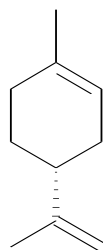


Chapter 3: Alkenes and Alkynes



Enone

General Properties

Alkenes contain double bonds and alkynes triple bonds. Both classes of compounds are hydrocarbons, containing only C and H atoms.

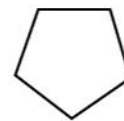
- a double bond consists of 1 σ and 1 π bond,
- a triple bond consists of 1 σ and 2 π bonds.



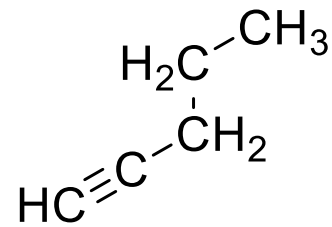
alkane



alkene



cyclic alkane



Alkynes



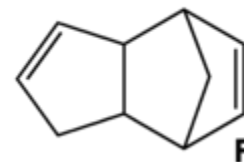
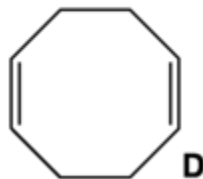
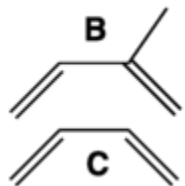
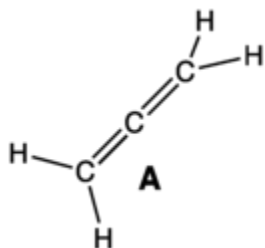
Every π bond results in the loss of a pair of H atoms.

General Properties (cont'd)

The Index of Hydrogen Deficiency (IHD) can give an idea of possible structures based on the ratio of C to H. This is a count of the number of H₂ molecules needed to obtain the corresponding saturated acyclic structure. The IHD is also equal to the number of rings and π bonds in the molecule.

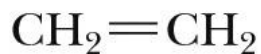
With multiple double (or triple) bonds three possible arrangements arise: cumulated, conjugated or isolated (non-conjugated). Conjugated are especially important as the π bonds can interact.

Cumulated	Conjugated	Isolated
$C=C=C$	$C=C-C=C$	$C=C-C-C=C$
$C=C=C=C$	$C\equiv C-C\equiv C$	$C\equiv C-C-C-C\equiv C$

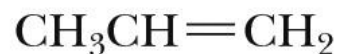


- IUPAC Nomenclature of alkenes
 - Use the Suffix **-ene** to show the presence of a carbon-carbon double bond.
 - Number the parent chain to give the 1st carbon of the double bond the lower number.
 - Follow IUPAC rules for numbering and naming substituents.
 - For a cycloalkene, the numbering of the atoms of the ring must begin with the two carbons of the double bond.

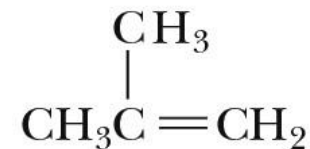
- Some alkenes, particularly low-molecular-weight ones, are known almost exclusively by their common names.



IUPAC name: Ethene
 Common name: Ethylene

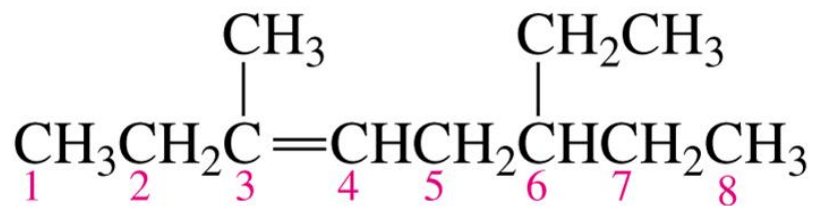


Propene
 Propylene

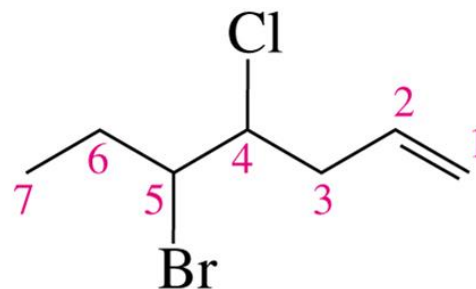


2-Methylpropene
 Isobutylene

Substituents are stated in alphabetical order.

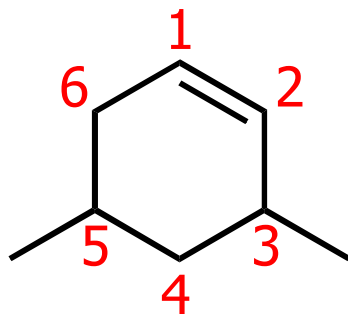
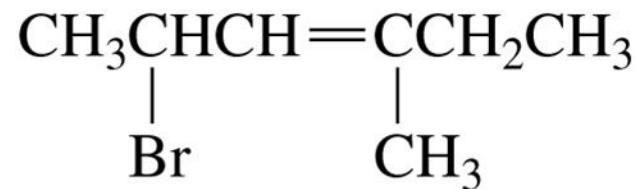
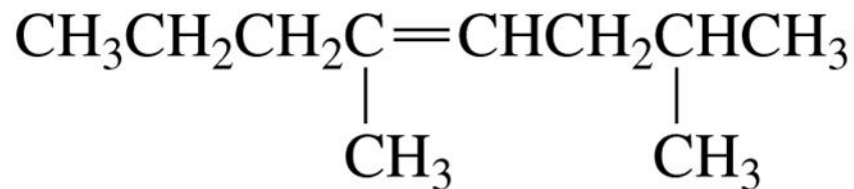


6-ethyl-3-methyl-3-octene



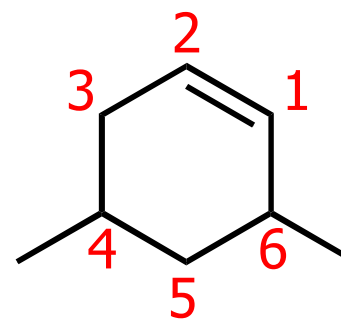
5-bromo-4-chloro-1-heptene

Hw:



3,5-Dimethylcyclohexene

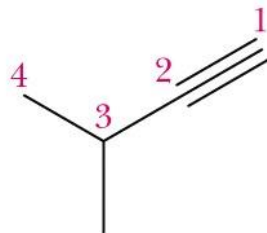
NOT



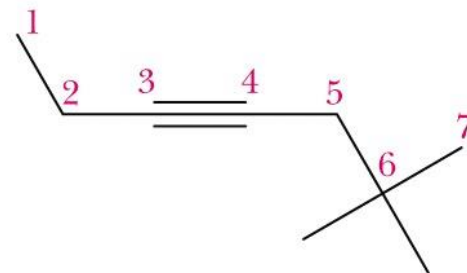
4,6-Dimethylcyclohexene

- IUPAC nomenclature of alkynes

- Use the infix **-yne** to show the presence of a carbon-carbon triple bond.
- Number the parent chain to give the 1st carbon of the triple bond the lower number.
- Follow IUPAC rules for numbering and naming substituents.



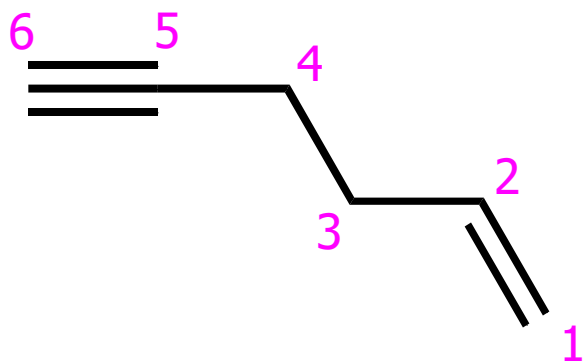
3-Methyl-1-butyne



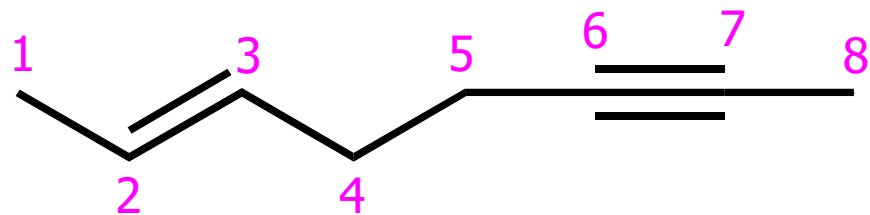
6,6-Dimethyl-3-heptyne

- Common Name:





Hex-1-en-5-yne

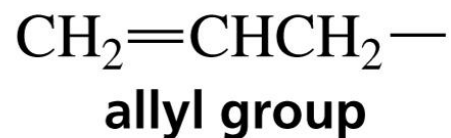
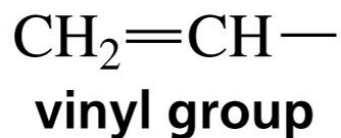


(2E)-Oct-2-en-6-yne

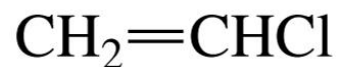
Vinyl and Allyl Groups

A **vinyl group** is the **smallest group** that contains a **vinyl carbon**.

An **allyl group** is the **smallest group** that contains an **allylic carbon**.

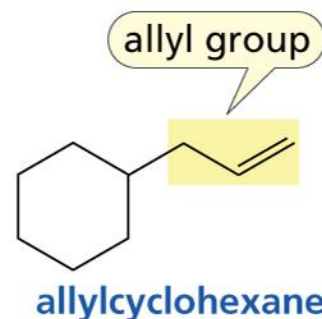
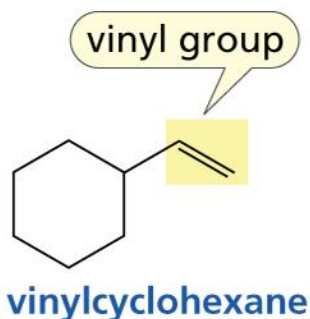


common name: vinyl chloride
systematic name: chloroethene



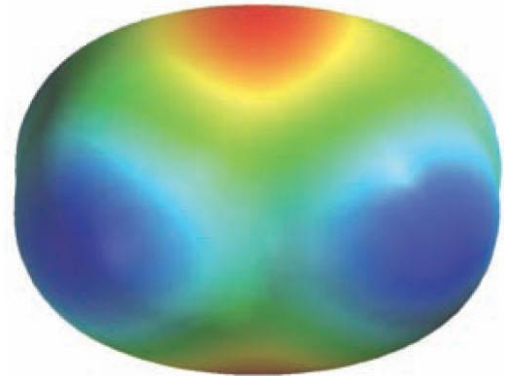
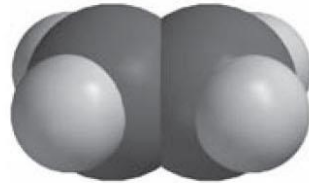
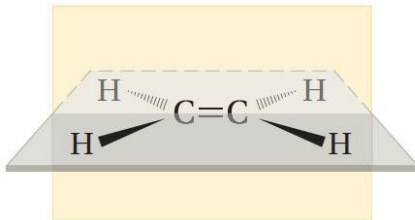
allyl bromide
3-bromopropene

The **substituent** is on the **vinyl** or **allylic** carbon.



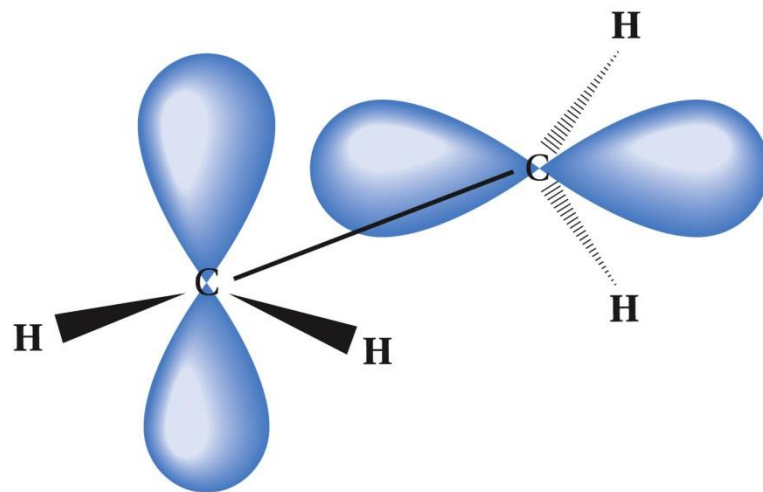
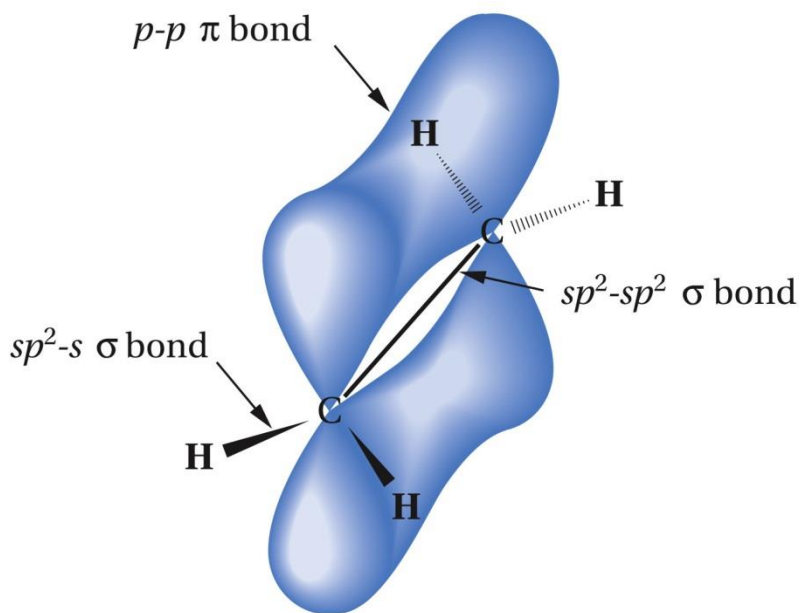
Bonding in Alkenes

- Alkenes are sp^2 hybridized
- Trigonal planar – bond angle $\sim 120^\circ$
- 3 σ and 1 π bond (or 2 single and 1 double)
- C=C double bond $\sim 1.34 \text{ \AA}$
- The π bond lock the geometry to planar

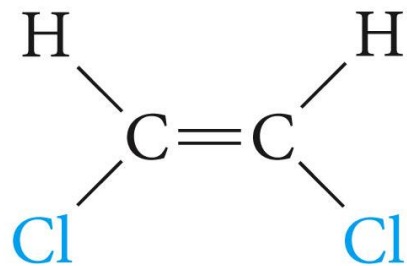


Cis – Trans Isomerism

The double bond in an alkene is rigid, that is it will not rotate freely. Therefore substituents on the carbon atoms will produce geometric isomers the same as on a cycloalkane ring.

