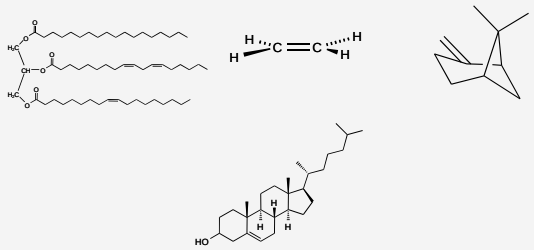
Today is November 2

Last day to change a class to or from the Pass/No Credit (P/NC) option.

Last day to drop a course.

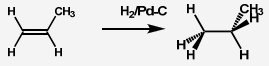
1

Alkenes: Addition Reactions



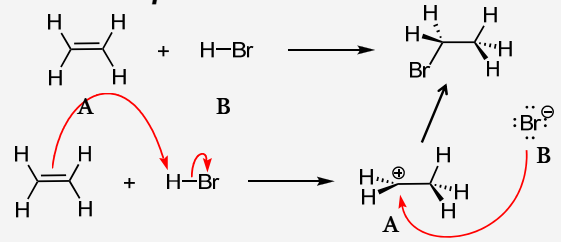
2

Alkene Additions



3

Electrophilic addition to an alkene



Which substrate acts as a base in the first step of this reaction?

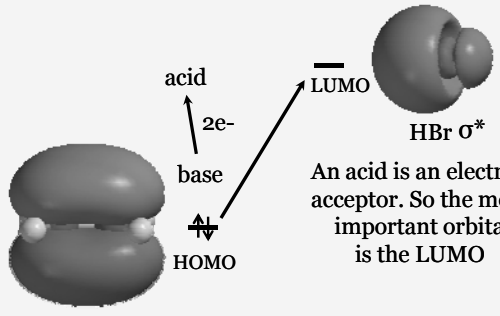
Which substrate acts as a base in the second step of this reaction?

The alkene acts as a base.
The HBr is an acid.

The bromide acts as a base.
The carbocation is an acid.

4

MO description

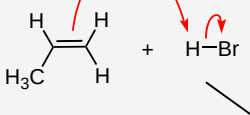


An acid is an electron acceptor. So the most important orbital is the LUMO

The alkene acts as a base.
So the most important orbital is the HOMO

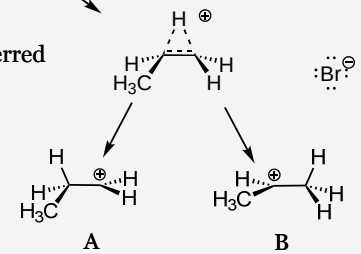
5

What if we use **propene** instead?

