Learning Guide for Chapter 12 - Alkenes (II)

I. Addition reactions of alkenes Introduction to addition reactions Catalytic hydrogenation of alkenes Hydroxylation of alkenes Epoxidation of alkenes Cyclopropanation of alkenes Addition of X_2 to alkenes Polymerization of alkenes II. Stereochemistry of alkene addition reactions IV. Oxidative cleavage of alkenes Table of alkene additions

I. Addition reactions of alkenes

Introduction to addition reactions

What happens in an addition reaction?



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



2. addition of HBr with peroxide



3. acid catalyzed hydration



4. oxymercuration-reduction

$$\underbrace{1. \text{Hg(OAc)}_2, \text{H}_2\text{O}}_{2. \text{NaBH}_4}$$

5. hydroboration-oxidation



Preview of reactions in this chapter:

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

6. addition of X₂



7. addition of X_2 with H_2O



8. catalytic hydrogenation



9. hydroxylation



10. epoxidation



11. cyclopropanation



12. polymerization



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

Catalytic hydrogenation of alkenes

During catalytic hydrogenation, what gets added to the double bond?

What kind of catalyst is needed?

How do these catalysts need to be handled?

Why would it be a good idea to recycle them?

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

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

Do we need to worry about regioselectivity?

What kind of apparatus is needed to perform this reaction?

What do we know about the mechanism of this reaction?

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

Hydroxylation of Alkenes

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

What kind of product results?

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

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

reagent:

used with:

advantage:

disadvantage:

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

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Why would KMnO₄ make a good chemical test, while OsO₄ would not?

Epoxidation of Alkenes

What is an epoxide?

What functional group are they a subset of?

How reactive are they, and why?

Why would we want to make them?

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

What do they look like?

Why are they so reactive? How are they abbreviated? How can you make a peroxyacid?

What happens to them during the reaction with alkenes?

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?

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



peroxyacidic acid



peroxybenzoic acid



m-chloroperoxybenzoic acid (MCPBA)



magnesium monoperoxyphthalate (MMPP)

What type of mechanism does this reaction have?



What role does the alkene play?

Why can the oxygen be attacked?

Explain the relative rates of the following reactions.



Cyclopropanation of Alkenes

What happens when an alkene reacts with a carbene?

What is a carbene?

Predict how a carbene will react with an alkene:

How can diazomethane be used to make a carbene?

 $CH_2N_2 =$

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

What problems are associated with this reaction?

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

Write a reaction using this reagent to make cyclopropylcyclopentane.

What happens when chloroform or bromoform react with potassium tert-butoxide?



Give the product of the reaction shown below.



How are the products of the two reactions below different?





What kind of compound is formed when Br₂ is added to an alkene?



What other halogens may be used?

What do we need when choosing a solvent?

What would happen if hexane were used?

What solvent is most often used?

Is it always written?



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

What happens first in the mechanism of this reaction?

What happens next?

What kind of product results if water is present?



When does the water participate in the mechanism?

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

What products would result from the following reaction?



Polymerization of alkenes

What is a polymer?

Under what conditions will an alkene form a polymer?

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



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



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

What can be done to prevent this?

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?



What alkene would be needed to make the following polymers?



How are the two reactions below different?



II. Stereochemistry of Alkene Reactions

What stereochemistry have we seen with substitution and elimination reactions?

What stereochemistry is possible with addition reactions?

Can an alkene have a stereocenter?



Can a stereocenter be formed by an alkene reaction?



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

What might cause an optically active mixture to be formed?

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

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

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

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

What determines which of these three options will happen?

What reactions give syn addition?

What do the syn additions have in common?

Hydrogenation

$$\begin{array}{c|c} & H_2 \\ \hline & Pt/C \end{array}$$

Hydroxylation

H_2O_2	
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Hydroboration-oxidation

H ₂ O ₂
NaOH

 H_2O_2

NaOH

Epoxidation

Cyclopropanation

What reactions give anti addition?

Why?

Addition of X₂

Br:

Addition of X₂ with H₂O

Which reactions give nonselective addition?

What do these reactions have in common?

Oxymercuration-reduction

$$\begin{array}{c} & Hg(OAc)_2 \\ \hline H_2O \end{array} \qquad \xrightarrow{\text{NaBH}_4} \end{array}$$

Addition of HX

HCl HCl

Addition of HBr with peroxide

Acid-catalyzed hydration

$$\begin{array}{c} & H_{3}PO_{4} \\ \hline H_{2}O \end{array}$$

Give all stereoisomers of the following reactions.

IV. Oxidative Cleavage of Alkenes

What happens to an alkene when it reacts with ozone?

What happens if dimethyl sulfide is present?

What happens if hydrogen peroxide is present?

What if one of the products has only one C?

What if the alkene is cyclic?

Is this a useful synthetic reaction?

Then why do we care?

What alkene could give the following sets of ozonolysis products?

Reaction	Reagents	Product	Mechanism?	Rearrangements?	Regioselectivity	Stereoselectivity
addition of HX 1) H	1) HI, HBr, or HCl	alkyl halide	yes	yes	X on <u>more</u> substituted C	nonselective
	2) HBr/ROOR	alkyl bromide	yes	no	Br on <u>least</u> substituted C	nonselective
hydration	1) H_2SO_4 or H_3PO_4 , H_2O	alcohol	yes	yes	OH on <u>more</u> substituted C	nonselective
	2) 1. Hg(OAc) ₂ , H ₂ O 2. NaBH ₄	alcohol	no	no	OH on <u>more</u> substituted C	nonselective
	3) 1. BH ₃ -THF 2. H ₂ O ₂ , NaOH	alcohol	no	no	OH on <u>least</u> 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 hydrogenatio	on 1) H ₂ , Pd/C	alkane	no	no	none	syn addition
hydroxylation	1) KMnO ₄ , NaOH, H ₂ O	vicinal diol	no	no	none	syn addition
	2) OsO_4, H_2O_2, H_2O	п	"	n	11	n
epoxidation	1) PhCO ₃ H	epoxide	no	no	none	syn addition
cyclopropanation	1) CH_2N_2 , heat	cyclopropane	yes	no	none	syn addition
	2) CH ₂ I ₂ , Zn/Cu	cyclopropane	no	n	"	'n
	3) CHX ₃ , (CH ₃) ₃ COK	dihalocyclopropane	yes	"	11	n
polymerization	1) H ₂ SO ₄	polymer	yes	no (3º)	none	nonselective
	2) ROOR	polymer	yes	no	"	n
oxidative cleavage	1) O ₃ , (CH ₃) ₂ S	ketone/aldehyde	no	no	none	none
	2) O_3, H_2O_2	ketone/carboxylic aci	d "	n	"	"