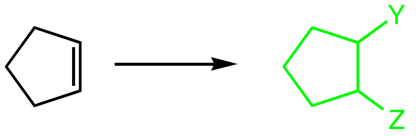
Learning Guide for Chapter 12 - Alkenes (II)

I. Addition reactions of alkenes

Introduction to addition reactions

What happens in an addition reaction?



C=C goes to C-C

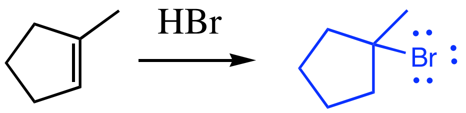
each side forms a bond to a new atom

this describes the result, not the mechanism!

Review of addition reactions from the previous chapter:

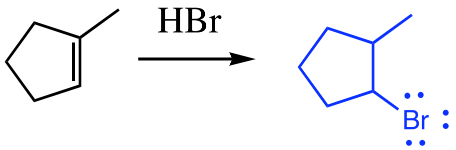
What new compounds result from the following reactions?
What type of product is formed?
What regioselectivity is demonstrated?
What type of mechanism occurs?

1. addition of HBr



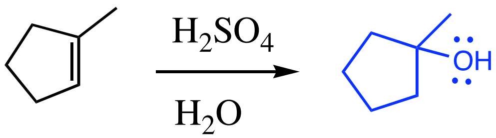
alkyl halide
Br goes to more subst side
carbocation mechanism (rearrangements)

2. addition of HBr with peroxide



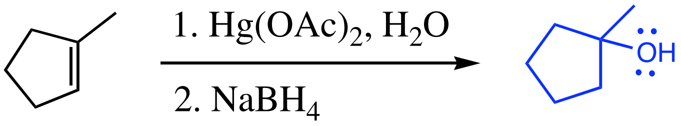
alkyl halide
Br goes to less subst side
radical mechanism

3. acid catalyzed hydration



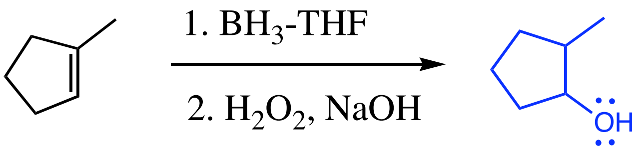
alcohol
OH goes to more subst side
carbocation mechanism (rearrangements)

4. oxymercuration-reduction



alcohol
OH goes to more subst side
no rearrangements

5. hydroboration-oxidation

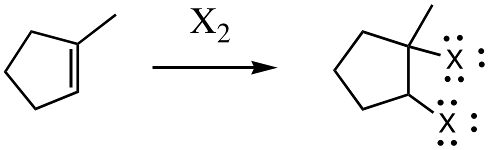


alcohol
OH goes to more less side
no rearrangements

Preview of reactions in this chapter:

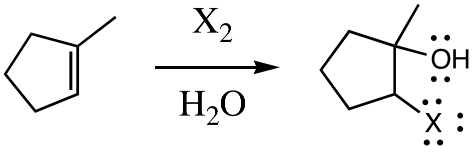
What type of product is formed?
What regioselectivity is demonstrated?

6. addition of X_2



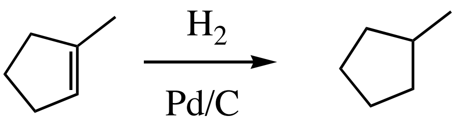
vicinal dihalide
a halogen goes to both sides
(no regioselectivity!)

7. addition of X_2 with H_2O



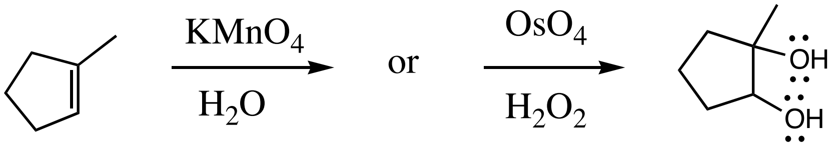
halohydrin
OH goes to more subst side

8. catalytic hydrogenation



alkane
H goes to both sides
reduction

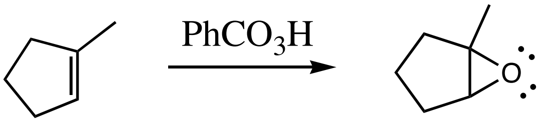
9. hydroxylation



vicinal diol
OH goes to
both sides

oxidation

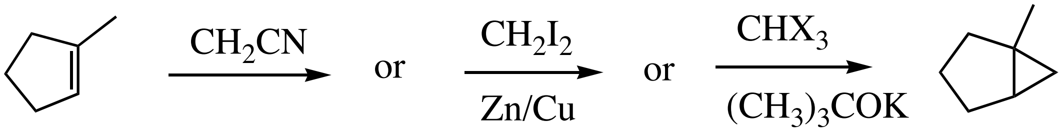
10. epoxidation



epoxide
same O bonded to both sides

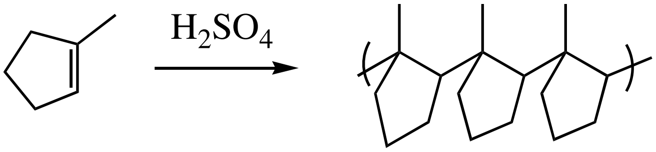
oxidation

11. cyclopropanation



cyclopropane
same O bonded to both sides

12. polymerization



polymer
C=C's attach to each other
end to end

So, what new compounds can we make from alkenes using addition reactions? Which of these are the most useful?

alkyl halides - can be used in S_N2 rxns

alcohols - very useful!

vicinal dihalides - not commonly needed

halohydrins - might be useful

alkanes - only way so far to make

vicinal diols - can be useful

epoxides - can be used to make other things

cyclopropanes - not very common, but this is the only way (in this class) to make them

polymers - plastics $$$

Catalytic hydrogenation of alkenes

During catalytic hydrogenation, what gets added to the double bond? two H's

What kind of catalyst is needed? metal such as Pd, Pt, Rh, or Ni

finely divided, precipitated on C

note relationship on Periodic Table; often called noble metals

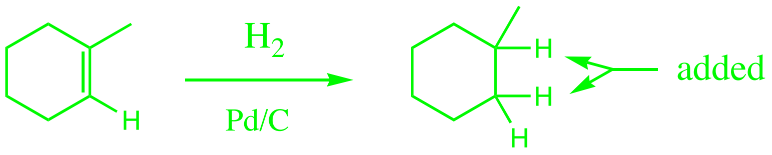
How do these catalysts need to be handled? very carefully - pyrophoric!

Why would it be a good idea to recycle them? expensive

What do we call it when the catalyst is a different state of matter than the reaction?

heterogeneous catalysis

Write a reaction for the catalytic hydrogenation of 1-methylcyclohexene.



Do we need to worry about regioselectivity? nope - both H's are the same

What kind of apparatus is needed to perform this reaction?

Parr shaker - H_2 tank, glass reaction bottle, motor to shake it show image

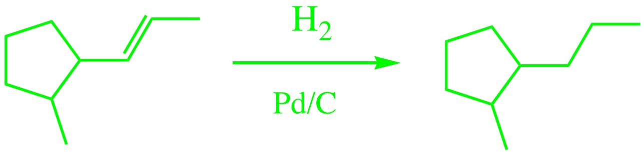
What do we know about the mechanism of this reaction?

no Nu or E

no rearrangements - no C+

H_2 and pi bond form weak bonds to metal surface, then to each other show diagram

How many alkenes with the formula C_9H_{16} could be used as the starting material to make 1-methyl-2-propylcyclopentane?



