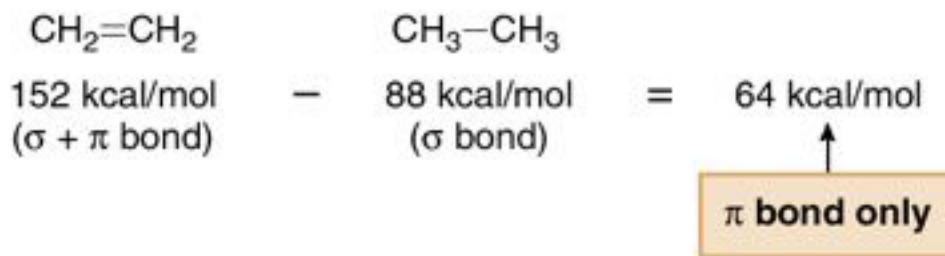
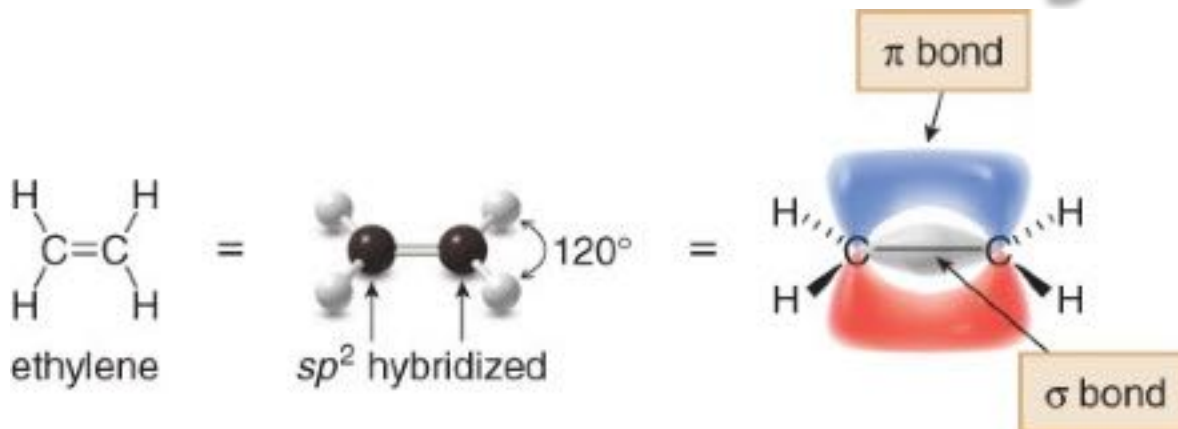


Alkenes (Olefins)

Chapters 7 & 8
Organic Chemistry, 8th *Edition*
John McMurry

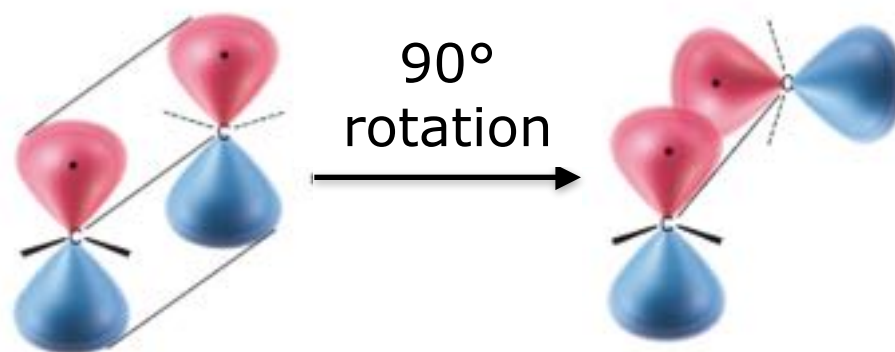
Structure and Bonding



- The π bond is much weaker than the σ bond of a C–C double bond, making it much more easily broken. As a result, alkenes undergo many reactions that alkanes do not.

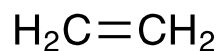
Structure and Bonding

Rotation around the C=C bond is restricted



The p orbitals are orthogonal
the π bond is broken

Simple Alkenes



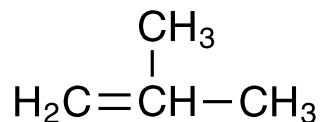
ethene

(ethylene)



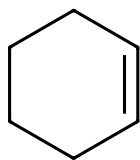
propene

(propylene)



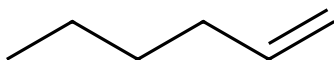
2-methylpropene

(isobutene)



cyclohexene

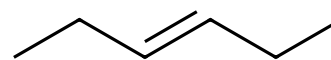
Positional isomers



1-hexene



2-hexene



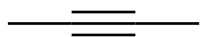
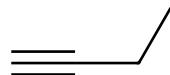
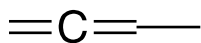
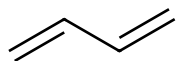
3-hexene

Unsaturation Degree

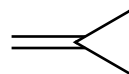
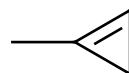
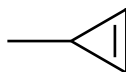
- Alkenes are **unsaturated hydrocarbons**.
- An acyclic alkene has the **general structural formula C_nH_{2n}** .
- Cycloalkanes also have the general formula C_nH_{2n} .
- Each π bond or ring removes two hydrogen atoms from a molecule, and this introduces one degree of unsaturation.

●es. C_4H_6

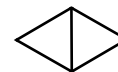
two π bonds



a π bond
and a ring



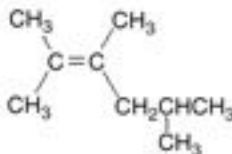
two rings



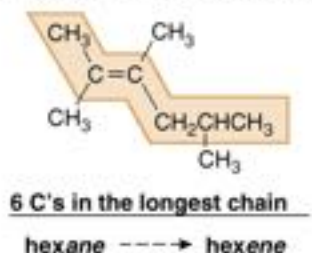
Nomenclature

How To Name an Alkene

Example Give the IUPAC name of the following alkene:



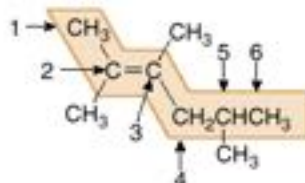
Step [1] Find the longest chain that contains *both* carbon atoms of the double bond.



• Change the **-ane** ending of the parent alkane to **-ene**.

Step [2] Number the carbon chain to give the double bond the lower number, and apply all other rules of nomenclature.

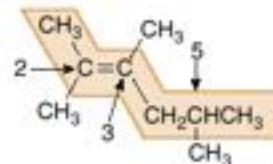
a. **Number** the chain, and name using the **first number** assigned to the C=C.



• Number the chain to put the C=C at C2, not C4.

2-hexene

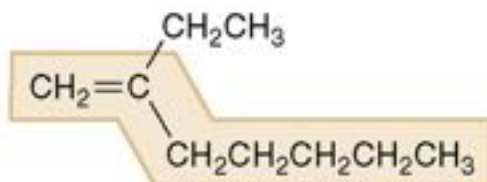
b. **Name** and **number** the substituents.



three methyl groups at C2, C3, and C5

Answer: 2,3,5-trimethyl-2-hexene

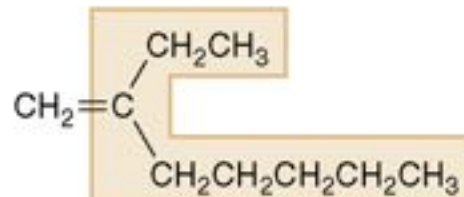
Nomenclature



7 C's ----> heptene

Both C's of the C=C are contained in this long chain.

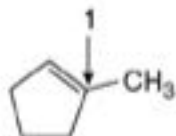
Correct: 2-ethyl-1-heptene



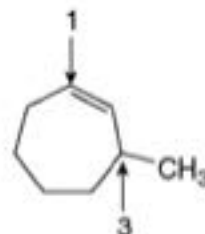
8 C's

Both C's of the C=C are NOT contained in this long chain.

Incorrect



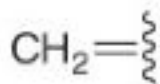
1-methylcyclopentene



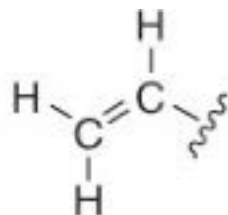
3-methylcycloheptene

[Number clockwise beginning at the C=C and place the CH₃ at C3.]

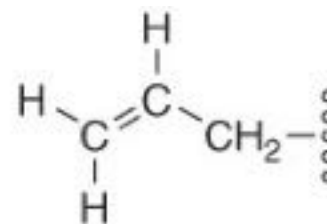
Nomenclature



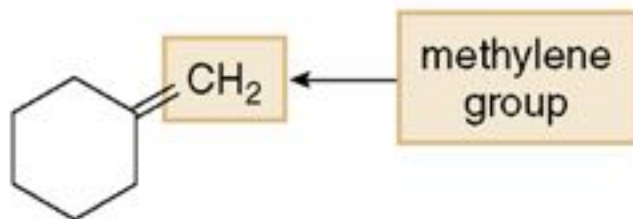
methylene group



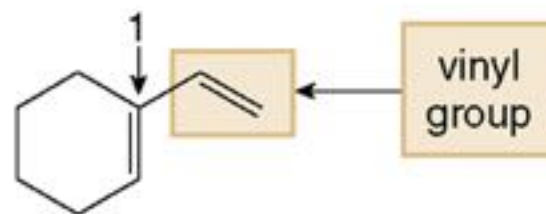
vinyl group



allyl group



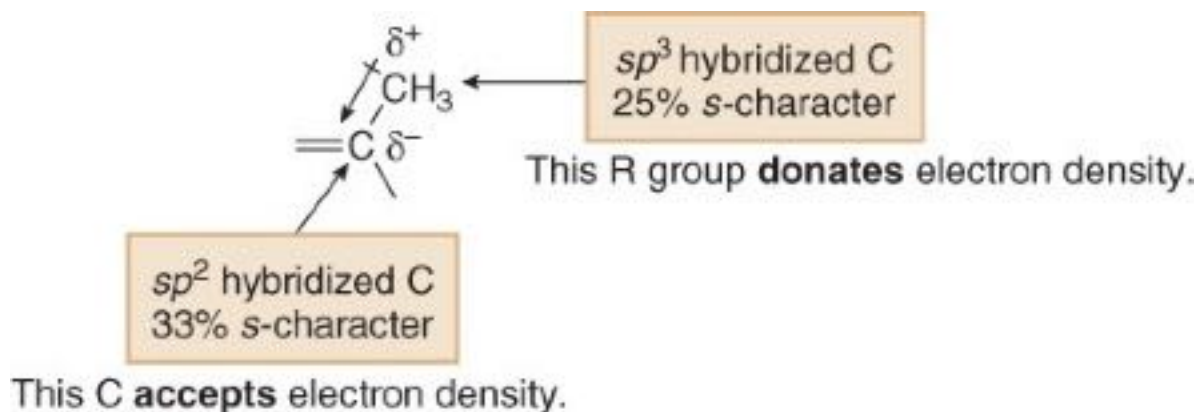
methylenecyclohexane



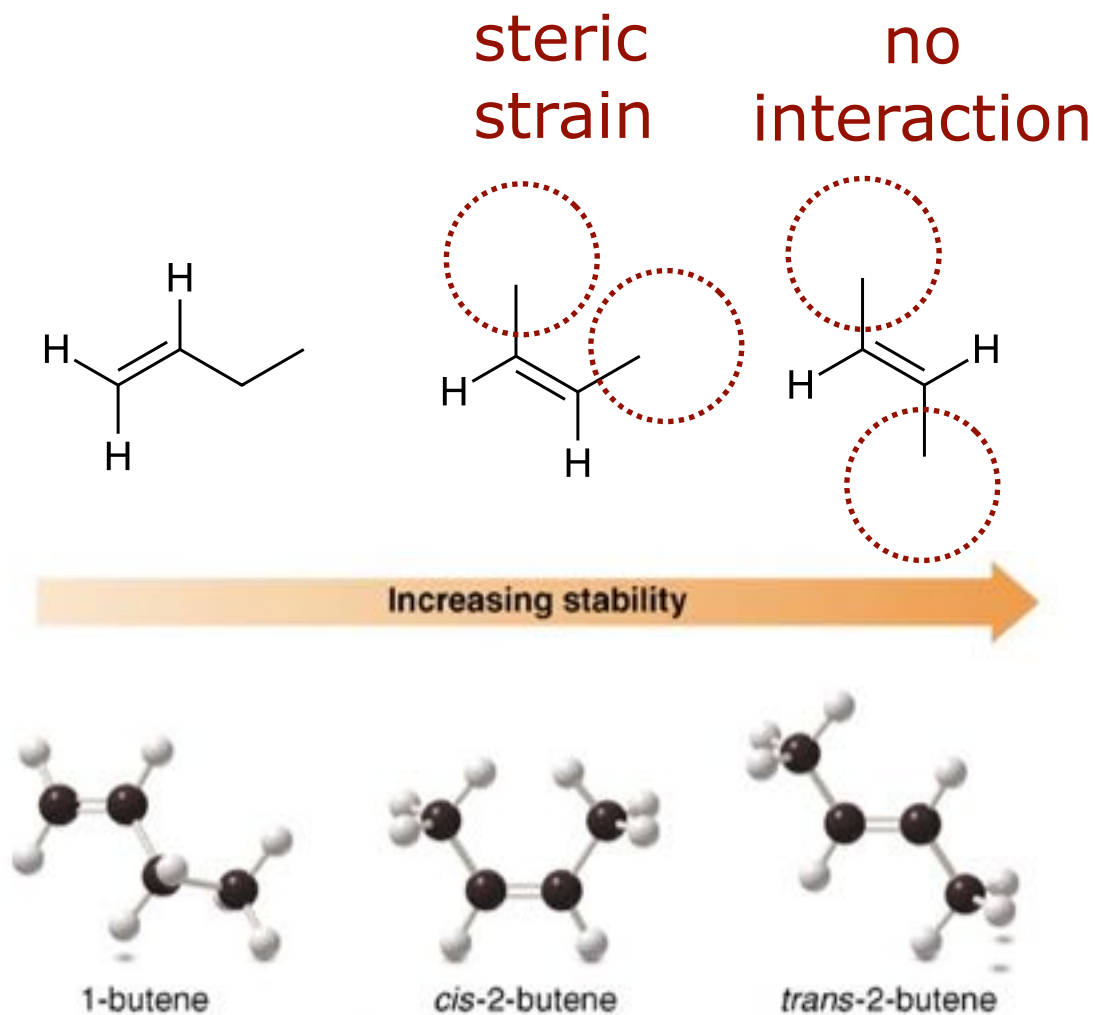
1-vinylcyclohexene

Physical Properties

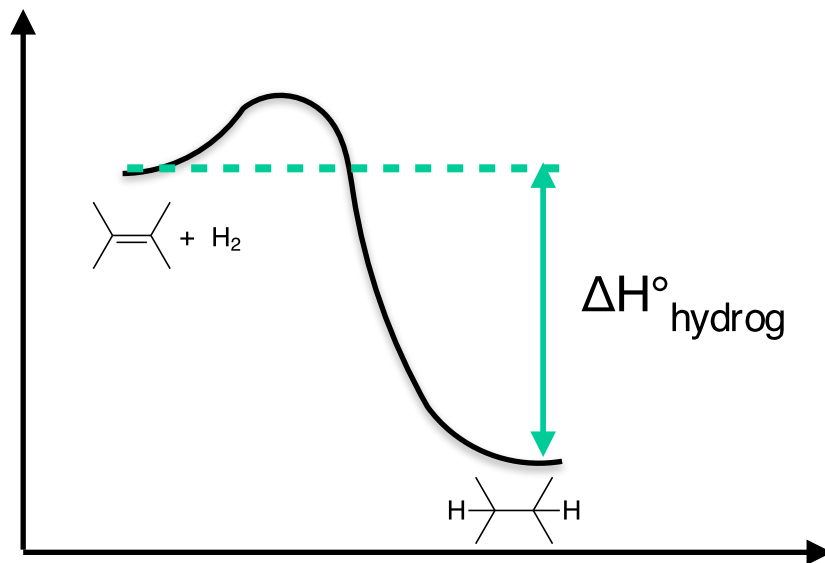
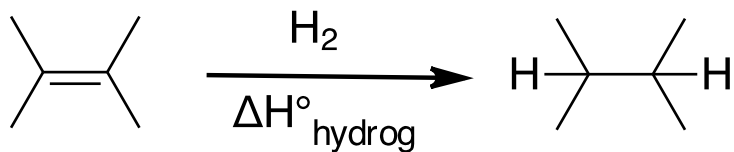
- Their physical properties are similar to alkanes of comparable molecular weight.
- Alkenes have low melting points and boiling points.
- M.p. and b.p. increase as the number of carbons increases because of increased surface area.
- Alkenes are soluble in organic solvents and insoluble in water.
- The C—C single bond between an alkyl group and one of the double bond carbons of an alkene is **slightly polar**.