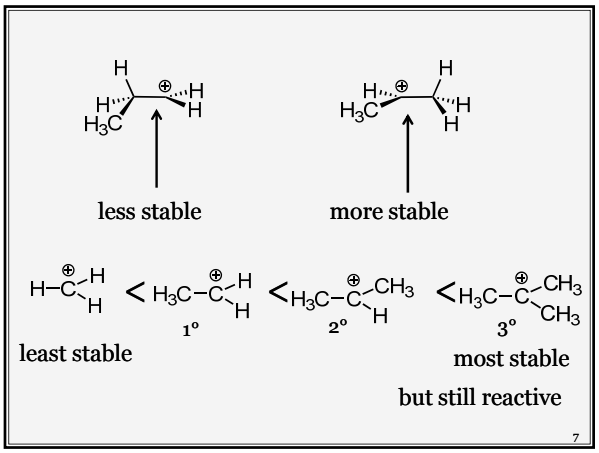


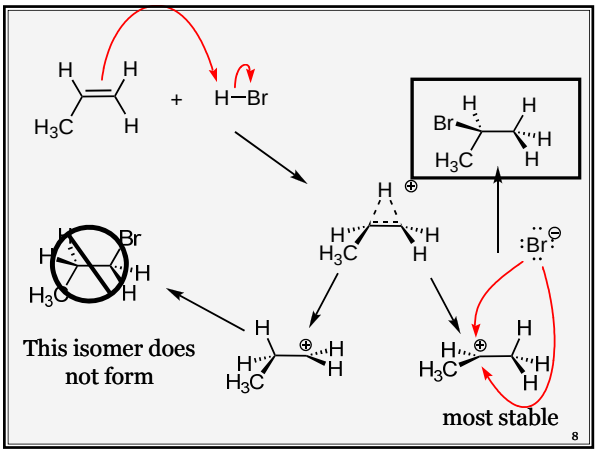
Unstable π–protonated alkene collapses to a more stable configuration

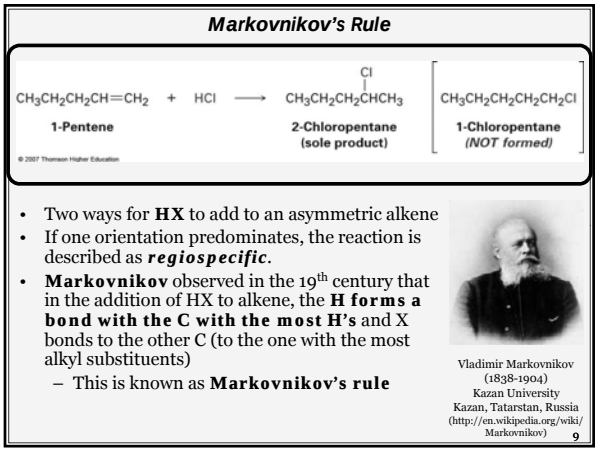
Which is the preferred carbocation?