11! (9 constitutional isomers + 2 stereoisomers)

Hydroxylation of Alkenes

What is added to the C=C in a hydroxylation reaction? OH to both sides

What kind of product results? vicinal diol (also called a glycol)

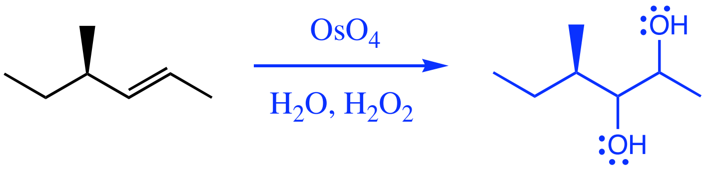
How is this different from oxymercuration-reduction and hydroboration-oxidation?

they only add one OH, form an alcohol

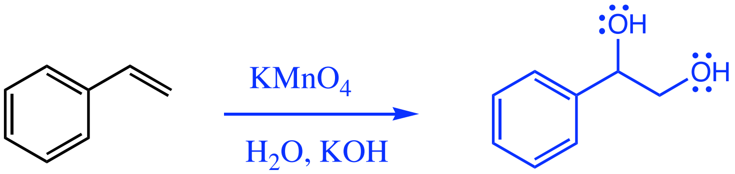
Fill in the table showing the two reagents commonly used in hydroxylation.

reagent:	$KMnO_4$	OsO_4
used with:	NaOH	H_2O_2
advantage:	cheap, easy to use	gives only the correct product
disadvantage:	gives side products	expensive, toxic, volatile

Which reagent would you used with the following starting materials? Write a reaction.



OsO_4 enantiomerically pure compound - don't want to lose any



MnO_2 cheap, readily available starting material

brown precip

purple soln

Why would $KMnO_4$ make a good chemical test, while OsO_4 would not?

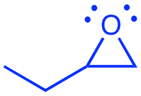
$KMnO_4$ gives a visible color change - purple to brown color - easy to see, also it is cheap, not too toxic

OsO_4 is too dangerous and difficult to work with, plus it gets regenerated

show demo with cyclohexene

Epoxidation of Alkenes

What is an epoxide? 3-membered ring w/ an O



What functional group are they a subset of? ethers

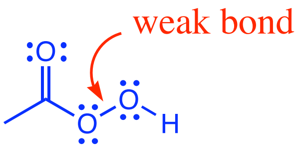
How reactive are they, and why? much more reactive than normal ethers - ring strain

Why would we want to make them? good intermediate
sometimes found in natural products

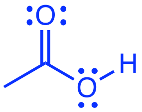
more about epoxides in ether chapter

What kind of reagent can we use to make epoxides from alkenes? peroxyacids

What do they look like? souped up carboxylic acids



peroxyacid

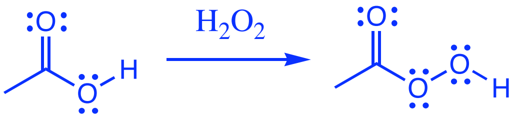


regular carboxylic acid

Why are they so reactive? O is very electronegative, O-O bonds are weak

How are they abbreviated? RCO_3H

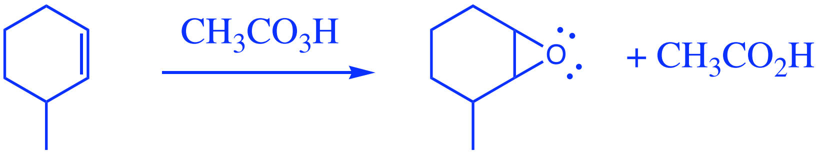
How can you make a peroxyacid? react a carboxylic acid with hydrogen peroxide



What happens to them during the reaction with alkenes?

go back to carboxylic acids

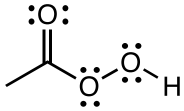
Draw a reaction in which 3-methyl-1-cyclohexene is converted to an epoxide using peroxyacetic acid.



Why are peroxyacids a good reagent to use when there are other functional groups in the molecule?

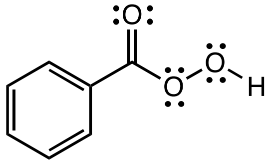
it only reacts with C=C

Give the solubility and any other special properties of the peroxyacids below.



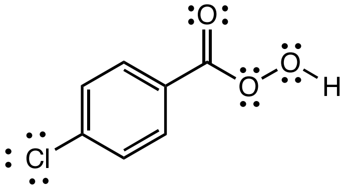
peroxyacidic acid

simplest stable peroxyacid
soluble in water, alcohols



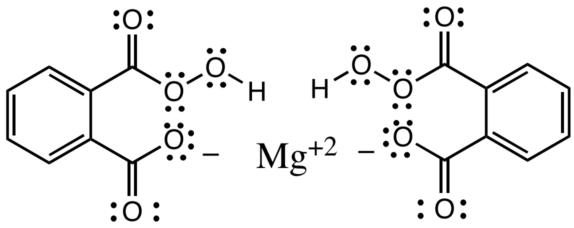
peroxybenzoic acid

soluble in low polarity solvents



m-chloroperoxybenzoic acid (MCPBA)

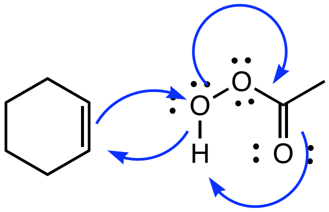
soluble in low polarity solvents
product crystallizes out of solution
somewhat shock sensitive



magnesium monoperoxyphthalate (MMPP)

soluble in water, alcohols
crystalline
stable

What type of mechanism does this reaction have?



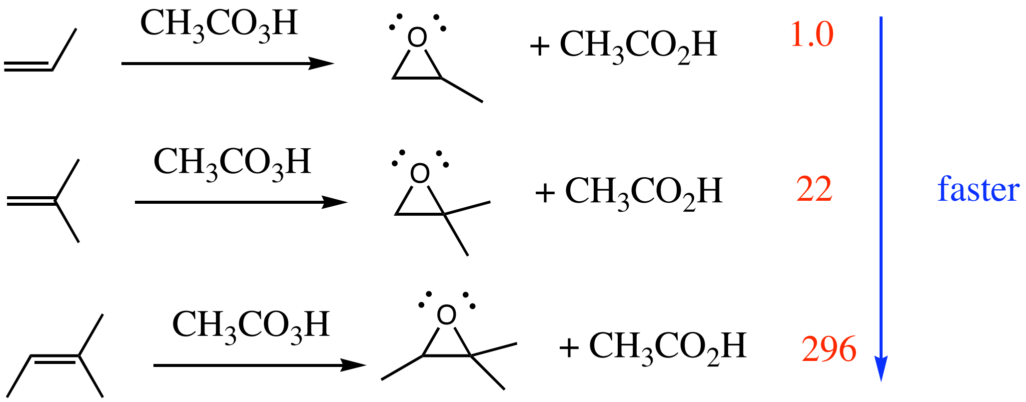
electrocyclic

What role does the alkene play? nucleophile

Why can the oxygen be attacked?

it wants electrons - the other O is pulling them away

Explain the relative rates of the following reactions.

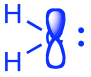


More C's attached; C is more EN than H, makes the alkene a better Nu

Cyclopropanation of Alkenes

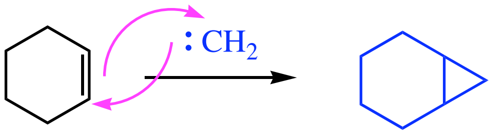
What happens when an alkene reacts with a carbene? a cyclopropane ring is formed

What is a carbene?



reactive intermediate
no charge, lone pair, empty orbital

Predict how a carbene will react with an alkene:



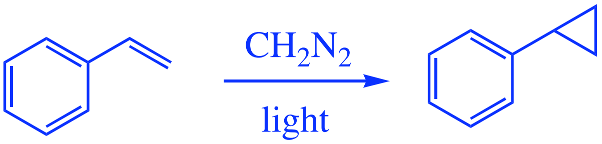
alkene is the Nu, attacks carbene, fills empty orbital, lone pair attacks the other C

How can diazomethane be used to make a carbene?

$$CH_2N_2 \quad = \quad H_2\underset{-}{\overset{..}{C}}-\underset{+}{N}\equiv N: \xrightarrow[\text{or light}]{\text{heat}} :CH_2 \quad + \quad :N\equiv N:$$

Write the reaction of diazomethane with vinylbenzene (also known as styrene).