Geometrical Isomerism



Stability of Alkenes



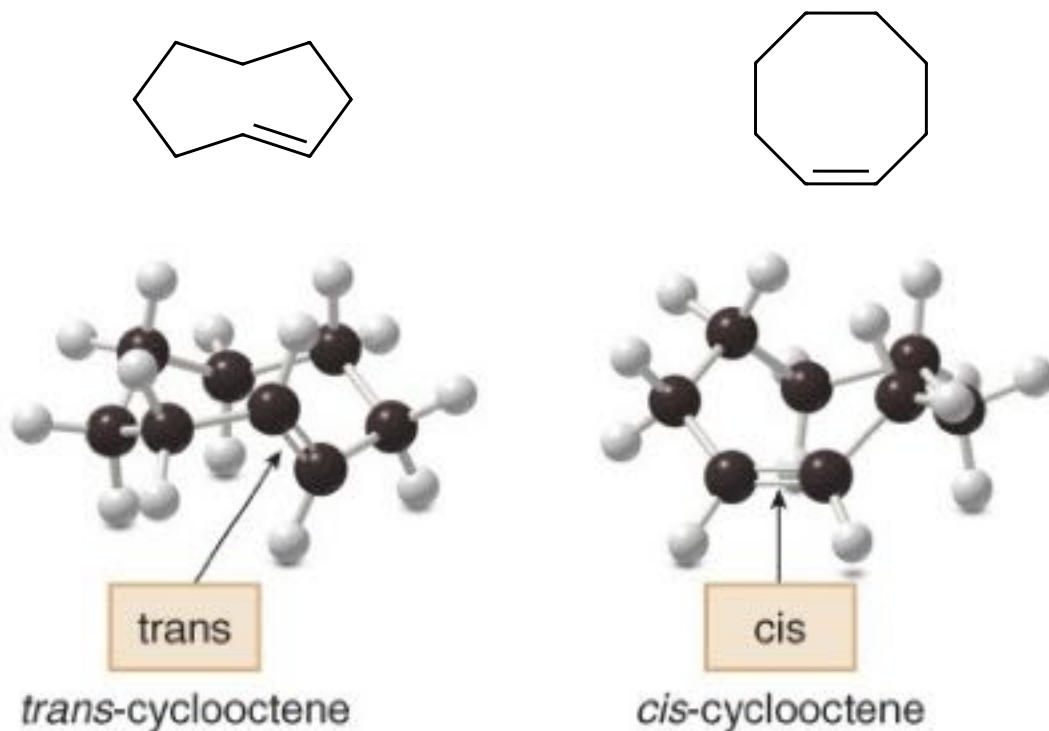
- Hydrogenation of alkenes is exothermic
- The heat of hydrogenation can be used as a measure of the relative stability of different alkenes.

Stability of Alkenes

Substitution	Alkene	$\Delta H^\circ_{\text{hydr}}$ (Kcal/mol)	stability
Unsubstituted	$\text{H}_2\text{C}=\text{CH}_2$	-32.8	less stable
Monosubstituted	$\text{CH}_3\text{CH}=\text{CH}_2$	-30.1	
Disubstituted	$(\text{CH}_3)_2\text{C}=\text{CH}_2$	-28.4	
	$\text{CH}_3\text{CH}=\text{CHCH}_3$ (cis)	-28.6	
	$\text{CH}_3\text{CH}=\text{CHCH}_3$ (trans)	-27.6	
Trisubstituted	$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	-26.9	
Tetrasubstituted	$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$	-26.6	more stable

Geometrical Isomerism

- *trans*-Cyclooctene is the smallest isolable trans cycloalkene, but it is considerably less stable than *cis*-cyclooctene, making it one of the few alkenes having a higher energy trans isomer.



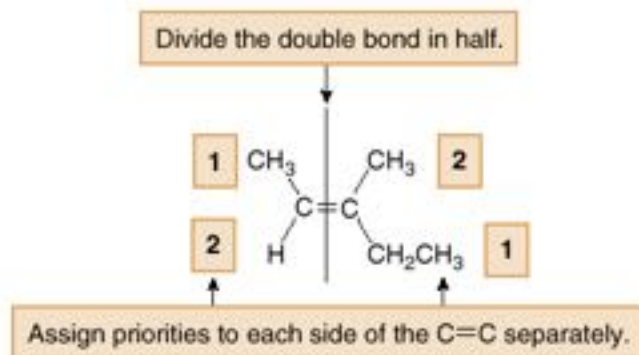
E/Z Nomenclature

How To

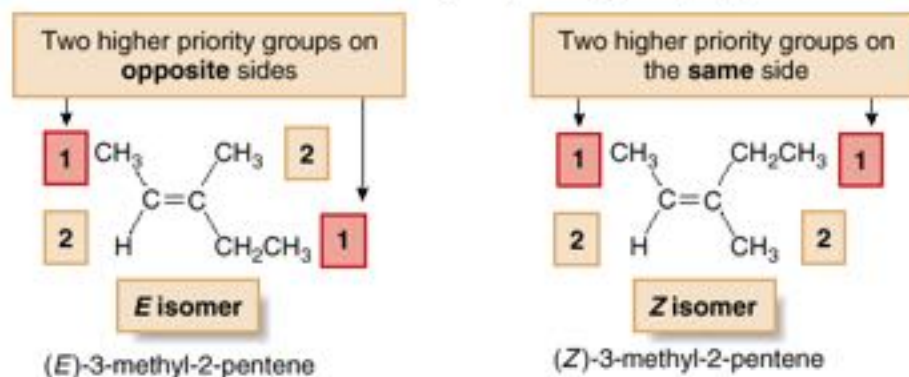
Assign the Prefixes *E* and *Z* to an Alkene

Step [1] Assign priorities to the two substituents on each end of the C=C by using the priority rules for *R,S* nomenclature (Section 5.6).

- Divide the double bond in half, and assign the numbers 1 and 2 to indicate the relative priority of the two groups on each end—the higher priority group is labeled 1, and the lower priority group is labeled 2.



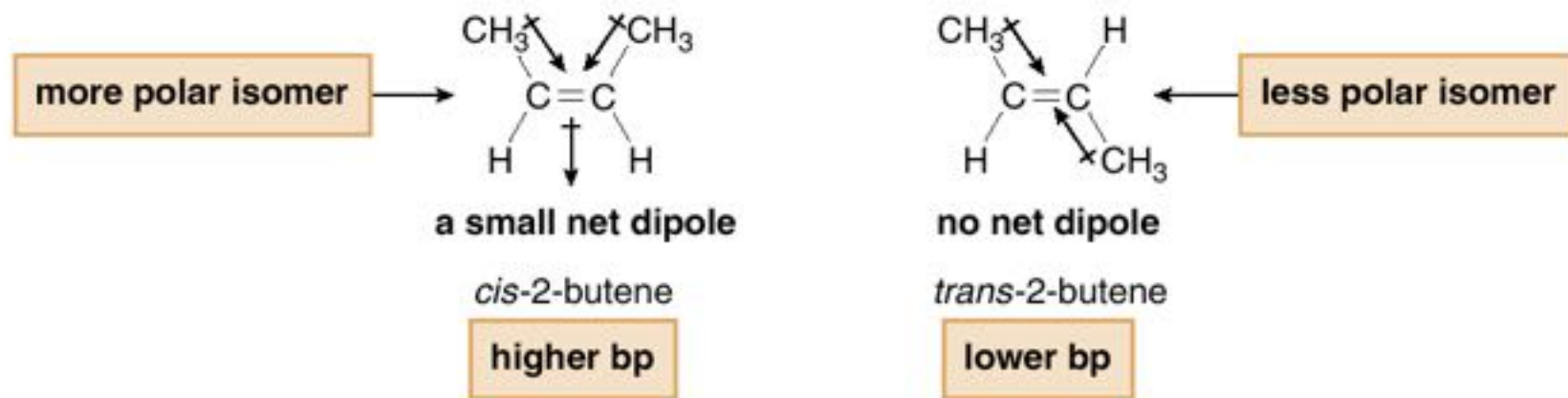
Step [2] Assign *E* or *Z* based on the location of the two higher priority groups (1).



- The *E* isomer has the two higher priority groups on the **opposite** sides.
- The *Z* isomer has the two higher priority groups on the **same** side.

Physical Properties

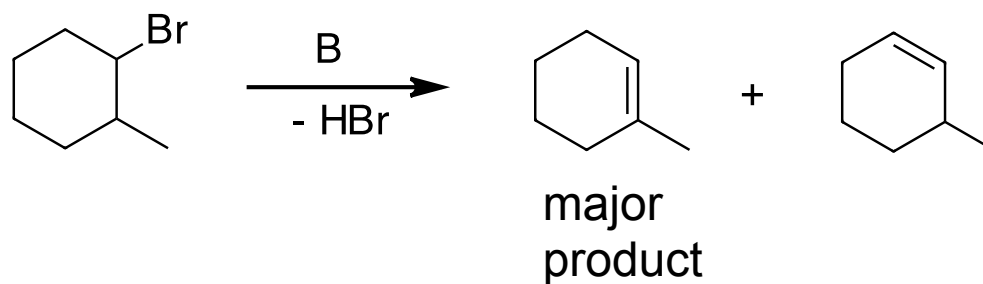
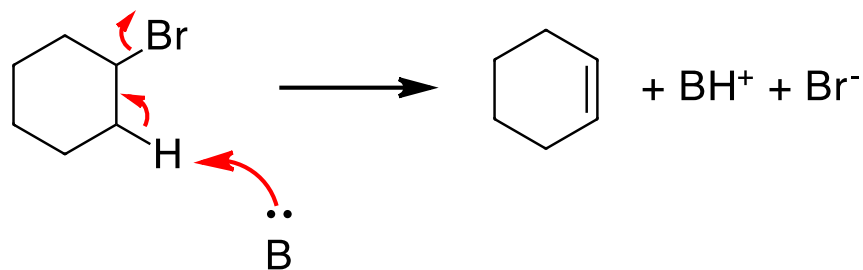
- A small dipole is associated with the C(sp²)-C(sp³) bond.
- A consequence of this dipole is that cis and trans alkenes often have different physical properties.
- *cis*-2-Butene has a higher b. p.(4°C) than *trans*-2-butene (1°C).



- A cis alkene is more polar than a trans alkene, giving it a slightly higher boiling point and making it more soluble in polar solvents.

Preparation of Alkenes.

1 Dehydrohalogenation

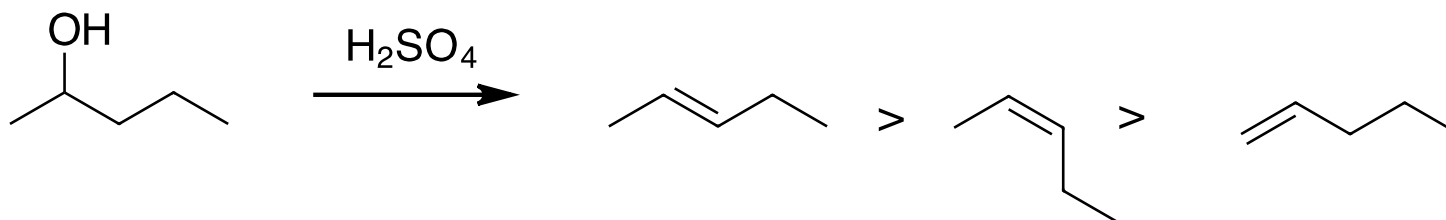
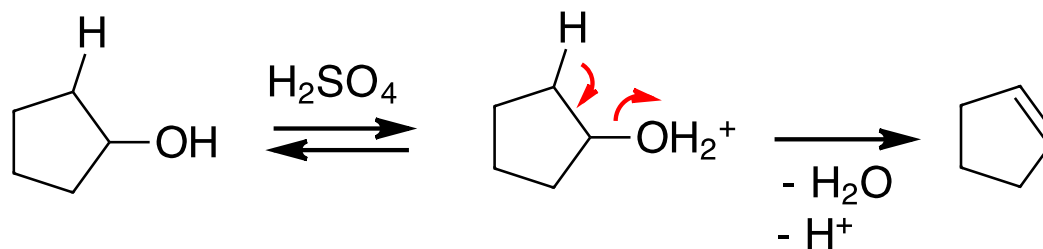


Saytzev's rule.

The more substituted alkene (more stable) is favoured

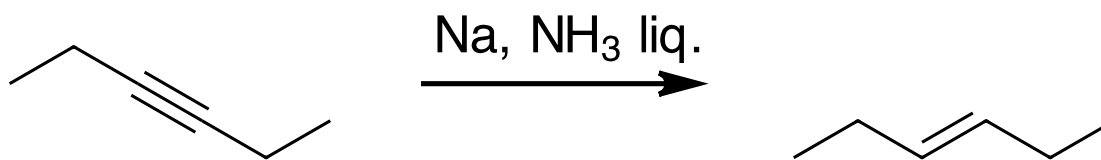
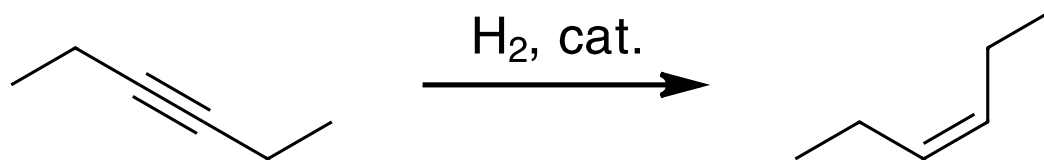
Preparation of Alkenes.

2 Dehydration



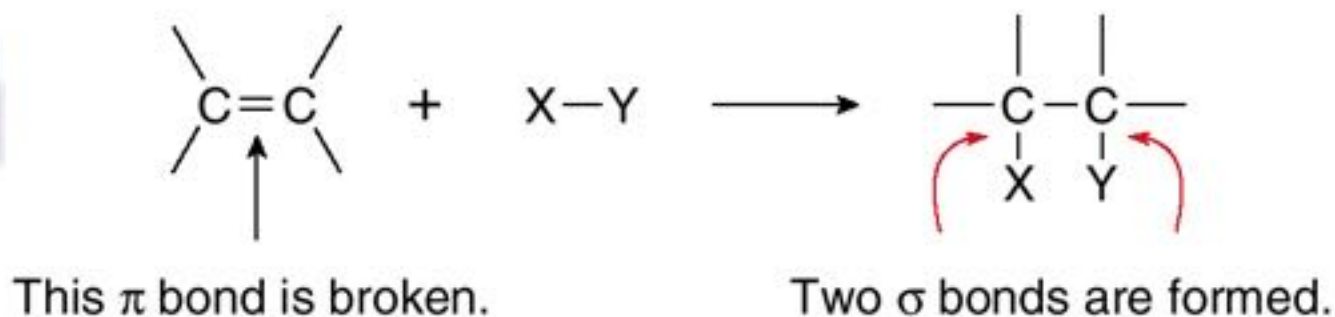
Preparation of Alkenes.

3 Hydrogenation/Reduction of Alkynes



Introduction to Addition Reactions

Addition reaction



- Alkenes are electron rich, with the electron density of the π bond concentrated above and below the plane of the molecule.
- Alkenes react with electrophiles.** Simple alkenes do not react with nucleophiles or bases.

Thermodynamics of Addition Reactions

- Addition reactions are exothermic because the two σ bonds formed in the product are stronger than the σ and π bonds broken in the reactants.

Overall reaction:



ΔH° calculation:

[1] Bonds broken

	ΔH° (kcal/mol)
$\text{CH}_2=\text{CH}_2$ π bond	+64
$\text{H}-\text{Br}$	+88
total	+152 kcal/mol

Energy needed to break bonds.

[2] Bonds formed

	ΔH° (kcal/mol)
$\text{BrCH}_2\text{CH}_2-\text{H}$	-98
$\text{CH}_3\text{CH}_2-\text{Br}$	-68
total	-166 kcal/mol

Energy released in forming bonds.

