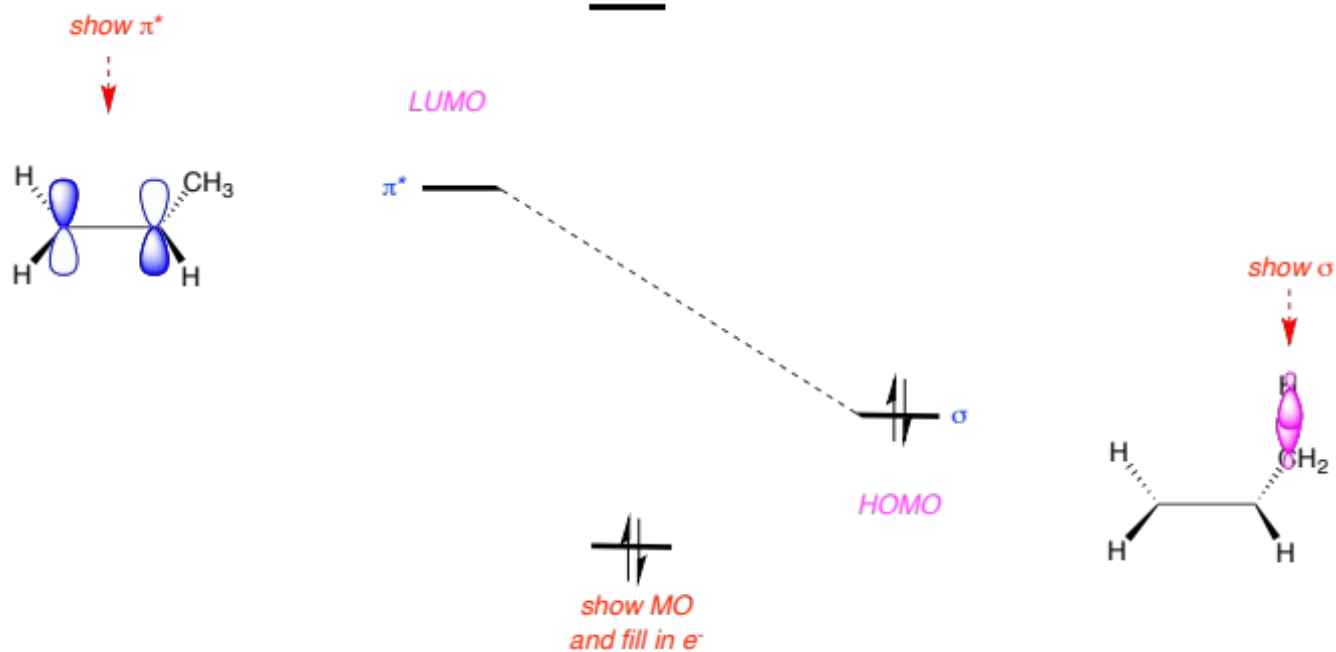
any instant because the other two *cannot achieve significant orbital overlap*.

A secondary propyl cation has **2** adjacent methyl groups, and therefore **2** σ filled C-H bonds
 Secondary propyl cations are *more* stable than ethyl or methyl cations because of this

A *tert*-butyl cation has **3** adjacent methyl groups, and therefore **3** filled σ C-H bonds that can stabilize by molecular orbital interactions. ^tBu-cations are *more* stable than ethyl or methyl cations because of this.

D. Alkenes Stabilities

Stabilities of most alkenes *increase with* the number of substituents.



Alkenes can only have the *stabilizing* interactions (above) if they have allylic C – H bonds.