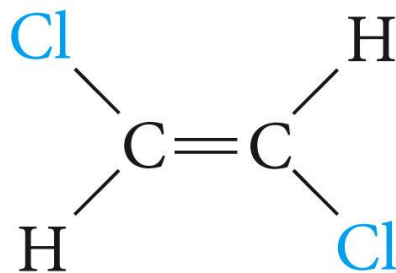


If the two non-hydrogen atoms or groups are on the same side of the double bond it is a *cis*- arrangement, on opposite sides a *trans*- arrangement, i.e.



cis-1,2-dichloroethene

bp 60°C, mp -80°C

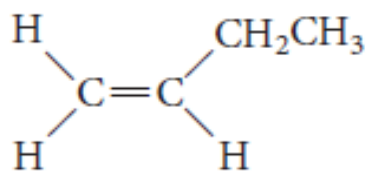


trans-1,2-dichloroethene

bp 47°C, mp -50°C

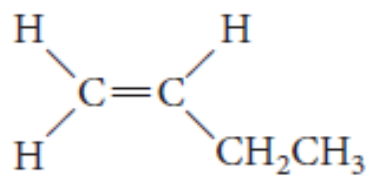
Note that they have different physical properties, this is because their dipole moments are different.

For *cis-trans* isomerism to occur in alkenes, *each* carbon of the double bond must have two different atoms or groups attached to it.



1-butene

is identical to



1-butene

Polar reagents can be divided into :

Nucleophiles

A nucleophile has

a **negative charge**,

a **lone pair**,

or a **π bond**.



these are nucleophiles because they



have a pair of electrons to share

Electrophiles

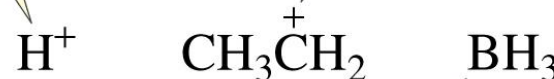
An electrophile has

a **positive charge**,

a **partial positive charge**,

or an **incomplete octet**.

these are electrophiles because they have a positive charge



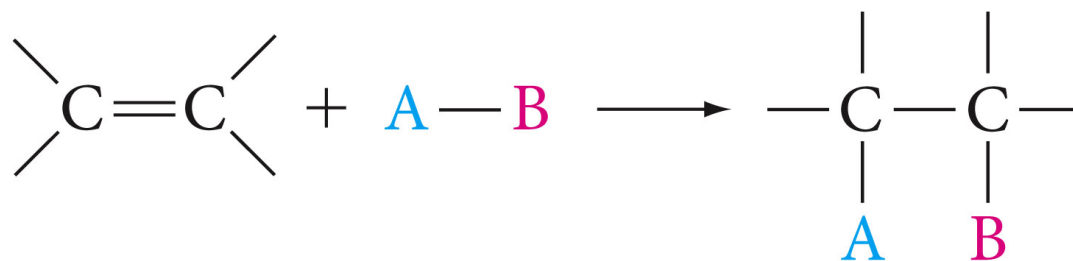
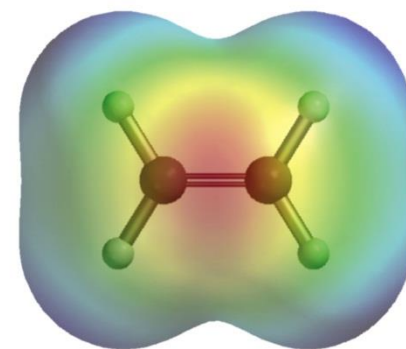
this is an electrophile because it has an incomplete octet

this is an electrophile because it has a partial positive charge



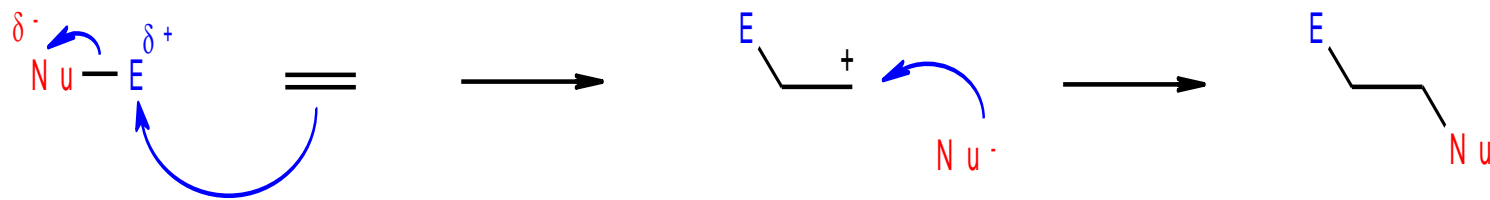
Chemical Reactivity

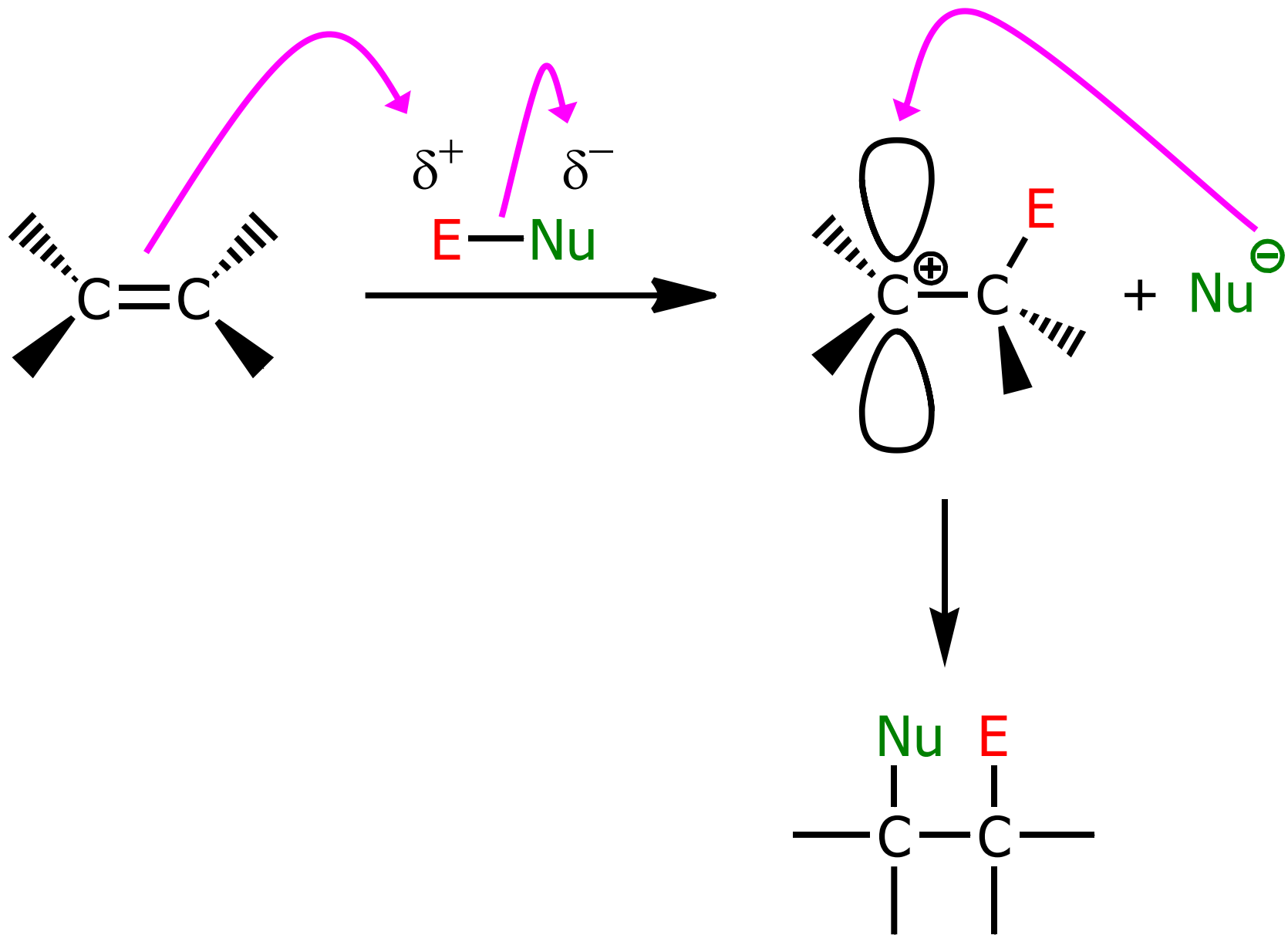
The chemical reactivity of alkenes arise from the π electrons. The π bond is weaker than the σ bond so these electron react first. The reagent will add across the double bond so these are *addition reactions*.



Electrophilic Addition Mechanism

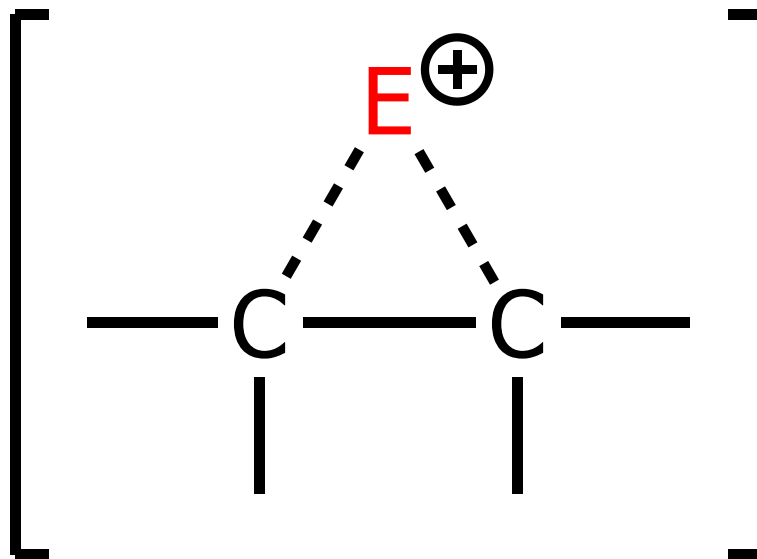
The basic mechanism is the same for all reagents, a two step reaction where an electrophile (**E**) add to the π bond in the first step creating a *carbocation* intermediate. A nucleophile (**Nu**) then adds to the carbocation in the second step.





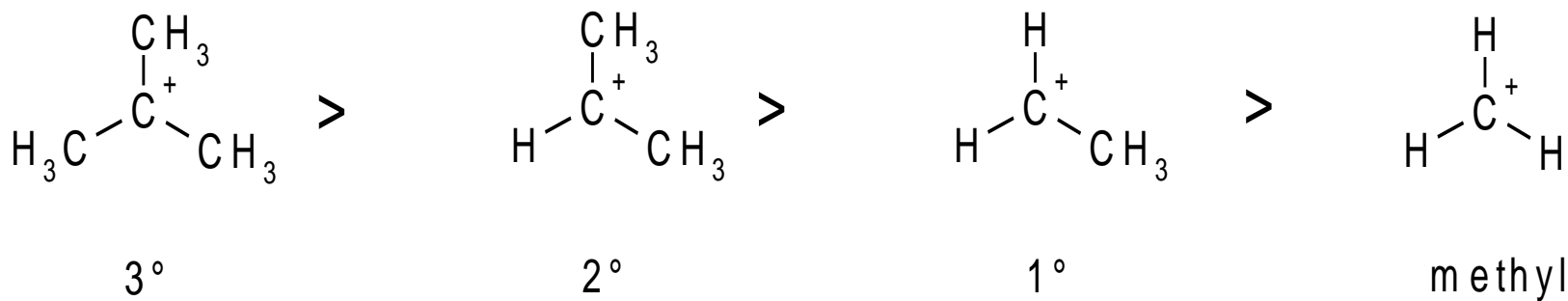
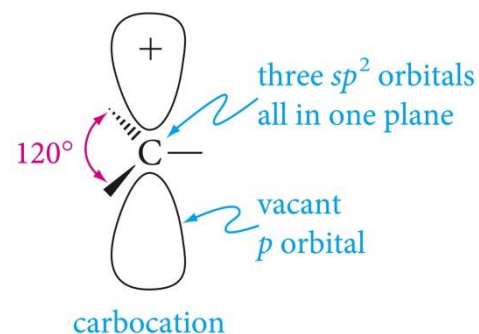
❖ Mechanism

- Sometimes do not go through a “free carbocation”, may go via



Carbocations

Are electron deficient and have an empty p orbital (sp^2 hybridized). Not all carbocations are equally stable so there are predictable patterns for which ones will form.

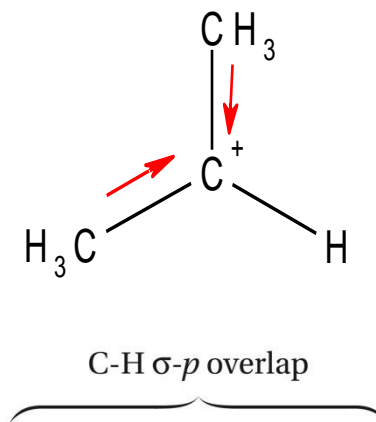


Note: this is the same order of stability as carbon radicals.