[3] Overall $\Delta H^\circ =$

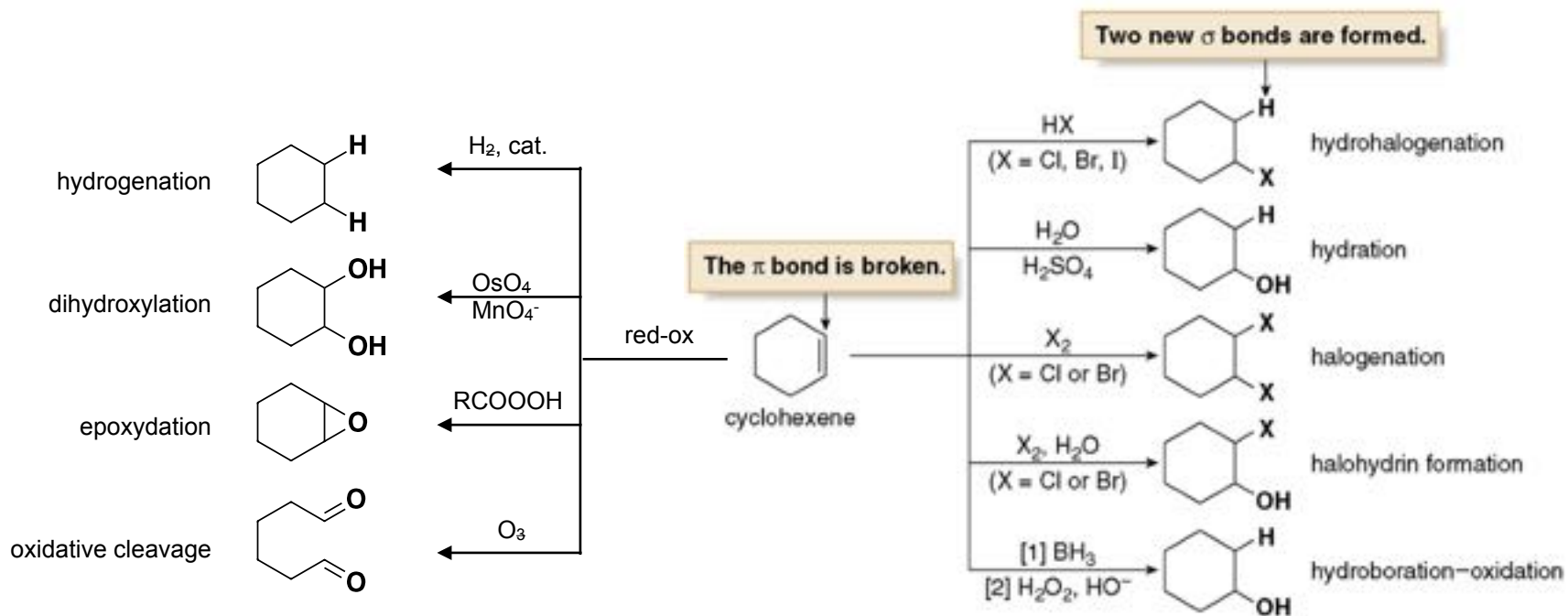
sum in Step [1]
+
sum in Step [2]

+152 kcal/mol
-166 kcal/mol

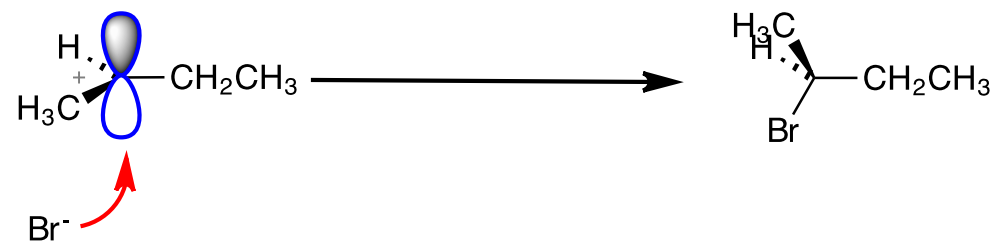
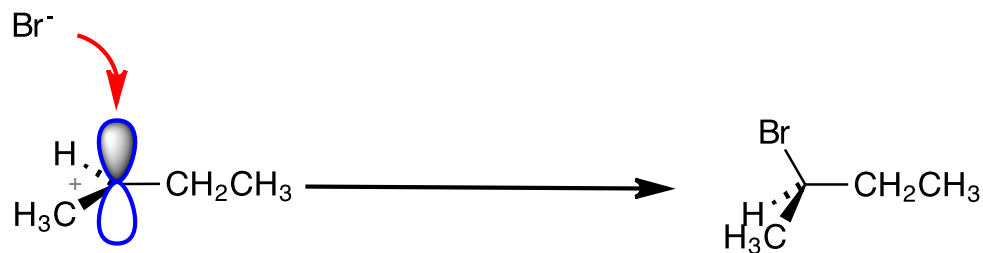
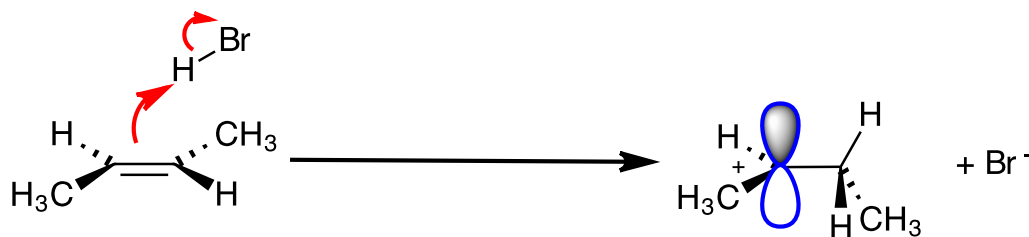
$\Delta H^\circ = -14$ kcal/mol

The reaction is exothermic.

Introduction to Addition Reactions

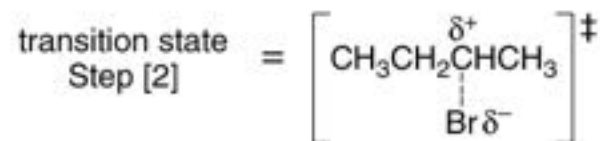
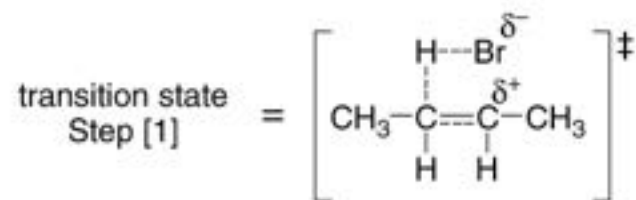
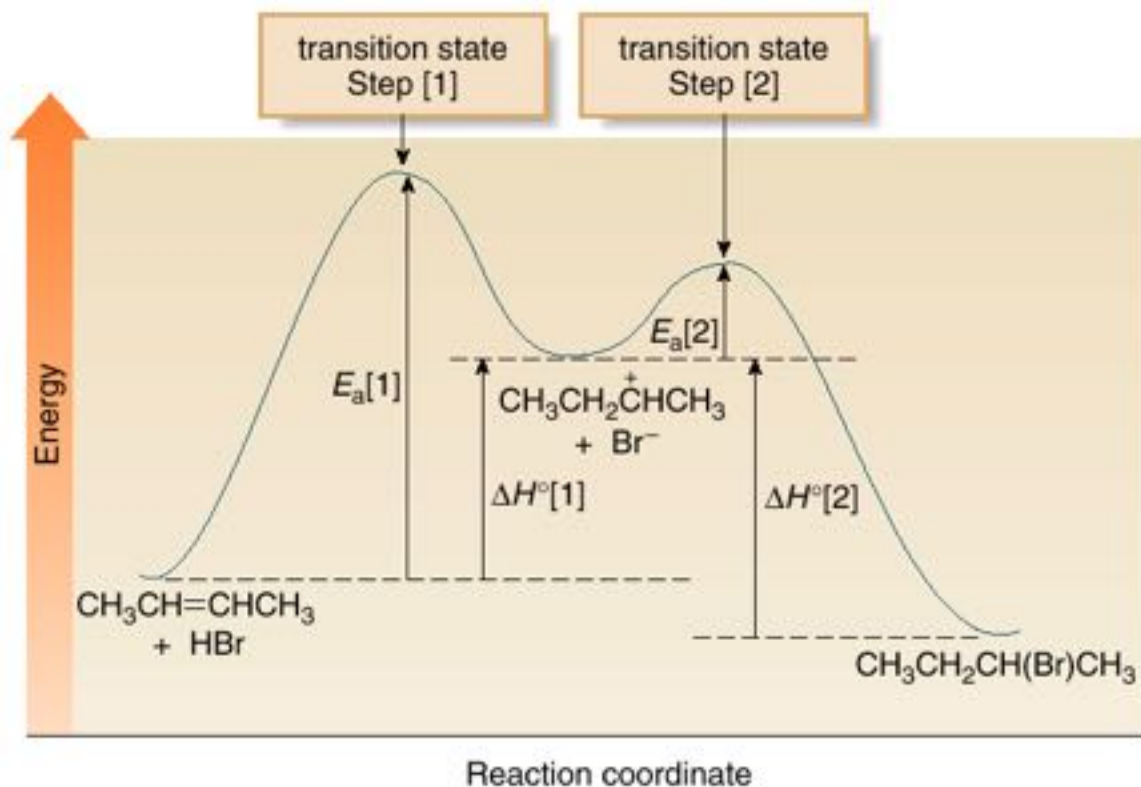


Hydrohalogenation. Mechanism



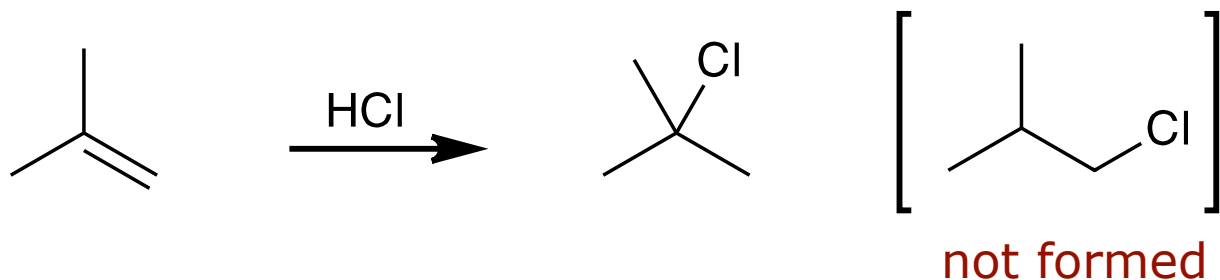
enantiomers

Hydrohalogenation

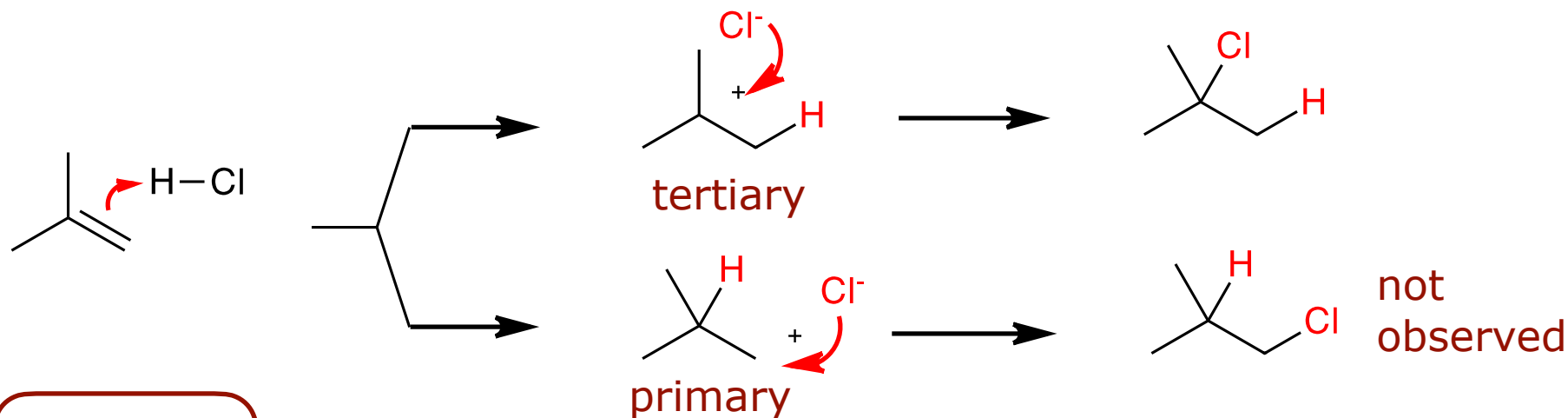


- The mechanism has two steps, so there are two energy barriers.
- Step [1] is rate-determining.

Hydrohalogenation — Markovnikov's Rule



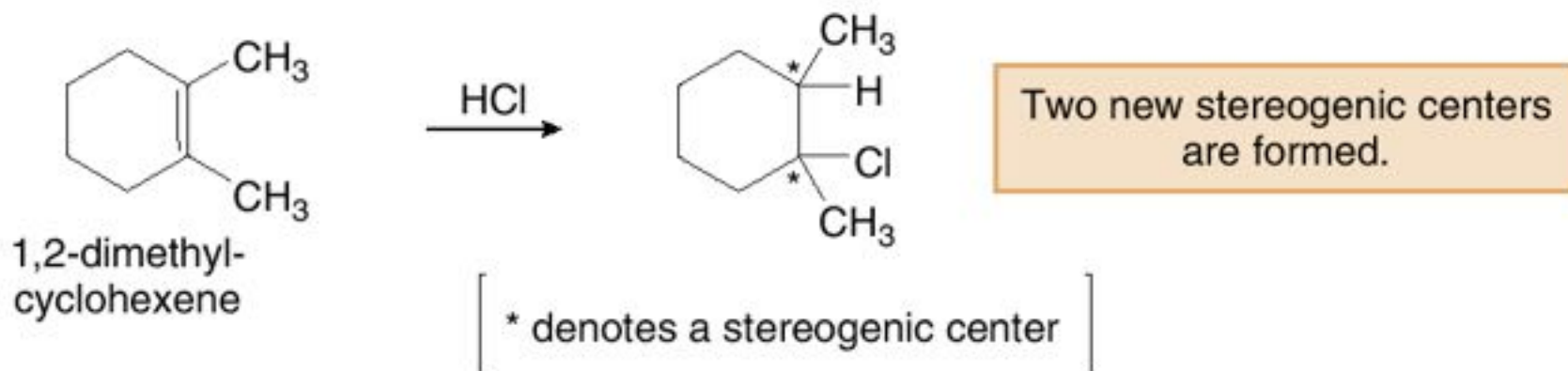
- The electrophile (H^+) adds to the less substituted carbon; the nucleophile (Cl^-) to the more substituted one.



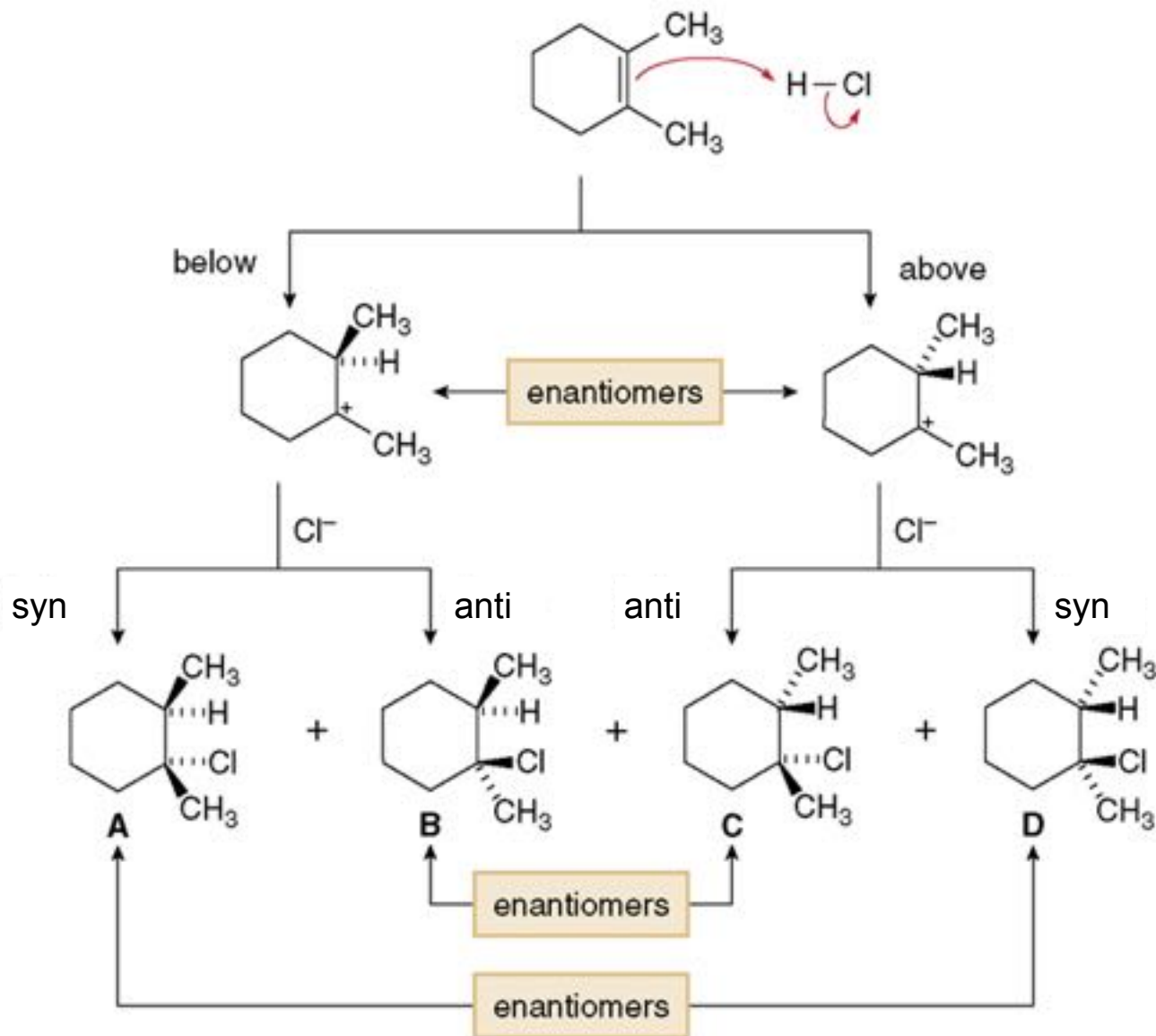
[video](#)