Interactions like this explain why more substituted alkenes have *enhanced* stabilities.



most stable

least stable

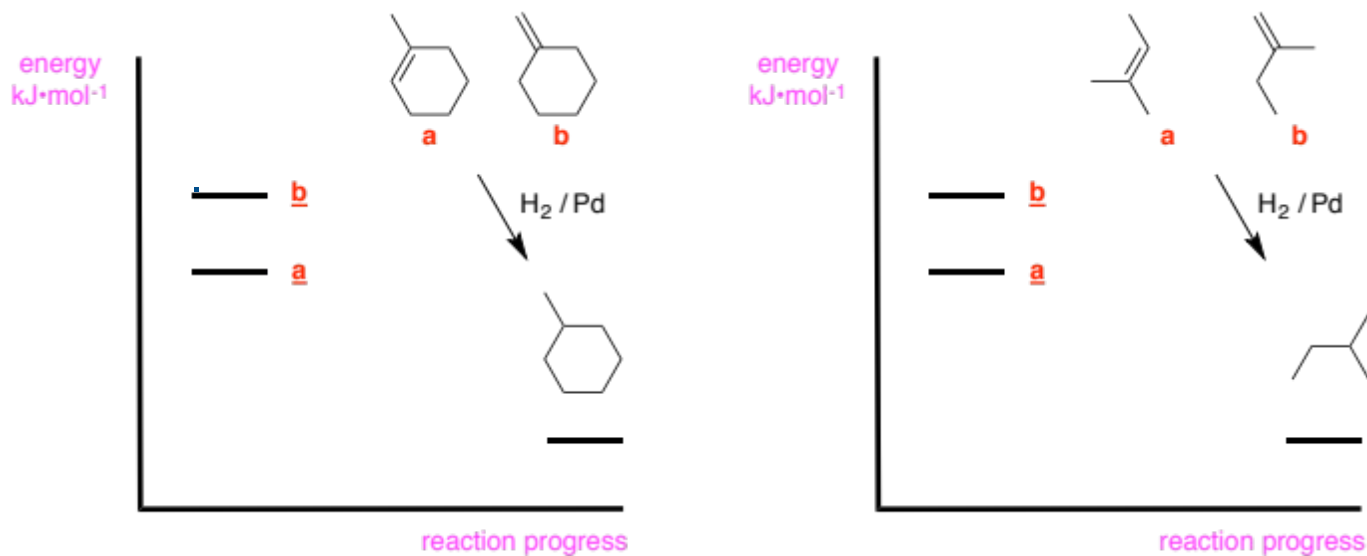
Heats Of Hydrogenation

Energy is *liberated* when hydrogen is added across a C=C bond.

Energies involved in such processes are called heats of *hydrogenation*.

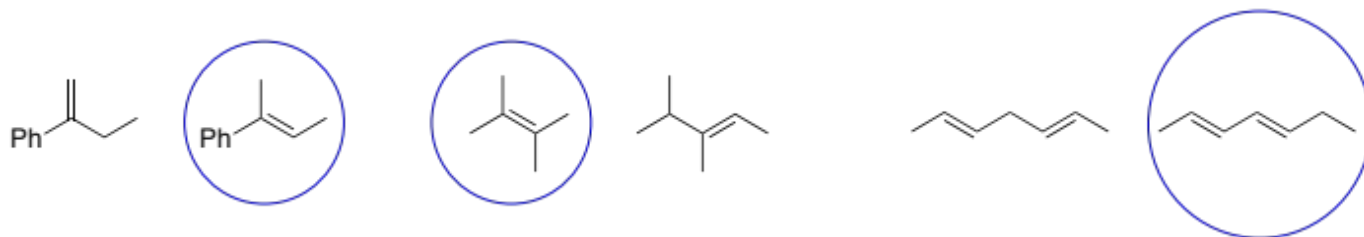
more stable alkenes will have *lower* heats of hydrogenation than less stable ones.

give the same or very similar products *can* be used to gauge the relative stabilities



b has the higher heat of hydrogenation, while in the diagram on the right it is *b*.