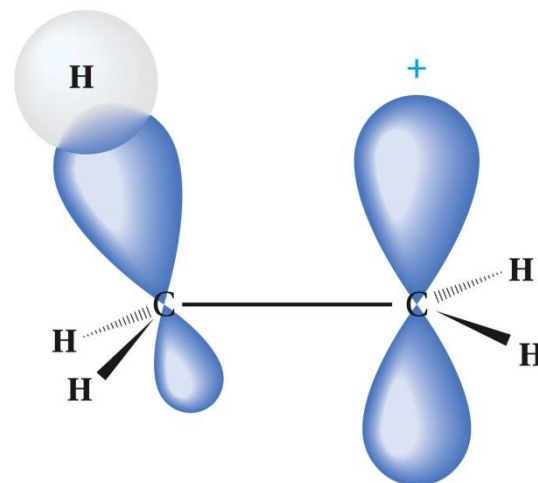
Carbocations (cont'd)

The order of carbocation stability arise from three sources.

1) **Inductive electron donation**: the electrons in C-C σ bonds will be pulled closer to the C^+ helping to minimize the charge. Note: this does not work for C-H bonds.

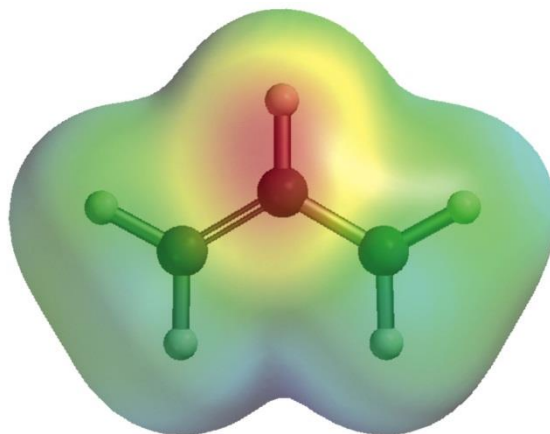
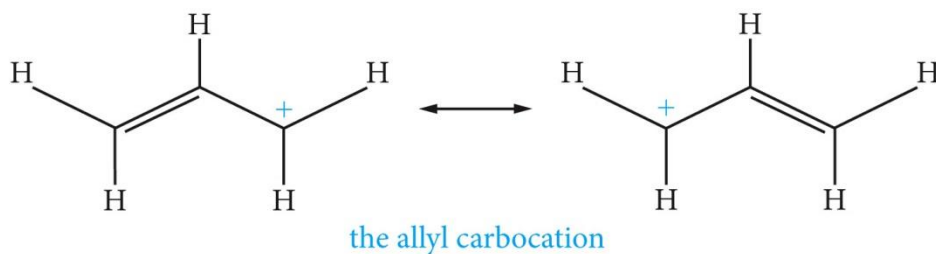


2) **Hyperconjugation**: this is an orbital interaction between adjacent C-H bonds that can overlap the empty p orbital of the C^+ , this again helps to minimize the charge on the C^+ .



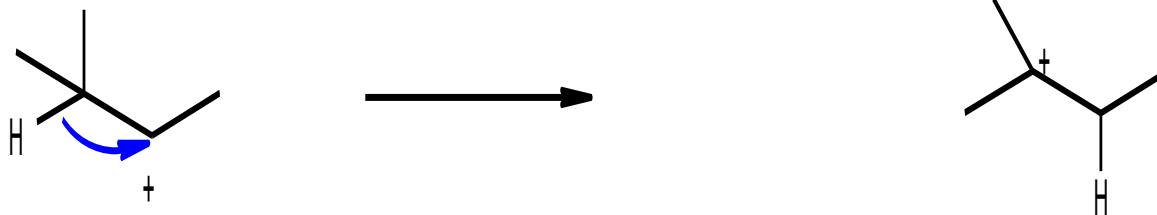
Carbocations (cont'd)

- 3) **Resonance**: a carbocation immediately adjacent to a π system (double bond, triple bond or aromatic ring) can be stabilized by resonance. This lowers the energy by spreading the charge over more atoms, i.e.



Carbocations (cont'd)

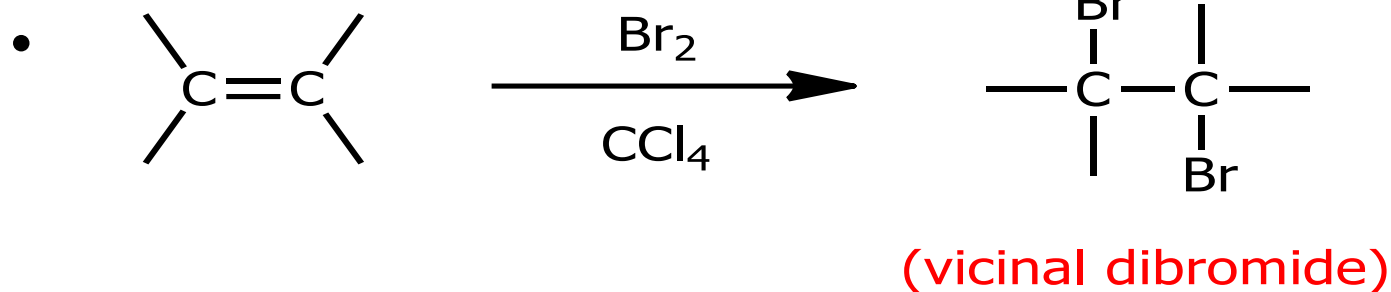
One final complexity for carbocations: rearrangement. Carbocations are susceptible to 1,2-hydride shifts, where an adjacent H atom (and its bonding electrons) shift to the C⁺ to produce a more stable carbocation, i.e.



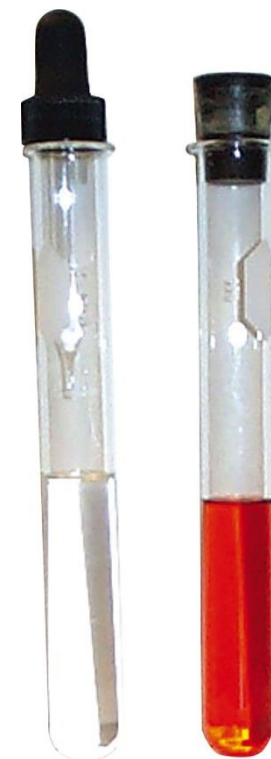
This is also possible for methyl groups. These shifts are common when a tertiary, allylic or benzylic carbocation is produced.

3.7.a Addition of Halogens

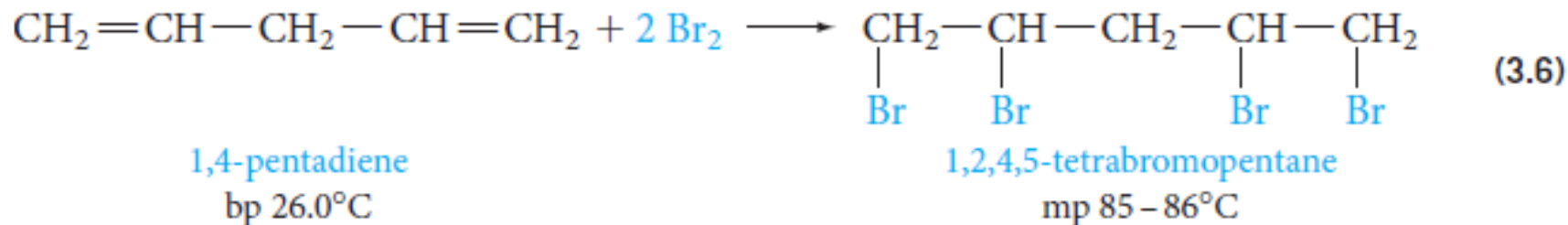
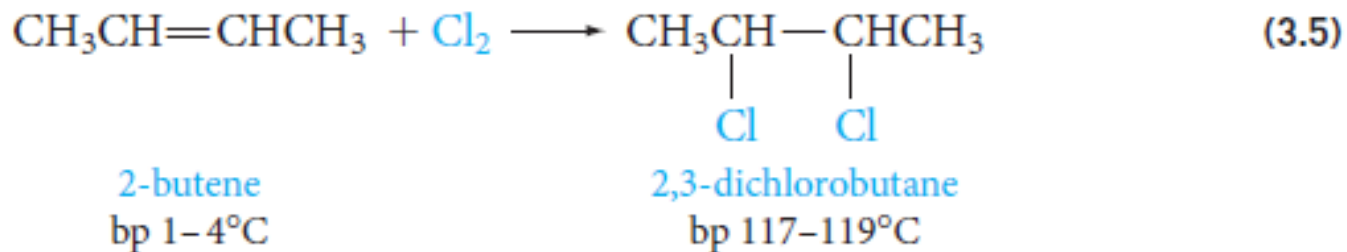
- Addition of Cl_2 or Br_2 across the double bond to product 1,2-dihalide alkane.



- Halogen is usually dissolved in chloroform or carbon tetrachloride.
- Reaction is rapid at room temperatures
- Addition of bromine is a common chemical test for the presence of double bonds as the red colored bromine solution turns colorless when it reacts with an alkene
- Reaction relies on the polarizability of the halogen bonds



Alkenes readily add chlorine or bromine.



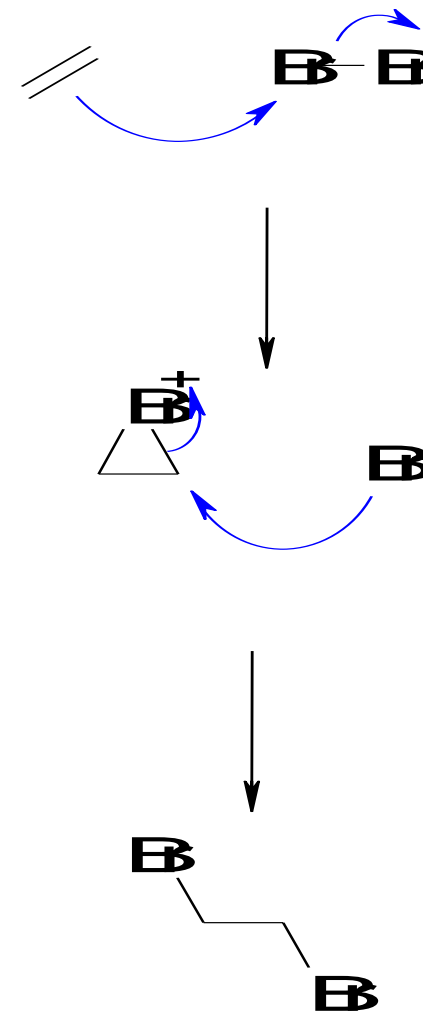
PROBLEM 3.8 Write an equation for the reaction of bromine at room temperature with a. propene b. 4-methylcyclohexene

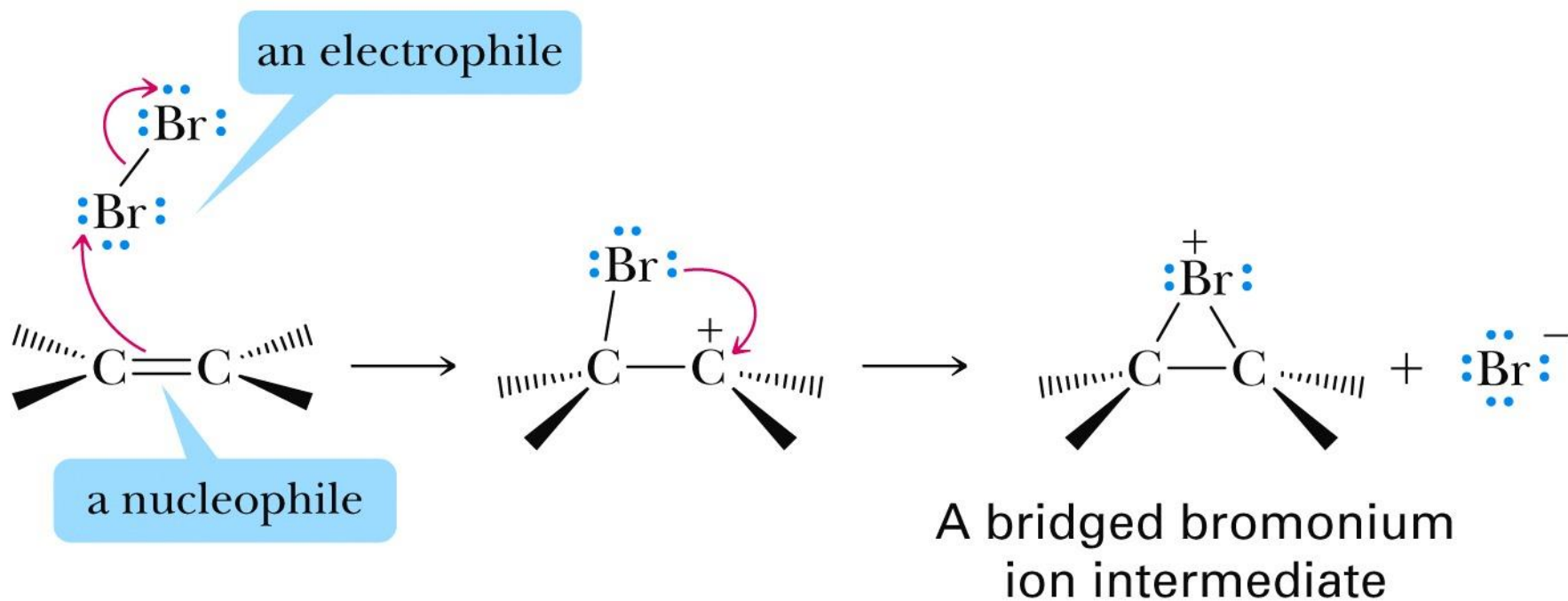
Halogenation (cont'd)

In the first step the π electrons act as a nucleophile attacking the bromine displacing a bromide ion and forming the cyclic bromonium cation intermediate.

