

Alkenes

Alkenes

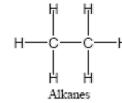


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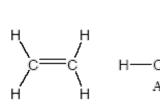
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Unsaturated Hydrocarbons

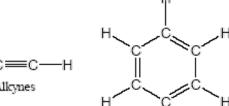
- **Saturated Hydrocarbons** — contain only carbon-carbon single bonds.



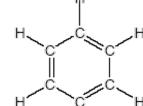
- **Unsaturated Hydrocarbons** — contain carbon-carbon double or triple bonds (more hydrogens can be added).



Alkenes



Alkynes



Aromatics

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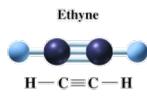
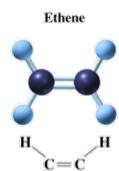
Alkenes and Alkynes

Saturated compounds (alkanes):
Have the maximum number of hydrogen atoms attached to each carbon atom.

Unsaturated compounds:
Have fewer hydrogen atoms attached to the carbon chain than alkanes.

Containing **double bond** are **alkenes**.
 C_nH_{2n}

Containing **triple bonds** are **alkynes**.
 C_nH_{2n-2}

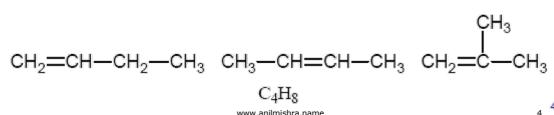
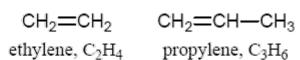


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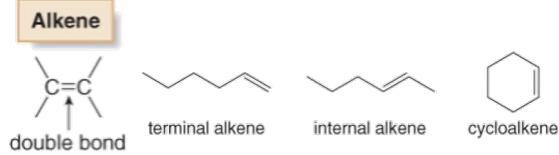
Alkenes

- Alkenes contain **carbon-carbon double bonds**.
 - General formula: C_nH_{2n} (for one double bond)
 - Suffix = **-ene**
- In the carbon-carbon double bond, two pairs of electrons are being shared, leaving the carbon free to bond to two other things.



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Classes of Alkenes

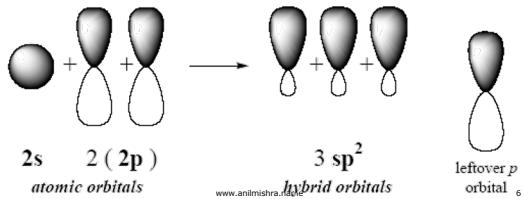


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Hybridization of Alkenes

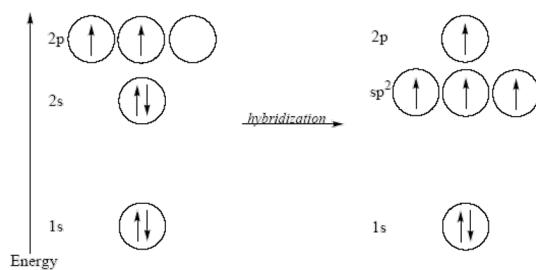
- When a carbon is connected to three other things (that is, one of the bonds is a double bond), the molecule is modeled by combining the $2s$ and two of the $2p$ orbitals to produce **three sp^2 orbitals**.
- Since only two of the $2p$ orbitals were hybridized, there is **one leftover p orbital** in an sp^2 -hybridized carbon atom.



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Hybrid Orbitals



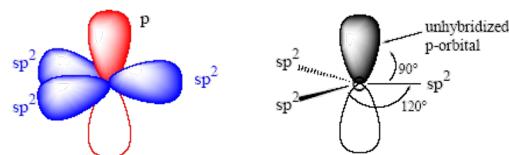
- All three sp^2 orbitals are at the same energy level, with one electron in each hybrid orbital, and one in the slightly higher-energy unhybridized $2p$ orbital.

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The Shape of an sp^2 Carbon

- The sp^2 orbitals are arranged in a **trigonal planar** shape around the central carbon atom, with bond angles of **120°**.
- The unhybridized p orbital is perpendicular to this plane.

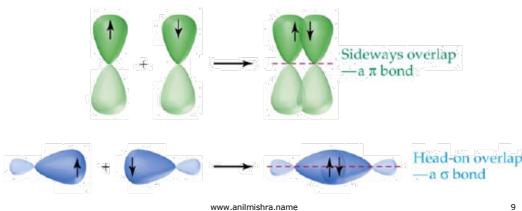


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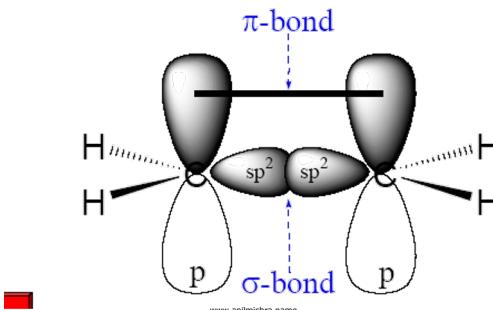
Sigma and Pi Bonds

- When two sp^2 -hybridized carbons are next to each other, two kinds of orbital overlap take place:
 - end-on-end overlap* of the sp^2 orbitals to make a **σ -bond** (sigma bond).
 - side-to-side overlap* of the unhybridized p orbitals to make a **π -bond** (pi bond).