E. Acid-mediated Alkene Isomerization



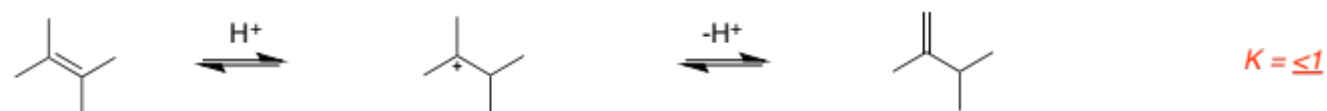
then lose a proton *from a different carbon* to give a different alkene that *is* an isomer of the first.

This reaction may be driven to form the most stable alkene, *ie* by *thermodynamics*.



carbocation

alkene



carbocation

alkene

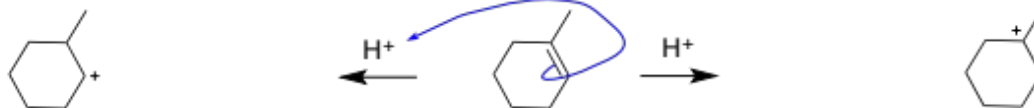


carbocation

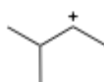
alkene

It is *conceivable* that carbocations can shift groups to isomerize faster than they can lose protons

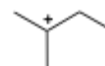
the most possible carbocation *intermediates* formed by protonation of the following alkenes



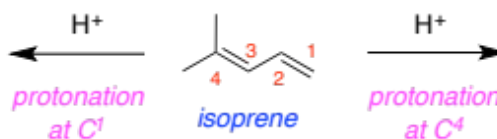
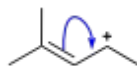
least favorable
2° carbonium ion



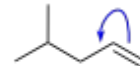
most favorable
3° carbonium ion



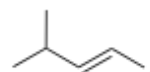
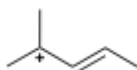
least favorable
2° carbonium ion



most favorable
3° carbonium ion



show resonance
stabilized forms

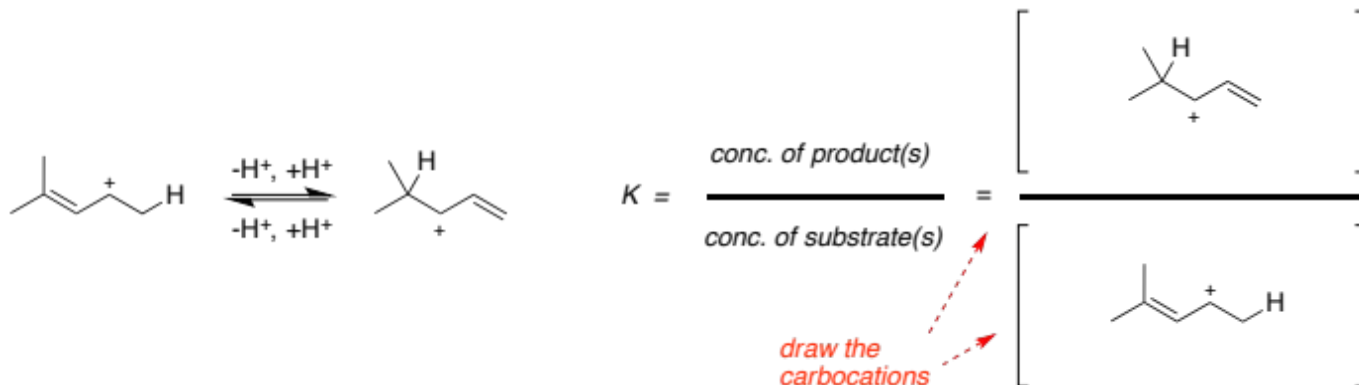


most favorable
3° carbonium ion

least favorable
1° carbonium ion

Protonation of isoprene at the diene termini (C^1 and C^4) *gives* a cation stabilized by allylic resonance protonation at the internal positions (C^2 and C^3) *does not*.

Free energy change for this reaction involves a *small* entropy factor because the number of starting materials *equals* the number of products.



The equilibrium constant featured above is *less than* one.