1



What problems are associated with this reaction?

carbene is very reactive - side products result

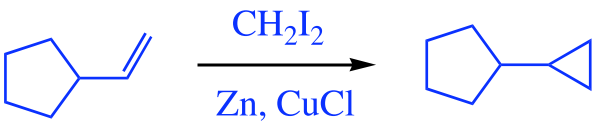
diazomethane is explosive and toxic

What two chemists discovered a reagent that gives better yields and isn't explosive?

Simmons & Smith

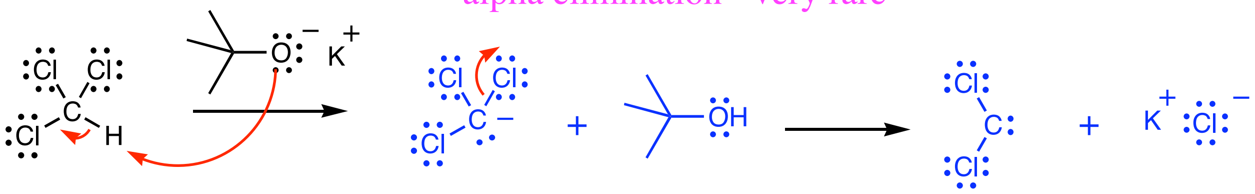
Write a reaction using this reagent to make cyclopropylcyclopentane.

2



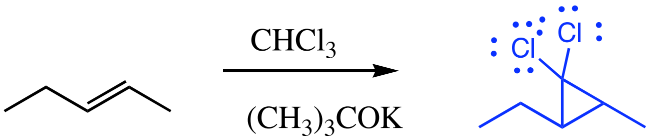
What happens when chloroform or bromoform react with potassium <u>tert</u>-butoxide?

alpha elimination - very rare



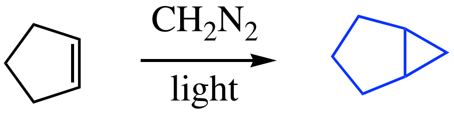
carbene

Give the product of the reaction shown below.

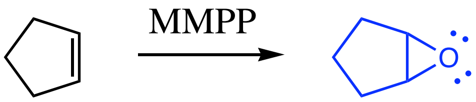


(Cl's can be removed using other reactions)

How are the products of the two reactions below different?

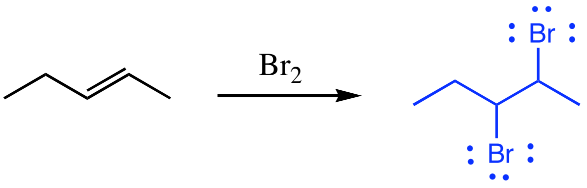


cyclopropane rings don't have an O



<u>Addition of X_2 to alkenes</u>

What kind of compound is formed when Br_2 is added to an alkene?



vicinal dihalide

What other halogens may be used? F, Cl, Br, I

Br_2 works

most commonly used

Cl_2 works

I_2 can be used, but the products decompose easily (why? sterics - I is huge)

F_2 is too reactive (will even react with glass!)

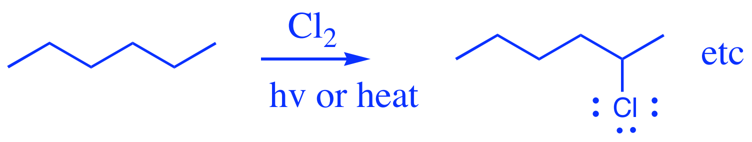
What do we need when choosing a solvent?

it has to dissolve alkene and halogen - nonpolar

also, can't react with the X_2

What would happen if hexane were used?

it would react with the halogen if light or heat were present

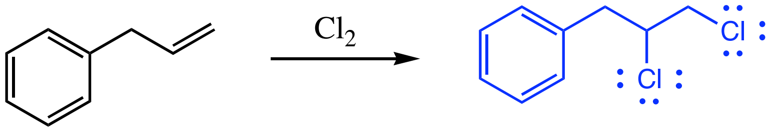


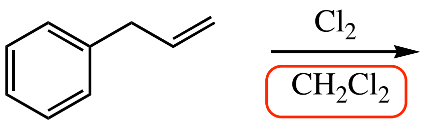
substitution rxn

radical goes to any 2° spot

What solvent is most often used? CH_2Cl_2

Is it always written? no





same thing!

solvent - don't freak out!

If you had two test tubes, one with cyclohexane and one with cyclohexene, how could you tell them apart?

both clear liquids

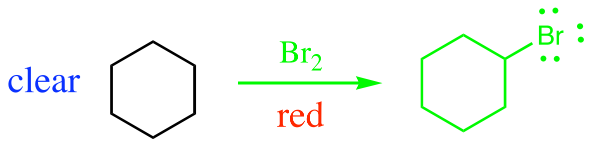
they smell different (if you had a labeled bottle, you could use this)

IR - look for C=C band, C-H on C=C band

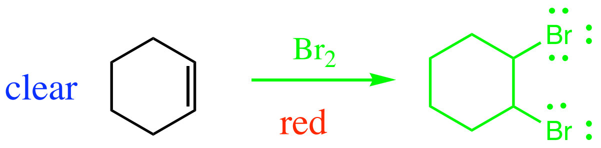
NMR - look for peaks at 4.5-6.5

chemical test - add Br_2 solution

show demonstration in 2 test tubes



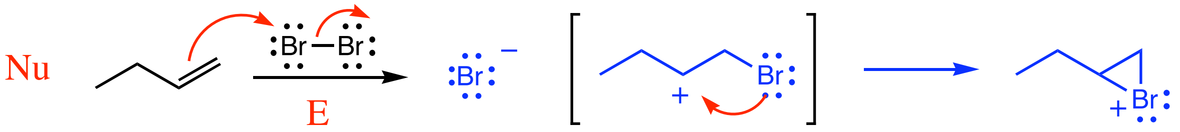
stays red - rxn is slow



goes clear - rxn is fast

What happens first in the mechanism of this reaction?

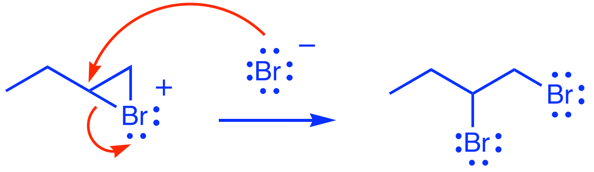
alkene attacks a Br, pushes the other one off, Br attaches to the other C



doesn't stop here

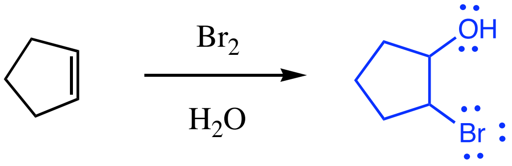
this is about the only time you'll ever see a halogen with a + charge

What happens next?