Bonding in Ethylene

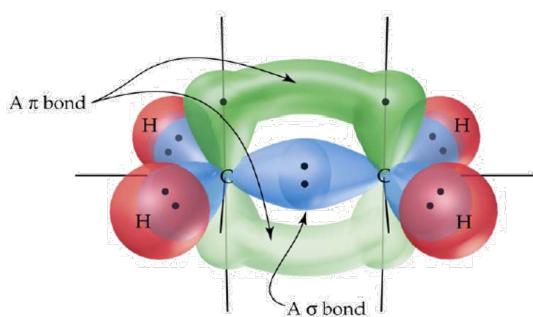
- Because of the π -bond, *free rotation is not possible* around carbon-carbon double bonds.



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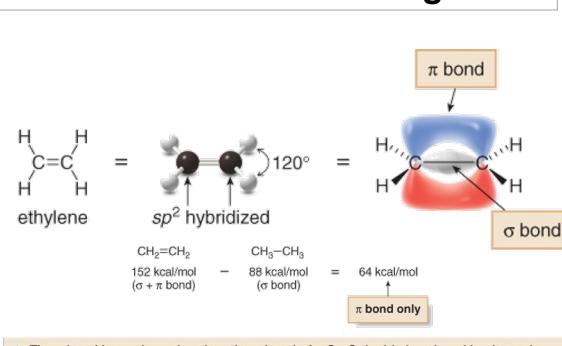
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Bonding in Ethylene



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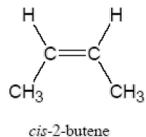
Structure and Bonding



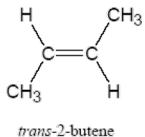
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Geometric Isomers in Alkenes

- Because free rotation is not possible around double bonds, there are two different forms of 2-butene, which are **geometric isomers** of each other:



cis-2-butene



trans-2-butene

- The prefix *cis*- is used when the two arms of the longest chain are on the **same side** of the double bond; the prefix *trans*- is used when they are on **opposite sides** of the double bond.
- Geometric isomers can have drastically different chemical and physical properties.

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Orbital Description

- Sigma bonds around C are *sp*² hybridized.
- Angles are approximately 120 degrees.
- No nonbonding electrons.
- Molecule is planar around the double bond.
- Pi bond is formed by the sideways overlap of parallel *p* orbitals perpendicular to the plane of the molecule.

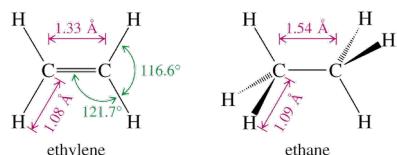
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Bond Lengths and Angles



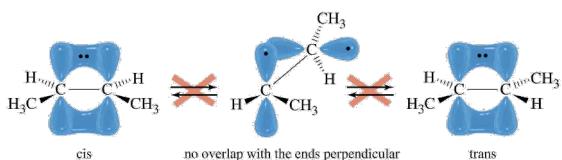
- Hybrid orbitals have more s character.
- Pi overlap brings carbon atoms closer.
- Bond angle with pi orbitals increases.
 - Angle C=C-H is 121.7°
 - Angle H-C-H is 116. 6°

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Pi Bond

- Sideways overlap of parallel *p* orbitals.
- No rotation is possible without breaking the pi bond (63 kcal/mole).
- Cis isomer cannot become trans without a chemical reaction occurring.



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Alkenes

IUPAC Nomenclature

- Parent is longest chain containing the double bond.
- ane changes to -ene. (or -diene, -triene)
- Number the chain so that the double bond has the lowest possible number.
- In a ring, the double bond is assumed to be between carbon 1 and carbon 2.

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Naming Alkenes & Alkynes

Using the IUPAC alkane names:

Alkene names change the end to -ene.

Alkyne names change the end to -yne

Comparison of Names for Alkanes, Alkenes, and Alkynes

Alkane	Alkene	Alkyne
$\text{H}_3\text{C}—\text{CH}_3$	$\text{H}_2\text{C}=\text{CH}_2$	$\text{HC}\equiv\text{CH}$
Ethane	Ethene (ethylene)	Ethyne (acetylene)
$\text{CH}_3—\text{CH}_2—\text{CH}_3$	$\text{CH}_3—\text{CH}=\text{CH}_2$	$\text{CH}_3—\text{C}\equiv\text{CH}$
Propane	Propene (propylene)	Propyne

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Guide to Naming Alkenes and Alkynes

STEP 1

Name of the longest carbon chain with a double or triple bond.

STEP 2

Number the carbon chain starting from the end nearest a double or triple bond.

→ Give the location for double and triple bond

STEP 3

Give the location and name of each substituent (alphabetical order) as a prefix to the name.

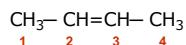
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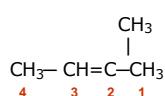
Naming Alkenes & Alkynes



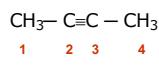
1-butene



2-butene



2-methyl-2-butene



2-butyne

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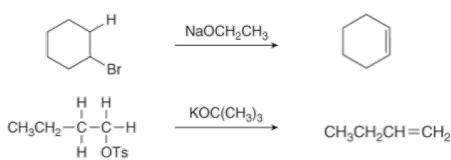
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Alkenes

Synthesis of Alkenes

Dehydrohalogenation

Examples



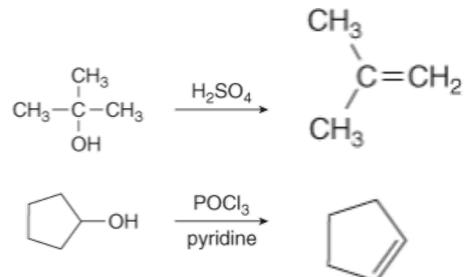
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Synthesis of Alkenes

Dehydration

Examples



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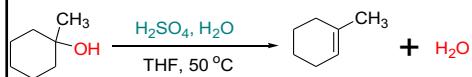
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Synthesis of Alkenes

Dehydration

- elimination of H-OH from an alcohol (**dehydration**)
 - require strong acids (sulfuric acid, 50 °C)



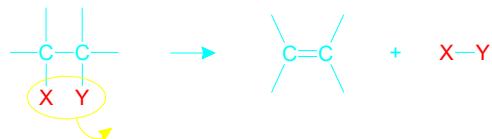
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Elimination Reactions

Dehydrohalogenation (-HX) and Dehydration (- H_2O) are the main types of elimination reactions.