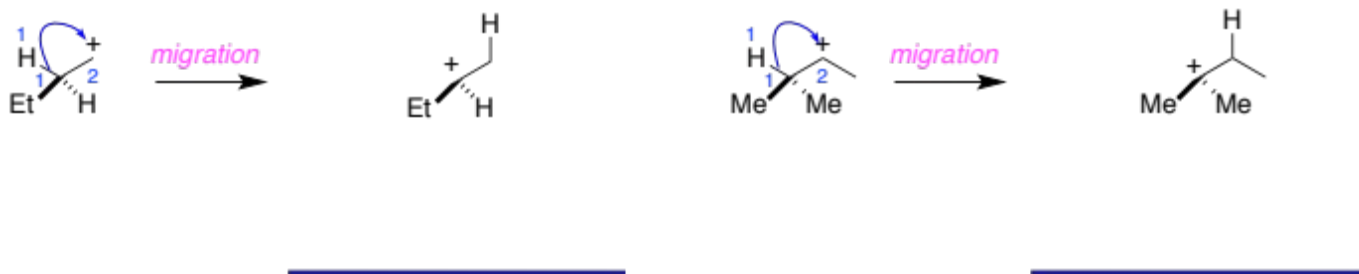
F. Carbocation Rearrangements

Hydride Shifts

two electrons this is called a *hydride* migration because a proton and two electrons is a *hydride anion*.

preferred one may be predicted by considering the relative stabilities of the carbocations produced: *true*.

Draw curly arrows to describe the following *1,2*-hydride migration reactions, and predict the products.





collisions of protons with *unsymmetrical* alkenes are *most* thermodynamically favorable

Alkyl Shifts

positive charge appears to shift in the *opposite*

Carbocation rearrangements are favorable if the cation formed is *more* stable than the original one.

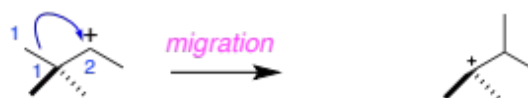
tend to undergo rearrangements if the products are *secondary / tertiary* carbocations

secondary ones tend to only migrate to form *tertiary* carbocations.

Show curly arrows for the *1,2-* migrational reactions shown below



draw curly arrows

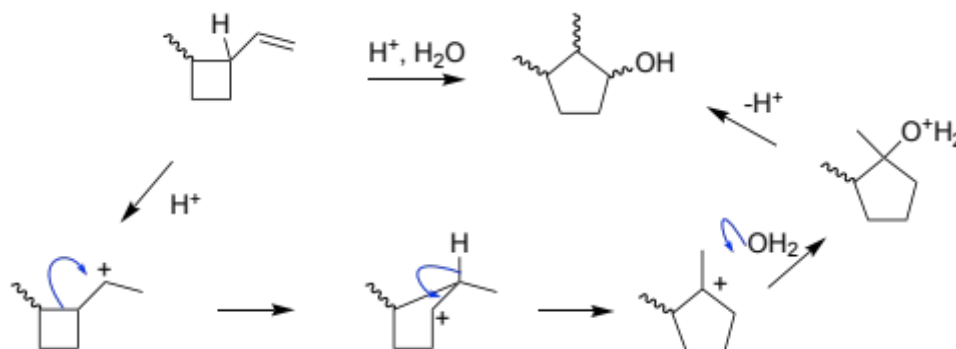


*draw curly arrows
and product*



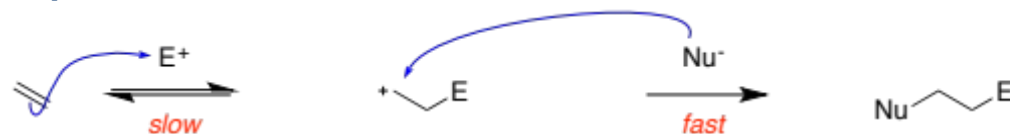
If the migrating group is an alkyl then these processes can be called *alkyl shift* reactions.