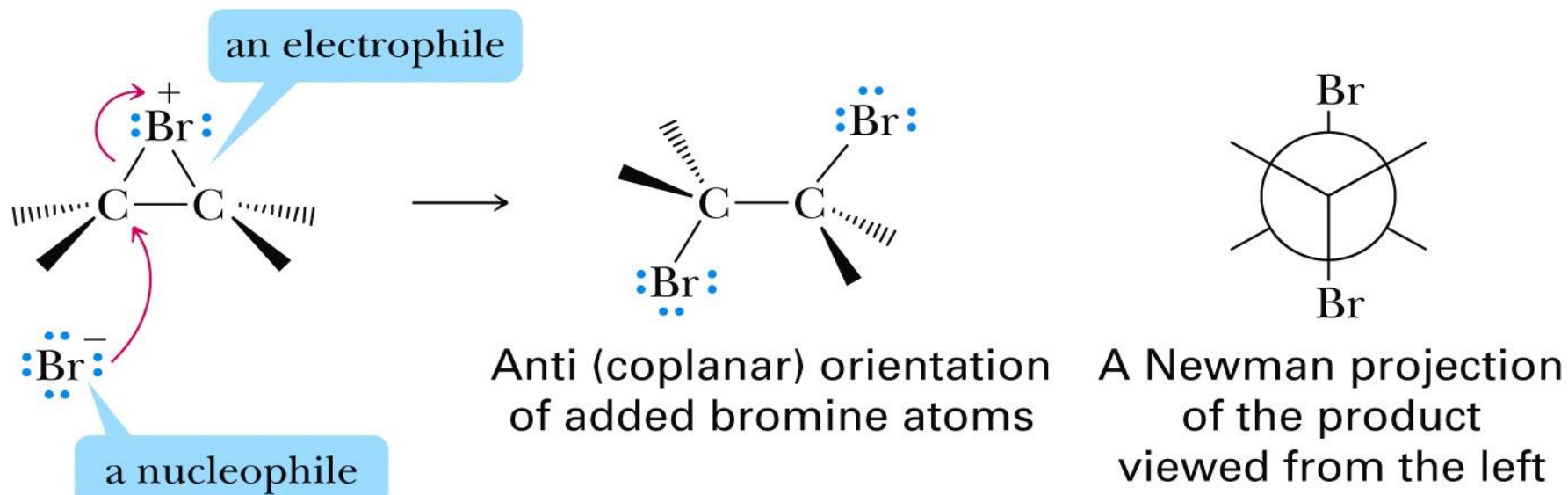
In the second step the nucleophilic bromide ion attacks the side of the bromonium ion away from the bromine atom opening the highly strain cyclic structure and producing the 1,2 dibromo hydrocarbon.

Note this is a trans addition since the two Br atoms add to opposite side of the double bond.



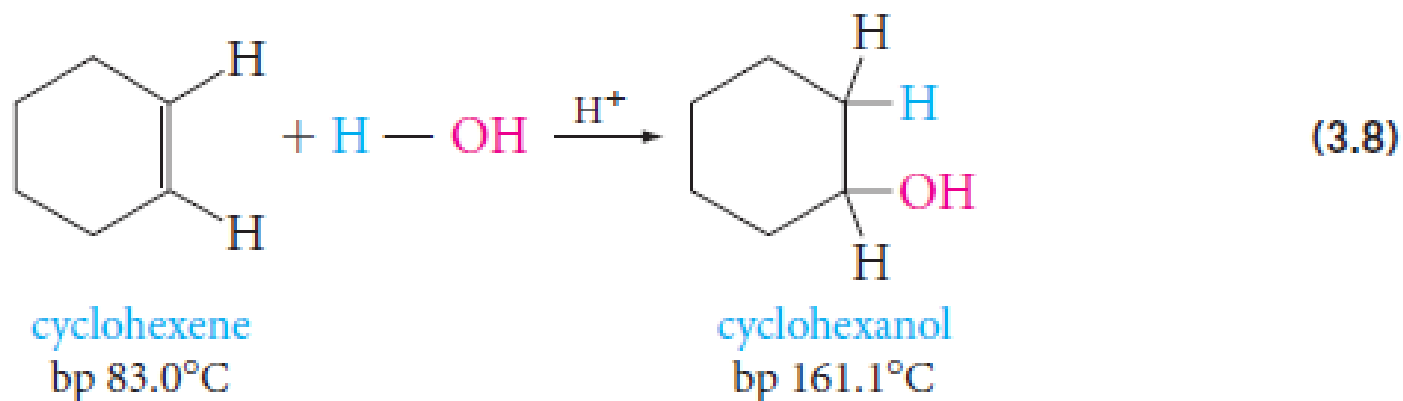
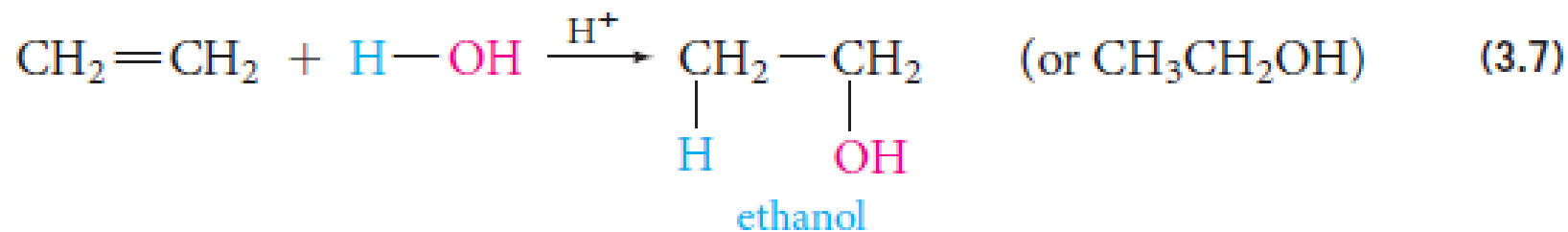


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3.7.b Addition of Water (Hydration)



Symmetry and Addition Reactions

The halogenation of ethene is a very symmetry reaction as both the reagent (Br_2) and the substrate (ethene) are symmetric. In this situation there can only be a single product. What about asymmetric reactions? Two products are possible now, which *regioisomer* will form?

Table 3.2 ▶ Classification of Reagents and Alkenes by Symmetry with Regard to Addition Reactions

	Symmetric	Unsymmetric
Reagents	$\begin{array}{c} \text{Br} - \text{Br} \\ \\ \text{Cl} - \text{Cl} \\ \\ \text{H} - \text{H} \end{array}$	$\begin{array}{c} \text{H} - \text{Br} \\ \\ \text{H} - \text{OH} \\ \\ \text{H} - \text{OSO}_3\text{H} \end{array}$
Alkenes	$\begin{array}{c} \text{CH}_2 = \text{CH}_2 \\ \\ \text{Cyclopentene} \end{array}$	$\begin{array}{c} \text{CH}_3\text{CH} = \text{CH}_2 \\ \\ \text{1-Methylcyclopentene} \end{array}$
	mirror plane	not a mirror plane

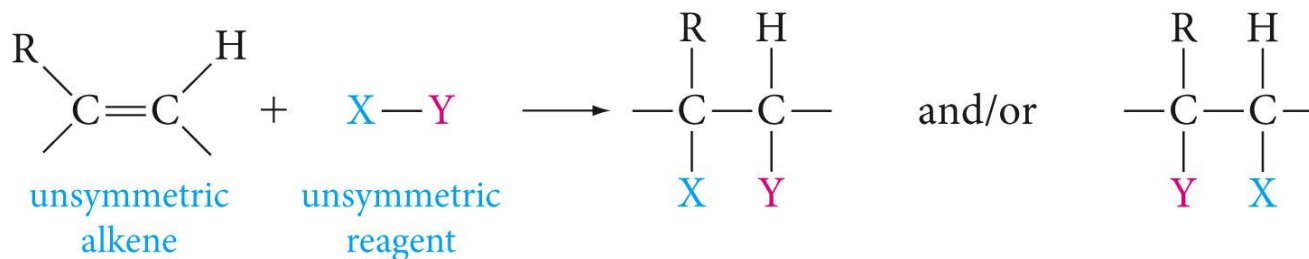

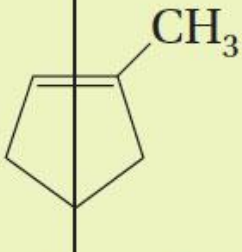
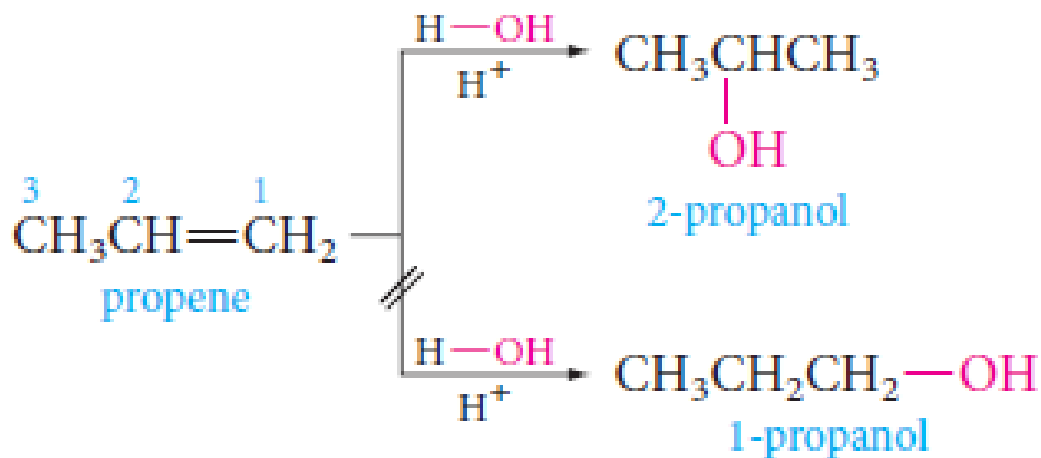


Table 3.2 ▀ **Classification of Reagents and Alkenes by Symmetry with Regard to Addition Reactions**

	Symmetric	Unsymmetric
Reagents	$\begin{array}{c} \text{Br} - \text{Br} \\ \\ \text{Cl} - \text{Cl} \\ \\ \text{H} - \text{H} \end{array}$	$\begin{array}{c} \text{H} - \text{Br} \\ \\ \text{H} - \text{OH} \\ \\ \text{H} - \text{OSO}_3\text{H} \end{array}$
Alkenes	$\begin{array}{c} \text{CH}_2 = \text{CH}_2 \\ \\ \text{Cyclopentene} \end{array}$	$\begin{array}{c} \text{CH}_3\text{CH} = \text{CH}_2 \\ \\ \text{1-Methylcyclopentene} \end{array}$
	 <p style="text-align: center; color: magenta;">mirror plane</p>	 <p style="text-align: center; color: magenta;">not a mirror plane</p>

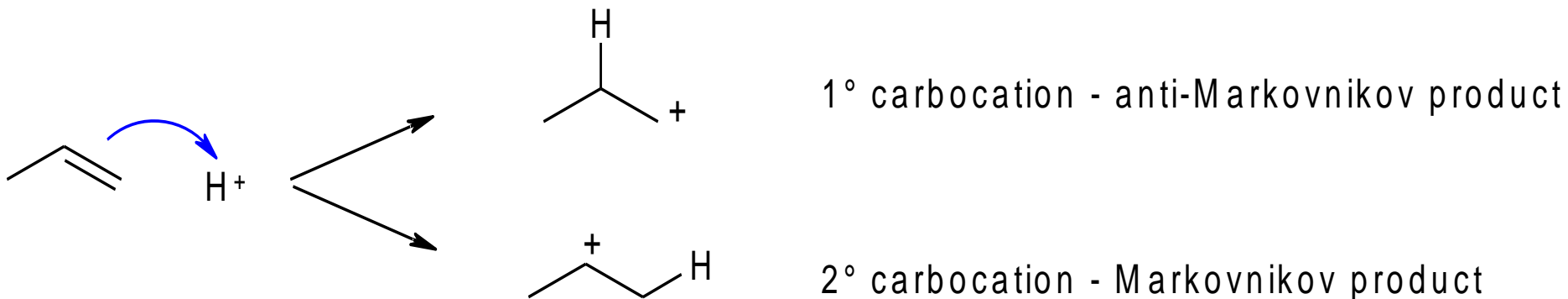
Markovnikov's Rule

Fortunately there is a simple rule of thumb to predict which product will form: Markovnikov's rule, which states that when **an unsymmetrical reagent adds to a double bond the electrophilic part of the reagent adds to the carbon with the most hydrogen atoms on it.**



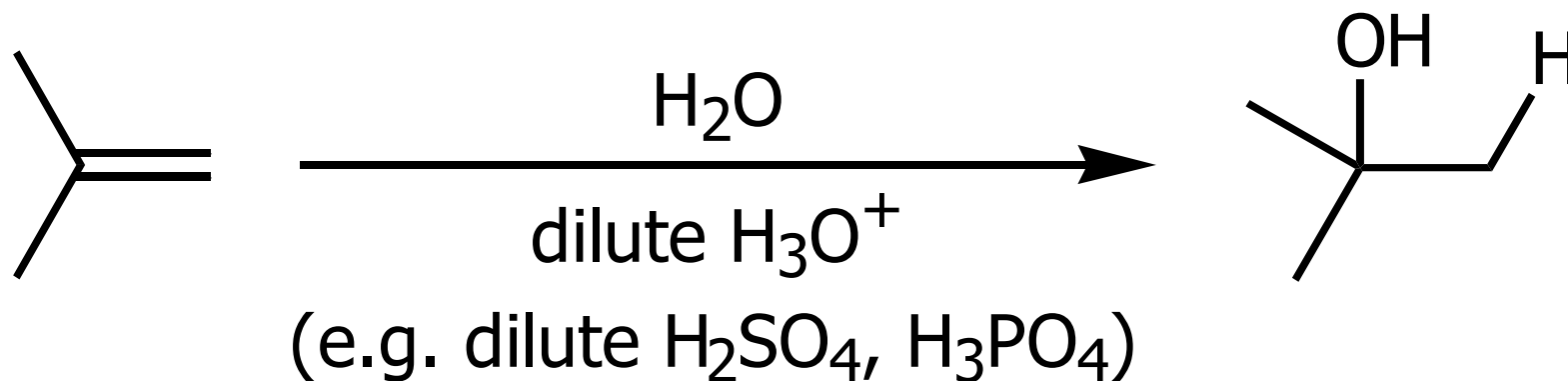
Markovnikov's Rule (cont'd)

Why? This mode of addition will always produce the most stable carbocation intermediate, i.e. consider the addition of H^+ to propene...