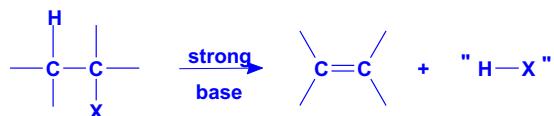


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Dehydrohalogenation (-HX)



$X = Cl, Br, I$

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Elimination Reactions

- An elimination reaction is a type of organic reaction in which two substituents are removed from a molecule in either a one or two-step mechanism.

• The one-step mechanism is known as the E2 reaction, and the two-step mechanism is known as the E1 reaction.

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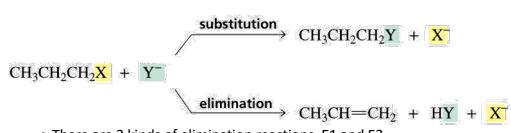
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Elimination Reactions

- A compound with an electronegative atom bonded to an sp^3 carbon, when approached by a nucleophile/base can undergo either a substitution reaction **OR** an elimination reaction



- There are 2 kinds of elimination reactions, E1 and E2.

- E1 stands for "Elimination unimolecular"
 - The E1 reaction is a two-step reaction
- E2 stands for "Elimination bimolecular"
 - The E2 reaction is a two-step reaction

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E1 Mechanism

- E1 is a model to explain a particular type of chemical elimination reaction. E1 stands for unimolecular elimination and has the following specificities.

• It is a two-step process of elimination: ionization and deprotonation.

- Ionization: the carbon-halogen bond breaks to give a carbocation intermediate.

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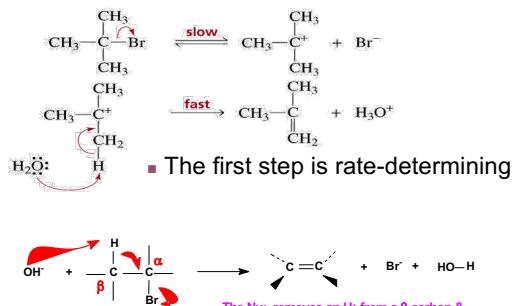
E1 Mechanism

- Deprotonation of the carbocation.
- E1 typically takes place with tertiary alkyl halides, but is possible with some secondary alkyl halides.
- The reaction rate is influenced only by the concentration of the alkyl halide because carbocation formation is the slowest step, aka the rate-determining step. Therefore, first-order kinetics apply (unimolecular).

E1 Mechanism

- The reaction usually occurs in the complete absence of a base or the presence of only a weak base (acidic conditions and high temperature).
- E1 reactions are in competition with SN1 reactions because they share a common carbocationic intermediate.

E1 Reactions



Mechanisms of Elimination—E1

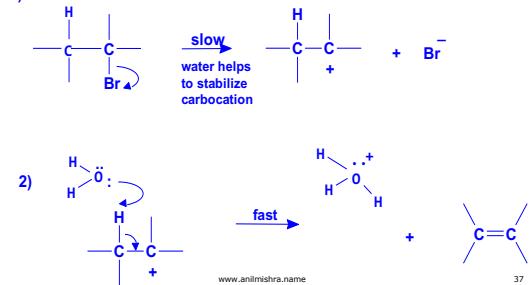
TABLE 8.3 Characteristics of the E1 Mechanism

Characteristic	Result
Kinetics	• First order
Mechanism	• Two steps
Identity of R	• More substituted halides react fastest
Base	• Rate: R ₃ CX > R ₂ CHX > RCH ₂ X
Leaving group	• Favored by weaker bases such as H ₂ O and ROH
Solvent	• A better leaving group makes the reaction faster because the bond to the leaving group is partially broken in the rate-determining step.
	• Polar protic solvents that solvate the ionic intermediates are needed.

E1 Mechanism

- This reaction is done in strong base at low concentration, such as **0.01 M NaOH in water**

1)

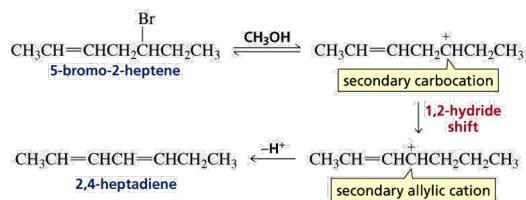


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The E1 Reaction

- E1 reaction involves a carbocation
- Therefore rearrangements must be considered

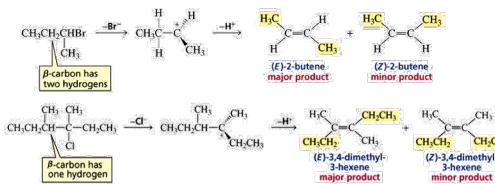


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The E1 Reaction: Stereochemistry

- With C⁺ both syn and anti elimination can occur, so E1 reaction forms both *E* and *Z* products regardless of whether β-carbon is bonded to one or two H's
- Product stability leads to stereoselectivity but not stereospecificity



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The Zaitsev (Saytzeff) Rule Z Rule

- What about dehydrohalogenations involving RX with hydrogen atoms on different β carbon atoms

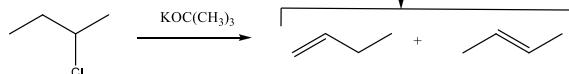


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The Zaitsev (Saytzeff) Rule Z Rule

Two possible organic products.
Which is the major product?

