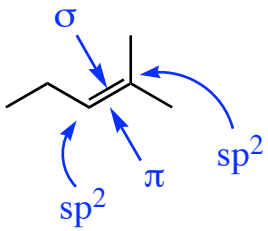
Learning Guide for Chapter 11 - Alkenes I

I. Introduction to alkenes

Bond structure

What is the hybridization, geometry, and molecular orbitals of an alkene?

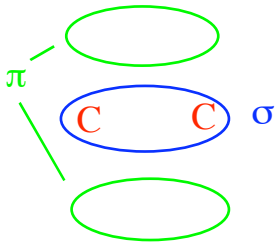


hybridization: sp^2

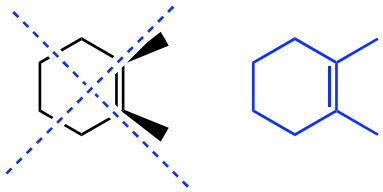
geometry: trigonal planar

molecular orbitals: $sp^2 + sp^2 \rightarrow \sigma$

$p + p \rightarrow \pi$



What is wrong with the following line structures?



C=C atoms are trigonal planar
can't go up and down

angle should be 120°
not tetrahedral

usually this problem occurs
when making C=C from 3° C

Which is higher in energy, the sigma or the pi bond? Why?

pi bond
farther from C nuclei

Classifying compounds with C=C's

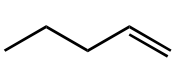
What is the difference between alkenes, aromatic compounds, and unsaturated compounds?

alkene: hydrocarbon with a C=C — we will focus on these

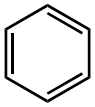
aromatic compound: any compound containing a benzene ring

unsaturated compound: any compound containing a C=C or C---C, can have O, N, X

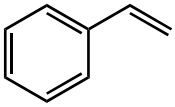
Label each of the following.



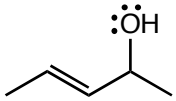
alkene
unsaturated



aromatic ring
(not an alkene)



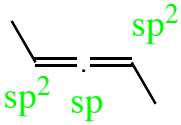
aromatic
alkene
unsaturated



unsaturated alcohol
(not an alkene)

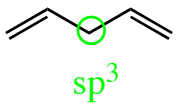
Compounds with more than one C=C are classified by how far apart they are. Which of the following structures is isolated, conjugated, and cumulated?

energy



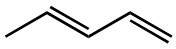
cumulated: 2 C=C's sharing a C

less stable than isolated, more reactive



isolated: at least one sp^3 C between the C=C

behave like normal alkenes



conjugated: 2 or more C=C's next to each other

all 4 C are sp^2

more stable than isolated

can absorb UV and visible light

Physical properties

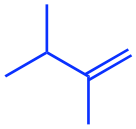
How do the physical properties of alkenes compare to those of alkanes? very similar

polarity: nonpolar

water solubility: very low

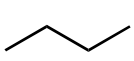
density: less than water

flammability: high

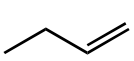


d = 0.65 g/ml

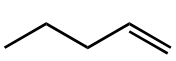
What can you conclude from the following boiling points?



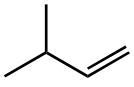
bp = 0°C



bp = -6°C



bp = 30°C



bp = 25°C

alkenes and alkane have similar bp's

alkene bp's increase as MW increases

branching causes a slight drop in bp (less surface area)

Reactivity

How does the reactivity of alkenes compare to alkanes? alkenes are more reactive!

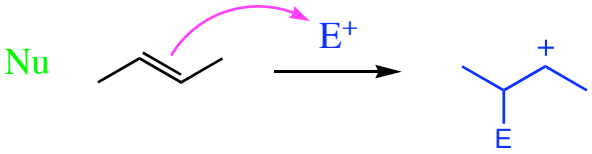
Which of the following would you predict that an alkene could react with? Why?

nucleophile **electrophile** **acid** base **radical**

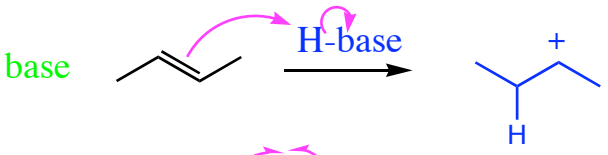
electrons in pi bond can attach a C or H or split apart

How strong of a reagent is an alkene? Why? not very strong
no charge, no lone pairs

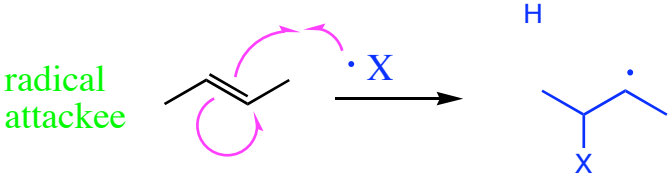
Predict the three types of mechanistic steps that an alkene can undergo.



carbocation — will continue the reaction by reaction as an electrophile



carbocation — ditto

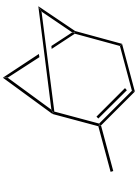


radical — will now act as a radical attacker

Occurence and uses of alkenes

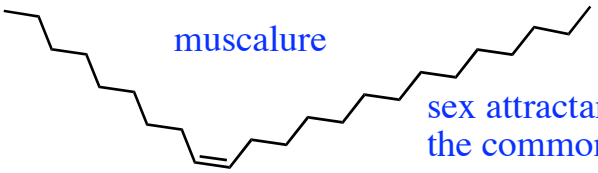
Are alkenes common in nature? no

Where are the following two compounds found?



α-pinene

extract of evergreen trees (terpentine)

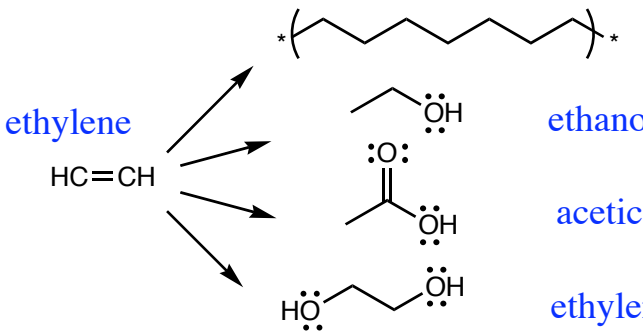


muscalure

sex attractant of the common housefly

Where do alkenes come from? petroleum

What is the most abundantly used organic compound, and what can you make with it?



polytheylene (HDPE, LDPE)

milk jugs, plastic bags

ethanol

acetic acid (vinegar)

also used to make fruit and tomatoes ripen after picking

ethylene glycol (antifreeze)

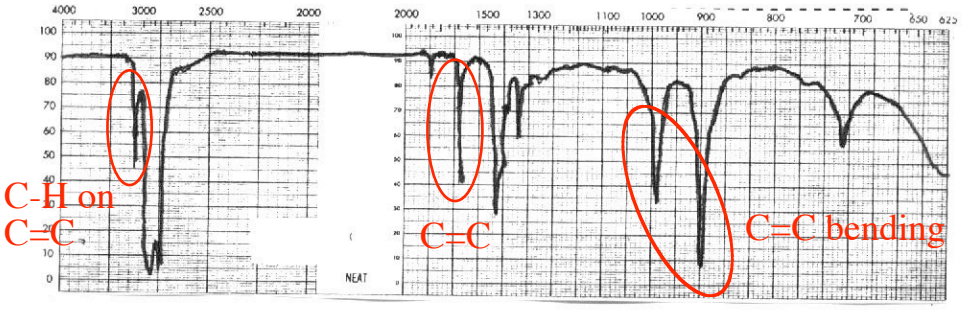
Spectroscopy

IR: What bands does an alkene have that an alkane does not?