1,2-migration then it is the one *most* able to support a positive charge that shifts preferentially. Me because methyl cations are *less* stable than Et^+ (though it does not actually shift as a complete carbocation, the shift involves a developing positive $\text{Et}^{\delta+}$; the group most able to support a positive charge shifts preferentially).



see: <https://youtu.be/Esqb6o510EY>

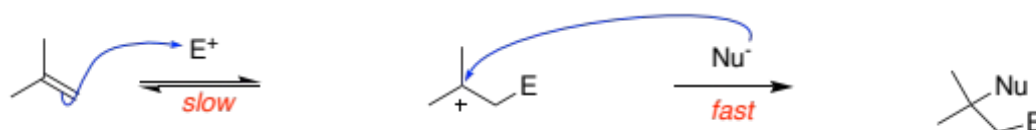
G. Electrophilic Addition Mechanisms



carbocation intermediate

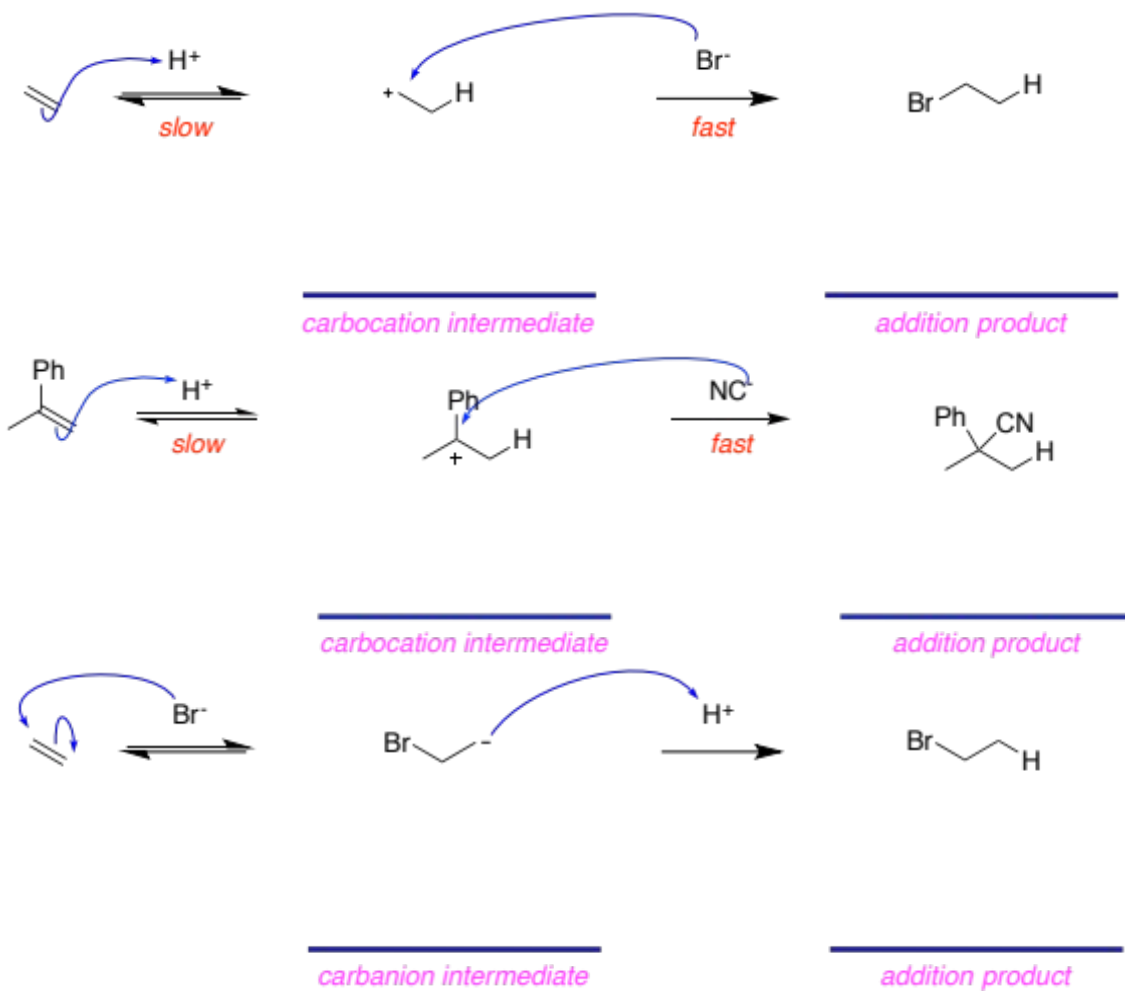
addition product

then the first step will be relatively *slow* compared with the second.



carbocation intermediate