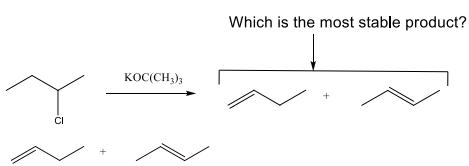


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The Zaitsev (Saytzeff) Rule Z Rule

Let's ask a different question about the products.



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The Zaitsev (Saytzeff) Rule Z Rule

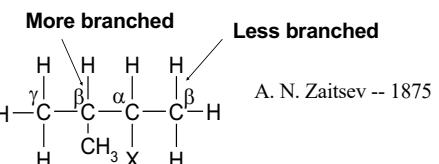
- When alkyl halides have two or more different β carbons, more than one alkene product is formed. When this happens, one of the products usually predominates.
- The major product is the more stable product—the one with the more **substituted double bond**.
- The alkene formed in greatest amount is the one that corresponds to removal of the hydrogen from the β -carbon having the fewest **hydrogen substituent**.

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The Zaitsev (Saytzeff) Rule Z Rule

- In reactions of removal of hydrogen halides from alkyl halides or the removal of water from alcohols, the **hydrogen** which is lost will come from the **more highly branched** β -carbon.



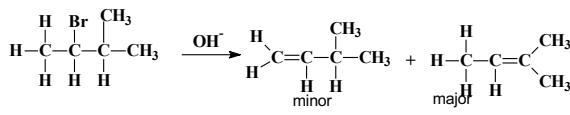
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The Zaitsev (Saytzeff) Rule

Z Rule

According to the **Z-rule**, the major product in a dehydrohalogenation is the **most stable product.**



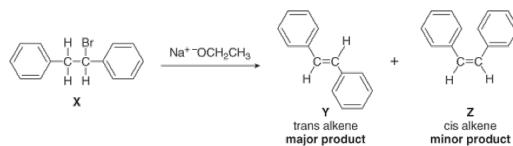
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The Zaitsev (Saytzeff) Rule

Z Rule

- When a mixture of stereoisomers is possible from a dehydrohalogenation, the major product is the more stable stereoisomer.
- A reaction is **stereoselective** when it forms predominantly or exclusively one stereoisomer when two or more are possible.
- The E2 reaction is **stereoselective** because one stereoisomer is formed preferentially.



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E2 Mechanism

- E2 stands for bimolecular elimination. The reaction involves a one-step mechanism in which carbon-hydrogen and carbon-halogen bonds break to form a double bond ($\text{C}=\text{C}$ Pi bond).

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E2 Mechanism

- The specifics of the reaction are as follows:
 - E2 is a single step elimination, with a single transition state.
 - It is typically undergone by primary substituted alkyl halides, but is possible with some secondary alkyl halides and other compounds.
 - The reaction rate is second order, because it's influenced by both the alkyl halide and the base (bimolecular).

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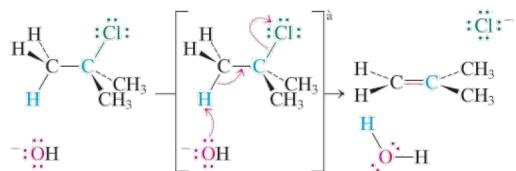
E2 Mechanism

- E2 typically uses a strong base. It must be strong enough to remove a weakly acidic hydrogen.
- In order for the pi bond to be created, the hybridization of carbons needs to be lowered from sp^3 to sp^2 .
- The C-H bond is weakened in the rate determining step and therefore a primary deuterium isotope effect much larger than 1 (commonly 2-6) is observed.
- E2 competes with the SN_2 reaction mechanism if the base can also act as a nucleophile (true for many common bases).

The E2 Mechanism

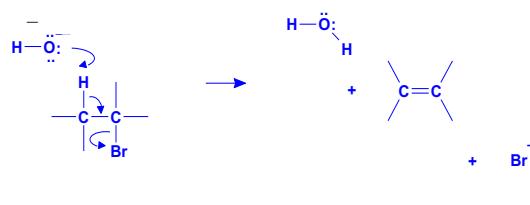
• E2: Deprotonation is First Step

The E2 Reaction Mechanism



E2 mechanism

- This reaction is done in *strong base at high concentration*, such as 1 M NaOH in water.



The E2 Mechanism

TABLE 8.2 Characteristics of the E2 Mechanism

Characteristic	Result
Kinetics	• Second order
Mechanism	• One step
Identity of R	• More substituted halides react fastest
Base	• Rate: R ₃ CX > R ₂ CHX > RCH ₂ X
Leaving group	• Favored by strong bases
Solvent	• Better leaving group → faster reaction
	• Favored by polar aprotic solvents

The E2 Reaction: Regioselectivity

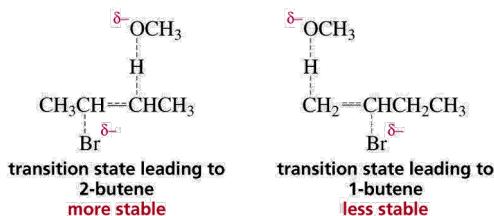
- 2-bromobutane has two structurally different β -carbons from which to abstract a hydrogen