Hydration

- Addition of water across the double bond
- Product is an alcohol
- Requires an acid as a catalyst as water is not acidic enough to produce the electrophile

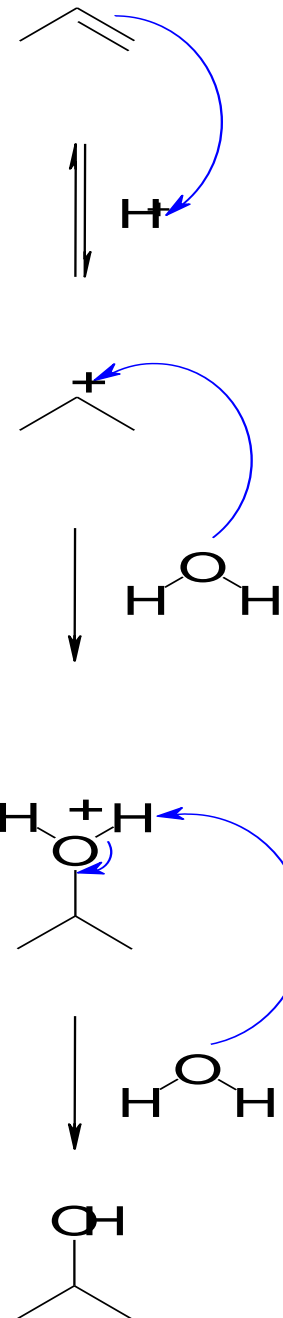


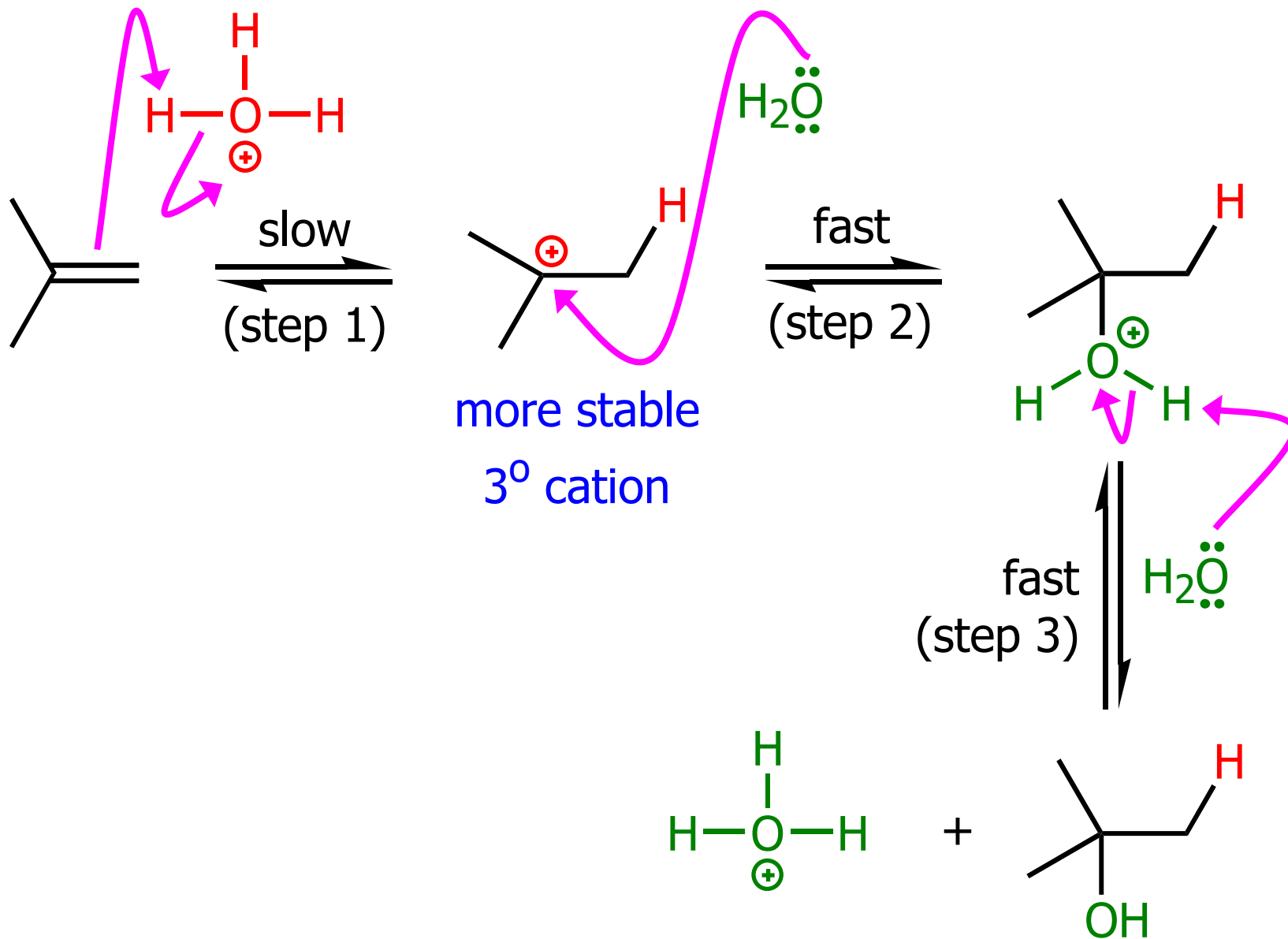
Hydration (cont'd)

First step is the protonation of the alkene in a Markovnikov orientation to generate the most stable carbocation.

The second step is the attack of the nucleophilic water molecule on the carbocation

Finally an acid/base reaction deprotonates the alkyloxonium ion to form the alcohol.



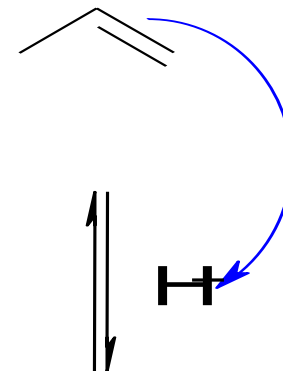


Hydrohalogenation

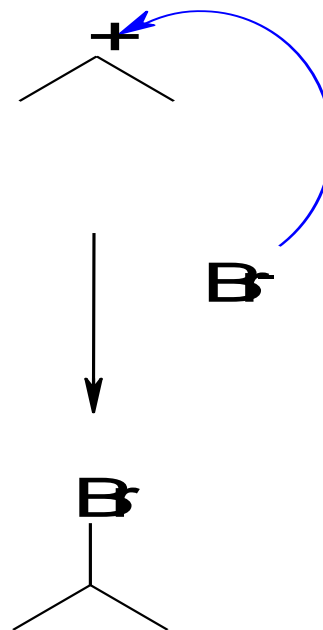
- Addition of HX across a double bond to produce a Markovnikov halide alkane
- Reactivity: $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$ (parallels acidity)
- HBr needs to be used in the dark and under an inert atmosphere to prevent a free radical addition process that produces the anti-Markovnikov product.
- Note: this same mechanism applies to other acids such as H_2SO_4

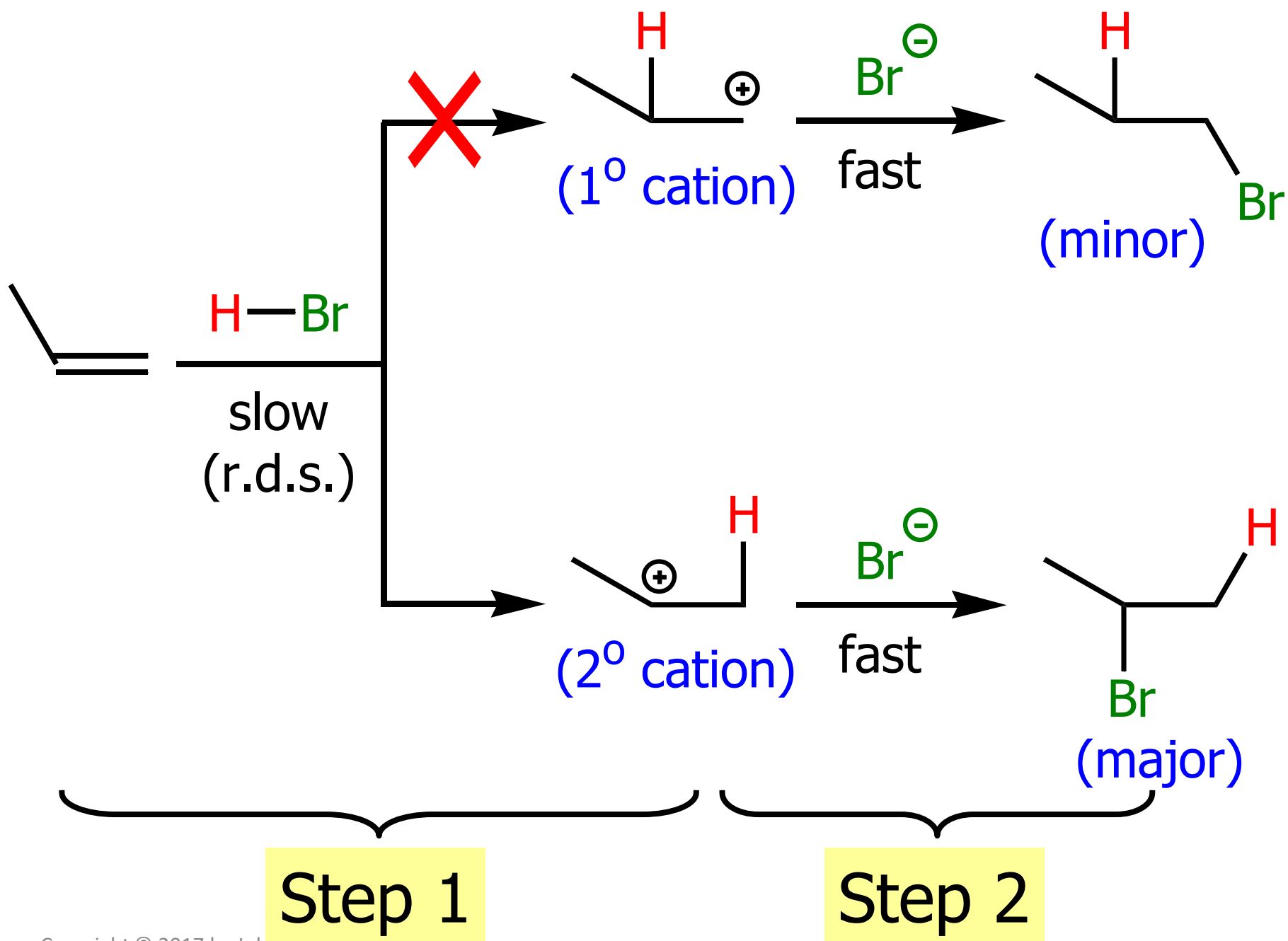
Hydrohalogenation (cont'd)

First step in the Markovnikov addition of the electrophilic acidic proton to produce the most stable carbocation intermediate.



The second step is the nucleophilic attack of the halide anion on the carbocation intermediate generating the alkyl halide product.



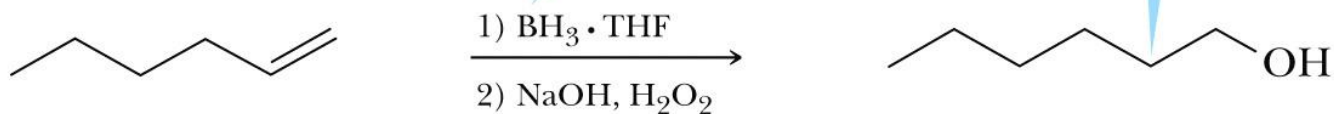


Hydroboration/Oxidation

- Final product is an anti-Markovnikov alcohol
- Two step reaction, BH_3 , $\text{H}_2\text{O}_2/\text{NaOH}$

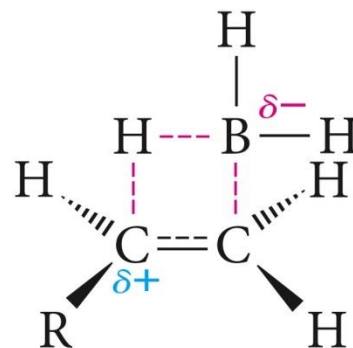
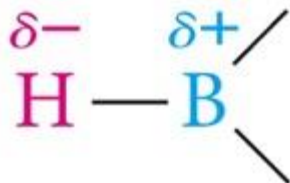
the net result of hydroboration-oxidation is the addition of H and OH across the C—C double bond

contrary to Markovnikov's rule, the hydrogen has added to the former double-bond carbon with the fewer hydrogens



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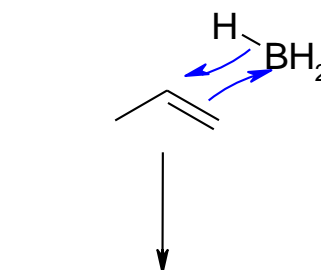
- Electrophile is the B atom (H is more EN than B!)
- Concerted addition reaction



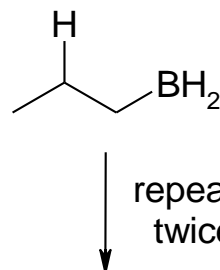
transition state
for hydroboration

Hydroboration (cont'd)

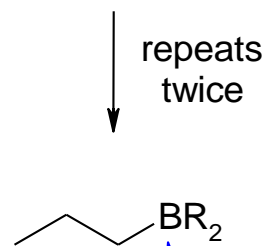
Step 1: alkene π electron acts as nucleophile and add to the electrophilic B, at the same time the H is transferred to the C atom.