Hydrohalogenation - Stereochemistry

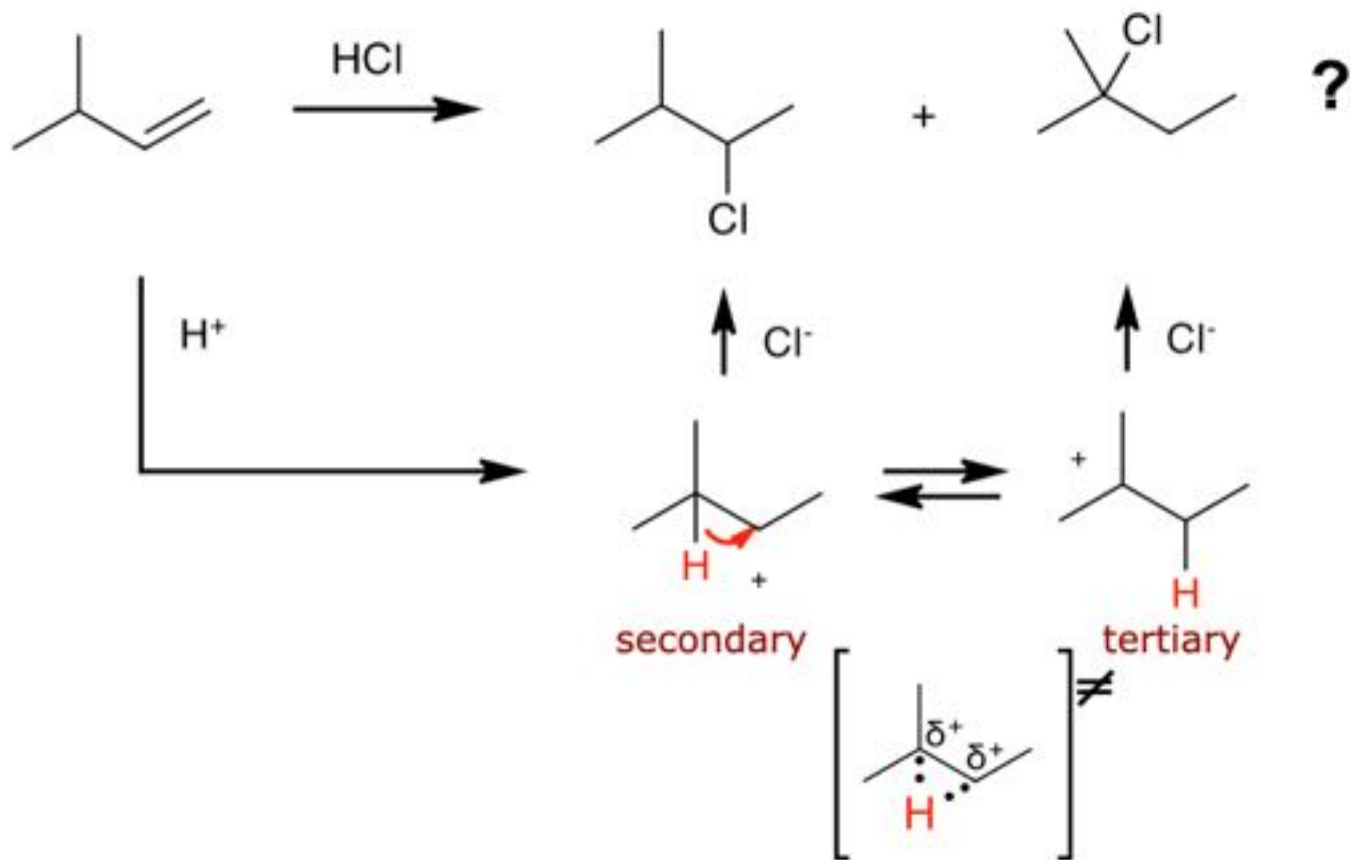
- Addition of HX to 1,2-dimethylcyclohexene forms two new stereogenic centers.



Hydrohalogenation—Stereochemistry

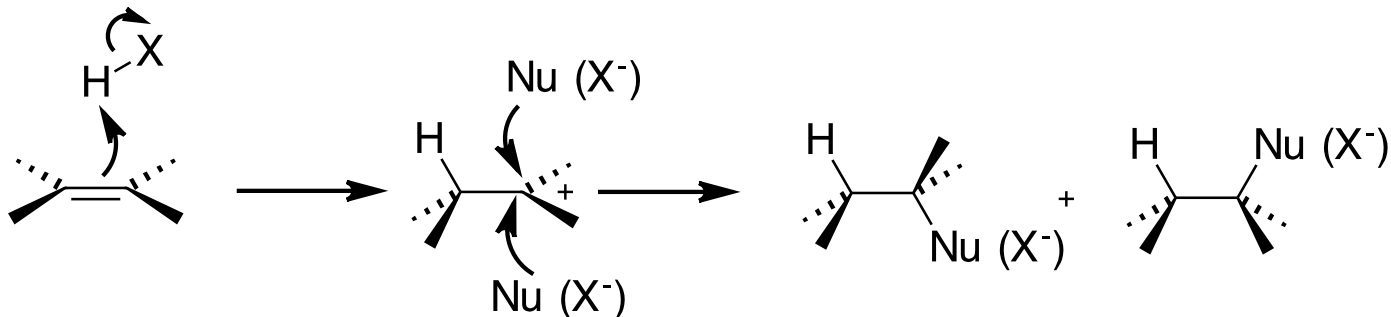


Carbocation Rearrangements



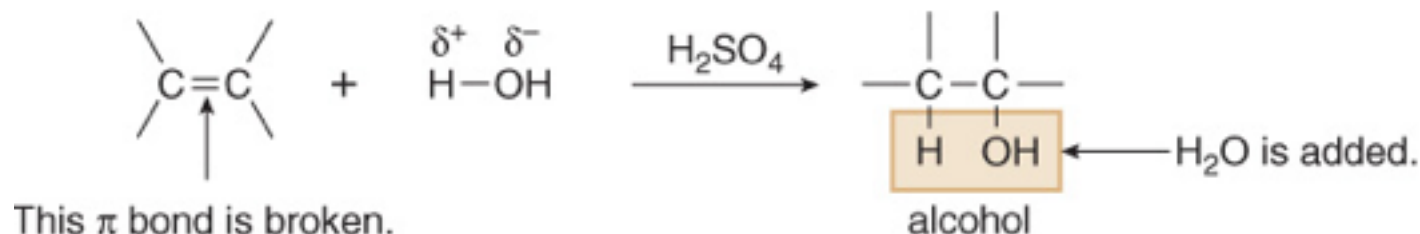
Groups prone to migration: H, Me, Ph

Hydrohalogenation—Summary

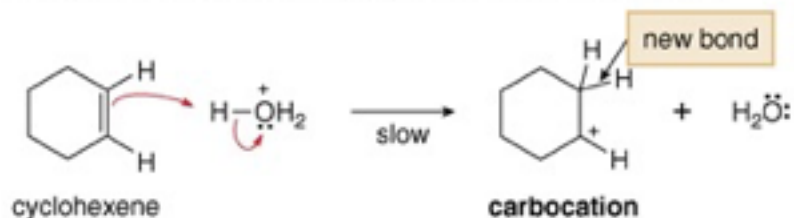


Mechanism	<ul style="list-style-type: none">• The mechanism involves two steps.• The rate-determining step forms a carbocation.• Rearrangements can occur.
Regioselectivity	<ul style="list-style-type: none">• Markovnikov's rule is followed. In unsymmetrical alkenes, H bonds to the less substituted C to form the more stable carbocation.
Stereochemistry	<ul style="list-style-type: none">• Syn and anti addition occur.

Hydration—Electrophilic Addition of Water

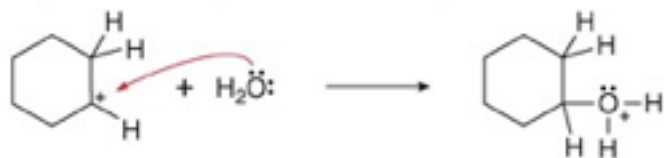


Step [1] Addition of the electrophile (H^+) to the π bond



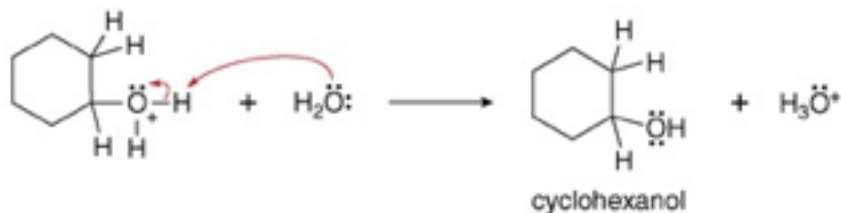
- The π bond attacks H_3O^+ , thus forming a new C–H bond while breaking the H–O bond. Because the remaining carbon atom of the original double bond is left with only six electrons, a **carbocation** intermediate is formed. This step is **rate-determining** because two bonds are broken but only one bond is formed.

Step [2] Nucleophilic attack of H_2O



- Nucleophilic attack of H_2O** on the carbocation forms the new C–O bond.

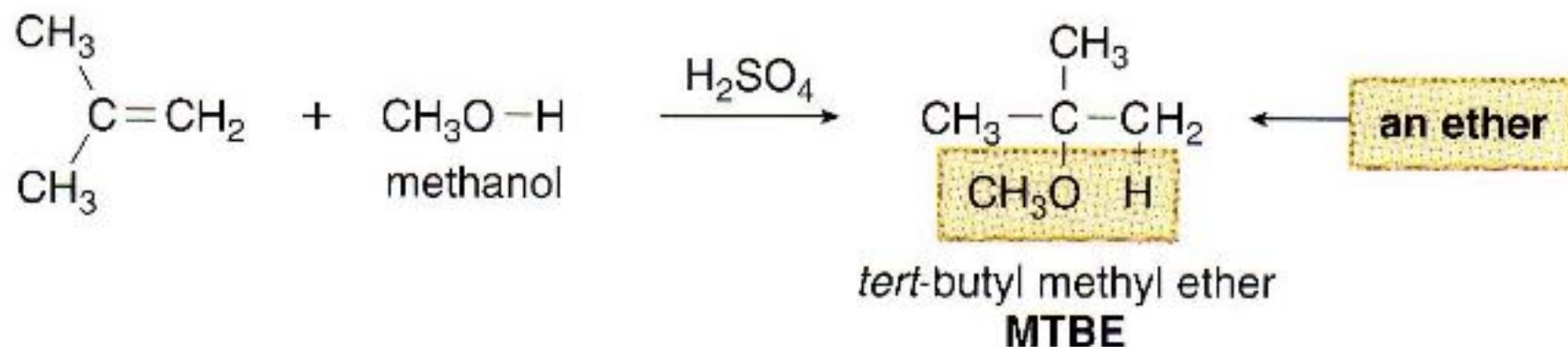
Step [3] Loss of a proton



- Removal of a proton with a base (H_2O) forms a neutral alcohol. Because the acid used in Step [1] is regenerated in Step [3], hydration is **acid-catalyzed**.

Electrophilic Addition of Alcohols

Alcohols add to alkenes, forming ethers by the same mechanism. For example, addition of CH_3OH to 2-methylpropene, forms *tert*-butyl methyl ether (MTBE), a high octane fuel additive.

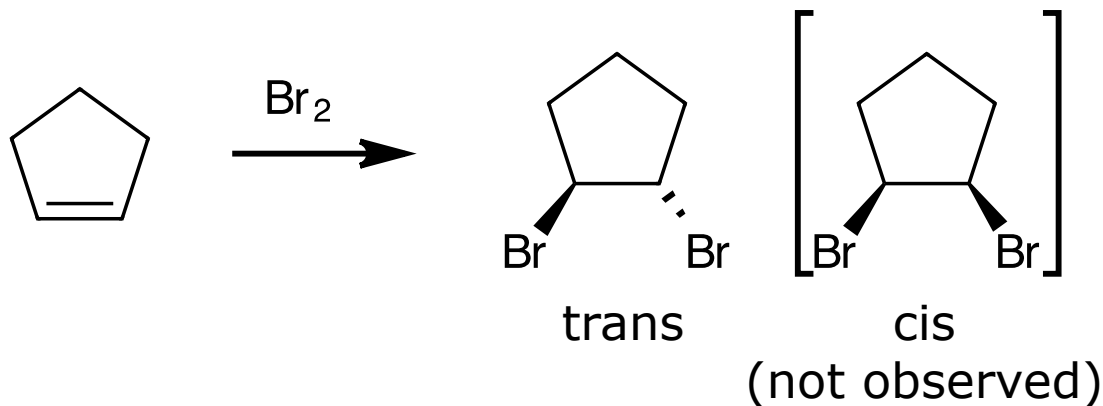


Halogenation - Addition of Halogens

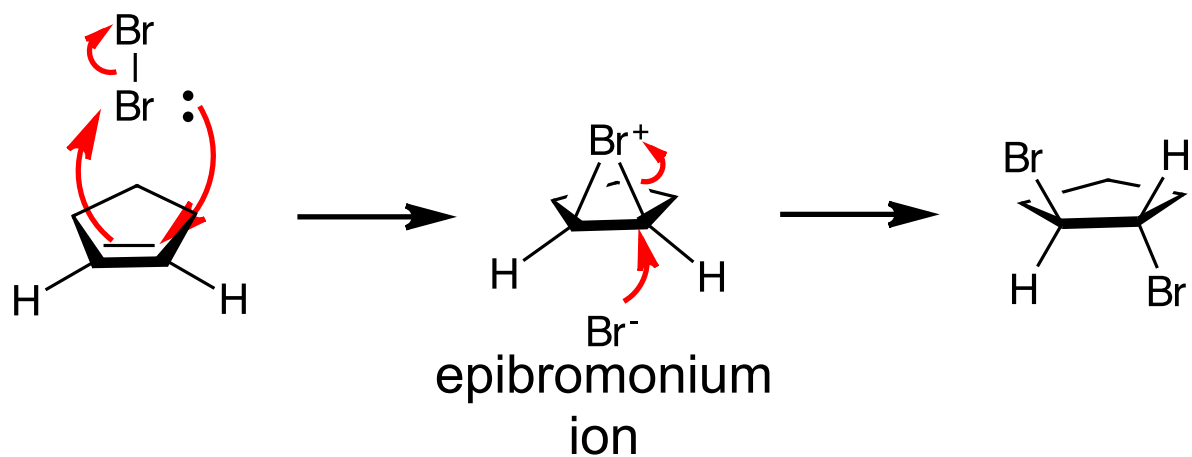
Halogenation



Anti addition



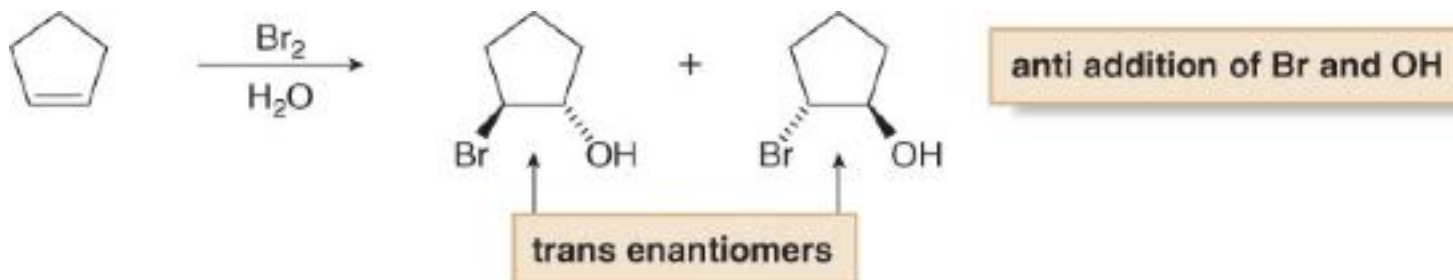
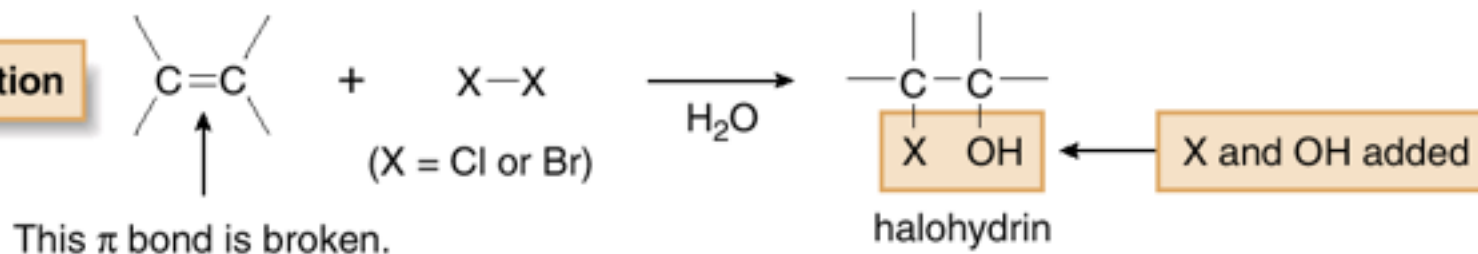
Halogenation - Mechanism