* C=C 1680-1620 cm^{-1} sharper, smaller than a C=O band (not very polar)
* C-H on C=C 3100-3000 cm^{-1} spike on the left side of the C-H (fewer of them)

C=C bending 960-730 cm^{-1} sometimes useful for stereochemistry

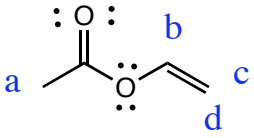
* memorize these



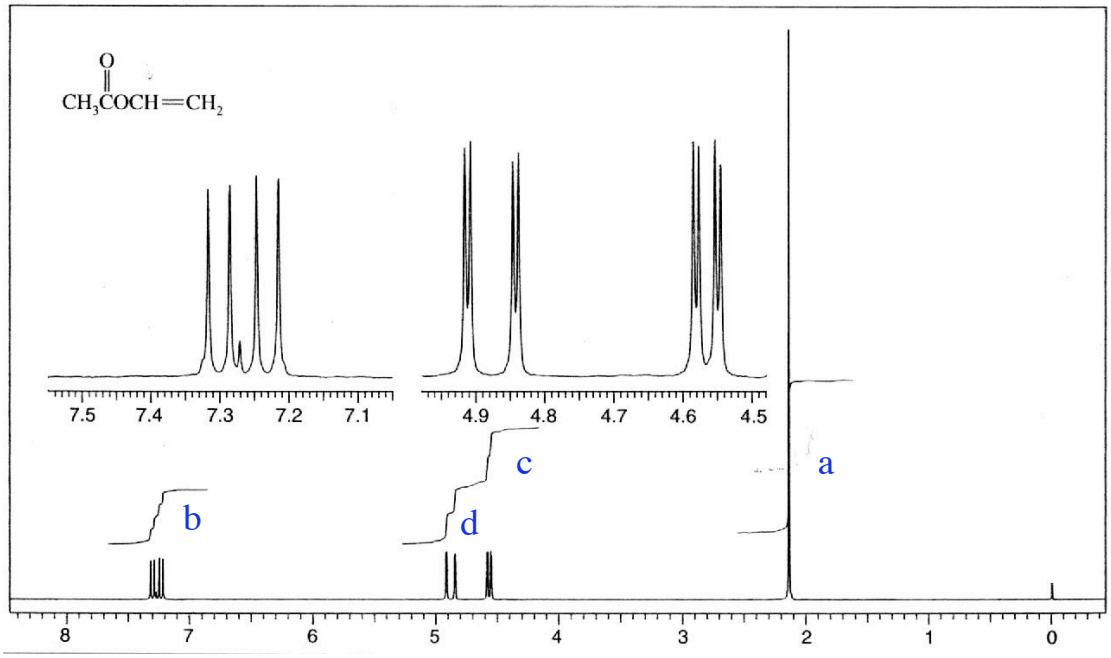
NMR: What chemical shift do H's on C=C's have? 4.5-6.5 ppm

What happens to the splitting in an alkene?

coupling constants are different - neighbor rule doesn't work

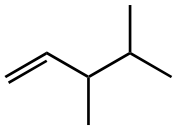


a - singlet 2-2.5 ppm
b - doublet of doublets 7.3 ppm (next to O and on C=C)
c, d - doublet of doublets 4.6 and 4.9 ppm (on C=C and near O)

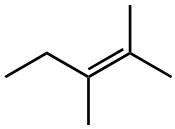


Stability of alkenes

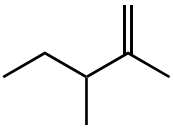
Put the following alkenes in order from most to least stable.



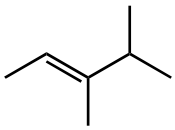
least stable
4



most stable
1



3



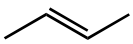
2

most substituted = most stable

4 C > 3 C > 2 C > 1 C

Now consider the alkenes below. Which is the most and least stable?

least crowded = most stable



trans
most stable

cis
least stable

geminal
in the middle

trans > geminal > cis

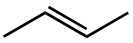
E > Z

Which of these two rules takes precedence?

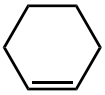
amount of substitution is more important than stereochemistry

Why are small cyclic alkenes less stable? ring strain

more reactive than other alkenes



normal angle:
120º



120º

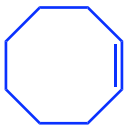
108º

90º

60º

What stereochemistry do most cyclic alkenes have? cis (or Z)

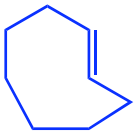
cis



stable

How big does a ring have to be before it is stable with a trans C=C?

at least 8 carbons



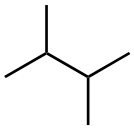
stable

less than 8 carbons is too strained

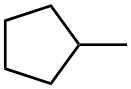
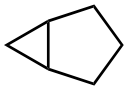
doesn't exist

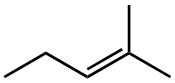
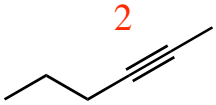
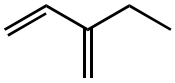
II. Unsaturation Number

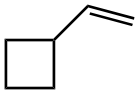
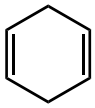
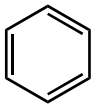
In chapter 2 we discussed molecular formulas for alkanes, cycloalkanes, and unsaturated hydrocarbons. What was the formula for a straight chain or branched alkane?

2C +2  C_6H_{14}  C_6H_{14}

What happens when a pi bond or ring is present? lose 2 H's for every pi bond or ring

rings:  1 C_6H_{12}  2 C_6H_{10}

pi bonds:  1 C_6H_{12} 2  C_6H_{10} 2  C_6H_{10}

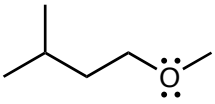
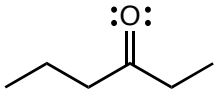
both:  2 C_6H_{10}  3 C_6H_8  4 H_2S

How can you write a formula to show the number of pi bonds and/or rings are present?

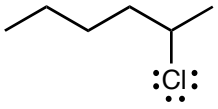
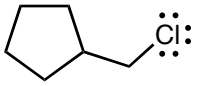
$$\frac{\text{maximum \# - actual \#}}{2} \qquad \frac{(2C+2) - H}{2} = \text{unsaturation number}$$

Now let's see what happens when we add other elements to the compounds.