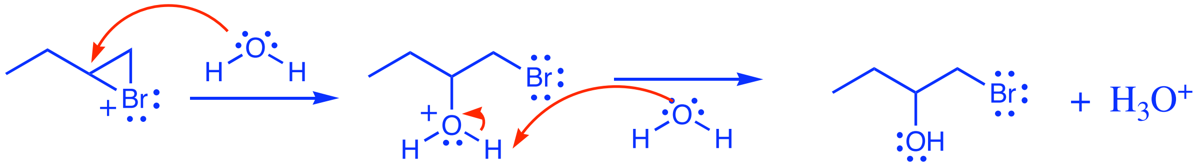
no rearrangments occur, so no C+ is formed

What kind of product results if water is present?

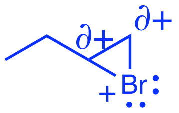


When does the water participate in the mechanism?

it takes the place of the bromide ion - there are more water molecules around

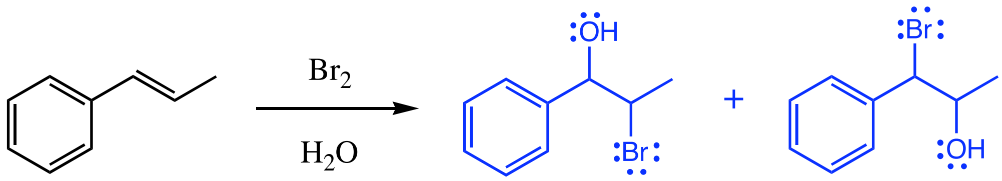


Why does the water attack the more substituted side of the ring?



more substituted C shares more of the charge with Br
Nu is attracted to this C

What products would result from the following reaction?



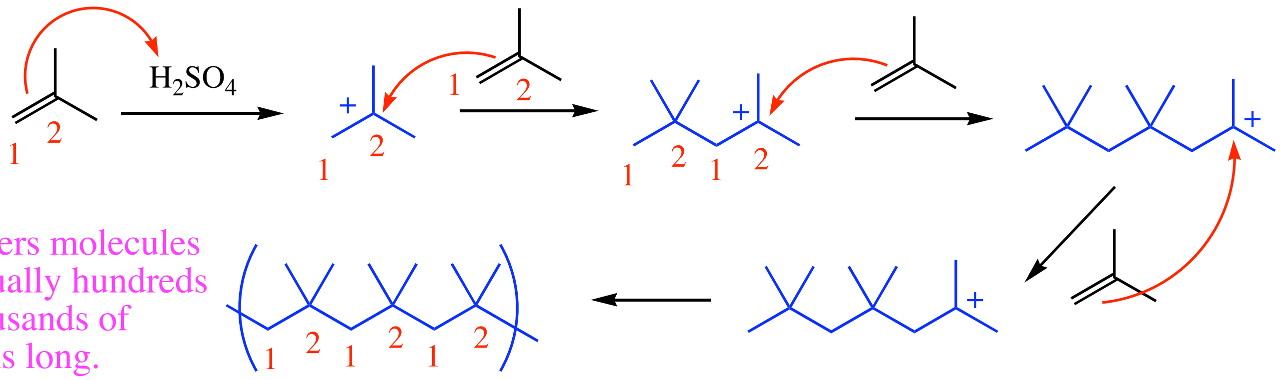
Polymerization of alkenes

What is a polymer? a long molecule made by attaching small ones together

Under what conditions will an alkene form a polymer?

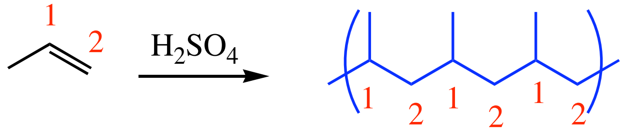
a small amount of a reagent that makes a carbocation or radical, no other reagents

Isobutylene is used to make a polymer that can substitute for rubber. How does it form in the presence of sulfuric acid?

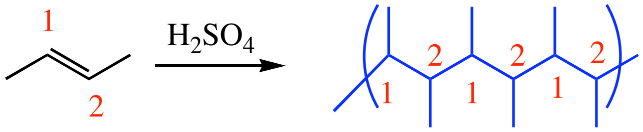


Polymers molecules are usually hundreds or thousands of carbons long.

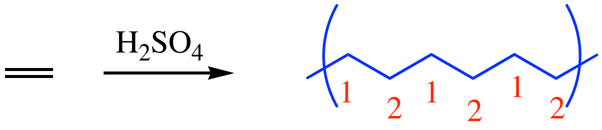
How would the polymer be different if the alkenes below were used?



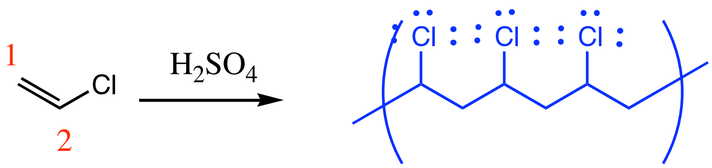
polypropylene



each of these polymers would have different properties



polyethylene



polyvinylchloride PVC

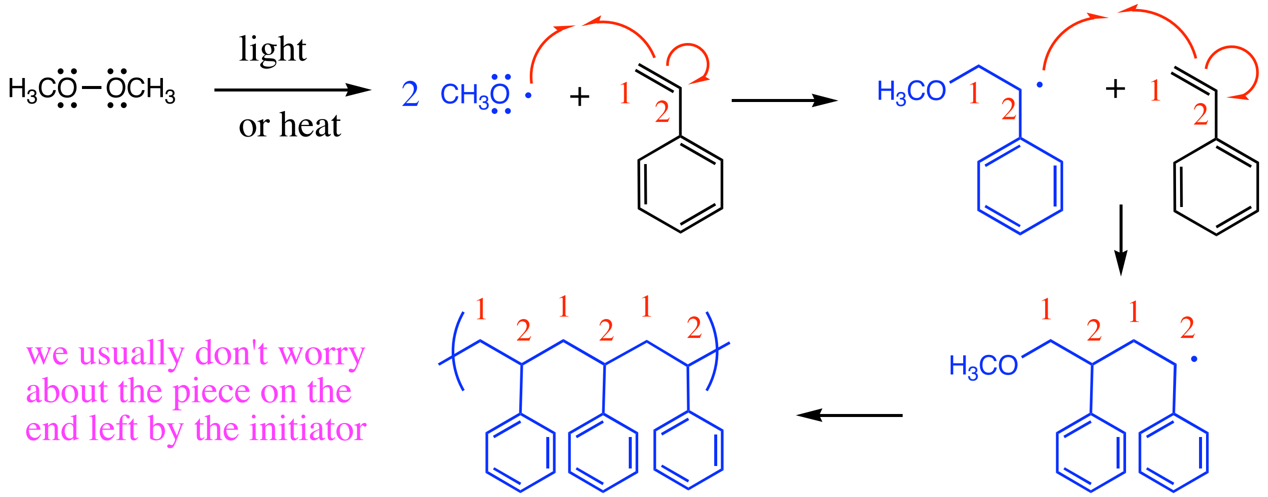
What problems can this reaction cause when storing alkenes or taking a boiling point?

they can turn to polymers in the bottle or while taking a BP

What can be done to prevent this?

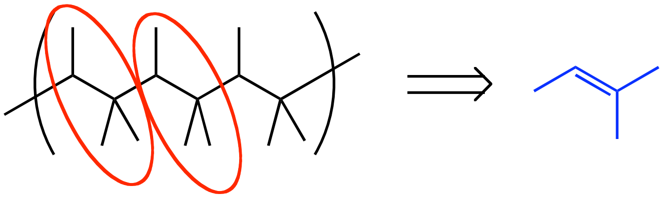
add inhibitors that react with C+ and C. to stop the chain reaction

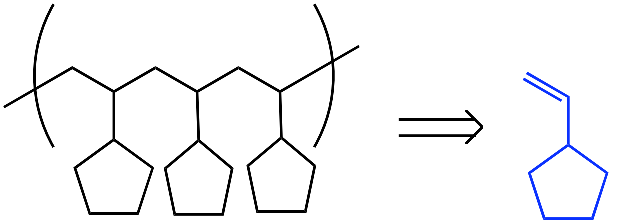
Polystyrene is a clear, brittle plastic used in drinking cups, CD cases, etc, and in making styrofoam. How can it be formed using an organic peroxide?