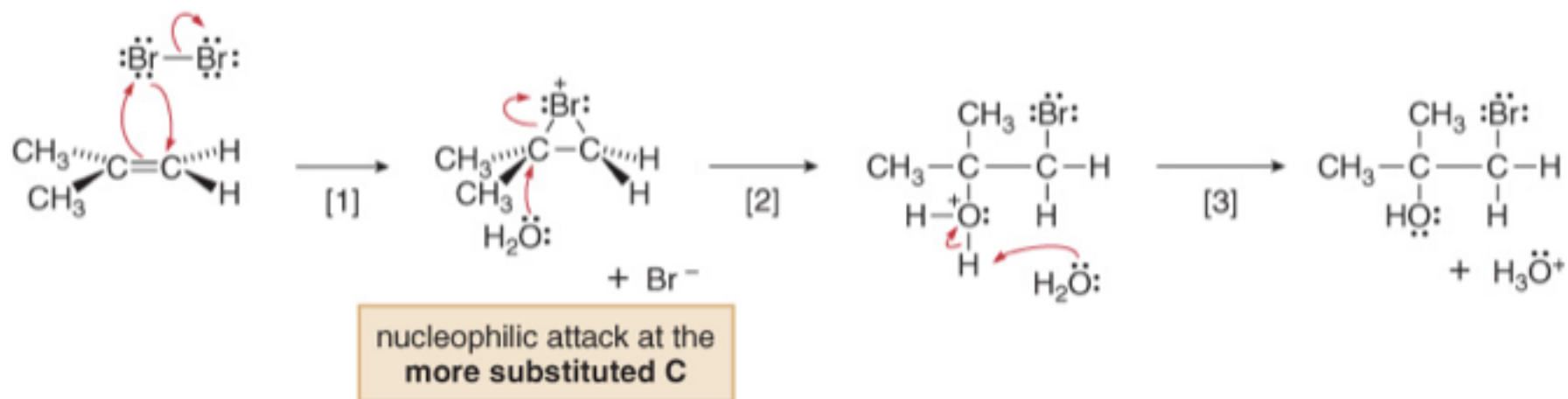
[video](#)

Halohydrin Formation

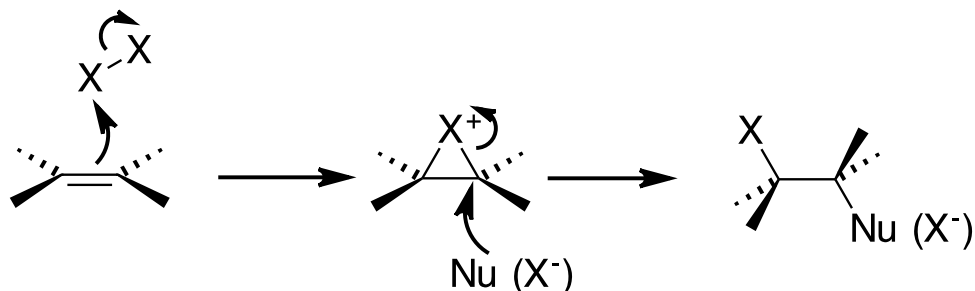
General reaction



Halohydrin Formation

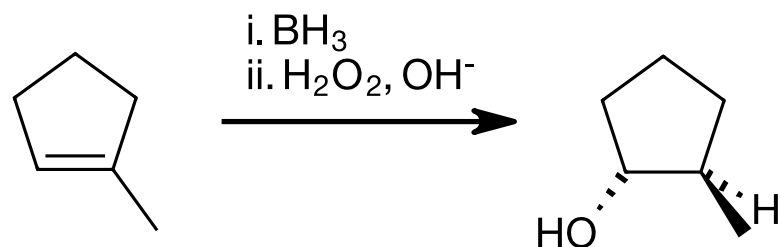


Halogenation and Halohydrin Formation



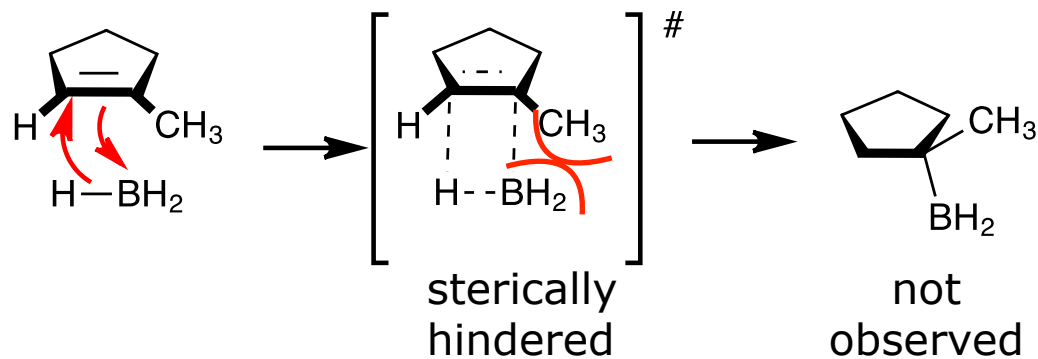
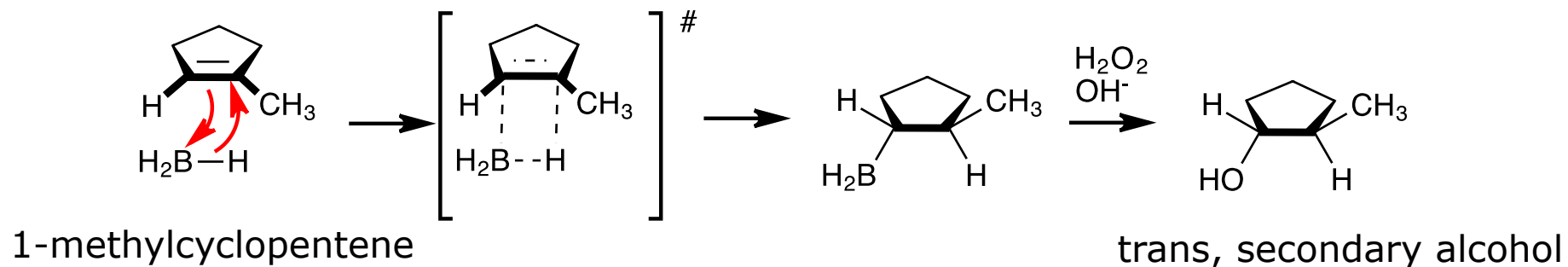
Mechanism	<ul style="list-style-type: none">• The mechanism involves two steps.• The rate-determining step forms a bridged halonium ion.• No rearrangements can occur.
Regioselectivity	<ul style="list-style-type: none">• Markovnikov's rule is followed. X^+ bonds to the less substituted carbon.
Stereochemistry	<ul style="list-style-type: none">• Anti addition occurs.

Hydroboration - Oxidation



anti-Markovnikov
stereoselective (sin addition)

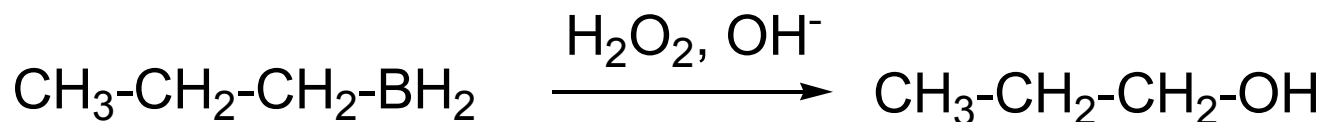
Hydroboration - Oxidation



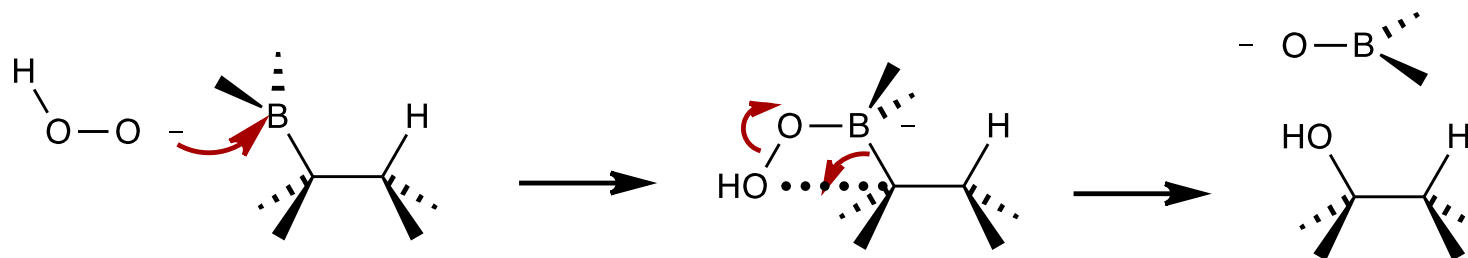
[video](#)

Hydroboration - Oxidation

Alkylboranes react rapidly with water and spontaneously burn when exposed to air; they are oxidized, without isolation, with basic hydrogen peroxide (H_2O_2 , OH^-).

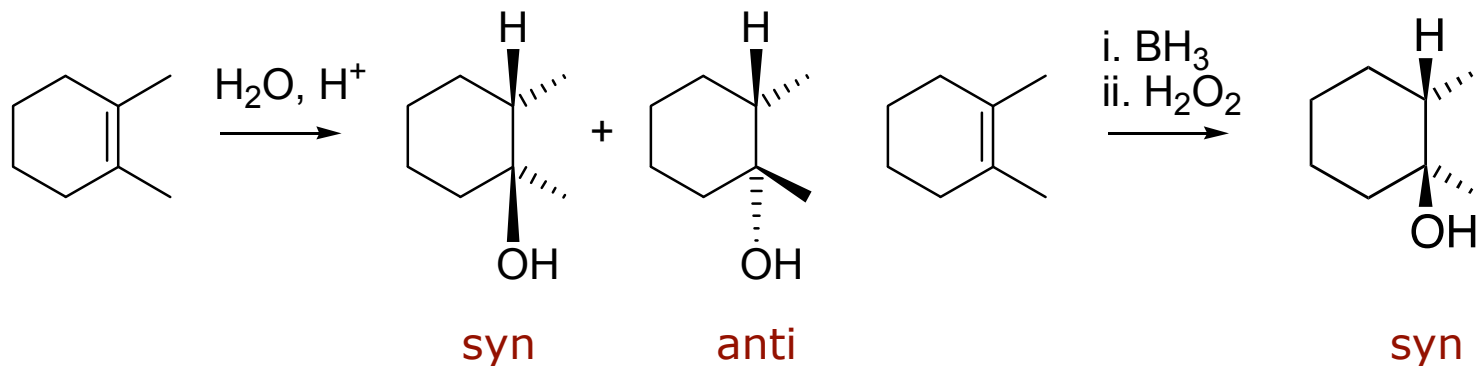
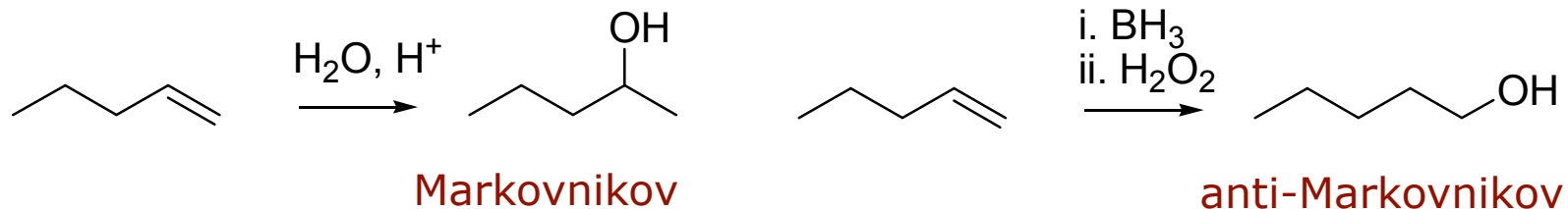


Oxidation replaces the C—B bond with a C—O bond, forming a new OH group with retention of configuration.



Hydroboration - Oxidation

- The overall result is syn addition of the elements of H and OH to a double bond in an “**anti-Markovnikov**” fashion.

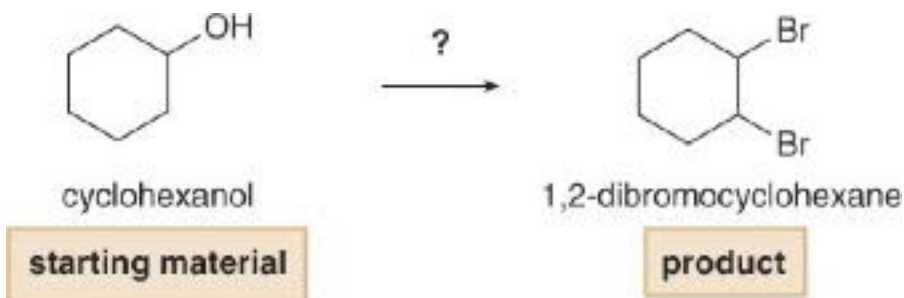


Hydroboration - Oxidation

Observation

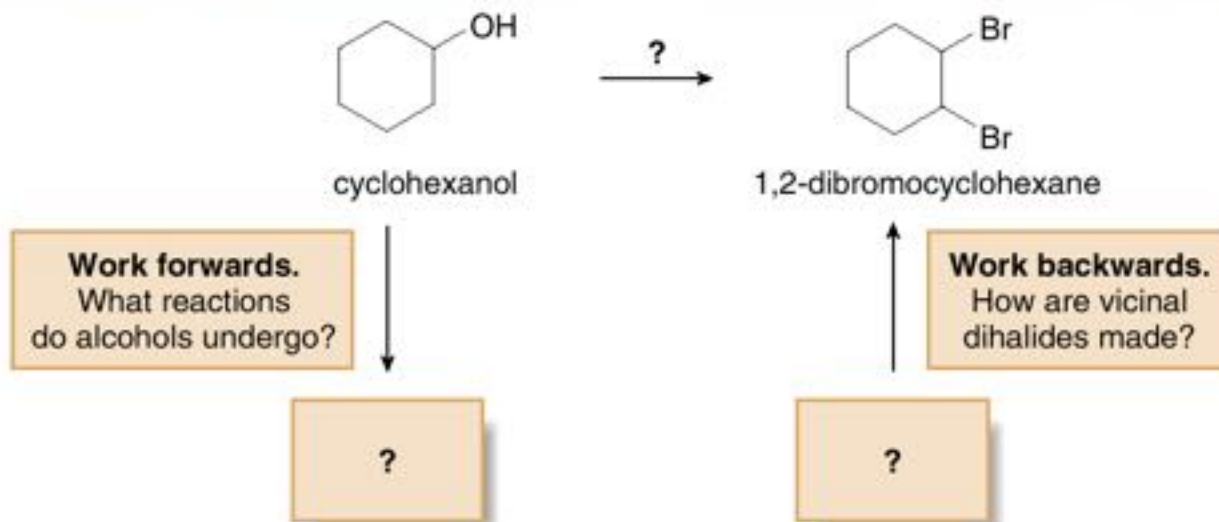
Mechanism	<ul style="list-style-type: none">• The addition of H and BH₂ occurs in one step.• No rearrangements can occur.
Regioselectivity	<ul style="list-style-type: none">• The BH₂ group bonds to the less substituted carbon atom.
Stereochemistry	<ul style="list-style-type: none">• Syn addition occurs.• OH replaces BH₂ with retention of configuration.

Alkenes in Organic Synthesis



To solve this problem we must:

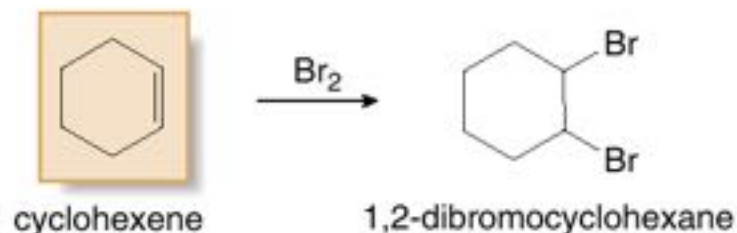
- Work backwards from the product by asking: What type of reactions introduce the functional groups in the product?
- Work forwards from the starting material by asking: What type of reactions does the starting material undergo?



Alkenes in Organic Synthesis

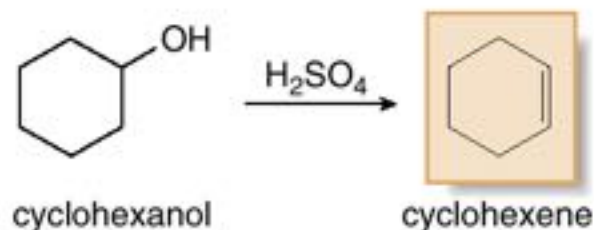
Working backwards:

[1] 1,2-Dibromocyclohexane, a vicinal dibromide, can be prepared by the addition of Br_2 to **cyclohexene**.



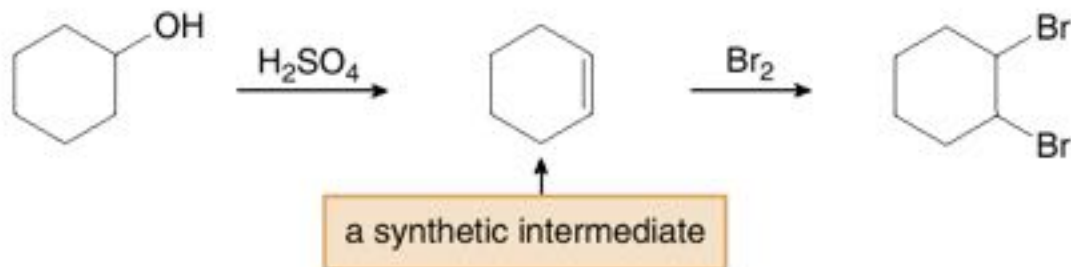
Working forwards:

[2] Cyclohexanol can undergo acid-catalyzed dehydration to form **cyclohexene**.