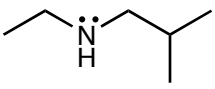
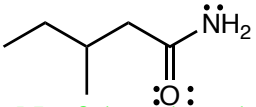
Oxygen: no change - same number of H's required

 $C_6H_{14}O$  $C_6H_{12}O$

Halogens: need one less H for every X (X takes the place of an H)

 $C_6H_{13}Cl$  $C_6H_{11}Cl$

Nitrogen: need one more H for every N

 $C_6H_{15}N$  $C_6H_{13}NO$

C - 4 bonds, add a carbon, add 2 H's; N - 3 bonds, add a N, add 1 more H)

Generate a formula for figuring out how many double bonds or rings you have:

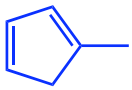
$$\text{unsaturation \#} = \frac{\text{maximum \# adjusted for N, X - actual \#}}{2}$$

$$\text{unsaturation \#} = \frac{(2C + 2 - X + N) - H}{2}$$

Practice - calculate the unsaturation number for each molecular formula. Then draw a possible structure.

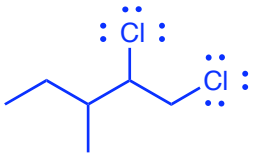
C_6H_8

3



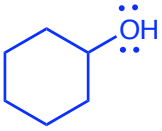
$C_6H_{12}Cl_2$

0



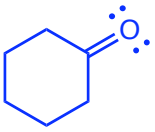
$C_6H_{12}O$

1



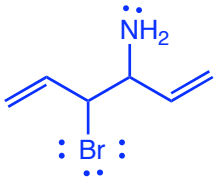
$C_6H_{10}O$

2



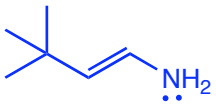
$C_6H_{10}NBr$

2



$C_6H_{13}N$

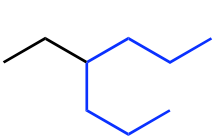
1



III. Nomenclature of Alkenes

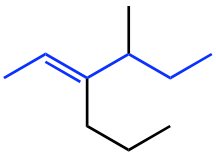
What are the priorities in choosing the principle chain for an alkane?

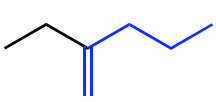
1. longest chain/ring
2. most substituents

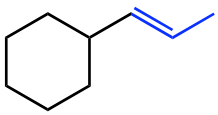


With alkenes, there is an addition, higher priority.

1. must contain the C=C
2. longest chain/ring
3. most substituents

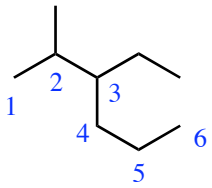






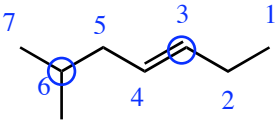
What are the priorities for numbering an alkane?

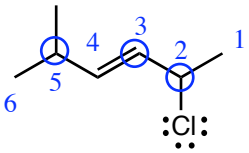
1. lowest # to first substituent (then second, etc)
2. alphabetize



With alkenes, the C=C takes priority. The numbers must go across the C=C, and the number of the first carbon is the number of the alkene.

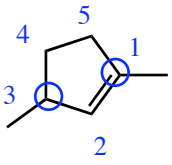
1. lowest # to C=C
2. lowest # to first substituent (then second, etc)
3. alphabet

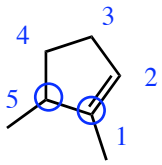




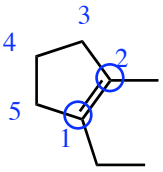
What about cyclic alkenes? start on C=C, go across it

no # needed

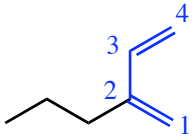


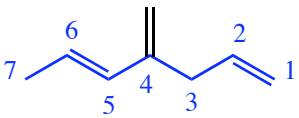


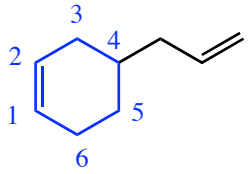
* 1,5
2,3

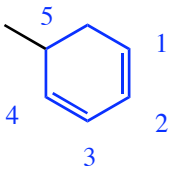


What if there are two or more C=C?









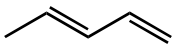
If alkanes end in "ane," what do you think alkenes end in? ene

How would you specify the location of the C=C? give the number before the name

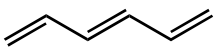
trans-2-hexene

cyclopentene

How will the name change where there is more than one C=C?



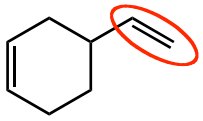
1,3-pentadiene



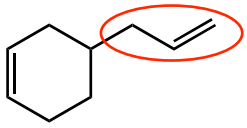
1,3,5-heptatriene

add "adi", "atri" before ending

If the C=C cannot be included in the principle chain, it must be named as a substitutent.
What are the two smallest ones called?



vinyl

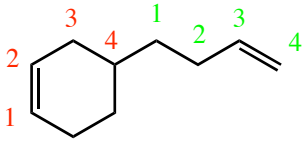


allyl

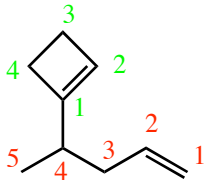
4-vinyl-1-cyclohexene

4-allyl-1-cyclohexene

For all other substitutents, the name comes from the alkyl name. insert "en" before "yl"
How is it numbered? from the point of attachment



but yl
^
en
butenyl



cyclobutenyl

4-(3-butenyl)-1-cyclohexene

4-(1-cyclobutenyl)-1-pentene

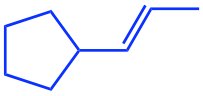
<u>Stereochemistry in nomenclature</u>

When is it necessary to specify the stereochemistry of an alkene?

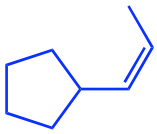
when there are two possible stereoisomers

When may <u>cis</u> and <u>trans</u> be used?

when there are only 2 substituents



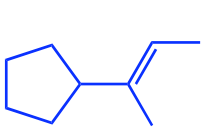
cis
E



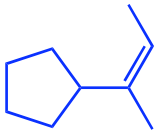
trans
Z

When are <u>E</u> and <u>Z</u> appropriate?

<u>can</u> be used anytime
<u>must</u> be used when there are 3 or 4 substituents
or when there is more than one C=C



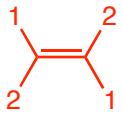
E



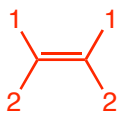
Z

What are the priorities for E and Z?