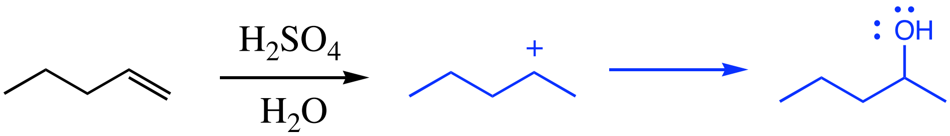
we usually don't worry about the piece on the end left by the initiator

What alkene would be needed to make the following polymers?

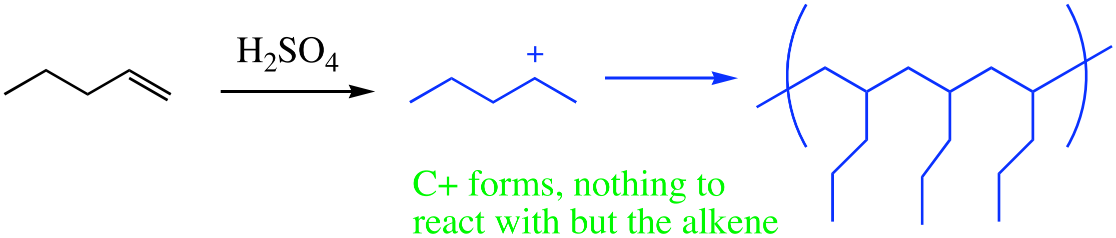




How are the two reactions below different?



C+ forms, reacts with water



C+ forms, nothing to react with but the alkene

II. Stereochemistry of Alkene Reactions

What stereochemistry have we seen with substitution and elimination reactions?

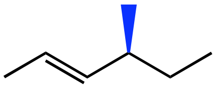
substitution - inverted (S_N2), racemized (S_N1)

elimination - anti elimination (E2)

What stereochemistry is possible with addition reactions? syn, anti, non-selective

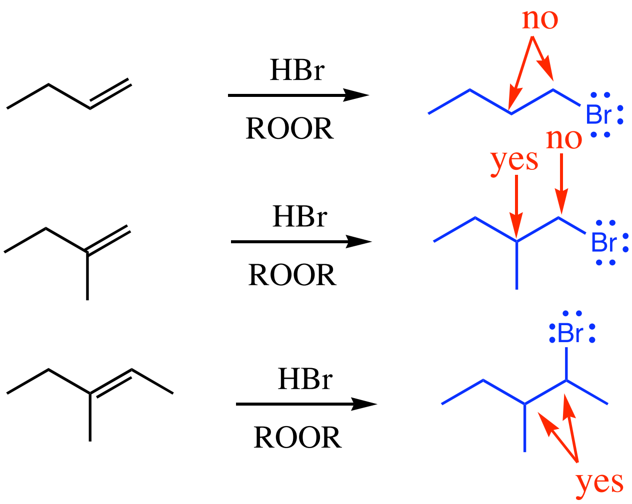
Can an alkene have a stereocenter?

yes - E/Z, but not a chiral one; at least not the C=C atoms



won't be changed by alkene reactions

Can a stereocenter be formed by an alkene reaction? yes!



no new stereocenters

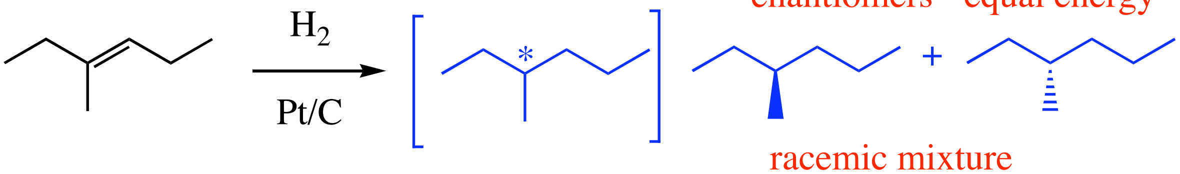
one new stereocenter

two new stereocenters

next page

If only one of the C=C carbons becomes a stereocenter, what should we expect to happen?

enantiomers - equal energy



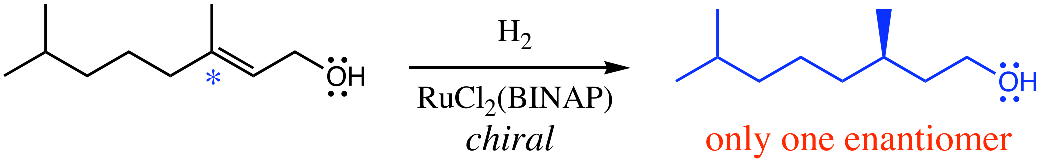
racemic mixture

What might cause an optically active mixture to be formed?

chiral reagent or starting material

figuring this out is graduate level - just be aware of the possibility

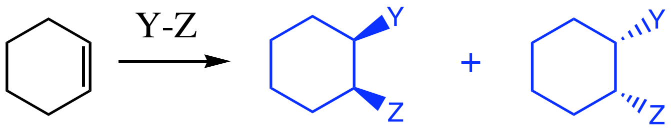
one new stereo-center



only one enantiomer

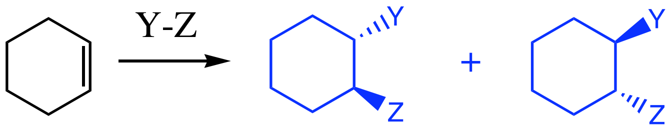
If both of the C=C carbons become stereocenters, what can happen?

1) syn addition - new substituents added to the same side



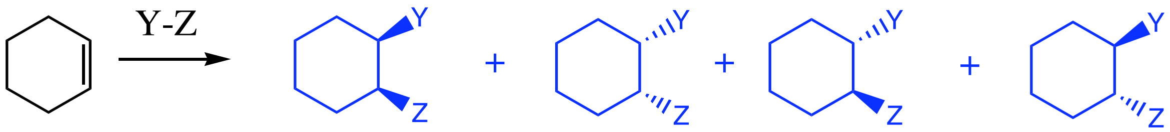
if Y=Z and there is a plane of symmetry, meso

2) anti addition - new substituents added to the opposite sides



even if Y=Z, there will be no plane of symmetry - 2 enantiomers

3) nonselective addition - new substituents are added to the same and opposite sides



What determines which of these three options will happen?

mechanism of the reaction

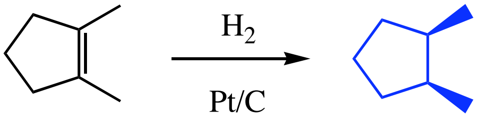
What reactions give syn addition?

hydroboration-oxidation
hydrogenation
hydroxylation
epoxidation
cyclopropanation

What do the syn additions have in common?

both new substituents added at the same time

Hydrogenation



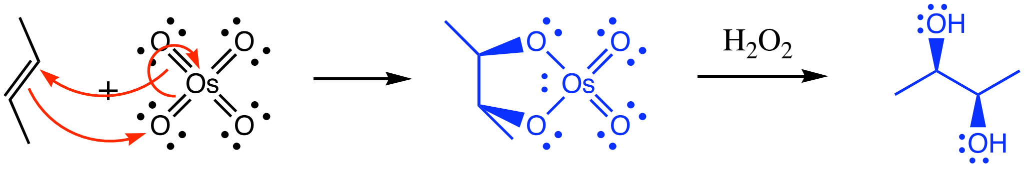
meso

H's added from the same face - the side that is toward the surface of the catalyst