Cyclohexene is called a **synthetic intermediate**, or simply an **intermediate**, because it is the **product of one step and the starting material of another**. We now have a two-step sequence to convert cyclohexanol to 1,2-dibromocyclohexane, and the synthesis is complete. Take note of the central role of the alkene in this synthesis.

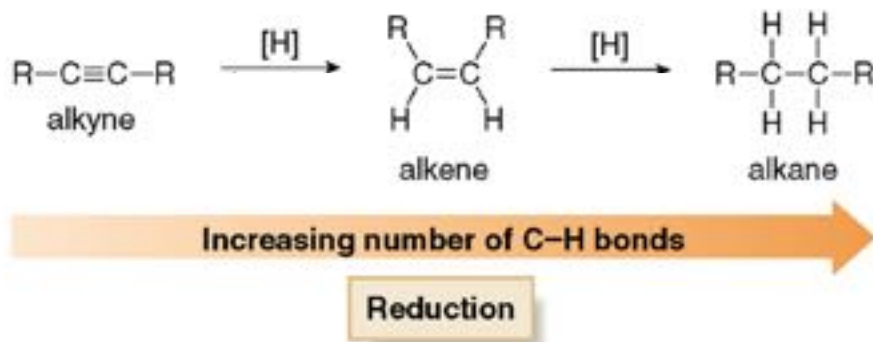
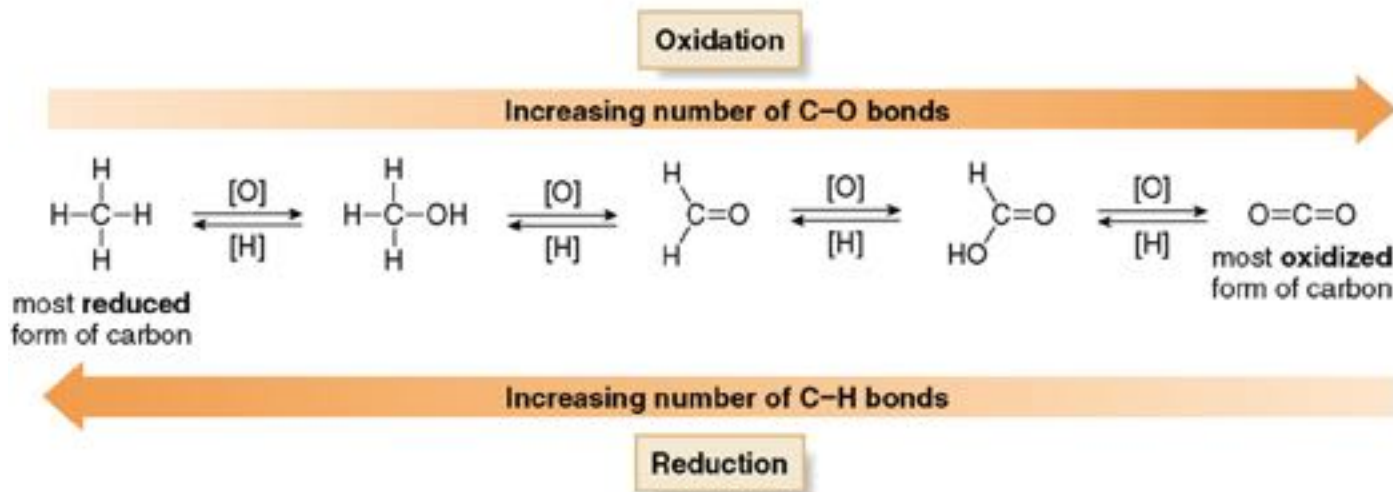
A two-step synthesis



Oxidation and Reduction

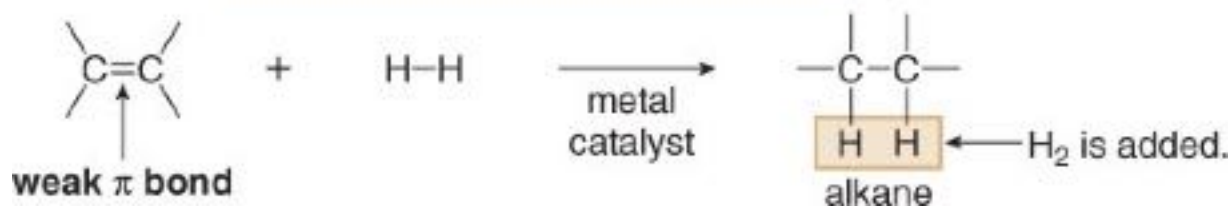
Oxidation: increase of C—O bonds or decrease of C—H bonds.

Reduction: decrease of C—O bonds or increase of C—H bonds.



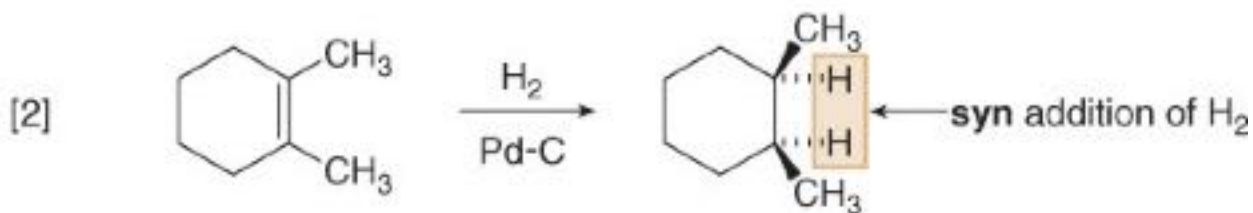
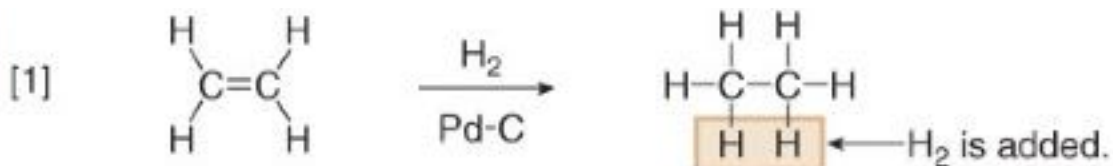
Catalytic Hydrogenation

Hydrogenation—General reaction

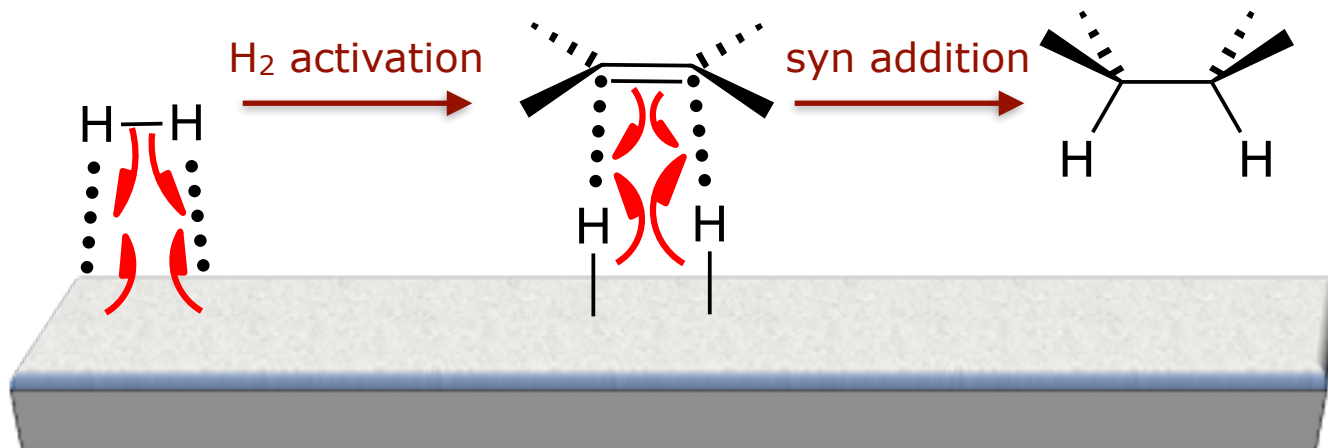


- The addition of H_2 occurs only in the presence of a metal catalyst (Pd, Pt, or Ni) adsorbed onto a finely divided inert solid, such as charcoal.
- H_2 adds in a **syn** fashion.

Examples

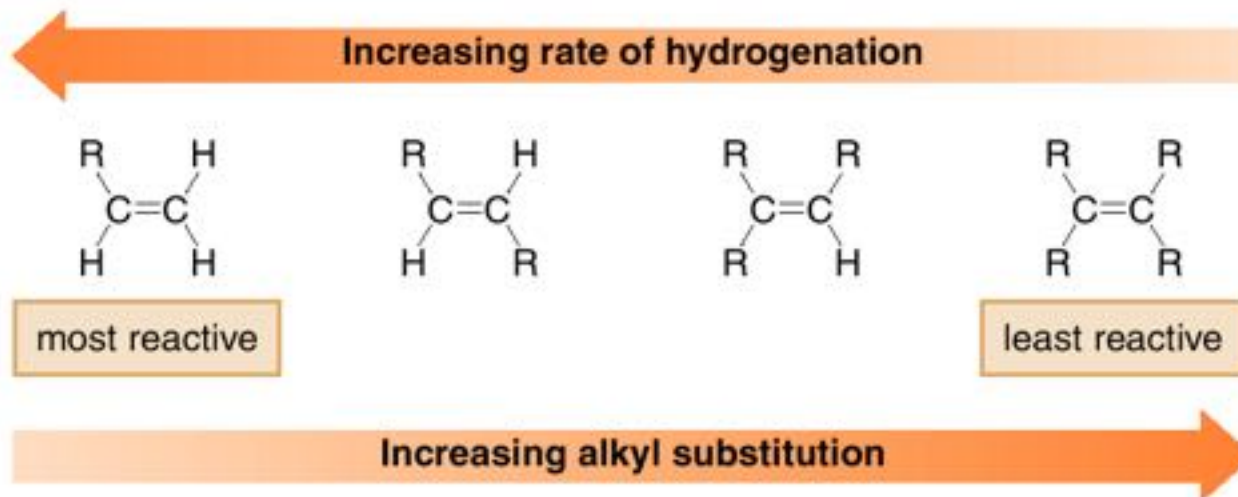


Catalytic Hydrogenation



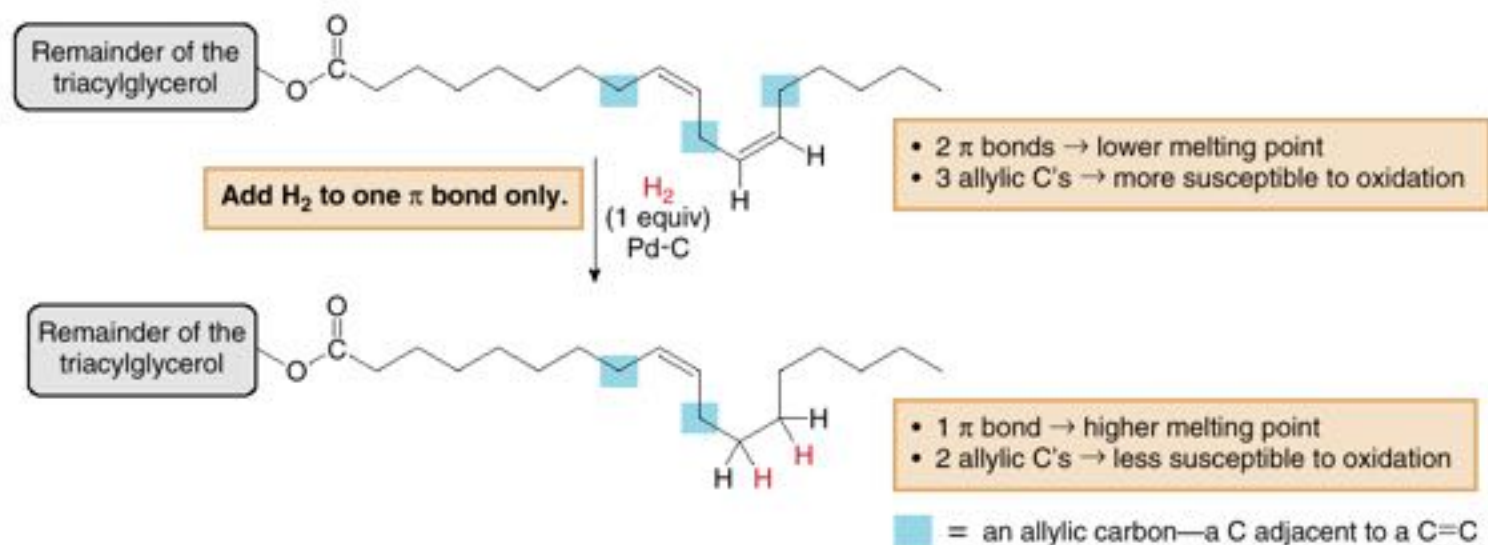
Catalytic Hydrogenation

- Rapid, sequential addition of H_2 occurs from the side of the alkene complexed to the metal surface, resulting in syn addition.
- Less crowded double bonds complex more readily to the catalyst surface, resulting in faster reaction.



Catalytic Hydrogenation

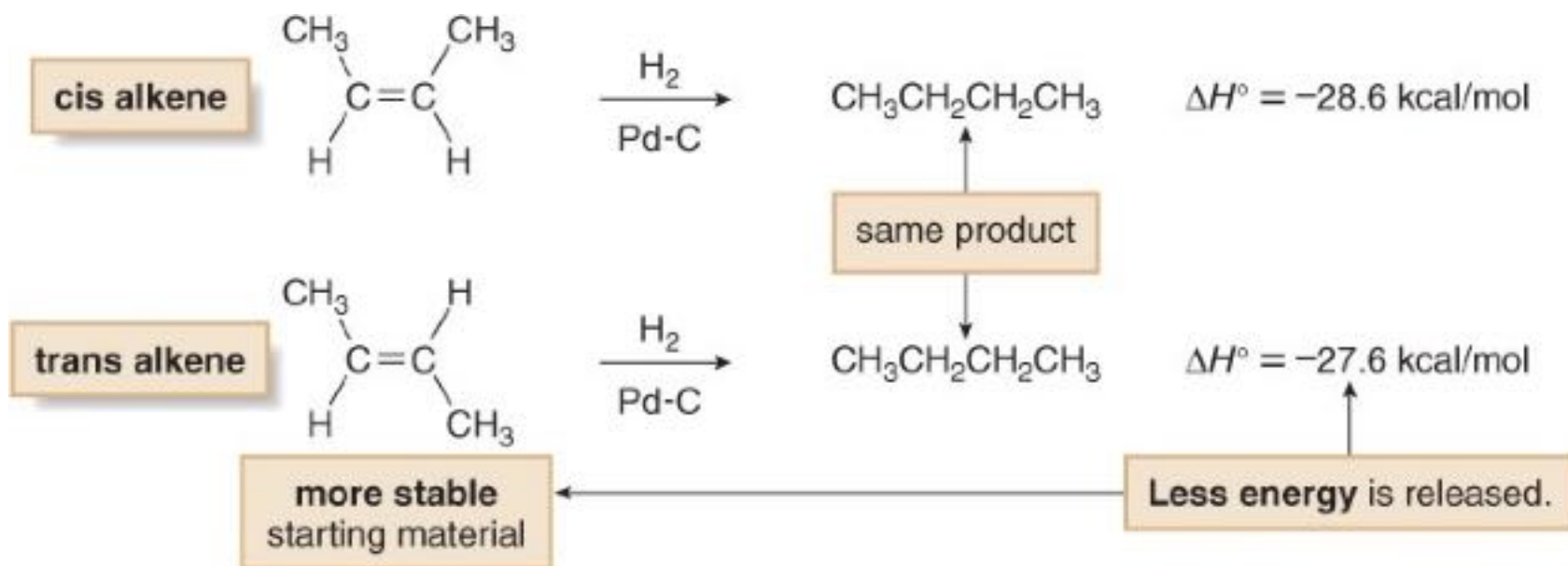
- When unsaturated vegetable oil is treated with hydrogen, some or all of the π bonds add H_2 . This increases the melting point of the oil.
- Margarine is prepared by partially hydrogenating vegetable oils to give a product with a consistency that more closely resembles butter.



- Decreasing** the number of degrees of unsaturation **increases** the melting point.
- When an oil is *partially* hydrogenated, some double bonds react with H_2 , whereas some double bonds remain in the product.
- Partial hydrogenation **decreases** the number of allylic sites, making a triacylglycerol **less** susceptible to oxidation, thereby increasing its shelf life.

Catalytic Hydrogenation

- Hydrogenation of alkenes is exothermic
- The heat of hydrogenation, can be used as a measure of the relative stability of two alkenes.