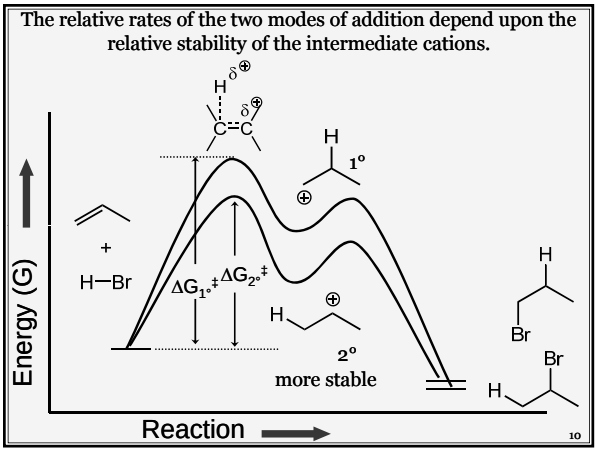


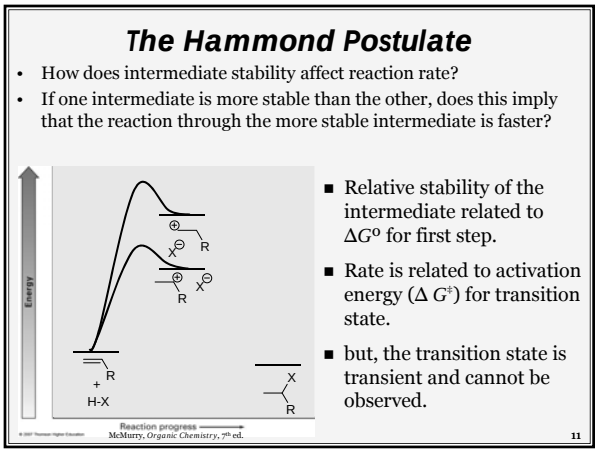
6

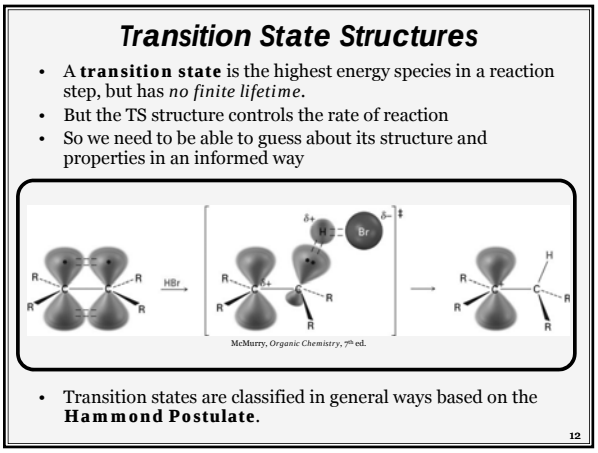

less stable
more stable
least stable
1°
2°
3°
most stable
but still reactive
7


This isomer does not form
most stable
8


Markovnikov's Rule
1-Pentene
2-Chloropentane (sole product)
1-Chloropentane (NOT formed)
Two ways for HX to add to an asymmetric alkene
If one orientation predominates, the reaction is described as regiospecific.
Markovnikov observed in the 19th century that in the addition of HX to alkene, the H forms a bond with the C with the most H's and X bonds to the other C (to the one with the most alkyl substituents)
– This is known as Markovnikov's rule
Vladimir Markovnikov (1838-1904) Kazan University Kazan, Tatarstan, Russia (http://en.wikipedia.org/wiki/Markovnikov)
9


The relative rates of the two modes of addition depend upon the relative stability of the intermediate cations.
Energy (G)
Reaction
1°
2°
more stable
10


The Hammond Postulate
How does intermediate stability affect reaction rate?
If one intermediate is more stable than the other, does this imply that the reaction through the more stable intermediate is faster?
Relative stability of the intermediate related to ΔG° for first step.
Rate is related to activation energy (Δ G‡) for transition state.
but, the transition state is transient and cannot be observed.
Energy
Reaction progress
McMurry, Organic Chemistry, 7th ed.
11


Transition State Structures
A transition state is the highest energy species in a reaction step, but has no finite lifetime.
But the TS structure controls the rate of reaction
So we need to be able to guess about its structure and properties in an informed way
McMurry, Organic Chemistry, 7th ed.
Transition states are classified in general ways based on the Hammond Postulate.
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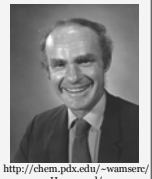
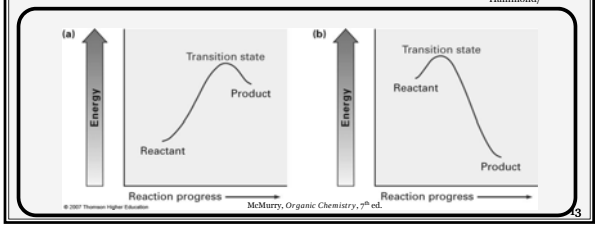
The Hammond Postulate

- *"If two states, for example, a transition state and an unstable intermediate, occur consecutively during a reaction process and have nearly the same energy content, their interconversion will involve only a small reorganization of the molecular structures."* —G. S. Hammond, 1955.
- A transition state should be similar in structure to the state that is closest in energy.



http://chem.pdx.edu/~wamserc/Hammond/



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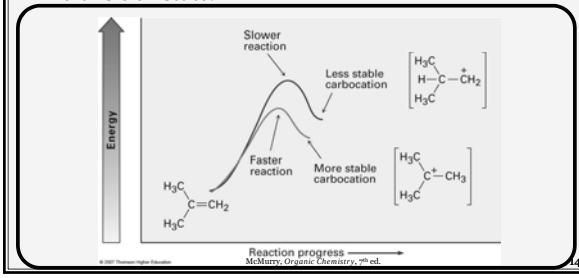
Competing Reactions and the Hammond Postulate

- ***Faster reaction*** should result from ***more stable*** intermediate.
- Transition state structure resembles nearest intermediate.
- Factors that ***stabilize the intermediate*** also ***stabilize transition state***.