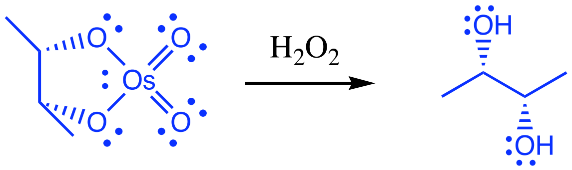
Hydroxylation

both O's attach at the same time

meso? NO! (use models
if you don't see it

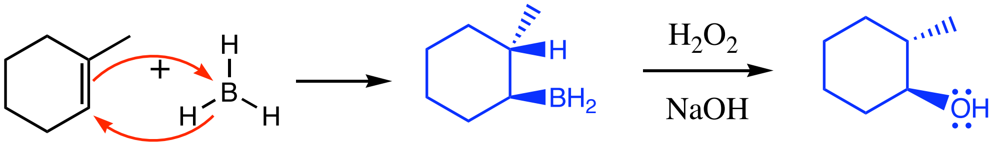


we're only looking at this
mech so you can see why it's syn

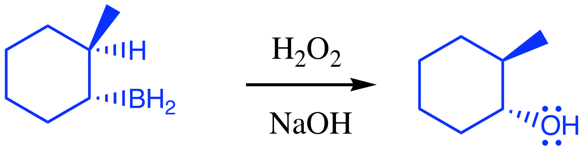


Hydroboration-oxidation

B and H attach at the same time, B --> O stereochem conserved



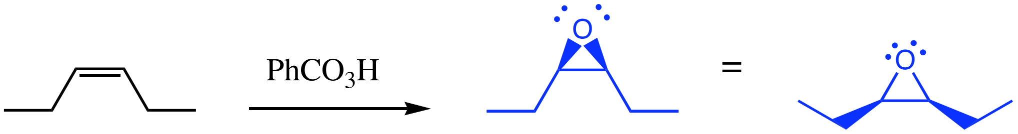
notice that the
focus is on the
new substituents,
not the ones
already there!



Epoxidation

O attaches to both C's at the same time

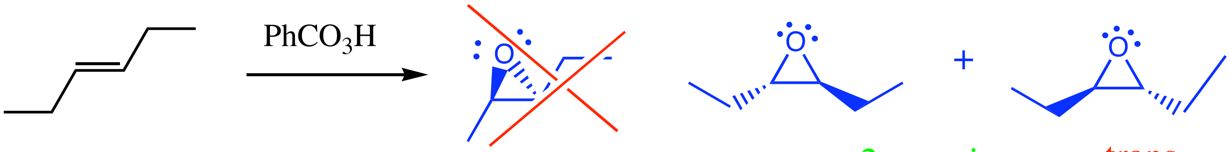
cis



cis

meso

trans



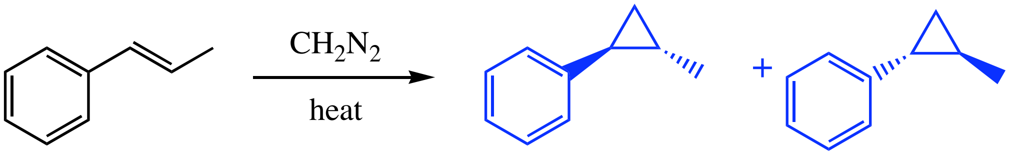
Notice that in syn addition, the
stereochemistry of the alkene is retained.

2 enantiomers

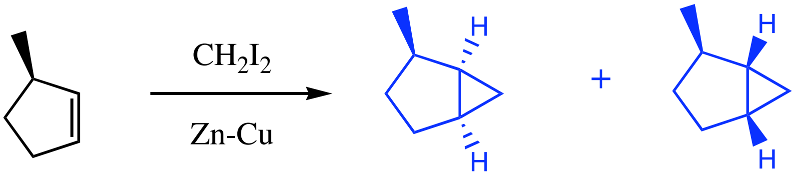
trans

Cyclopropanation

carbene attaches to both C's at the same time



2 enantiomers



note that a pre-existing
stereocenter is not changed!

2 diastereomers
stereoselective - chiral
starting material

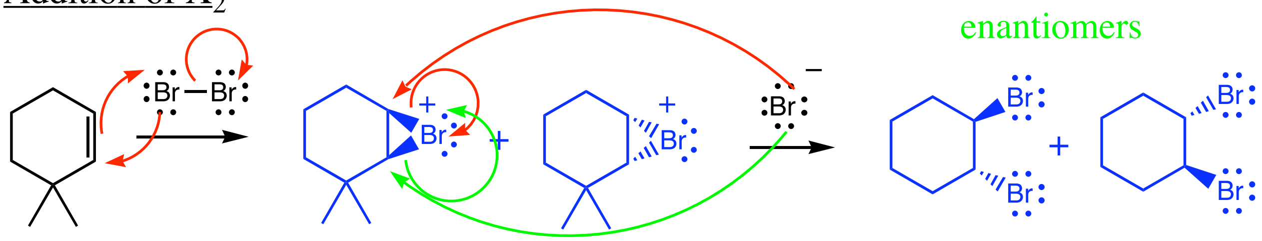
What reactions give anti addition?

addition of X_2

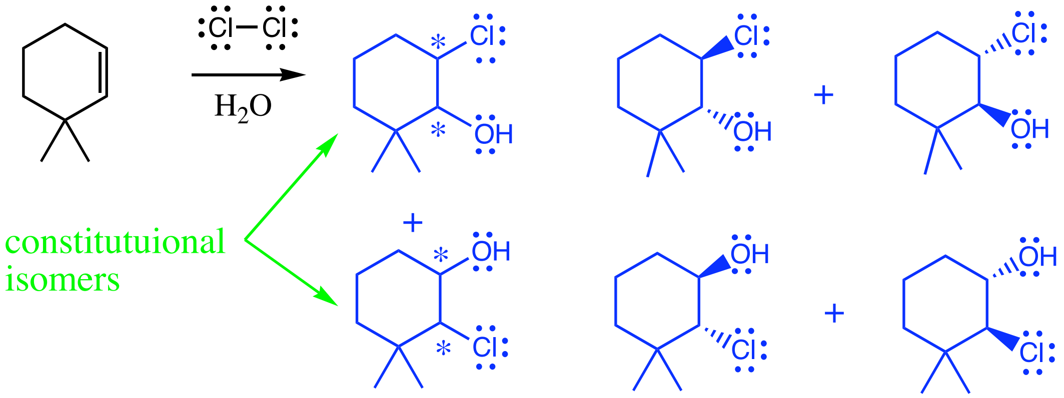
addition of X_2 with H_2O

Why? bromide ion (or water) must attack from behind the ring

Addition of X_2



Addition of X_2 with H_2O



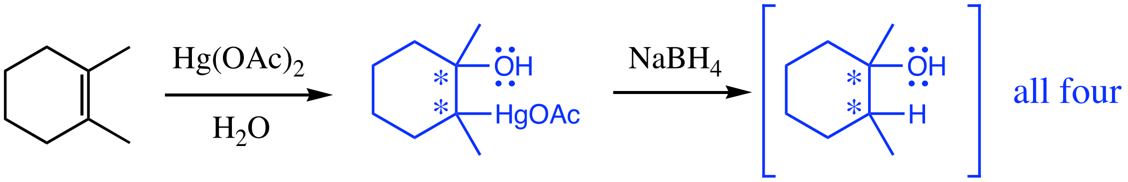
Which reactions give nonselective addition?