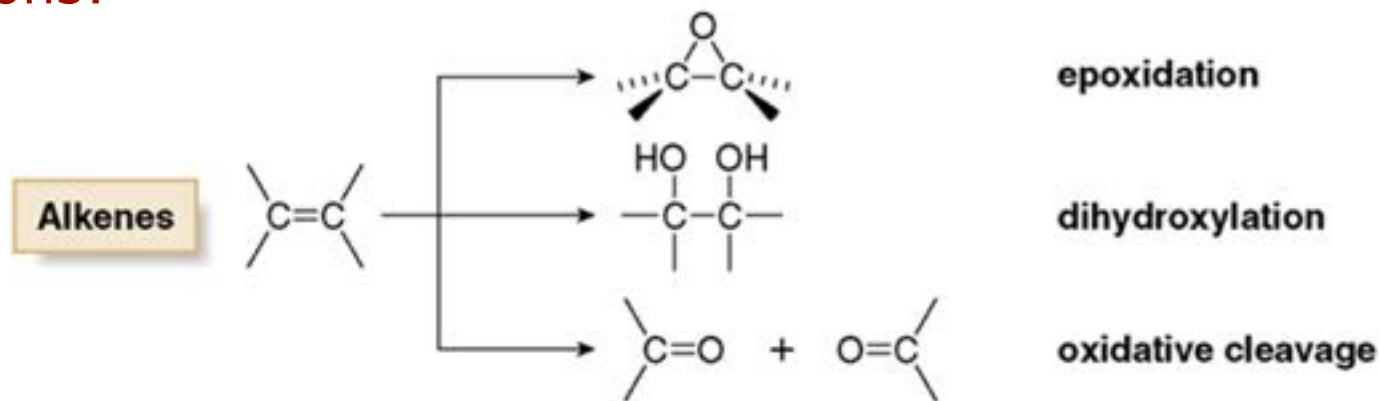


Oxidations

Oxidizing agents:

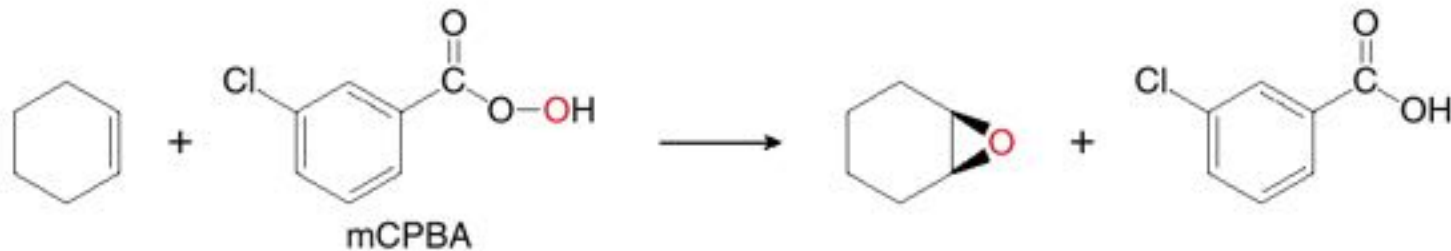
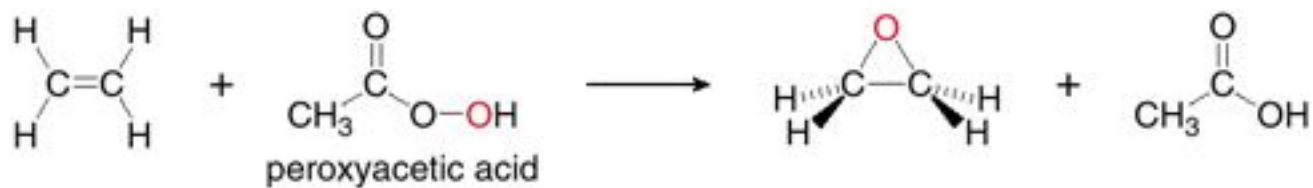
- Reagents containing an O—O bond: O_2 , O_3 , H_2O_2 , $ROOH$, $RCOOOH$.
- Reagents containing metal-oxygen bonds: $Cr(VI)$, $Mn(VII)$, $Os(VIII)$.

Reactions:



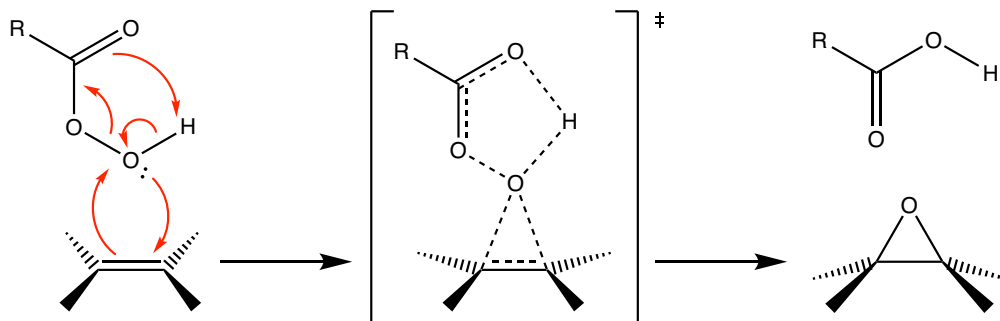
Epoxidation

Examples

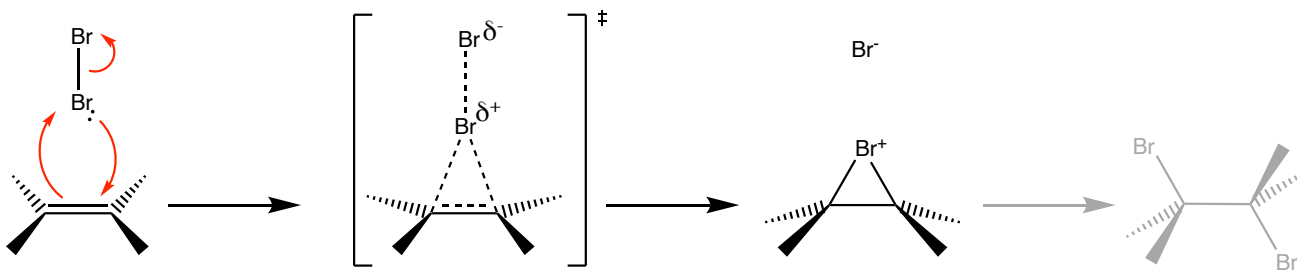


Epoxidation

One step: all bonds are broken/formed in a single step



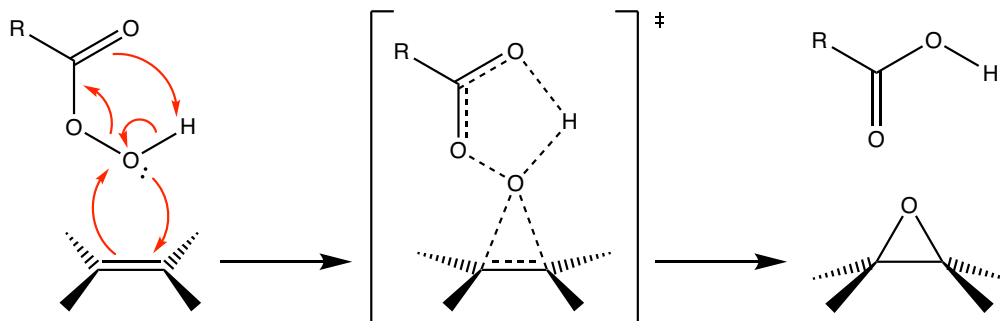
epoxidation and halogenation have similar mechanisms



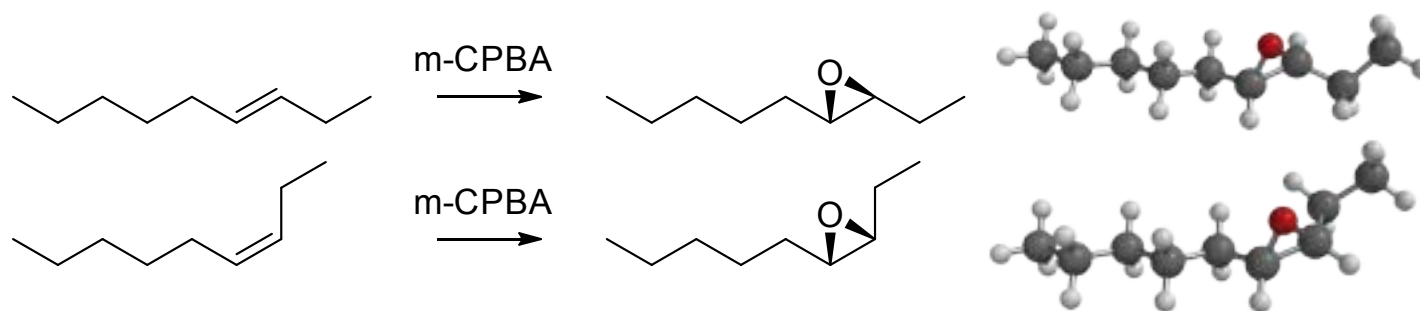
[video](#)

Epoxidation

One step: all bonds are broken/formed in a single step

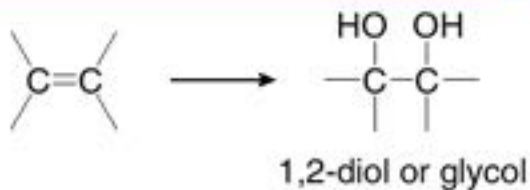


Epoxidation is stereospecific.