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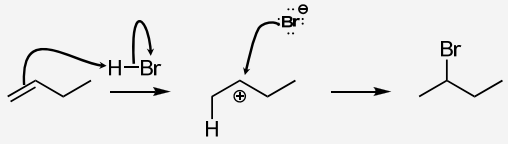
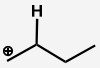
Regioselectivity of Alkene Addition

The addition of acids to alkenes follows the pathway with the most stable intermediate cation.

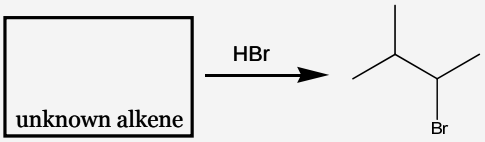


2° most stable carbocation

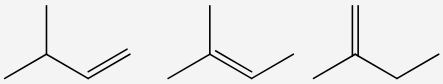
1° less stable carbocation



15



Draw the <u>best</u> alkene starting reagent you could use for the synthesis of this bromide.

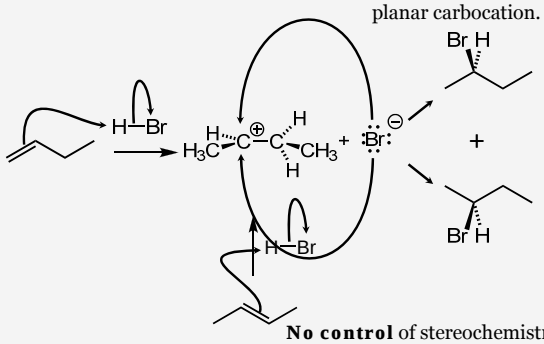


A. B. C.

16

Stereochemistry of H-Br addition.

Br^- adds to either side of planar carbocation.



No control of stereochemistry

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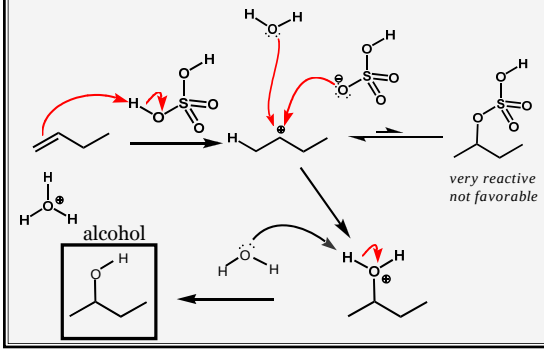
What if you use H_2SO_4 instead of HX?

HSO_4^- is a very weak base. Is there a better base around?



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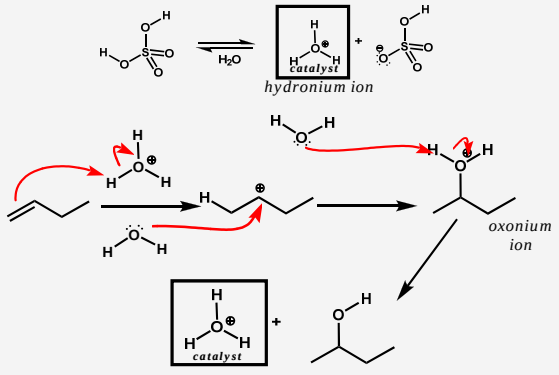
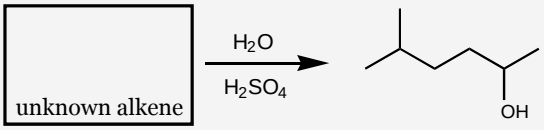
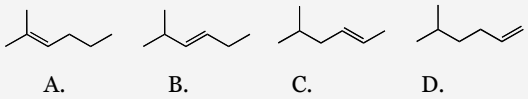
Alcohol synthesis: acid-catalyzed hydration of alkenes