1. mass of atom attached to C=C
2. mass of 3 atoms attached to that atom, etc

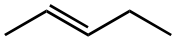


<u>E</u>

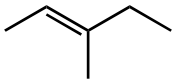


<u>Z</u>

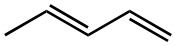
When is a number needed in the name with the E or Z? when there is more than one both are stereoisomers



trans-2-pentene or (E)-2-pentene — could be either - 2 substituents, no number



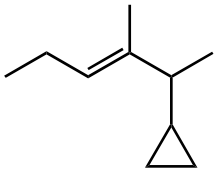
(E)-3-methyl-2-pentene — has to be E/Z - 3 substitutents, no number



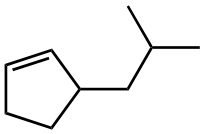
(E)-1,3-pentadiene or trans-1,3-pentadiene — could be either - only one C=C has stereochemistry, no number

(2E, 4Z)-2,4-hexadiene — has to be E/Z - 2 double bonds, give numbers!

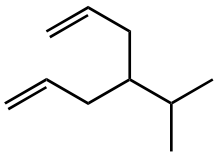
Practice:



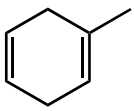
(E)-2-cyclopropyl-3-methyl-3-hexene



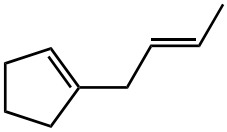
3-isobutyl-1-cyclopentene or 3-(2-methylpropyl)-1-cyclopentene



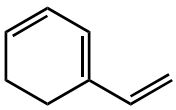
4-isopropyl-1,6-heptadiene or 4-(1-methylethyl)-1,6-heptadiene



1-methyl-1,4-cyclohexadiene



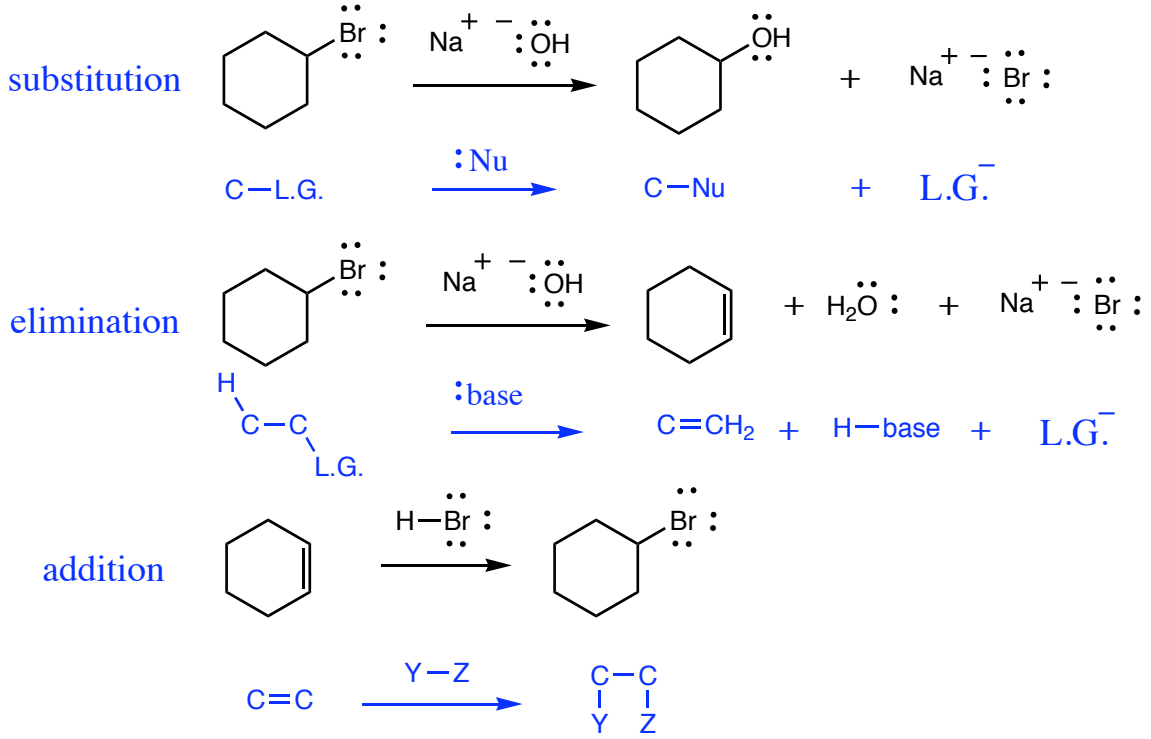
trans-1-(2-butenyl)-1-cyclopentene



1-vinyl-1,3-cyclohexadiene

IV. Introduction to C=C reactions

The following are three basic types of reactions - substitution, elimination, and addition.

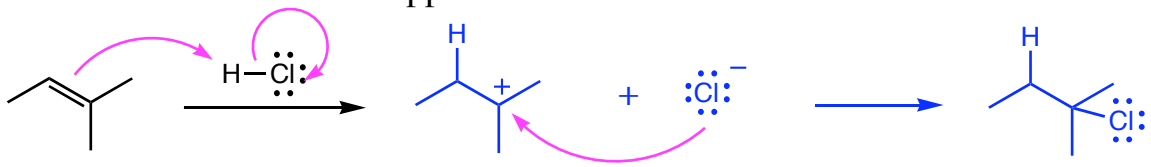


Addition reactions of C=C are NOT effective on benzene rings. These pi bonds arespread across the whole ring, and therefore don't behave the same as isolated C=C.

V. Addition of HX to alkenes

<u>Carbocation mechanism</u>

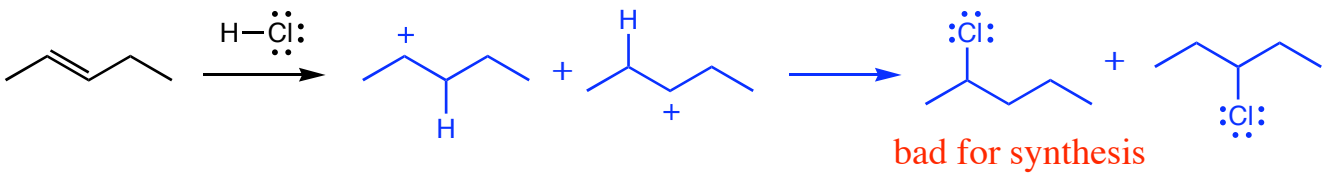
Alkyl halides can be formed by the reaction of alkenes with hydrogen halide acids like HI, HBr, and HCl. How could this happen?



Which side will the halogen end up on, and why?