E2 reactions give more stable alkene if possible

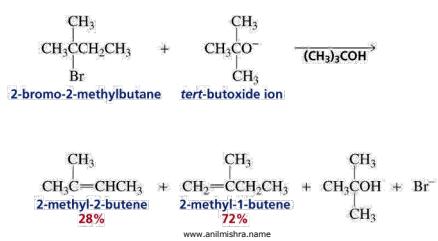
The E2 Reaction: Regioselectivity

- Zaitsev's rule (Saytzeff Rule):** The more substituted alkene will be formed in elimination reactions



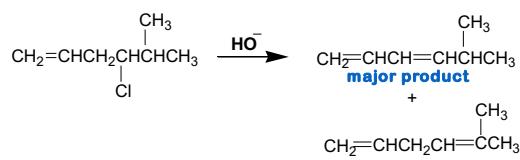
The E2 Reaction: Regioselectivity

- Zaitsev's rule does not apply when the base is bulky
- E2 Rxn is kinetically-controlled

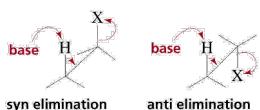


The E2 Reaction: Regioselectivity

- Zaitsev's rule may not apply when conjugated dienes might be formed

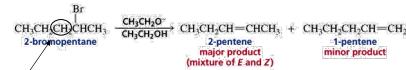


The E2 Reaction: Stereochemistry



- If the elimination reaction removes two substituents from the same side of the molecule it is **syn elimination**
- If the elimination reaction removes two substituents from opposite sides of the molecule it is **anti elimination**

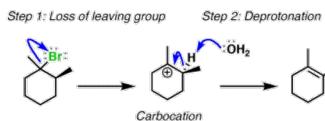
The E2 Reaction: Stereochemistry



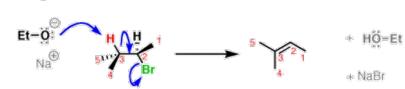
- The E2 Reaction is **stereoselective**, but **not stereospecific**
 - If 2 β H's are available on carbon bearing eliminated H, The H leading to more stable E isomer is selected to be extracted from β carbon regardless of stereochemistry at α carbon

E1 VS E2 Mechanisms

The E1 Mechanism



The E2 Mechanism



E1 VS E2 Mechanisms

- Here's what each of these two reactions have in common:

- In both cases, we form a new C-C π bond, and break a C-H bond and a C-(leaving group) bond
- In both reactions, a species acts as a base to remove a proton, forming the new π bond
- Both reactions follow Zaitsev's rule (where possible)
- Both reactions are favored by heat.

E1 VS E2 Mechanisms

	E1	E2
Rate Law	Unimolecular (depends on concentration of substrate)	Bimolecular (depends on concentration of both substrate and base)
"Big Barrier"	Formation of carbocation $3^\circ > 2^\circ >> 1^\circ$	None
Requires strong base?	No	Yes
Stereochemistry	No requirement	Leaving group must be <i>anti</i> to hydrogen removed

E1 VS E2 Mechanisms

In E1 Mechanism

- The rate of the E1 reaction depends only on the substrate,
 - Since the rate limiting step is the formation of a carbocation.
- The more stable that carbocation is, the faster the reaction will be.
 - Forming the carbocation is the "slow step"; a strong base is not required to form the alkene, since there is no leaving group that will need to be displaced.
- Finally there is no requirement for the stereochemistry of the starting material;
 - The hydrogen can be at any orientation to the leaving group in the starting material

E1 VS E2 Mechanisms

In E2 Mechanism

- The rate of the E2 reaction depends on both substrate and base,
 - Since the rate-determining step is bimolecular (concerted).
- A strong base is generally required, one that will allow for displacement of a polar leaving group.
- The stereochemistry of the hydrogen to be removed must be *anti* to that of the leaving group
 - The pair of electrons from the breaking C-H bond donate into the antibonding orbital of the C-(leaving group) bond, leading to its loss as a leaving group.

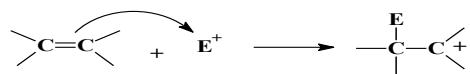
Reactivity of C=C

- Electrons in pi bond are loosely held.
- Electrophiles are attracted to the pi electrons.
- Carbocation intermediate forms.
- Nucleophile adds to the carbocation.
- Net result is addition to the double bond.

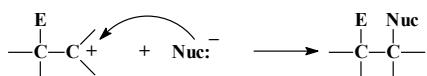
Alkenes

Electrophilic Addition

- Step 1: Pi electrons attack the electrophile.



- Step 2: Nucleophile attacks the carbocation.



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Types of Additions

Reagent	Type of Addition [Elements Added] ^a	Product
H_2O	hydration	
H_2 , a reduction	hydrogenation	
HOOH , an oxidation	hydroxylation	
IO_3 , an oxidation	oxidative cleavage	
O_2 , an oxidation	epoxidation	
X_2 , an oxidation	halohydrin formation	
HX	HX addition	
CH_3	cyclopropanation	

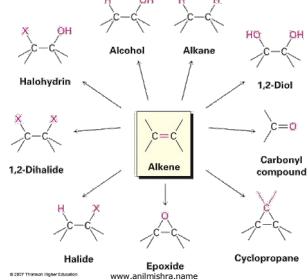
^aThese are not the reagents used but simply the groups that appear in the product.

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Diverse Reactions of Alkenes

- Alkenes react with many electrophiles to give useful products by addition (often through special reagents)



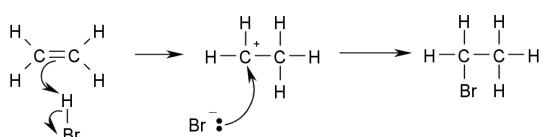
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Addition of HBr to an Alkene

- Step 1: Formation of a carbocation

- Step 2: Nucleophilic addition of bromide



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Addition of HBr to an Alkene

- Regiospecificity

- Markovnikov's Rule: The proton of an acid adds to the carbon in the double bond that already has the most H's. "Rich get richer."