Reverse of mechanism for acid-catalyzed E1 dehydration of alcohols 19

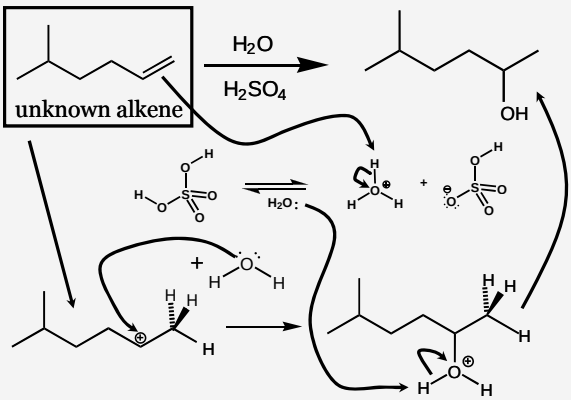


Draw the *best* alkene starting reagent you could use for the synthesis of this alcohol.



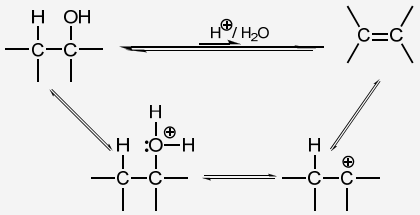
A. B. C. D.

20



21

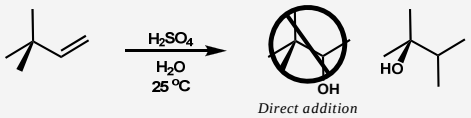
Aqueous acid (dilute H^+) or lower temperature (< 100°) favors hydration



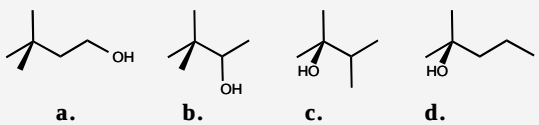
(Concentrated acid or higher temperature (> 100°) favors dehydration)

22

Predict the product and draw a mechanism based on what we know about carbocations



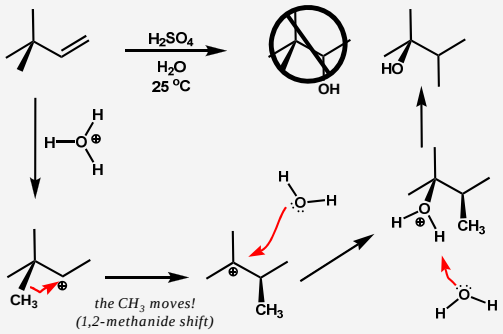
Direct addition product



a. **b.** **c.** **d.**

23

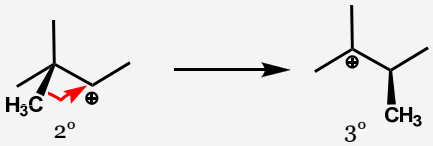
actual product



the CH_3 moves! (1,2-methanide shift)

24

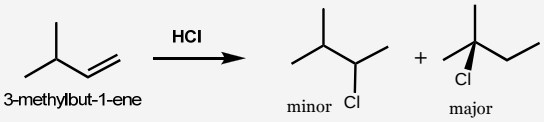
Carbocation Rearrangement



Secondary carbocations rearrange to form tertiary carbocations.

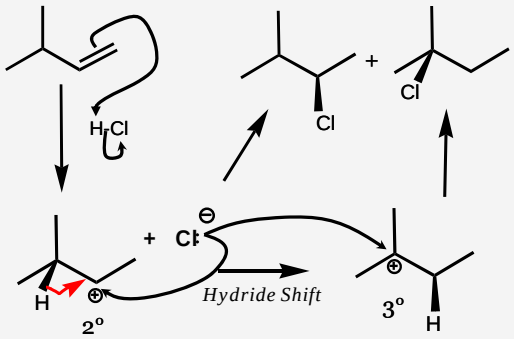
25

This reaction gives two products in a 75/25 ratio. What do you think they are?