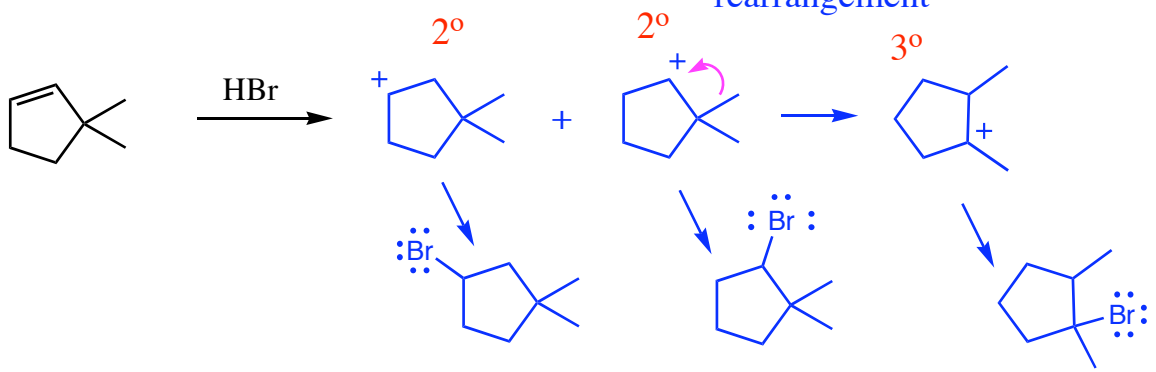
on the side where the more stable C+ was formed - more substituted side

What if two carbocations of equal energy could be formed? a mixture of products will be formed

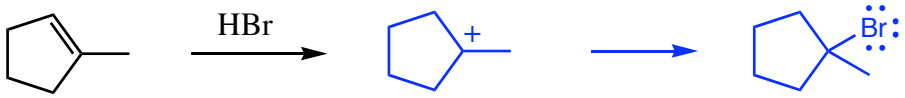


bad for synthesis

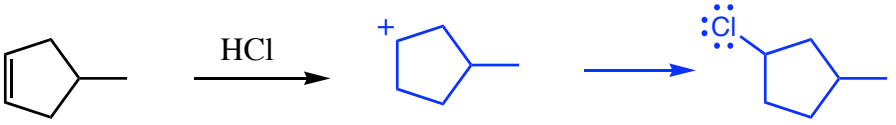
What will happen if the carbocation can rearrange? products form before and after rearrangement



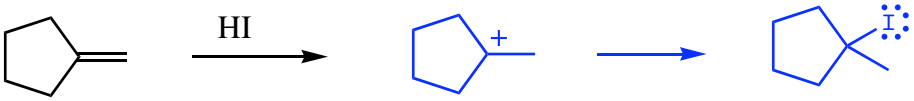
Show the carbocation(s) and product(s) of the following reactions.



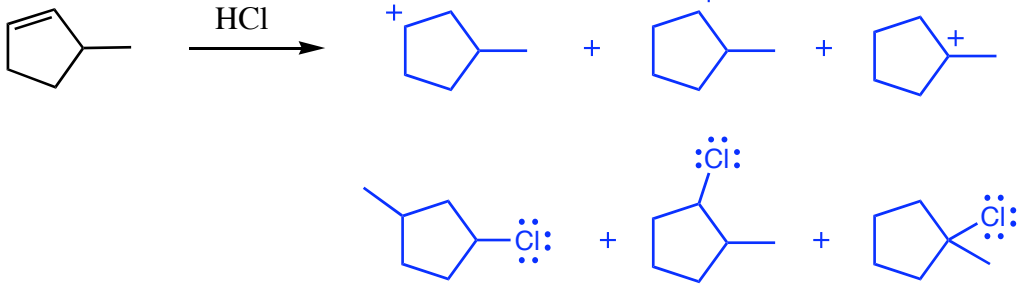
only 3° C+ forms



symmetrical - 2° C+ are the same

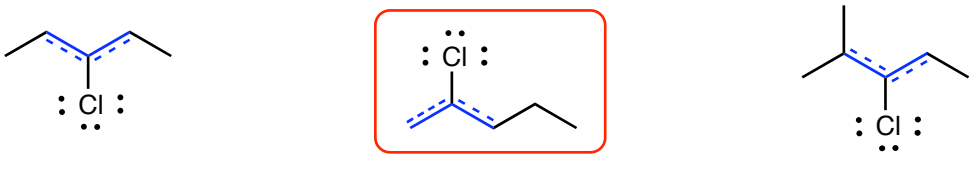


only 3° C+ forms

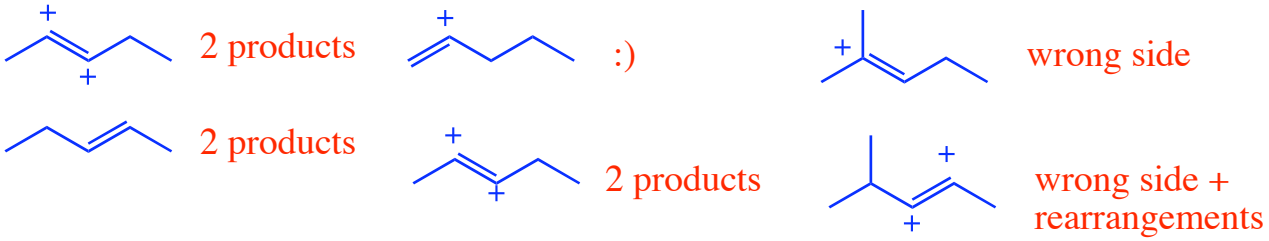


two 2° C+ form, one can rearrange

Which of these alkyl halides could be synthesized using this reaction?



same

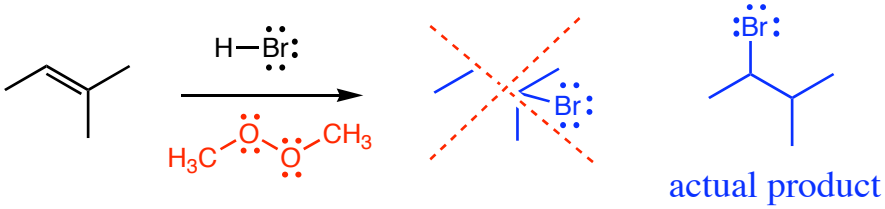


2 products :) wrong side

2 products 2 products wrong side + rearrangements

Radical mechanism

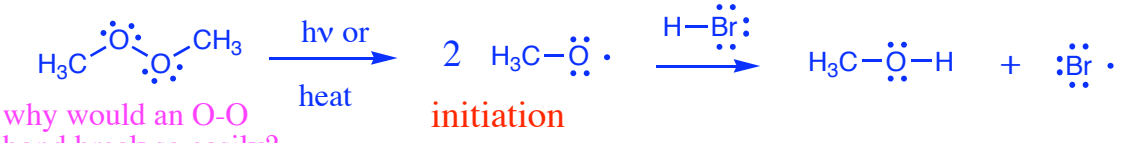
When chemists were first investigating this reaction, they noticed that once in a while with HBr, the products were opposite of what they expected. The halogen was on the spot where the less stable C+ would have been. Therefore, a C+ must not be involved in the reaction.



actual product

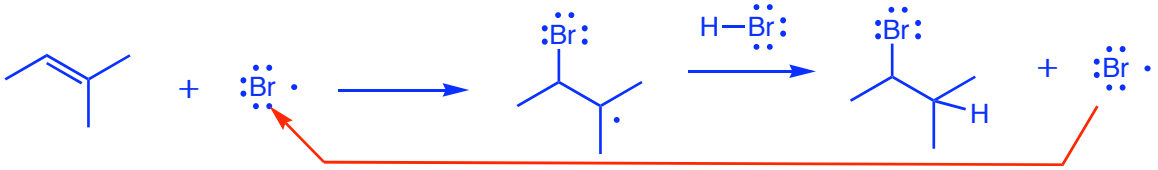
only with HBr, doesn't happen with HCl or HI

Eventually they discovered that this only occurred when trace amounts of organic peroxides were present. These caused a radical reaction to occur instead.



why would an O-O bond break so easily?

initiation

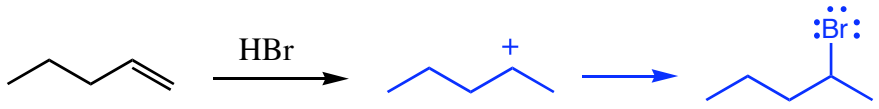


Why is only a small amount of peroxides necessary to change the products?