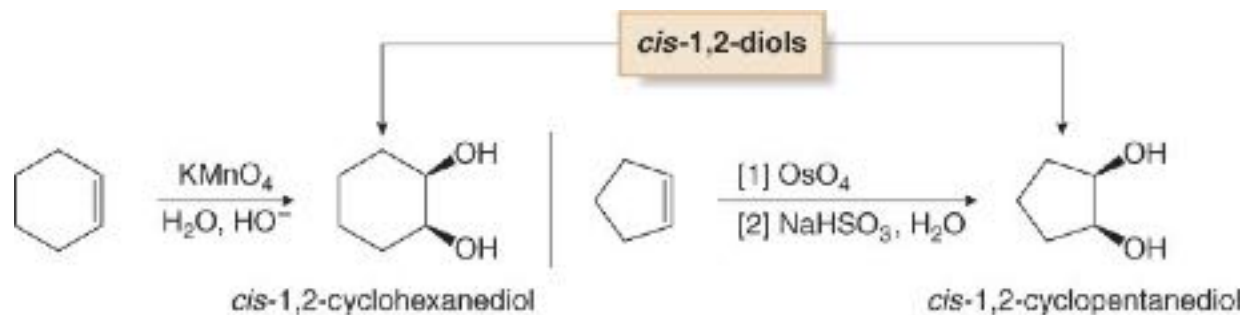


Dihydroxylation

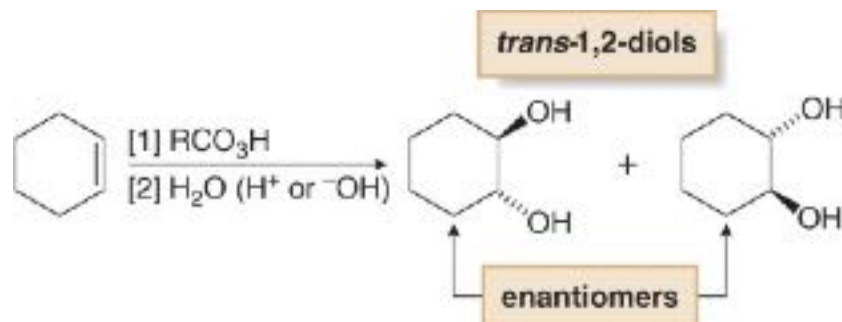
Dihydroxylation—General reaction



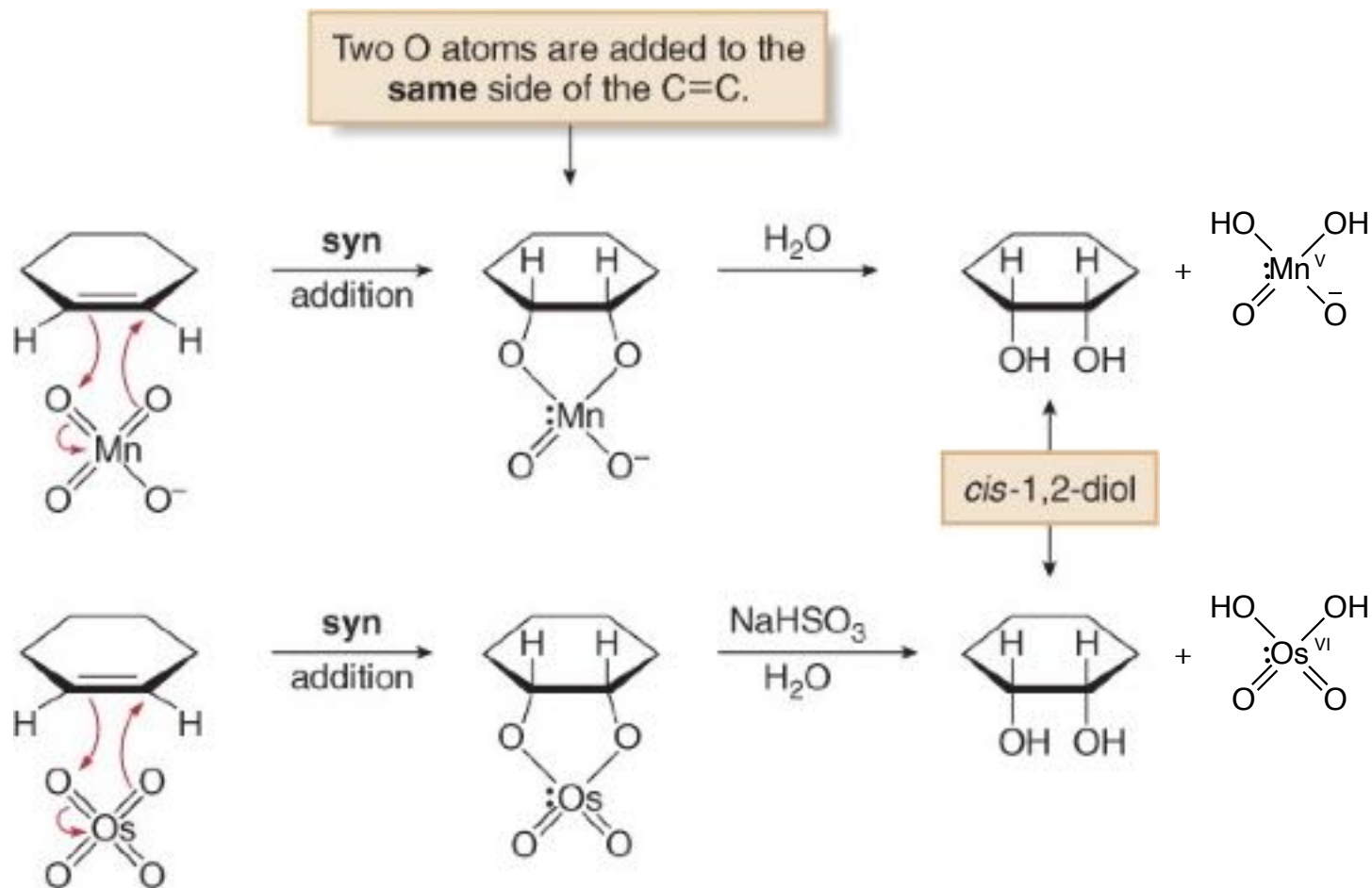
Syn dihydroxylation



Anti dihydroxylation

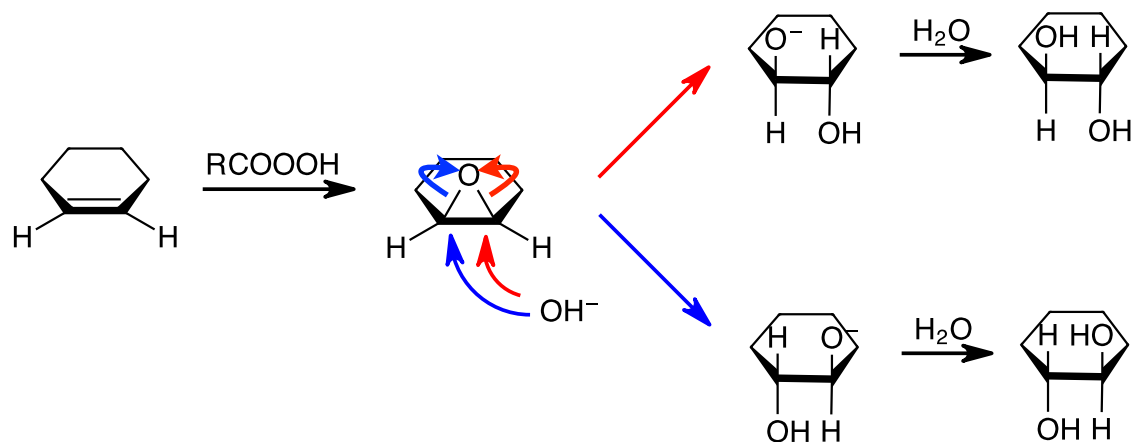


Syn Dihydroxylation



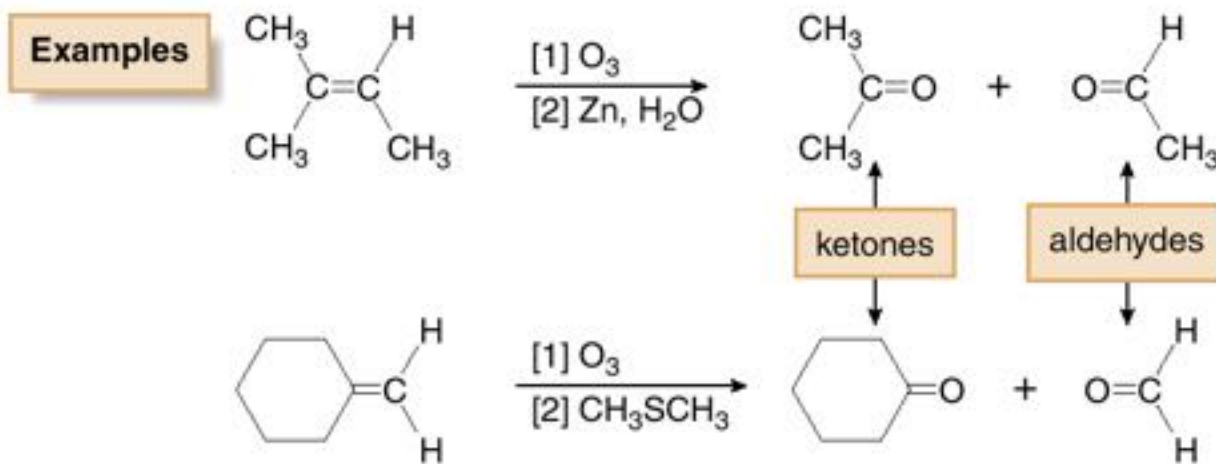
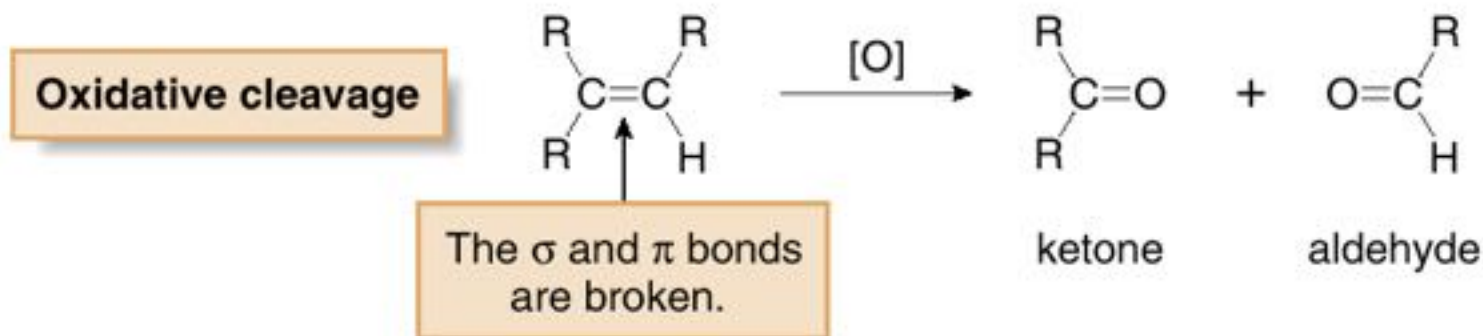
[video](#)

Anti Dihydroxylation



Oxidative Cleavage

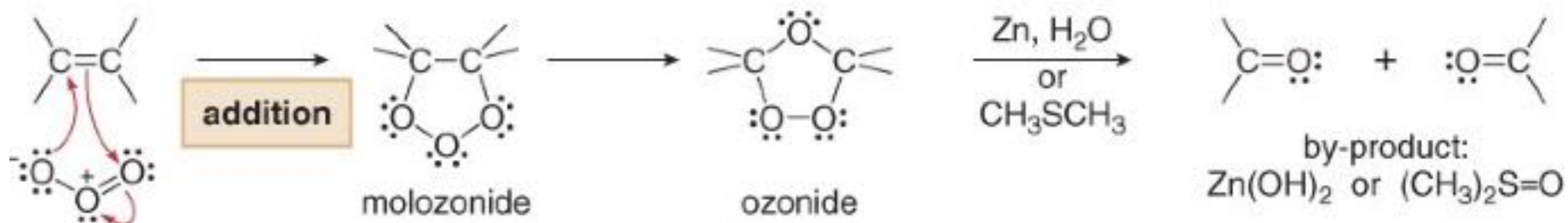
- Oxidative cleavage of an alkene breaks both the σ and π bonds of the double bond to form two carbonyl compounds. Cleavage with ozone (O_3) is called **ozonolysis**.



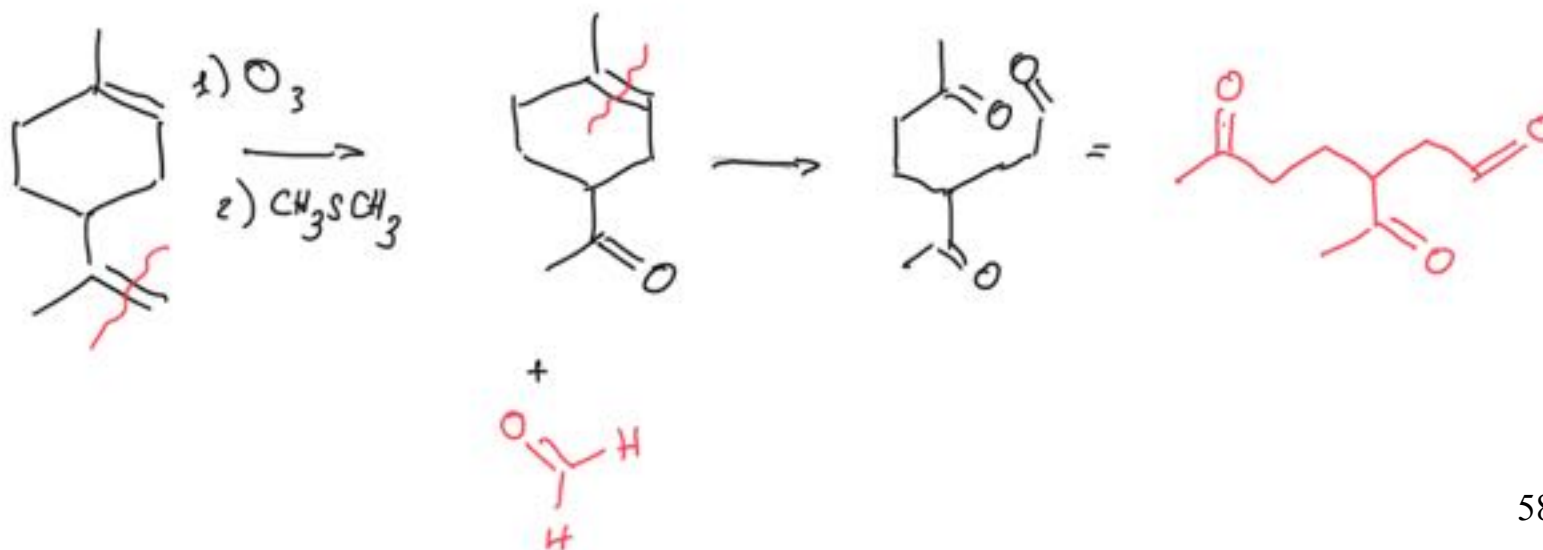
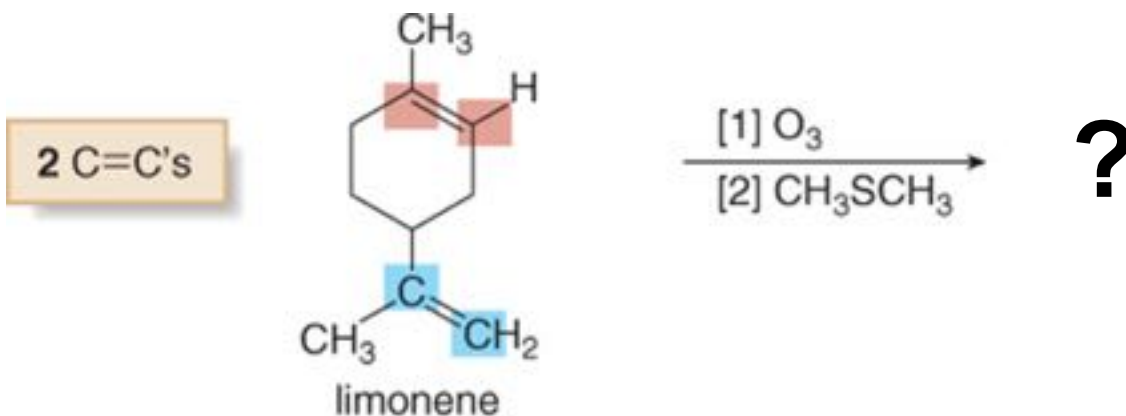
Oxidative Cleavage

- Addition of O_3 to the π bond of an alkene forms a **molozonide**, which rearranges to an **ozonide** in a stepwise process.
- The unstable ozonide is reduced to afford carbonyl compounds.

The key intermediates in ozonolysis



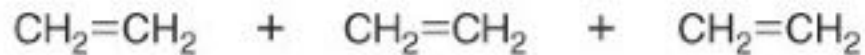
Oxidative Cleavage



Polymers and Polymerization

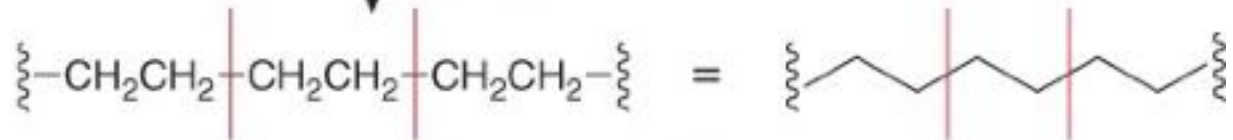
- **Polymers** are large molecules made up of repeating units of smaller molecules called **monomers**. They include biologically important compounds such as proteins and carbohydrates, as well as synthetic plastics such as polyethylene, polyvinyl chloride (PVC) and polystyrene.
- **Polymerization** is the joining together of monomers to make polymers. For example, joining ethylene monomers together forms the polymer polyethylene, a plastic used in milk containers and plastic bags.

Ethylene
monomers



polymerization

Polyethylene
polymer

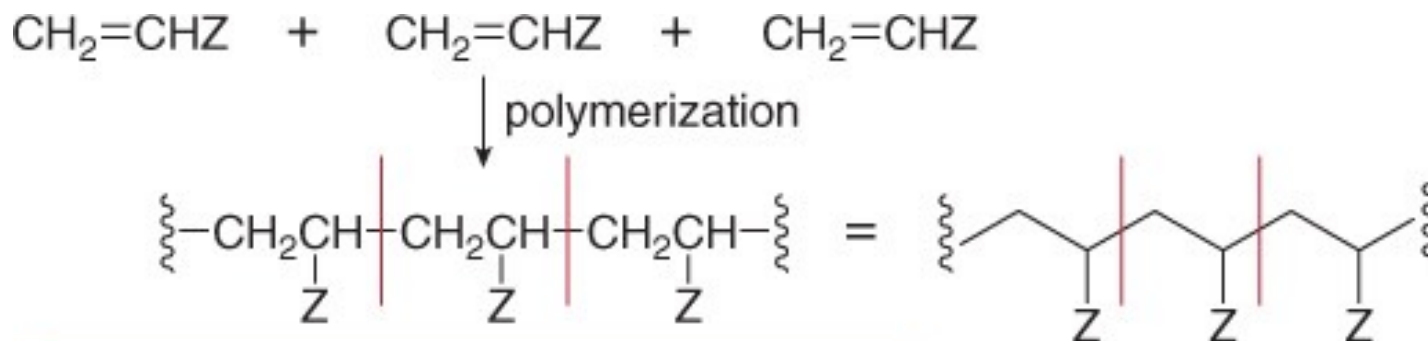


three monomer units joined together

Polyethylene
(PE)

Polymers and Polymerization

- Many ethylene derivatives having the general structure $\text{CH}_2=\text{CHZ}$ are also used as monomers for polymerization.
- The identity of Z affects the physical properties of the resulting polymer.
- Polymerization of $\text{CH}_2=\text{CHZ}$ usually affords polymers with Z groups on every other carbon atom in the chain.

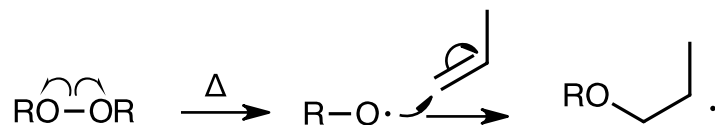


three monomer units joined together

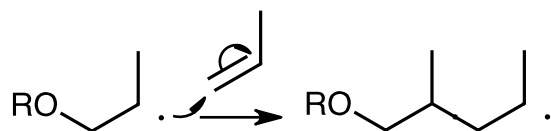
Polymers and Polymerization

Radical Polymerization

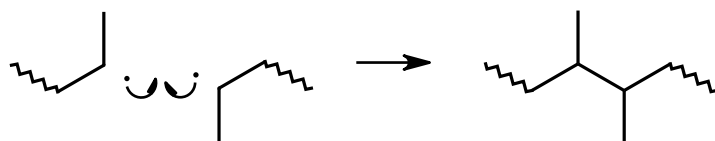
(with a radical initiator, e.g. RO-OR)



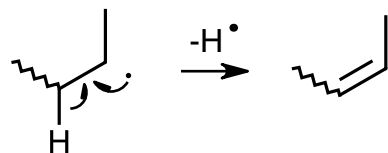
Initiation



Propagation

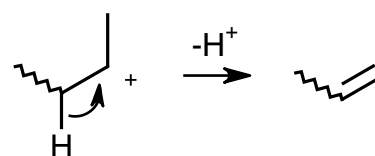
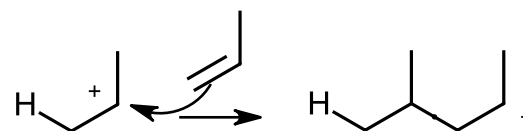
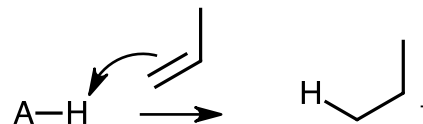


Termination



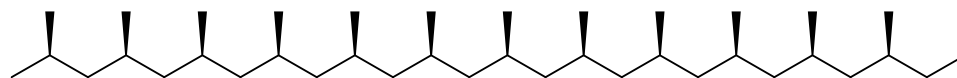
Cationic Polymerization

(with a Brønsted or a Lewis acid
e.g. AlCl_3 , TiCl_3)

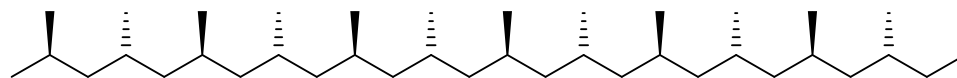


The more substituted radical/cation always adds to the less substituted end of the monomer, a process called **head-to-tail polymerization**.

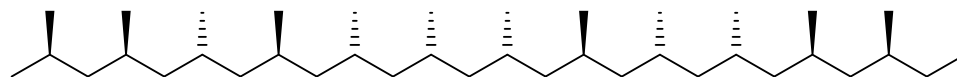
Polymers and Polymerization



isotactic (TiCl_3 , AlEt_2Cl)



syndiotactic (TiCl_4 , AlR_3)







atactic (TiCl_3 , AlCl_3)

Cationic polymerization - Ziegler-Natta catalysts

Polymers and Polymerization

Table 15.2

Common Industrial Monomers and Polymers

Monomer	Polymer	Consumer product
$\text{CH}_2=\text{CHCl}$ vinyl chloride	$\text{---} \text{CH}_2 \text{---} \text{CH}(\text{Cl}) \text{---} \text{CH}_2 \text{---} \text{CH}(\text{Cl}) \text{---} \text{CH}_2 \text{---} \text{CH}(\text{Cl}) \text{---}$ poly(vinyl chloride) PVC	 PVC pipes
$\text{CH}_2=\text{CHCH}_3$ propene	$\text{---} \text{CH}_2 \text{---} \text{CH}(\text{CH}_3) \text{---} \text{CH}_2 \text{---} \text{CH}(\text{CH}_3) \text{---} \text{CH}_2 \text{---} \text{CH}(\text{CH}_3) \text{---}$ polypropylene	 polypropylene carpeting
$\text{CH}_2=\text{CH}$  styrene	$\text{---} \text{CH}_2 \text{---} \text{CH}(\text{C}_6\text{H}_5) \text{---} \text{CH}_2 \text{---} \text{CH}(\text{C}_6\text{H}_5) \text{---} \text{CH}_2 \text{---} \text{CH}(\text{C}_6\text{H}_5) \text{---}$ polystyrene	 Styrofoam products

Esercizio

Un composto di formula bruta C_6H_{12} reagisce con ozono, in presenza di zinco, per dare 2 molecole di aldeide propionica (CH_3CH_2CHO) e reagisce con i peracidi organici per dare un prodotto non chirale. Risalire alla struttura del composto incognito.

C_6H_{12} ha grado di insaturazione = 1: può essere un alchene lineare o un cicloalcano; reagisce con O_3 , quindi è un alchene.