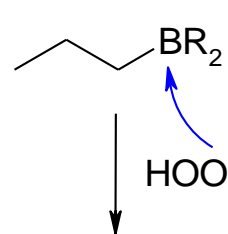
Step 2: step1 repeats twice more



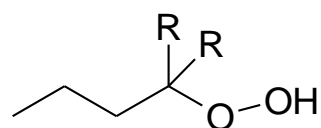
Step 3: peroxide ion acts as nucleophile with the B atom.



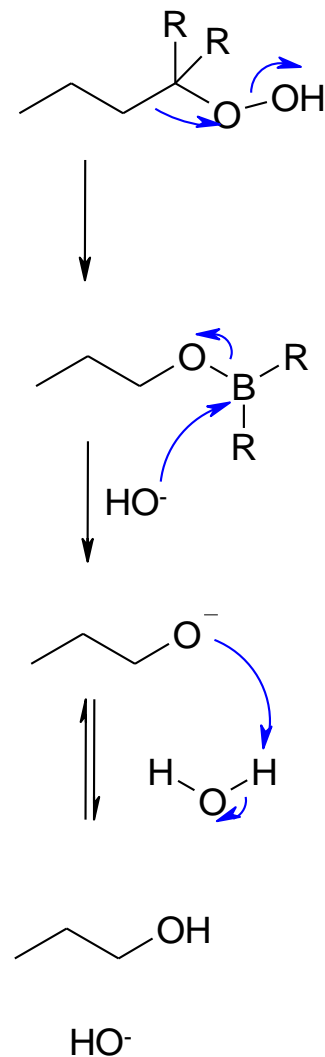
Step 4: migration of the C-B bond to form a C-O bond and displace hydroxide



Step 5: nucleophilic attack by hydroxide on B displacing it as BOH

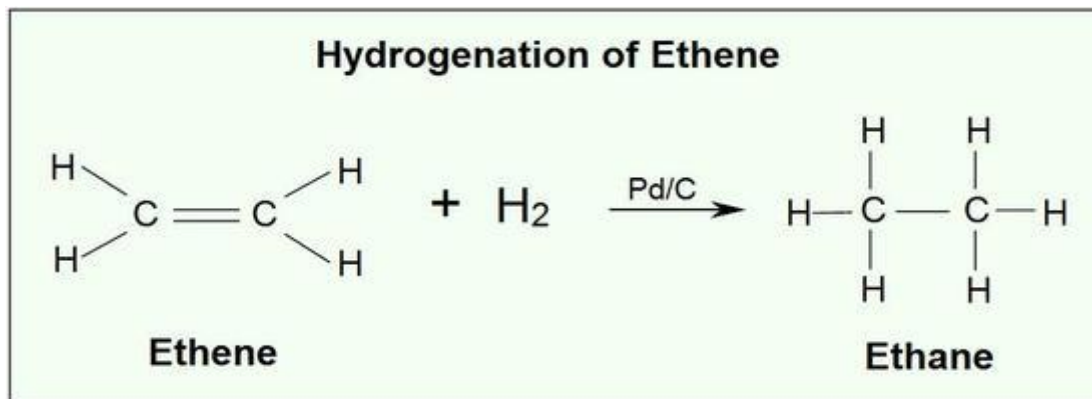


Step 6: acid/base reaction to protonate the alcohol



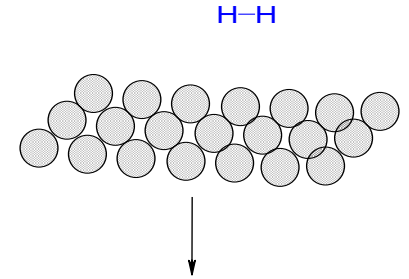
Hydrogenation

- Addition of H₂ across the double bond to produce an alkane
- Requires a metal catalyst, Pt, Pd, Ni or Rh
- “syn” addition, both atoms add to the same side of the double bond.

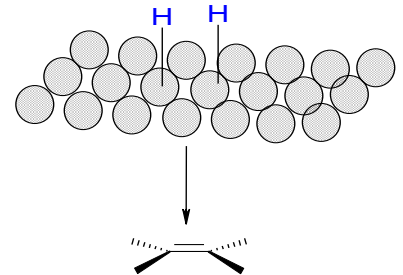


Hydrogenation

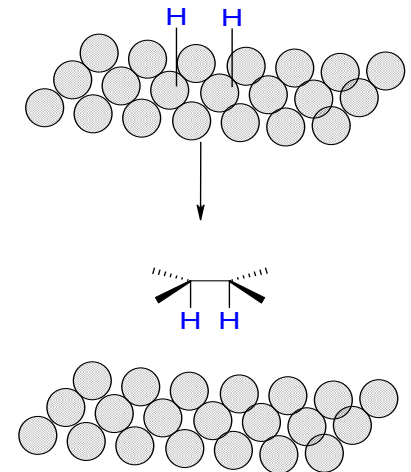
Step 1: hydrogen adsorbs onto the face of the metal



Step 2: alkene approaches H atoms

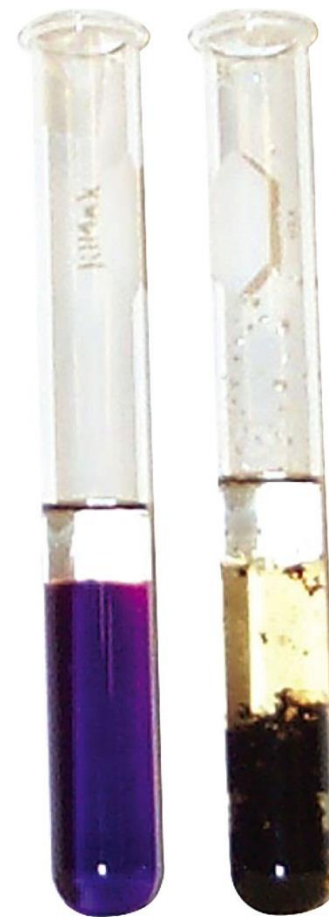


Step 3: H atoms add to the two C atoms producing an alkane



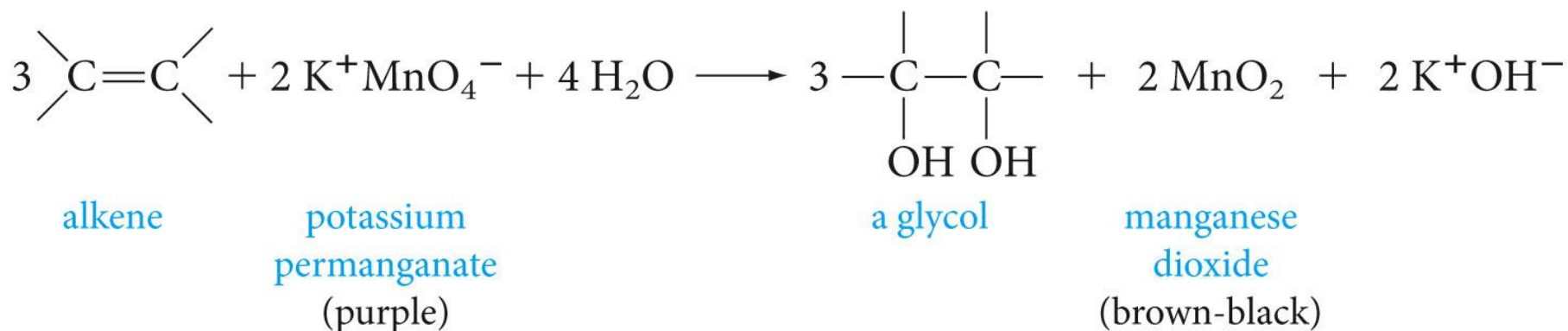
Oxidation: Permanganate

- Used as a chemical test
- Product is a glycol (1,2-diol) and manganese oxide
- Color change from purple to brown-black MnO_2 solid
- OsO_4 also used to make 1,2-diols



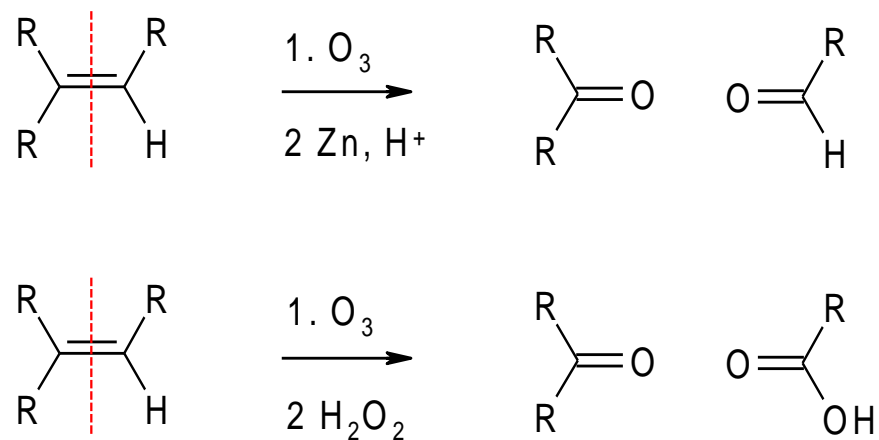
Oxidation: Permanganate (cont'd)

- Complex reaction mechanism
- Reactive via a five membered cyclic ester intermediate.
- Both O atoms are transferred from the permanganate ion.



Oxidation: Ozonolysis

- Cleaves the double bonds in half generating two carbonyl groups
- In Zn/H^+ get aldehydes or ketones (reductive products)
- In H_2O_2 ketones or carboxylic acids (oxidative products)
- Was primarily used for structure determination since ozone only reacts with C-C multiple bonds.
- Generates smaller molecules that are easier to identify.



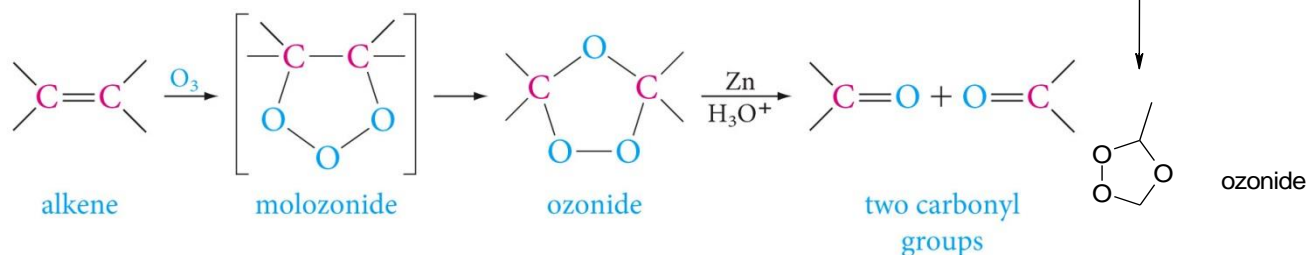
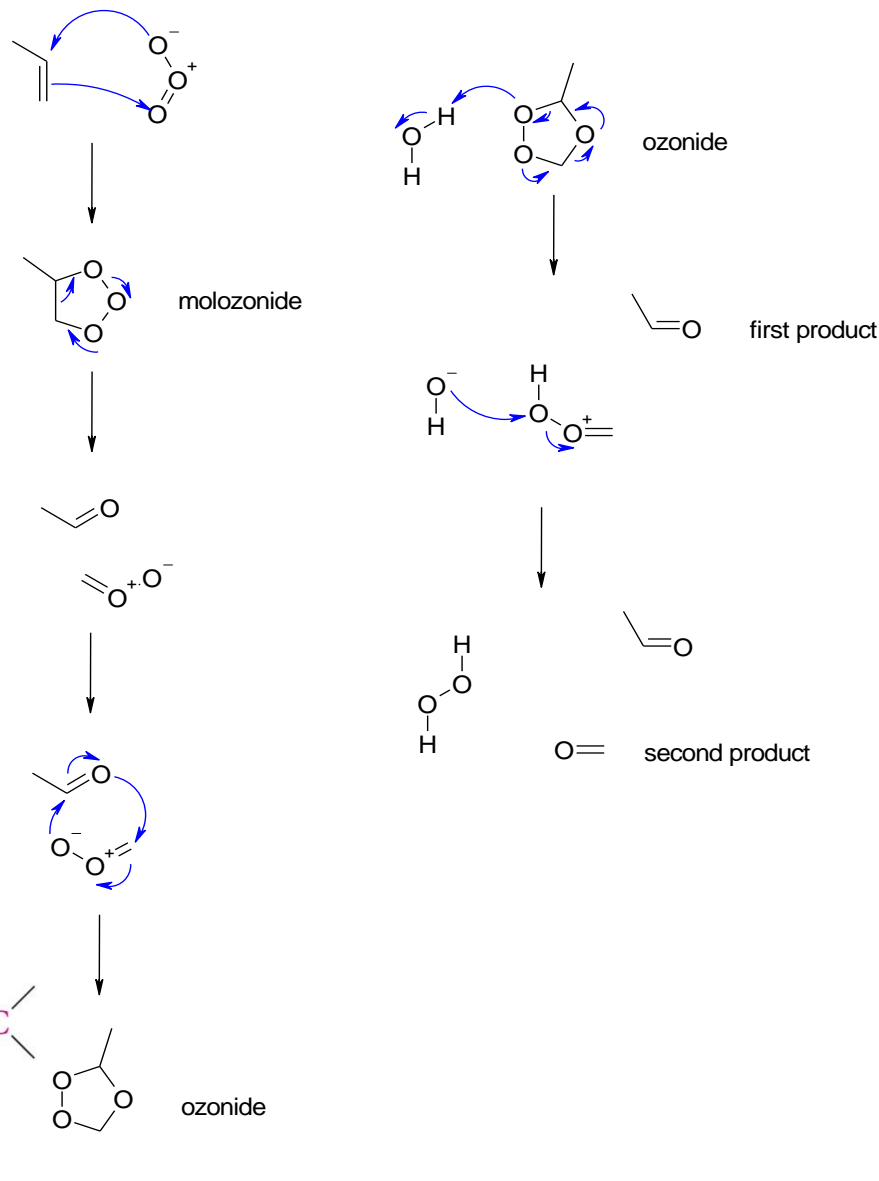
Oxidation: Ozonolysis (cont'd)

Step 1: π electrons act as nucleophile attacking the ozone at the electrophilic terminal O atom. A second C-O bond is formed by a nucleophilic attack of the other terminal O atom

Step 2: the molozonide rearranges to an ozonide

Step 3: the ozonide peroxide O acts as a base to a water molecule producing one of the final products.