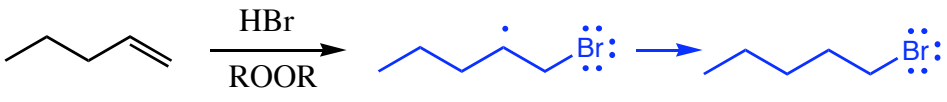
it is catalytic - once Br is produced, it keeps being regenerated

Will rearranged products form? no - radicals don't rearrange

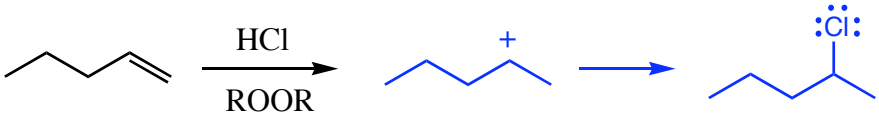
Give the reactive intermediate, then the products of the following reactions.



no organic peroxide
more subst. side



radical mechanism
less subst. side



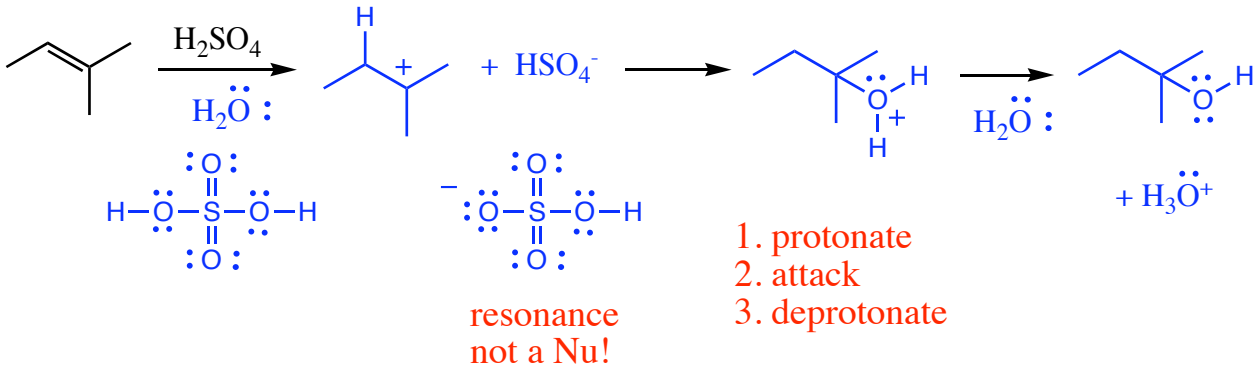
no effect on HCl or HI
- more subst. side

no rearrangements

VI. Hydration of alkenes

Acid-catalyzed hydration

If sulfuric acid is used instead of HBr or HCl, a different product is formed.



Why is this reaction different from the reaction with HX?

X^- is a Nu, HSO_4^- is not

If H_2SO_4 in water solution is used, what is the acid that actually reacts with the alkene?

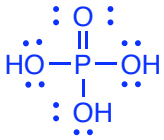
$H_2SO_4 + H_2O \rightarrow HSO_4^- + H_3O^+$ this reaction may be written with just H_3O^+ as the reagent

How much acid is needed to make the reaction work?

only a drop - is it regenerated (catalytic)

Why do you think this reaction is called "hydration of an alkene"?

water is added - an H to one side, an OH to the other

Would phosphoric acid (H_3PO_4) work?  yes

If one side of the C=C is more substituted than the other, which side gets the OH? Why?

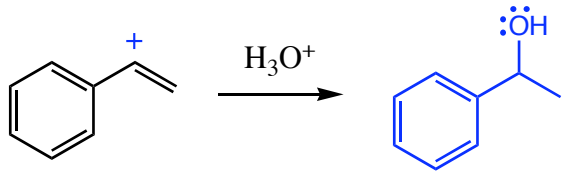
OH goes to the more subst side - that's where the more stable C+ forms

If both sides are equally substituted, what will happen?

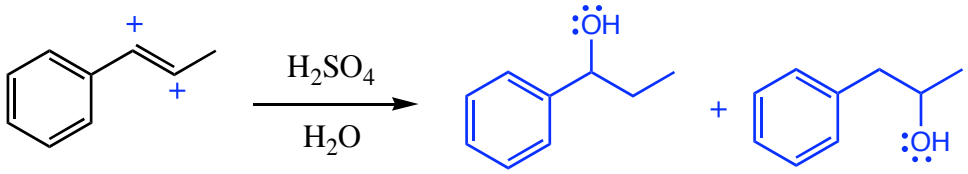
mixture of two products will form - OH on either side :(

Will rearrangements occur? yes - if the C+ could become more stable

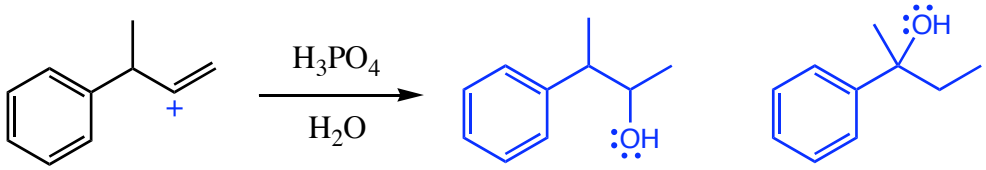
Predict the products of the following reactions:



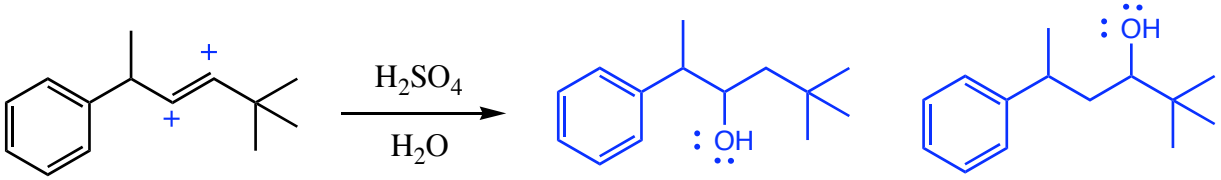
2° C+ is more stable than 1°



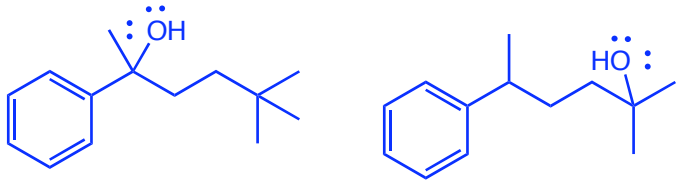
both C+ are 2°



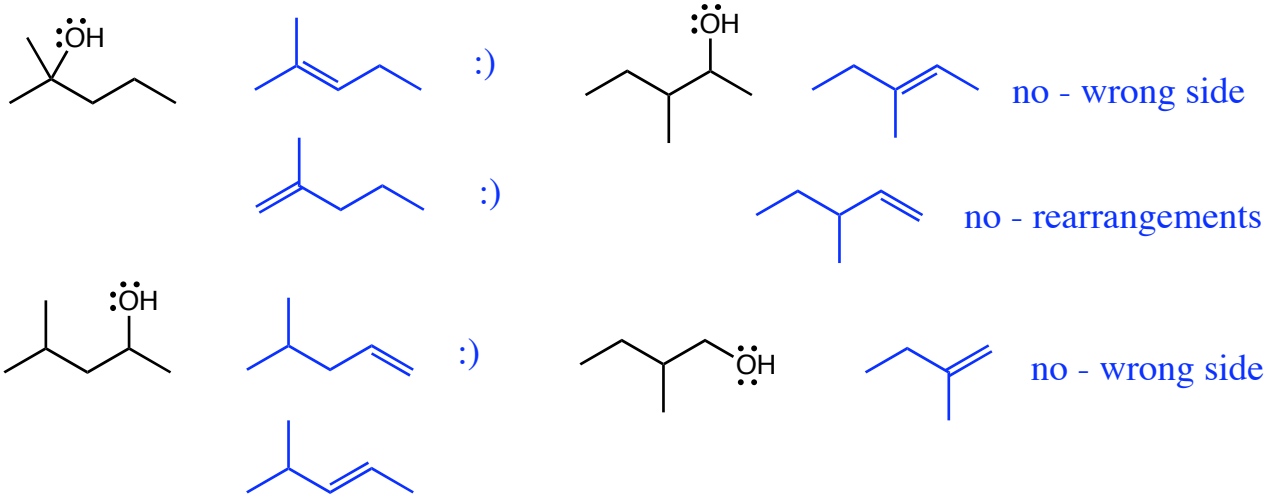
2° C+ forms,
then rearranges



two 2° C+ form,
then both can rearrange



Which of the following alcohols could be formed as the **only** products of a hydration reaction?



no - wrong side

no - rearrangements

no - wrong side

no - both sides
plus rearrangements

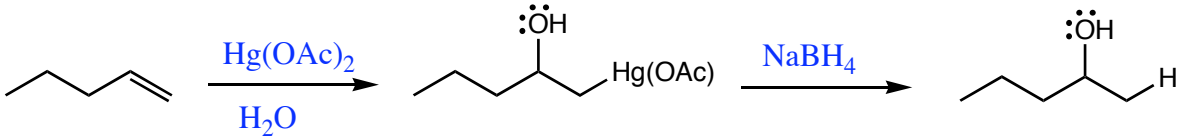
What limitations does acid-catalyzed hydration have when using it for synthesis?

forms C+, rearrangements
OH always goes to the more substituted side
equally substituted C=C give two products

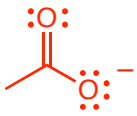
Two other hydration reactions have been developed which solve some of these problems; however, they have more complex mechanisms.

Oxymercuration-reduction

What are the reagents necessary for the two steps of oxymercuration-reduction?



What is does OAc stand for?



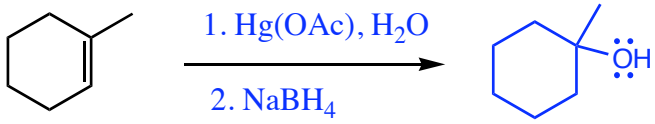
What happens in the first step?

OH is added to one side, Hg to the other

What happens in the second step?

C-Hg bond is broken, C-H bond is formed

How can both steps be shown with one arrow?



What is the regioselectivity of this reaction?

OH goes to the more substituted carbon

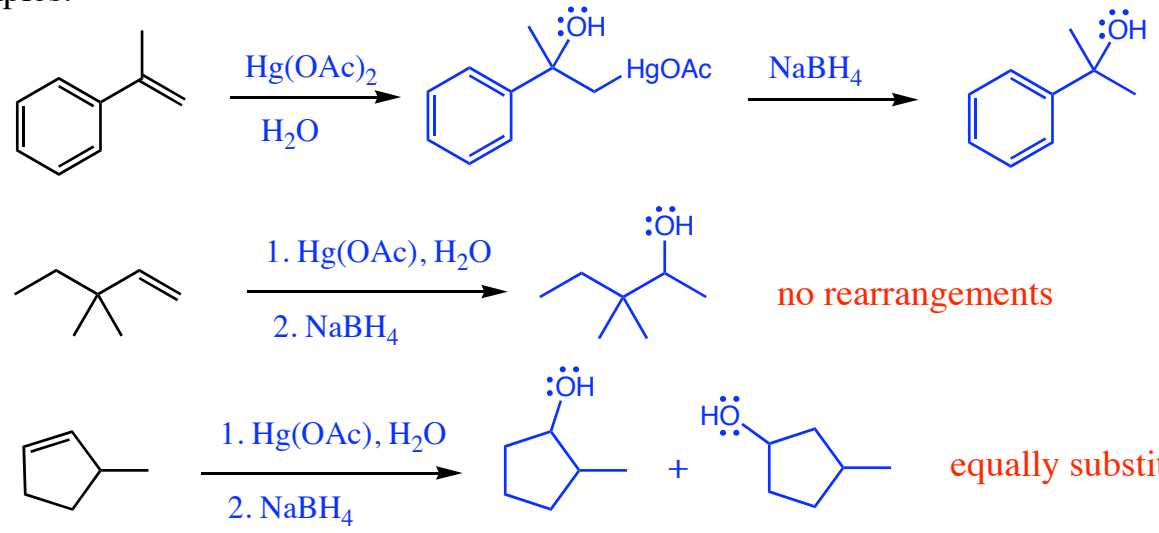
Will we learn the mechanism for this reaction?

Nope - too complex, not necessary to understand results

No rearrangements occur in this reaction - what does this imply?

no carbocation is formed

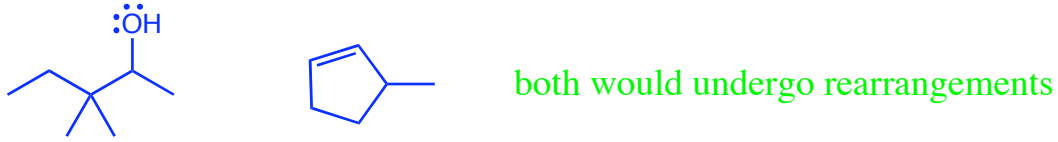
Examples:



Which of the problems with acid-catalyzed hydration does this solve?