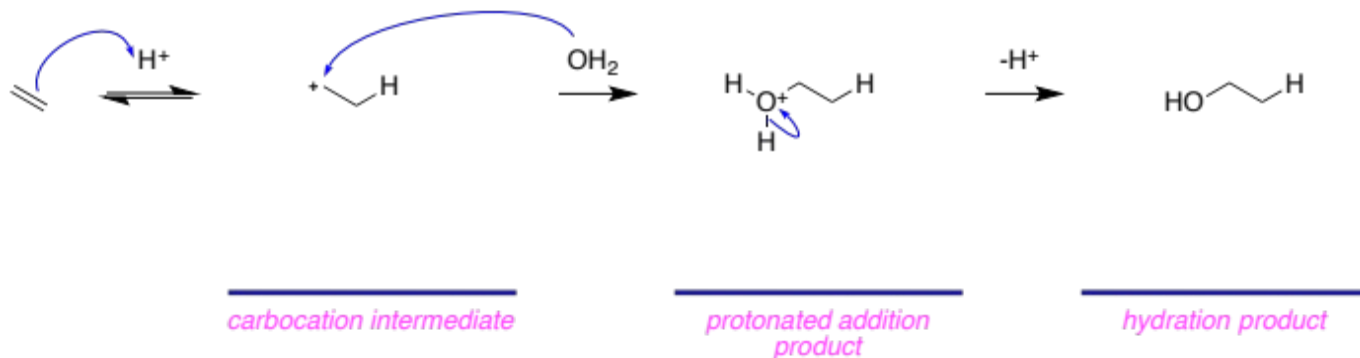
addition product



Addition of HBr to ethene *does not* proceed in this way.

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

so a positively charged entity, usually a *proton*, must be lost to give a neutral addition product.



H. Acid-mediated Hydration Of Alkenes

less favorable than for most other alkenes because the carbocation formed 1° .

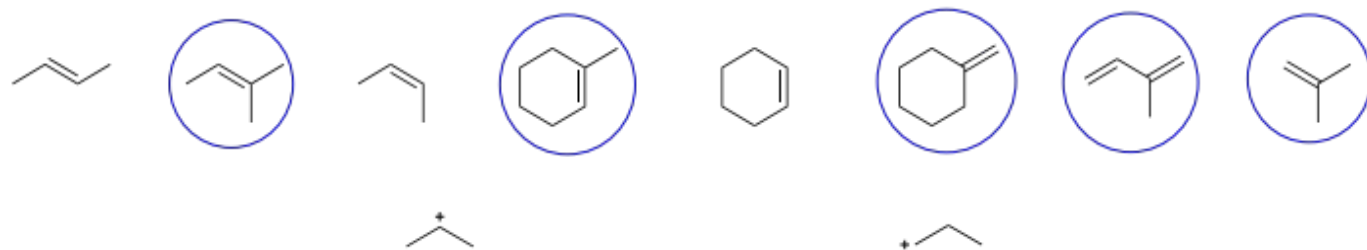
Hydration of propene could give *two* possible hydration products in which the *H* and *OH* groups become attached to different carbon atoms, *ie regioisomers*;



Reactions which form one regioisomer selectively are called *regioselective*.