Step 4: the hydroxide attacks the hydroxy O forming a peroxide and the second carbonyl compound



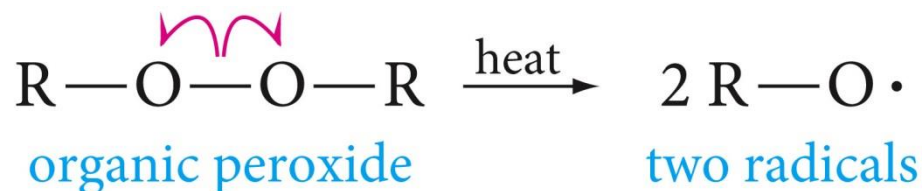
Radical Addition Reactions: Polymers

One of the most useful reactions of small alkenes is a free radical polymerization. Polyethylene, polypropylene and polybutylene are all very common plastics used throughout society.

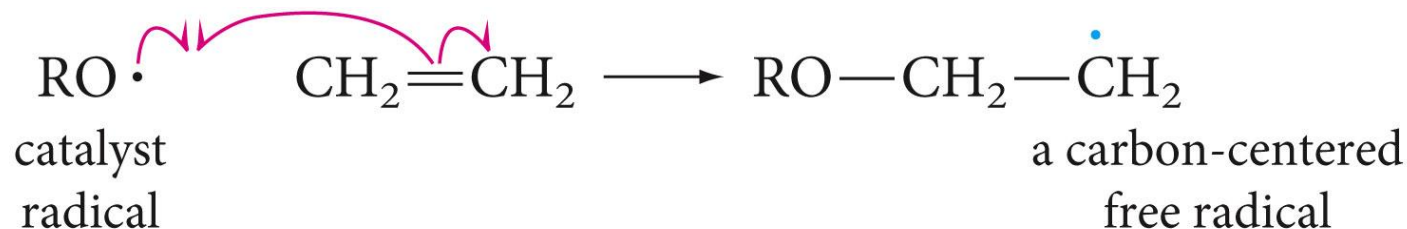
As with the other free radical reaction we have seen, this requires an initiation step, followed by chain growth and finally a termination step.

Radical Addition Reactions: Polymers

Initiation is commonly done using peroxides since they break at moderate temperatures.

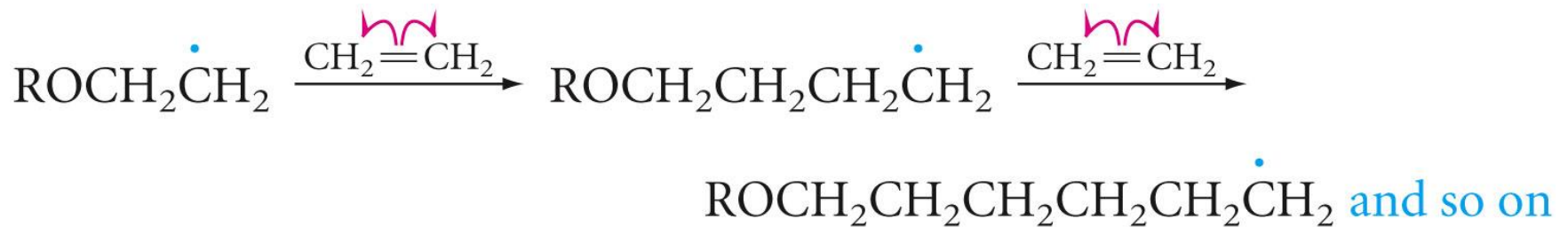


In contrast to the free radical substitution reaction in a free radical addition the initiator adds to the monomer rather than removing a H atom.



Radical Addition Reactions: Polymers

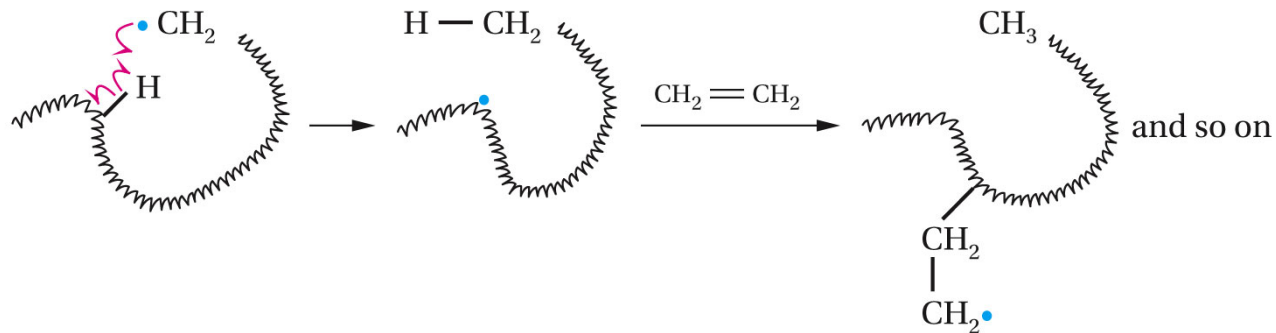
Chain growth occurs as the carbon radical reacts with additional monomers.



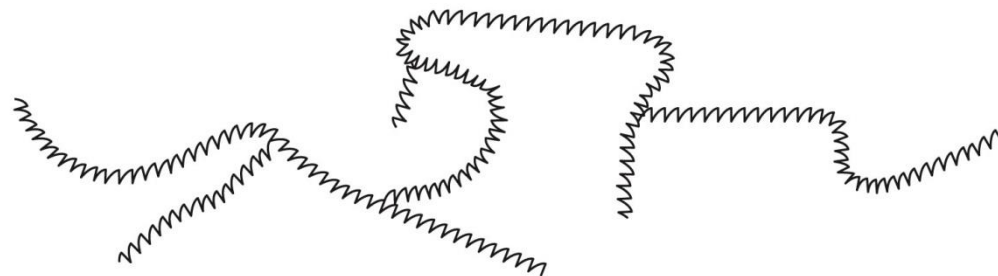
Termination usually occurs when two carbon radical react with each other.

Radical Addition Reactions: Polymers

During chain growth a branch point can be introduced if the chain wraps back on itself and abstracts a H atom from the middle of the chain. Growth will then proceed from this point.



The result is a complex branched polymer.



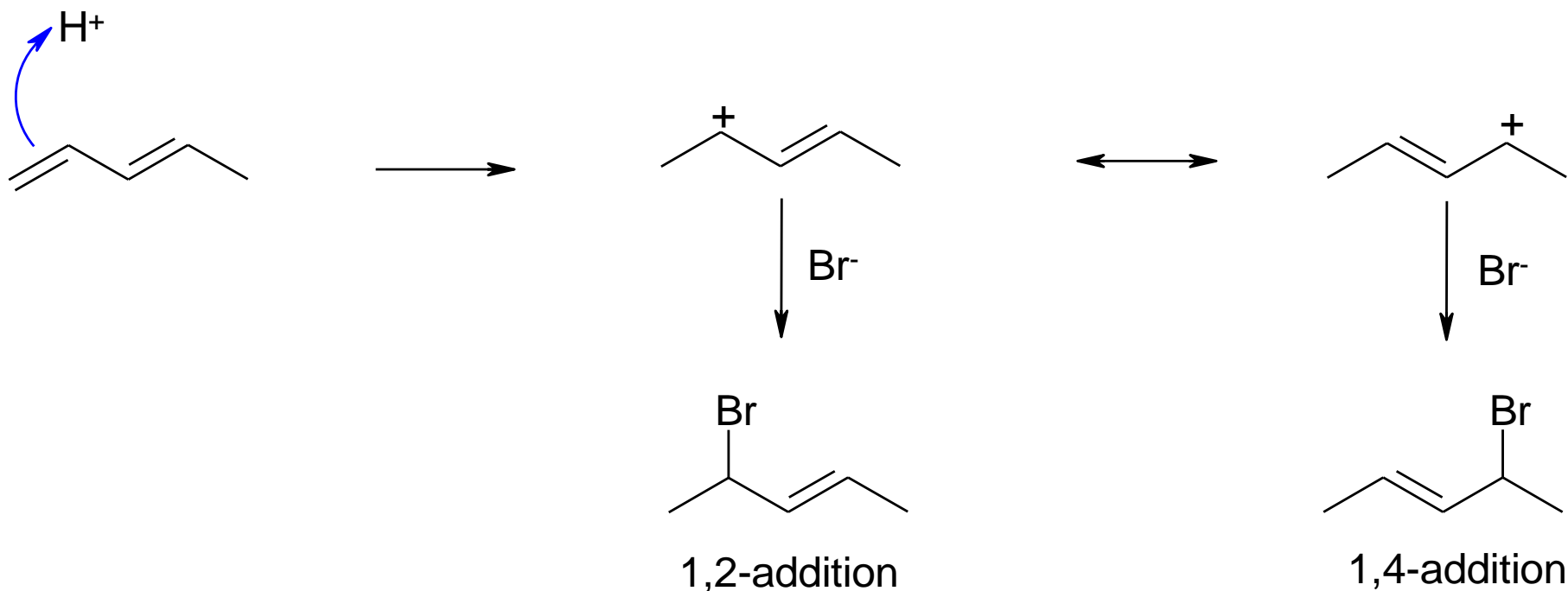
branched polyethylene

Radical Addition Reactions: Polymers

The exact structure of the polymer, chain length and amount of branching, can be controlled to some degree by the choice of initiator, use of catalysts, use of additional monomer types to introduce branching and reaction conditions. This include the relative concentrations of initiator and monomer, and reaction temperature.

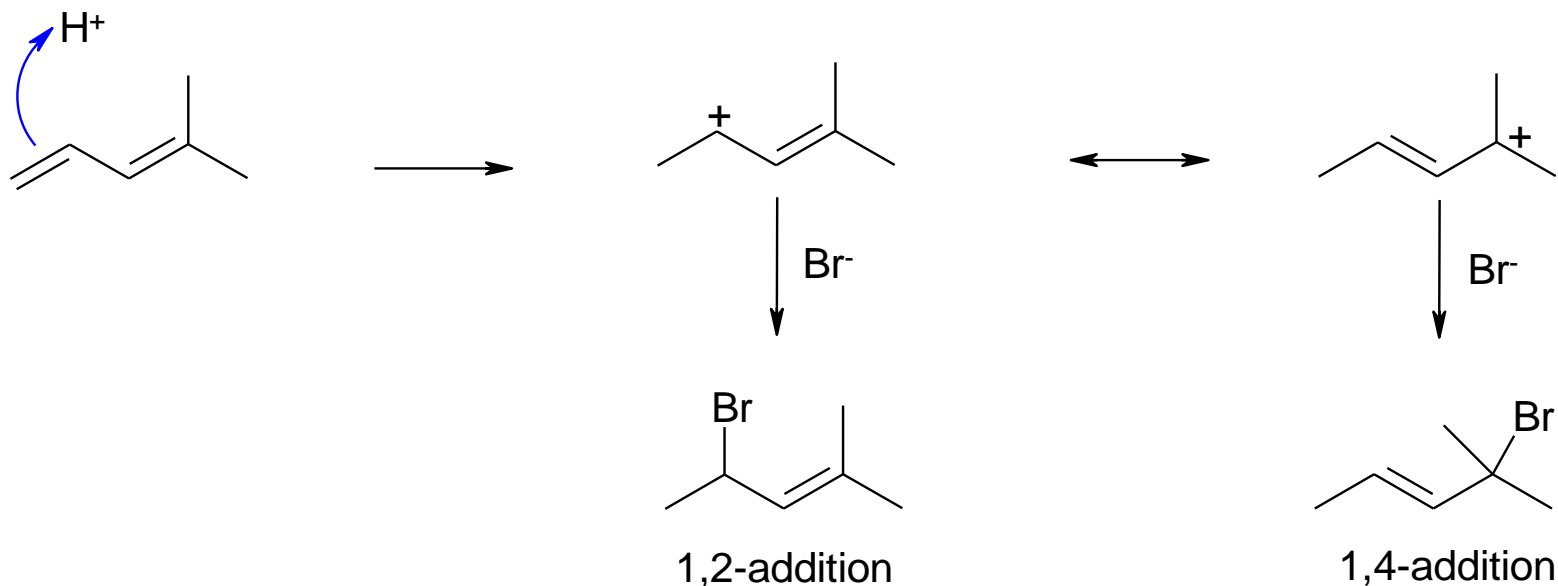
Additions to Conjugated Systems

Conjugated systems provide an extra complication for addition reactions. The first step is an electrophilic addition generating a carbocation. But since the two double bonds are conjugated resonance is possible for the carbocation intermediate, i.e.



Additions to Conjugated Systems

There will usually be both the 1,2 and 1,4 addition products from conjugated alkenes. The only time a single product will dominate is if the carbocations have unequal stability, i.e.



In this case there will be more of the 1,4 addition product as it reacts through a 3° carbocation which is more stable than the 2°.