addition of HX
addition of HBr with organic peroxide
acid-catalyzed hydration
oxymercuration-reduction

What do these reactions have in common? a racemizing step (usually C+ or radical)

Oxymercuration-reduction

reduction step is racemizing

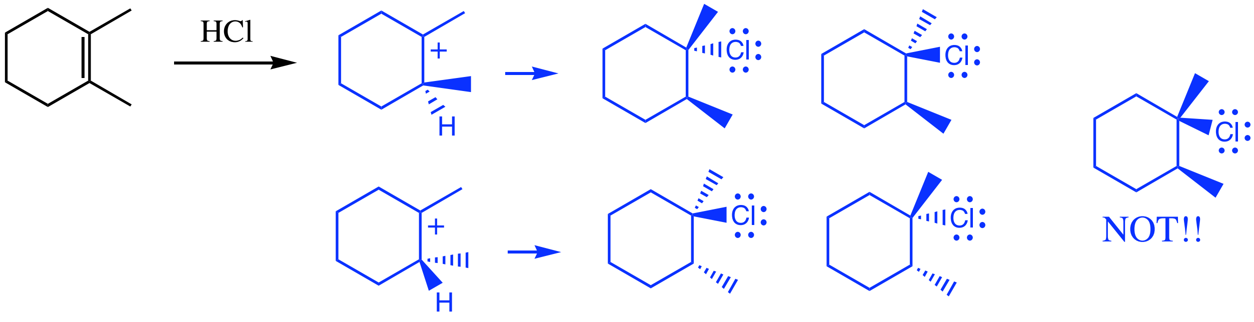


this step is actually anti

but this step is random, so the connection is destroyed

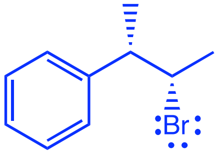
Addition of HX

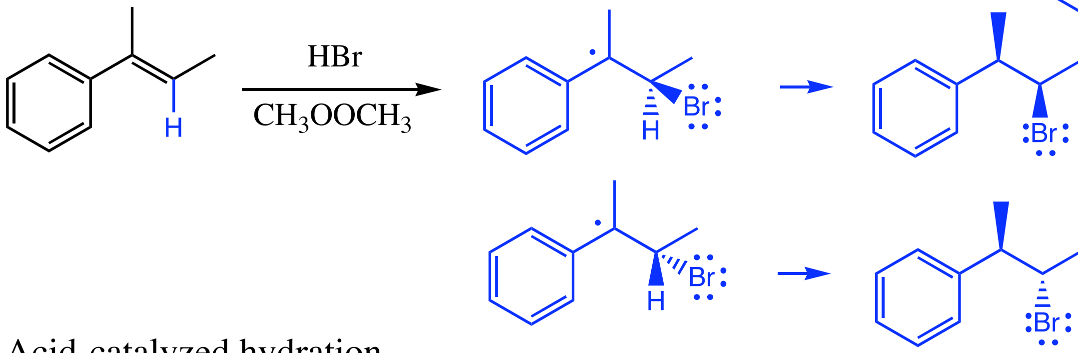
H can come from the top or bottom of the alkene; Cl can come from top or bottom of the carbocation - both are trigonal planar



Addition of HBr with peroxide

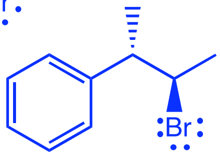
Br radical can attack C=C from top or bottom, H can attack radical from the top or bottom

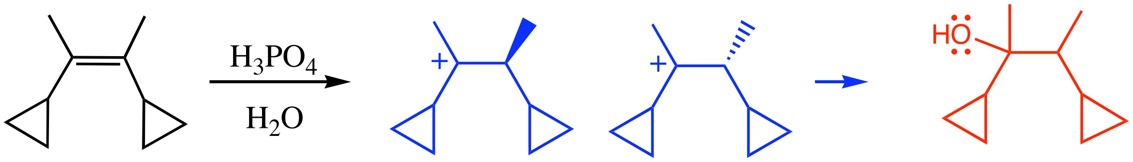




Acid-catalyzed hydration

H, then water can come from either side





all four

What steps should you follow when writing out the products with stereochemistry?

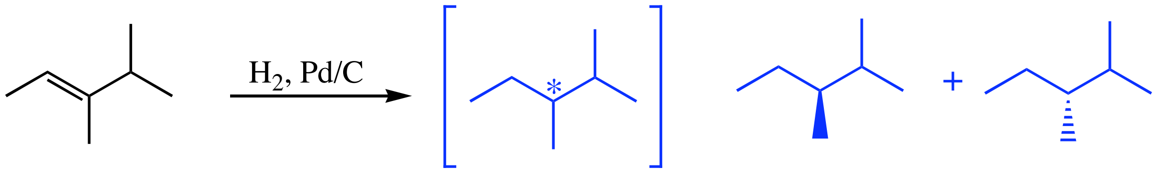
1. Draw all products without stereochemistry (watch for constitutional isomers).
2. Identify the stereocenters in the product.
3. Count them. 0 - you're done.

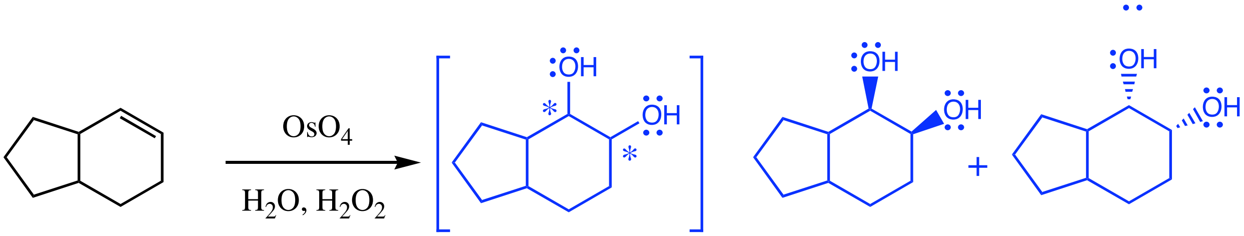
   1 - look for chiral reagent or SM; if not, racemic mixture of enantiomers, if yes, stereoselective, one is favored

   2 - is the reaction syn, anti, or non-selective?

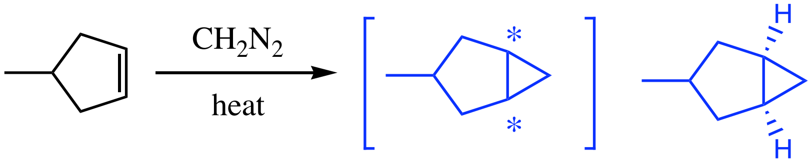
Give all stereoisomers of the following reactions.

doesn't matter that it's syn addition - the other C isn't a stereocenter



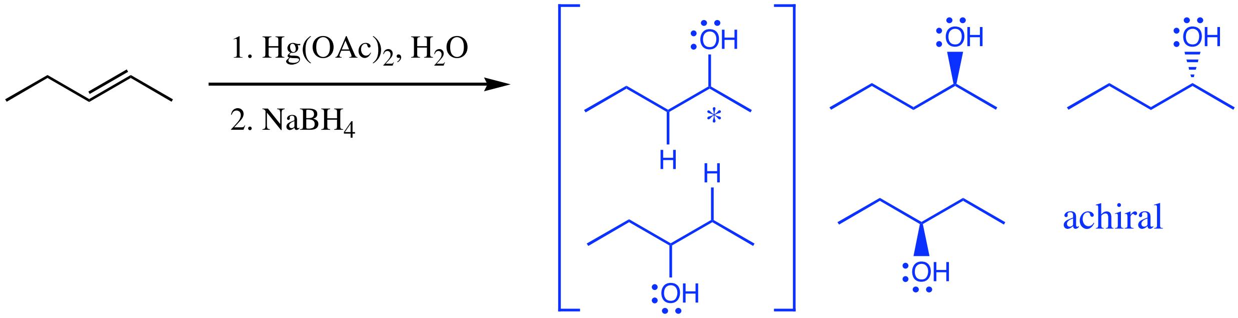


syn addition, 2 enantiomers



meso

don't forget bridgehead carbons!