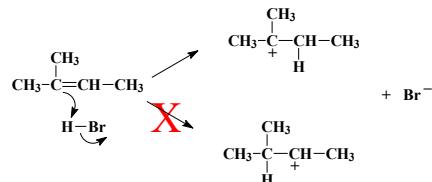
Addition of HBr to an Alkene

- More general Markovnikov's Rule: In an electrophilic addition to an alkene, the electrophile adds in such a way as to form the most stable intermediate.

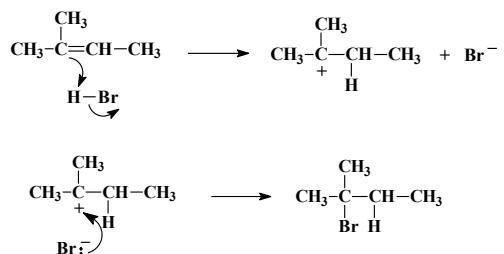
- HCl, HBr, and HI add to alkenes to form Markovnikov products.

Addition of HBr to an Alkene

Protonation of double bond yields the most stable carbocation. Positive charge goes to the carbon that was not protonated.



Addition of HBr to an Alkene

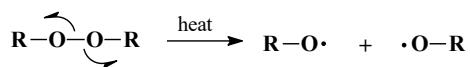


Free-Radical Addition of HBr

- In the presence of peroxides, HBr adds to an alkene to form the "anti-Markovnikov" product.
- Only HBr has the right bond energy.
- HCl bond is too strong.
- HI bond tends to break heterolytically to form ions.

Free Radical Initiation

- Peroxide O-O bond breaks easily to form free radicals.



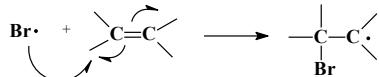
- Hydrogen is abstracted from HBr.



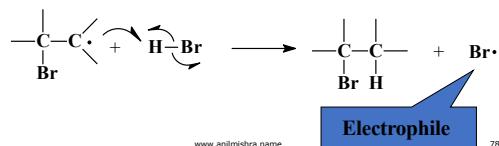
Electrophile

Propagation Steps

- Bromine adds to the double bond.

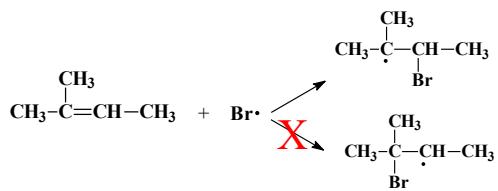


- Hydrogen is abstracted from HBr.



Electrophile

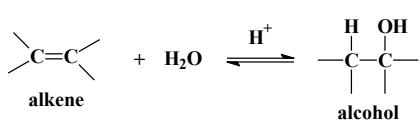
Anti-Markovnikov ??



- Tertiary radical is more stable, so that intermediate forms faster.

Alkenes

Hydration of Alkenes

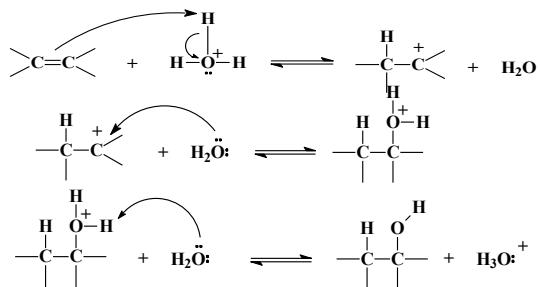


- Reverse of dehydration of alcohol
- Use very dilute solutions of H_2SO_4 or H_3PO_4 to drive equilibrium toward hydration.

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Mechanism for Hydration



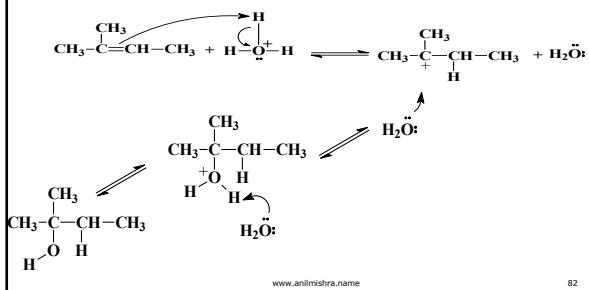
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Orientation for Hydration

- Markovnikov product is formed.



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Indirect Hydration

- Oxymercuration-Demercuration
 - Markovnikov product formed
 - Anti addition of H-OH
 - No rearrangements
- Hydroboration
 - Anti-Markovnikov product formed
 - Syn addition of H-OH

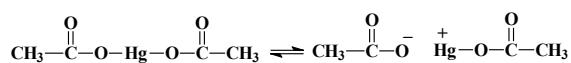
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Oxymercuration (1)

- Reagent is mercury(II) acetate which dissociates slightly to form ${}^+ \text{Hg(OAc)}$.
- ${}^+ \text{Hg(OAc)}$ is the electrophile that attacks the pi bond.

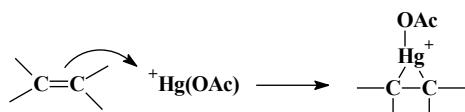


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Oxymercuration (2)

- The intermediate is a cyclic mercurinium ion, a three-membered ring with a positive charge.