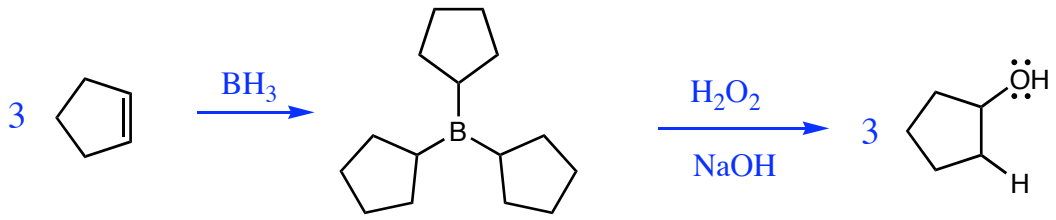
no C+, no rearrangements

Which of the products above couldn't be synthesized with acid-catalyzed hydration, but could be with oxymercuration-reduction.

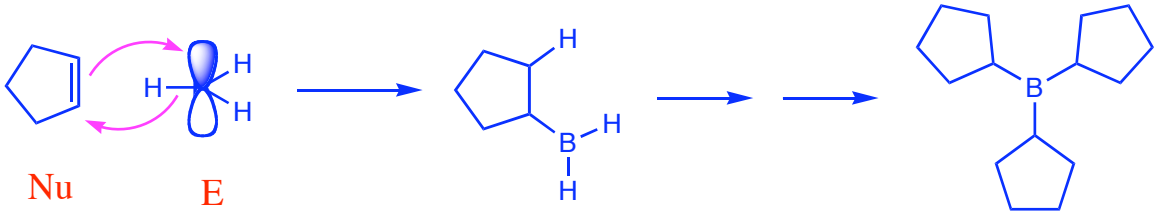


<u>Hydroboration-oxidation</u>

What are the reagents necessary for the two steps of hydroboration-oxidation?



What happens in the first step?



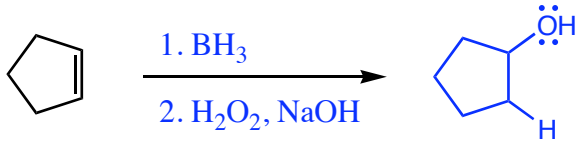
Write in the actual stoichiometry of the reaction.

What happens in the second step?

the C-B bond is broken, C-OH bond is formed

don't worry about the mechanism of this step

How can both steps be shown with one arrow?



The stoichiometry of this reaction is usually not shown.

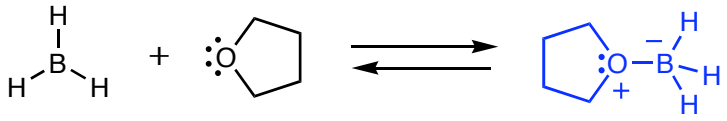
The regioselectivity of this reaction is controlled by sterics. Which side do you think is most likely to attach to the B? How does this affect the product?

less substituted side attached to B, so the OH ends up there

Why is BH_3 difficult to work with? its a gas

How else can BH_3 be represented? B_2H_6 - forms a dimer in the gas phase

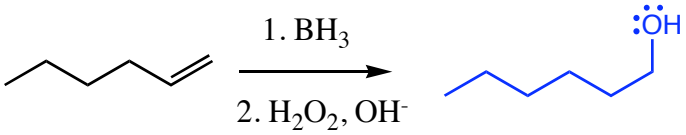
Why is it often dissolved in THF? it forms a more stable complex



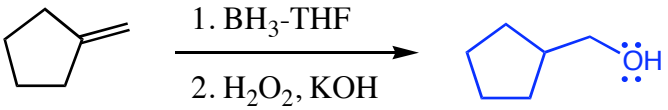
Do rearrangements occur in this reaction?

no - no C+ is formed

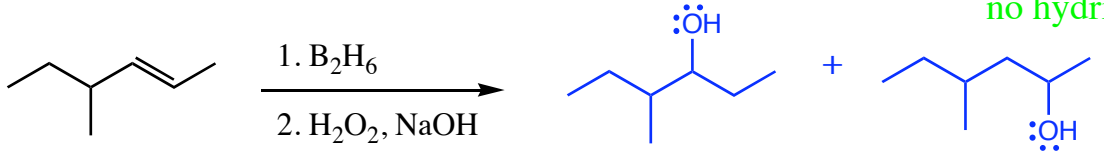
Predict the products of the following reactions.



OH goes to less subst. side

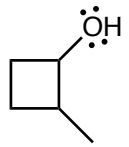


ditto

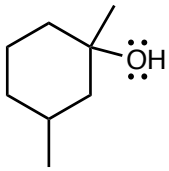
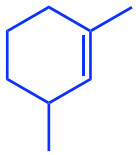
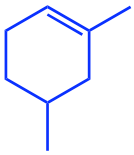
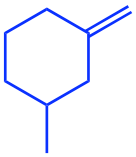


equally substituted
no hydride shift

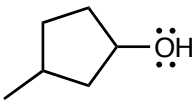
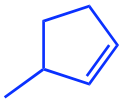
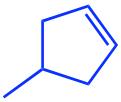
Draw all alkenes from which the following alcohols could be synthesized. Then decide if oxymercuration-reduction or hydroboration-oxidation could be used to give only the desired product.



HB-Ox :) :(2 products with either reaction

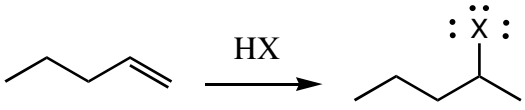





OM-red :) OM-red :) OM-red :)

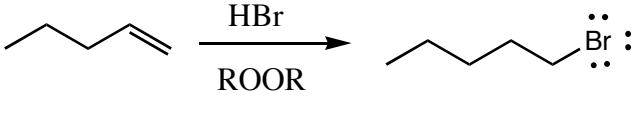




:(2 products OM-red or HB-ox :)

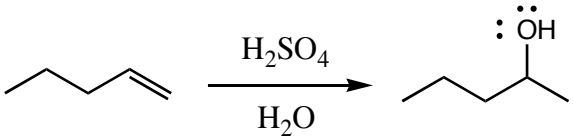
Summary of reactions:



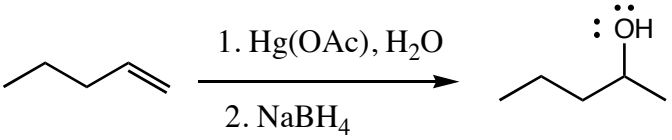
X goes to more subst. side
rearrangements



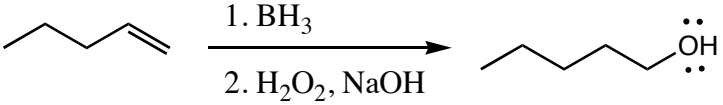
Br goes to less subst. side
no rearrangements



OH goes to more subst side
rearrangements



OH goes to more subst. side
no rearrangements



OH goes to less subst. side
no rearrangements