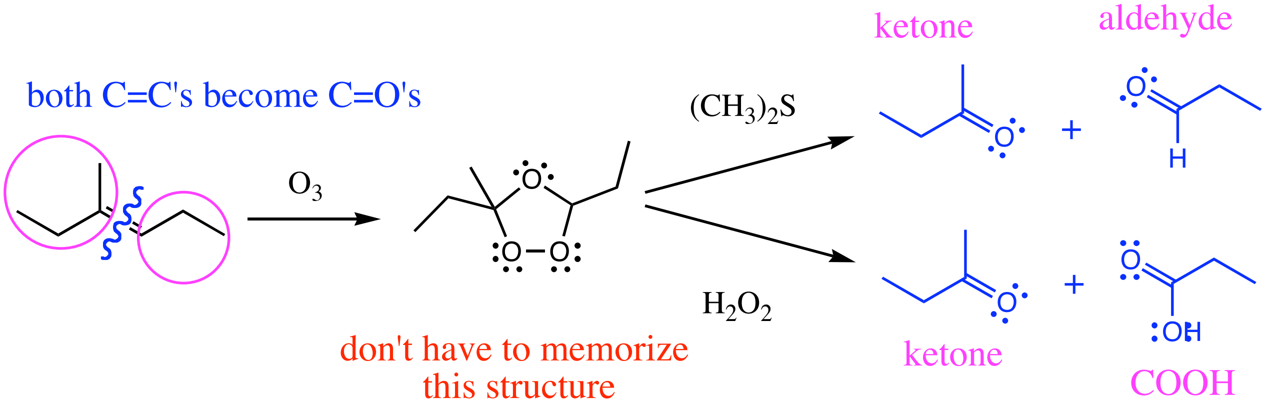
achiral

IV. Oxidative Cleavage of Alkenes

What happens to an alkene when it reacts with ozone?

the C=C bond is completely broken, both C's are oxidized

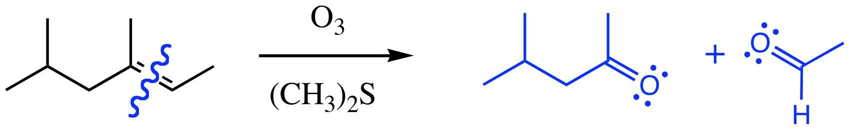
both C=C's become C=O's



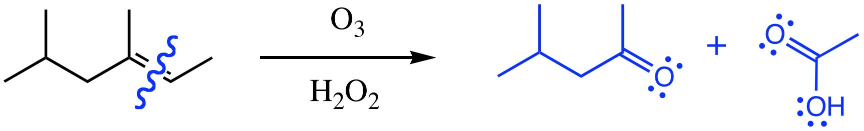
don't have to memorize
this structure

not an addition rxn!

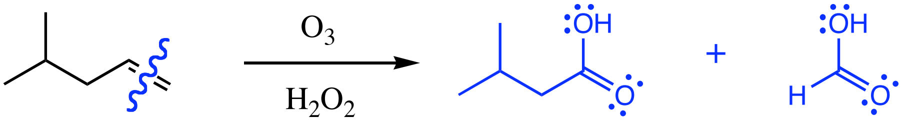
What happens if dimethyl sulfide is present? C's are oxidized to aldehydes and/or ketones



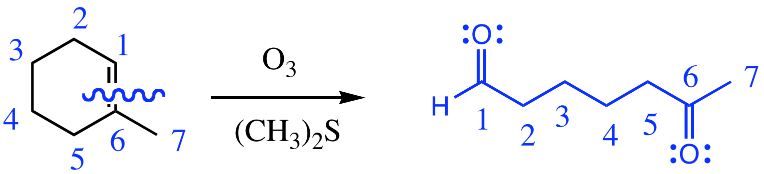
What happens if hydrogen peroxide is present? C's are oxidized to ketones and/or carboxylic acids



What if one of the products has only one C?



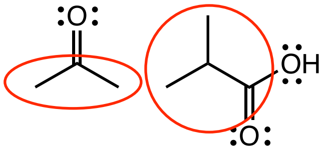
What if the alkene is cyclic?

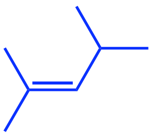


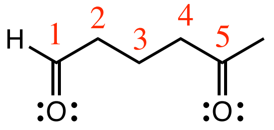
Is this a useful synthetic reaction? not likely - it makes smaller pieces

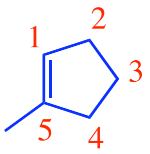
Then why do we care? it used to be a method for determining alkene structure (before spectroscopy)

What alkene could give the following sets of ozonolysis products?

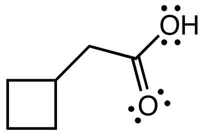


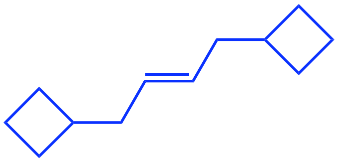






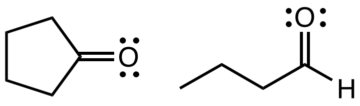
it helps to number cyclic ones

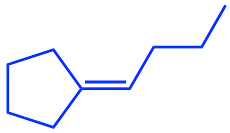




could be cis or trans

only one product = symmetrical





Reaction	Reagents	Product	Mechanism?	Rearrangements?	Regioselectivity	Stereoselectivity
addition of HX	1) HI, HBr, or HCl	alkyl halide	yes	yes	X on more substituted C	nonselective
	2) HBr/ROOR	alkyl bromide	yes	no	Br on least substituted C	nonselective
hydration	1) H_2SO_4 or H_3PO_4, H_2O	alcohol	yes	yes	OH on more substituted C	nonselective
	2) 1. $Hg(OAc)_2$, H_2O 2. $NaBH_4$	alcohol	no	no	OH on more substituted C	nonselective
	3) 1. BH_3-THF 2. H_2O_2, NaOH	alcohol	no	no	OH on least substituted C	syn addition
addition of X_2	1) I_2, Br_2, or Cl_2	vicinal dihalide	yes	no	none	anti addition
	2) I_2, Br_2, or Cl_2 and H_2O	halohydrin	yes	no	OH on more substituted C	anti addition
catalytic hydrogenation	1) H_2, Pd/C	alkane	no	no	none	syn addition
hydroxylation	1) $KMnO_4$, NaOH, H_2O	vicinal diol	no	no	none	syn addition
	2) OsO_4, H_2O_2, H_2O	"	"	"	"	"
epoxidation	1) $PhCO_3H$	epoxide	no	no	none	syn addition
cyclopropanation	1) CH_2N_2, heat	cyclopropane	yes	no	none	syn addition
	2) CH_2I_2, Zn/Cu	cyclopropane	no	"	"	"
	3) CHX_3, $(CH_3)_3COK$	dihalocyclopropane	yes	"	"	"
polymerization	1) H_2SO_4	polymer	yes	no (3°)	none	nonselective
	2) ROOR	polymer	yes	no	"	"
oxidative cleavage	1) O_3, $(CH_3)_2S$	ketone/aldehyde	no	no	none	none
	2) O_3, H_2O_2	ketone/carboxylic acid	"	"	"	"