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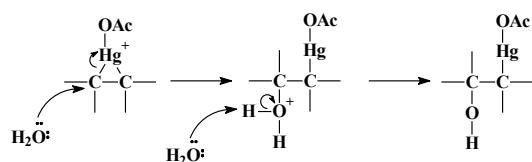
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Oxymercuration (3)

- Water approaches the mercurinium ion from the side opposite the ring (anti addition).
- Water adds to the more substituted carbon to form the Markovnikov product.

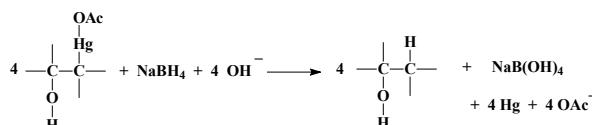


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Demercuration

- Sodium borohydride, a reducing agent, replaces the mercury with hydrogen.



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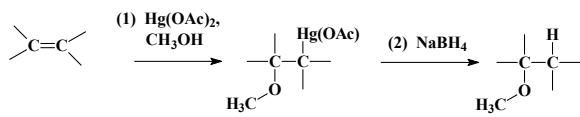
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Alkoxymercuration - Demercuration

- If the nucleophile is an alcohol, ROH, instead of water, HOH, the product is an ether.

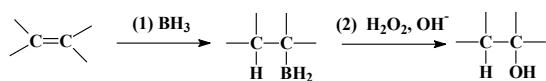


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Hydroboration

- Borane, BH_3 , adds a hydrogen to the most substituted carbon in the double bond.
- The alkylborane is then oxidized to the alcohol which is the anti-Mark product.



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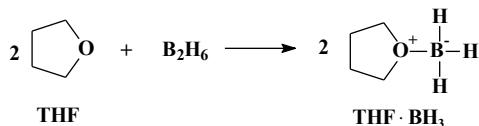
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Borane Reagent

- Borane exists as a dimer, B_2H_6 , in equilibrium with its monomer.
- Borane is a toxic, flammable, explosive gas.
- Safe when complexed with tetrahydrofuran.

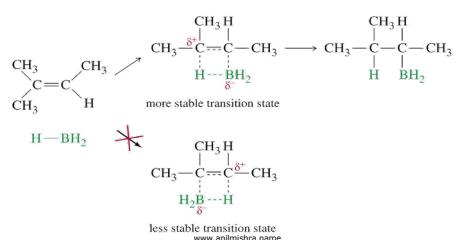


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Mechanism

- The electron-deficient borane adds to the least-substituted carbon.
- The other carbon acquires a positive charge.
- H adds to adjacent C on same side (syn).



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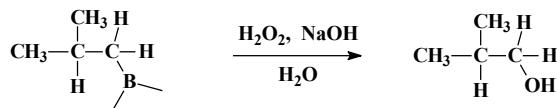
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Oxidation to Alcohol

- Oxidation of the alkyl borane with basic hydrogen peroxide produces the alcohol.
- Orientation is anti-Markovnikov.

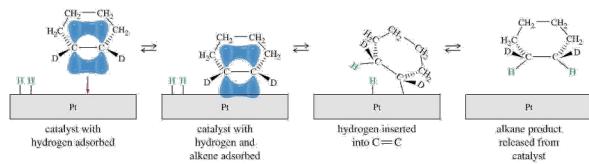


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Hydrogenation

- Alkene + H₂ → Alkane
- Catalyst required, usually Pt, Pd, or Ni.
- Finely divided metal, heterogeneous
- Syn addition



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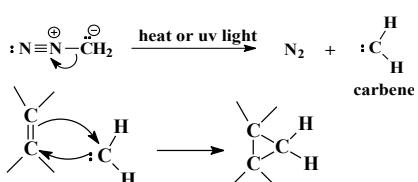
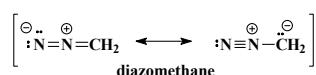
Addition of Carbenes

- Insertion of -CH₂ group into a double bond produces a cyclopropane ring.
- Three methods:
 - Diazomethane
 - Simmons-Smith: methylene iodide and Zn(Cu)
 - Alpha elimination, haloform

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Diazomethane



Extremely toxic and explosive.

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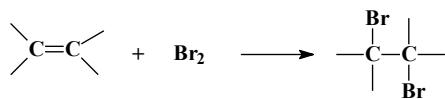
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Addition of Halogens

- Cl_2 , Br_2 , and sometimes I_2 add to a double bond to form a vicinal dibromide.
- Anti addition, so reaction is stereospecific.

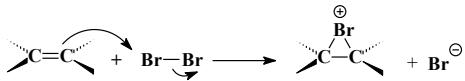


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Mechanism for Halogenation

- Pi electrons attack the bromine molecule.
- A bromide ion splits off.
- Intermediate is a cyclic bromonium ion.



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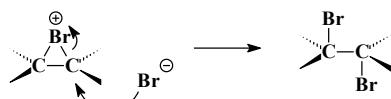
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Mechanism for Halogenation

- Halide ion approaches from side opposite the three-membered ring.



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Test for Unsaturation

- Add Br_2 in CCl_4 (dark, red-brown color) to an alkene in the presence of light.
- The color quickly disappears as the bromine adds to the double bond.
- “Decolorizing bromine” is the chemical test for the presence of a double bond.

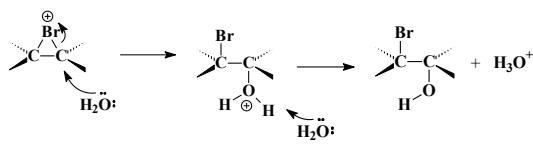
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Formation of Halohydrin

- If a halogen is added in the presence of water, a halohydrin is formed.
- Water is the nucleophile, instead of halide.