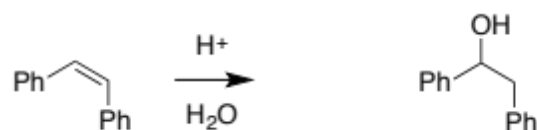
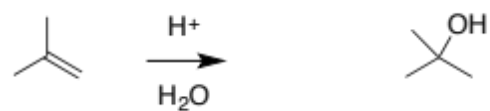
one chemical functional group in preference to others are called *chemoselective*.

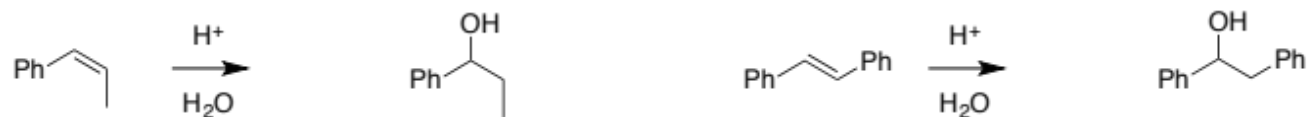
one enantiomer in preference to another, and preferential formation of one diastereomer: *enantioselective* and *diastereoselective*



gives 2-propanol
more stable

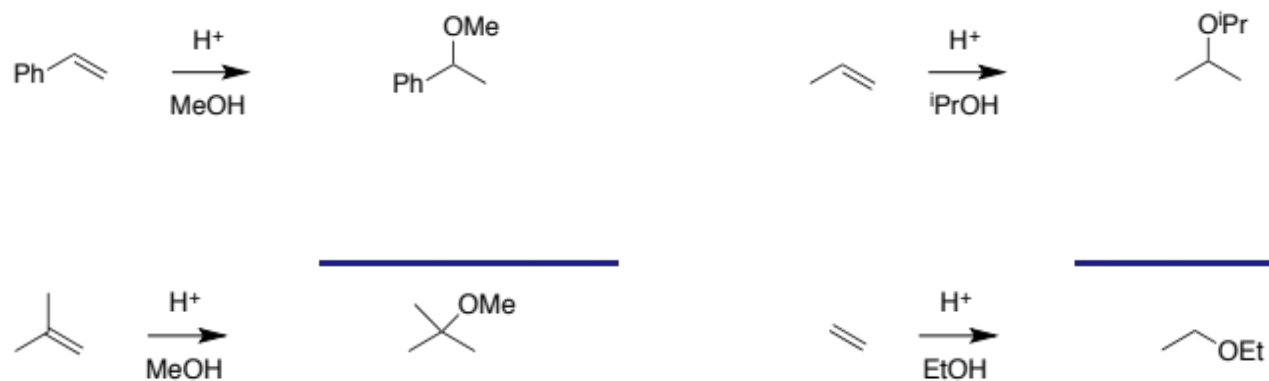
gives 1-propanol
less stable



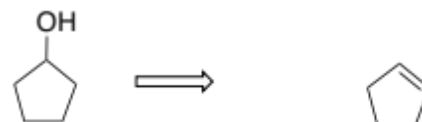
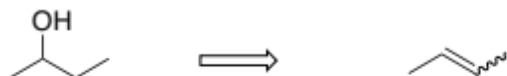
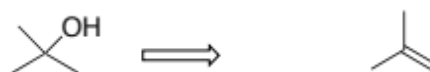
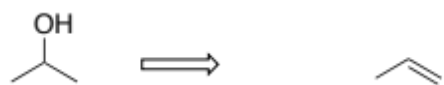


In the absence of water the reverse reaction (alcohol to alkene) would occur via a(n) *E1* pathway.

Predict the products of the following reactions to form *ethers*.



The reactions above *are not* hydration reactions, but they are mechanistically similar.



1-butene would give mixtures of alcohol regioisomers