What happened?

26



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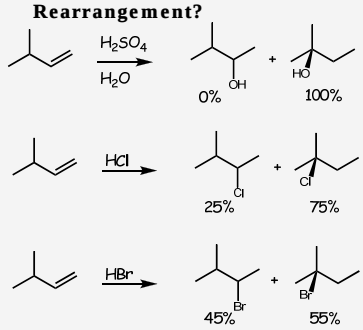
Alkene Electrophilic Additions

Rearrangement?



Nu:⁻

H_2O

Cl^-

Br^-

better nucleophile

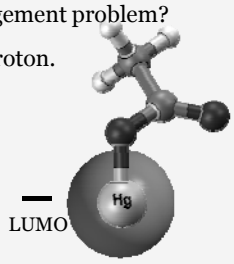
Direct addition more competitive with rearrangement

28

How can you avoid the rearrangement problem?

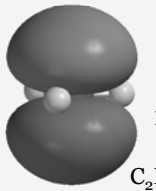
A Hg^{+2} ion can act like a giant proton.

Hg^{+2} $5d^{10}6s^0$



LUMO

$Hg(O_2CCH_3)^+$



π

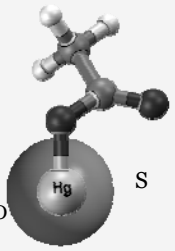
HOMO

C_2H_4

29

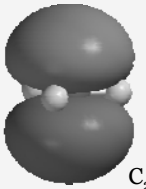
A Hg^{+2} ion can act like a giant proton.

S-S HOMO – LUMO interaction – allowed reaction



LUMO

S



π

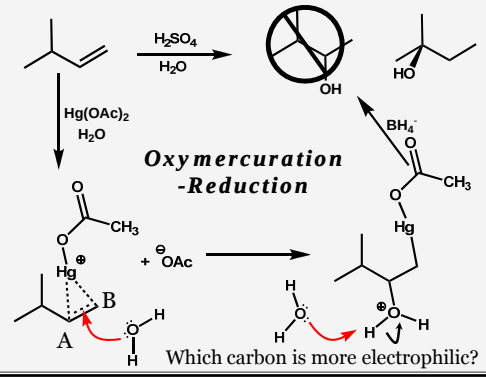
S

HOMO

C_2H_4

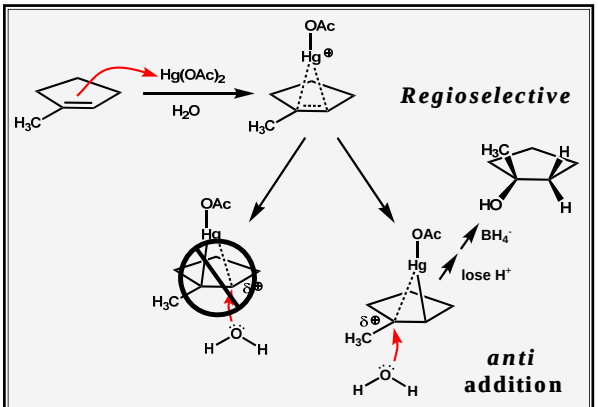
30

How do you avoid the rearrangement problem?



Which carbon is more electrophilic?

31



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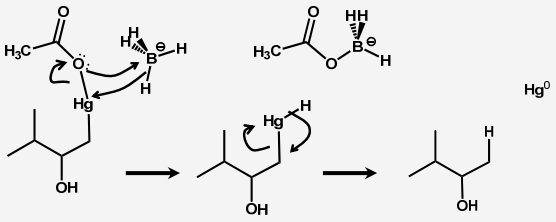
Demercuration.



The Hg^{+2} is reduced by BH_4-.

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