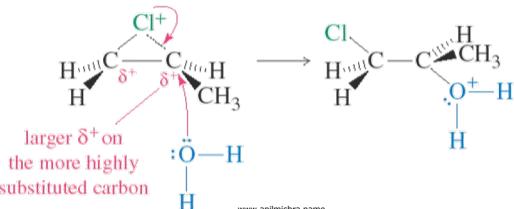


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Regiospecificity

- The most highly substituted carbon has the most positive charge, so nucleophile attacks there.



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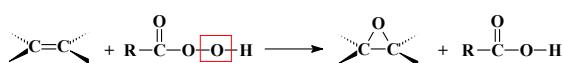
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Epoxidation

- Alkene reacts with a peroxyacid to form an epoxide (also called oxirane).
- Usual reagent is peroxybenzoic acid.

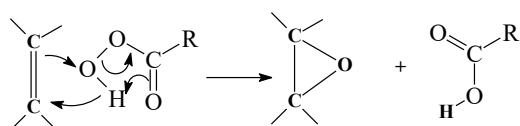


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Mechanism

- One-step concerted reaction. Several bonds break and form simultaneously.



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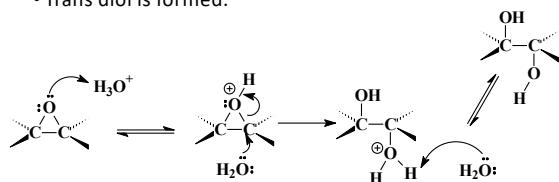
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Opening the Epoxide Ring

- Acid catalyzed.
- Water attacks the protonated epoxide.
- Trans diol is formed.



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Syn Hydroxylation of Alkenes

- Alkene is converted to a *cis*-1,2-diol,
- Two reagents:
 - Osmium tetroxide (expensive!), followed by hydrogen peroxide *or*
 - Cold, dilute aqueous potassium permanganate, followed by hydrolysis with base

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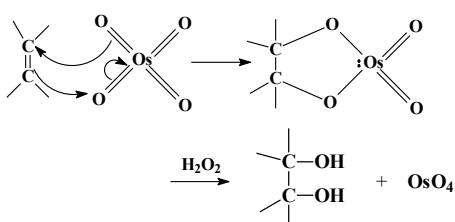
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Mechanism with OsO_4

- Concerted *syn* addition of two oxygens to form a cyclic ester.



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Oxidative Cleavage

- Both the pi and sigma bonds break.
- $\text{C}=\text{C}$ becomes $\text{C}=\text{O}$.
- Two methods:
 - Warm or concentrated or acidic KMnO_4 .
 - Ozonolysis
- Used to determine the position of a double bond in an unknown molecule.

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Alkenes

Cleavage with MnO_4^-

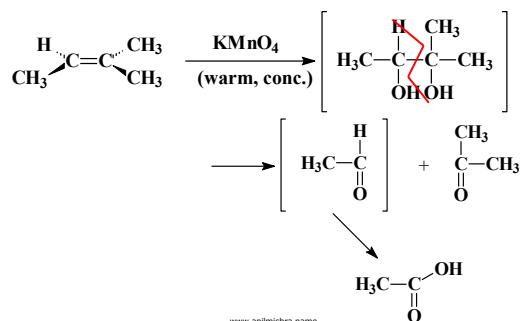
- Permanganate is a strong oxidizing agent.
- Glycol initially formed is further oxidized.
- Disubstituted carbons become ketones.
- Monosubstituted carbons become carboxylic acids.
- Terminal $=\text{CH}_2$ becomes CO_2 .

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Example



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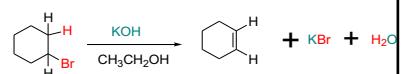
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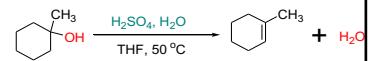
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Synthesis of Alkenes

1) dehydrohalogenation



2) dehydration



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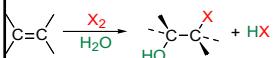
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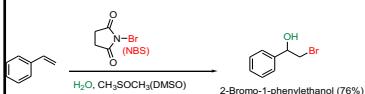
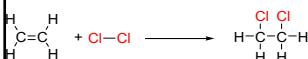
Alkenes

Reaction of Alkenes

1) Addition of Halogens to Alkenes



2) Halohydrin Formation

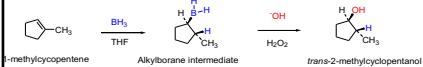


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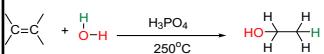
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Reaction of Alkenes

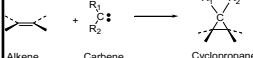
3) Addition of Water to Alkenes



4) Hydroboration-Oxidation Alcohol Formation



5) Carbene Formation – Cyclopropane synthesis



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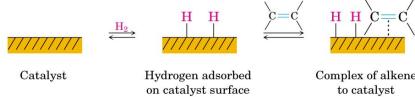
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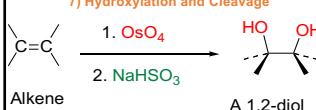
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Reaction of Alkenes

6) Catalytic Hydrogenation



7) Hydroxylation and Cleavage

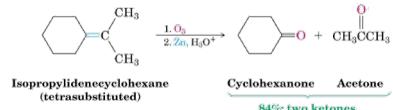


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Breakdown of Alkenes

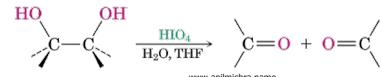
1) Ozonolysis



2) Permanganate Oxidation



3) Periodic Acid Oxidation, Cleavage of 1,2-diols



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