Cycloadditions: the Diels-Alder Reaction

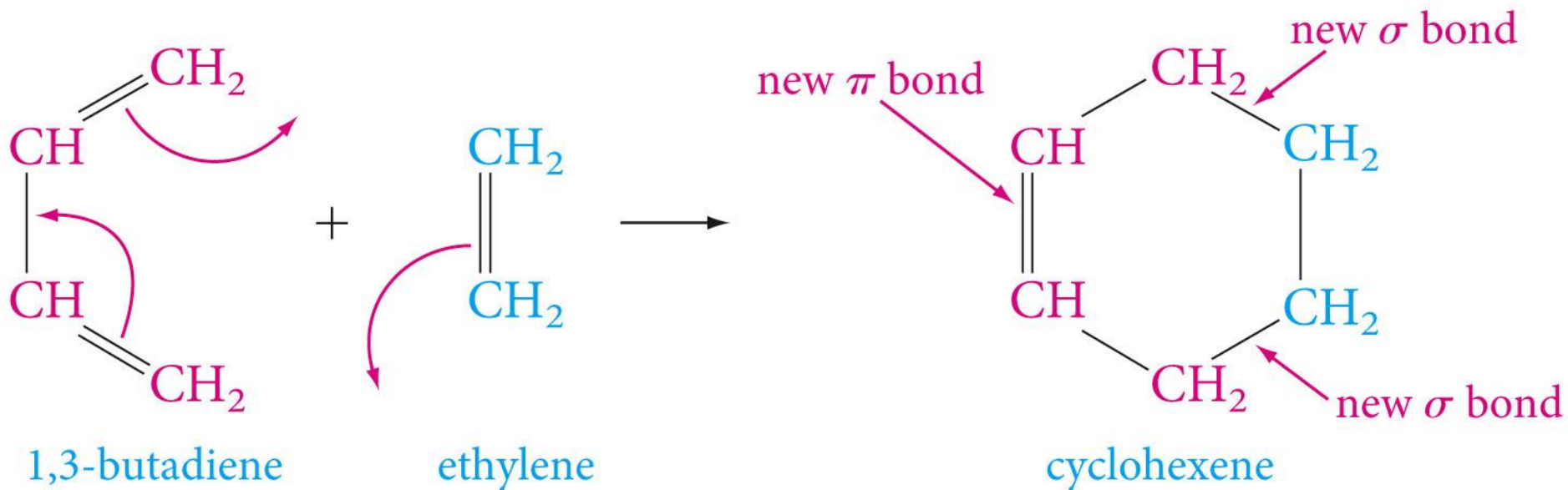
There is an additional type of reaction for conjugated alkenes, a cycloaddition. This is a very important reaction as it is an easy way to generate cycloalkenes in very high yields. The reaction involves a conjugated diene and an alkene or alkyne. There is a rearrangement of the π electrons that will produce two new σ bonds forming the ring.

Cycloadditions: the Diels-Alder Reaction

Diene: 1,3-butadiene

Dienophile: ethene

Product: cyclohexene



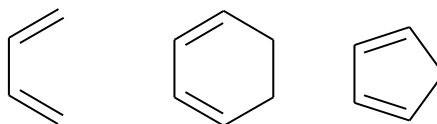
Cycloadditions: the Diels-Alder Reaction

The reaction proceeds best when an electron withdrawing group is attached to the dienophile.

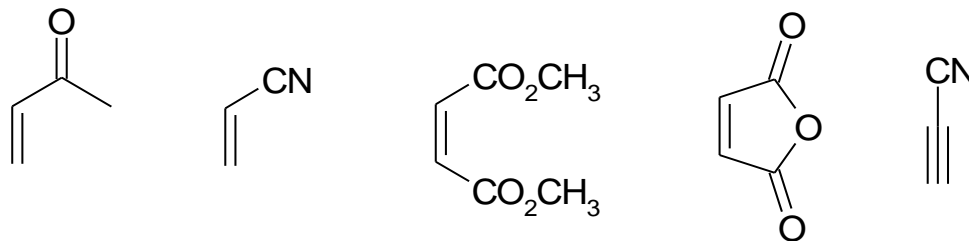
Electron withdrawing groups are groups of atoms that will withdraw electron density of the dienophile π bond which makes it a better electrophile.

Common electron withdrawing groups include: carbonyl ($-\text{C}(=\text{O})\text{R}$), cyano ($-\text{C}\equiv\text{N}$) and esters ($-\text{CO}_2\text{R}$).

dienes

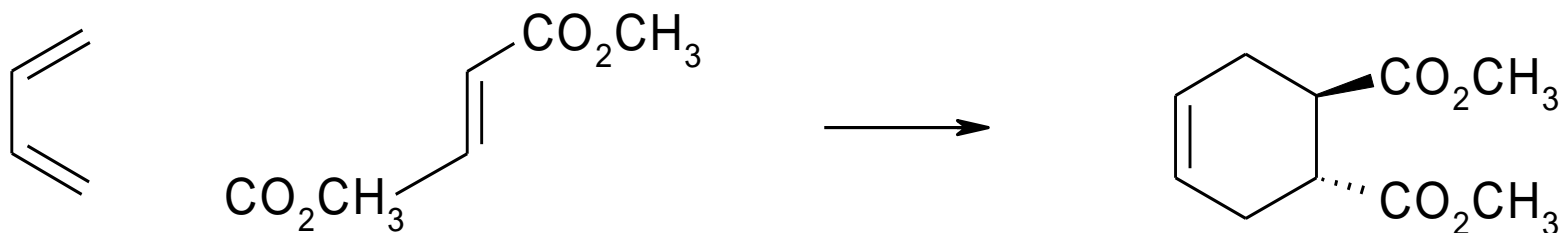
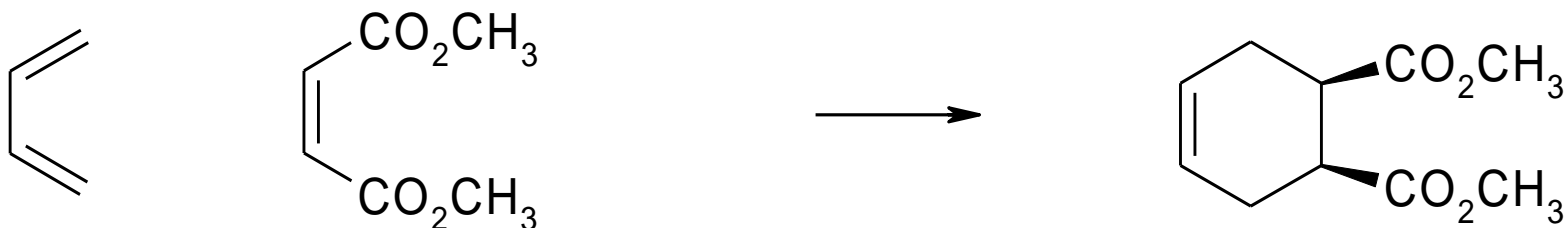


dienophiles



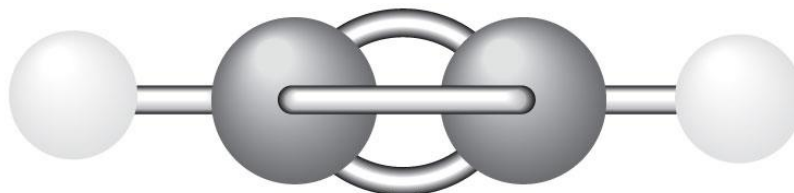
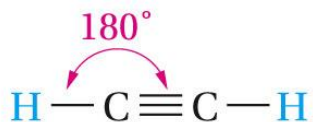
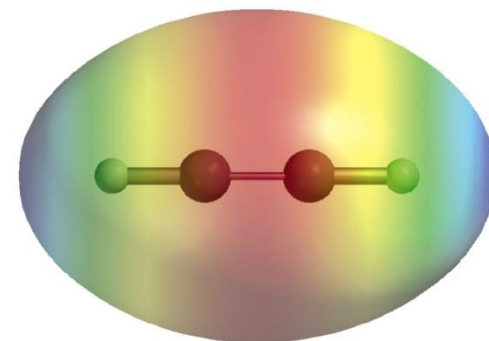
Cycloadditions: the Diels-Alder Reaction

The stereochemistry of the reactants is preserved in the product, i.e. a cis-dienophile give cis substituents in the product, a trans-dienophile give trans substituents in the product, i.e.



Alkynes

- Alkynes are sp hybridized
- Linear – bond angle 180°
- 2 σ and 2 π bond (or 1 single and 1 triple)
- $C\equiv C$ double bond $\sim 1.21 \text{ \AA}$



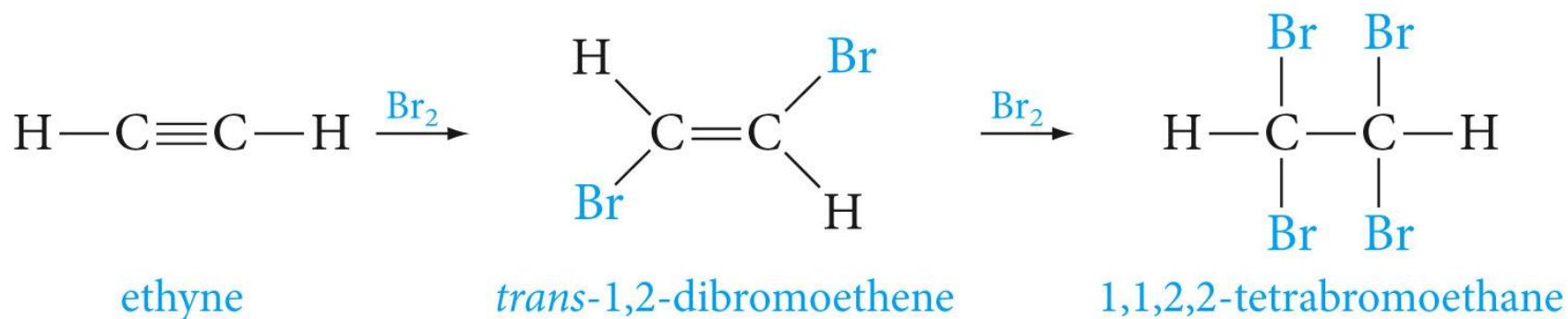
Alkynes: Reactions

Most of the reactions discussed for alkenes also apply to alkynes, although the alkynes usually react slower.

There are a couple of differences.

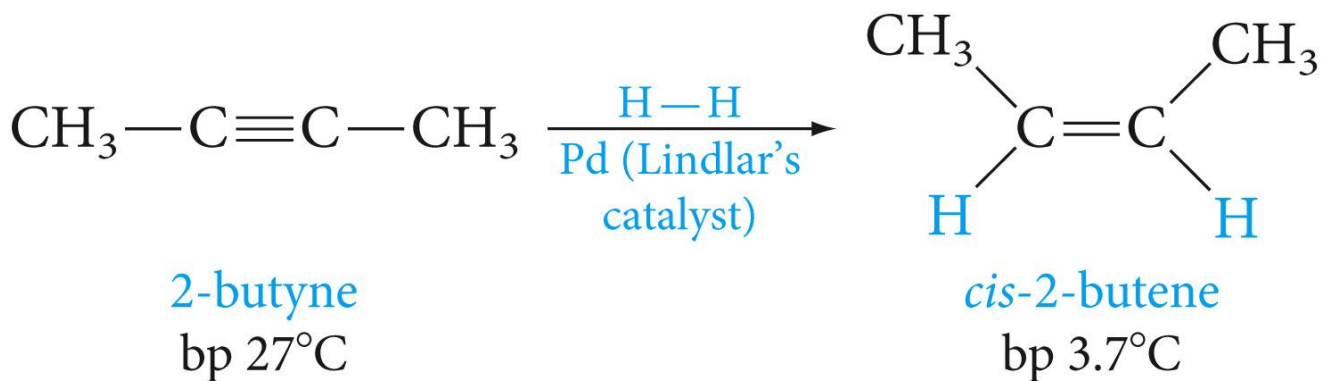
Alkynes: Reactions

Bromination: the first bromine adds trans to the alkyne. It can be stopped at this by controlling the amount of Br_2 present, but a second addition is possible.



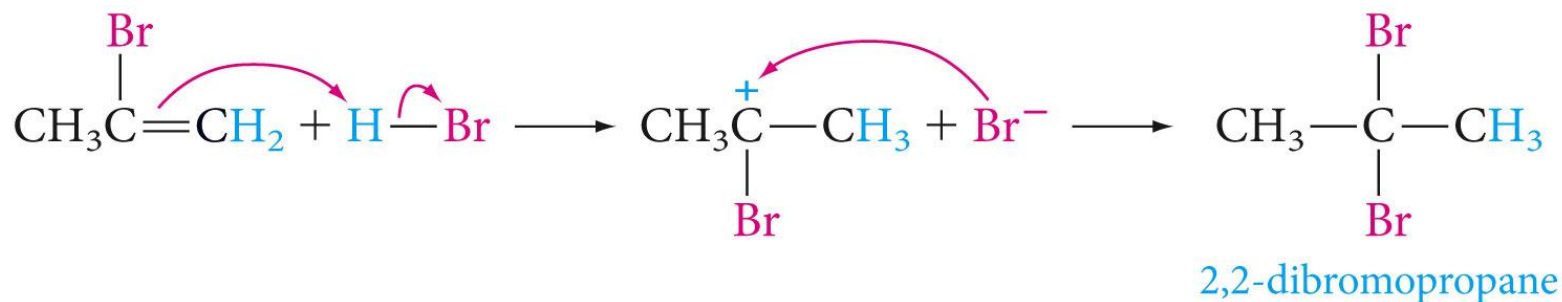
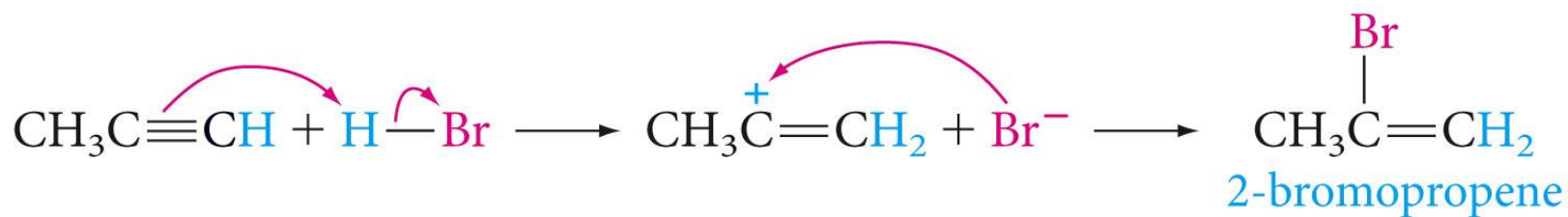
Alkynes: Reactions

Hydrogenation: ordinary Pt or Ni catalysts produce alkanes. However a special Pd catalyst called *Lindlar's reagent* causes only 1 H₂ in a syn addition to produce a cis-alkene



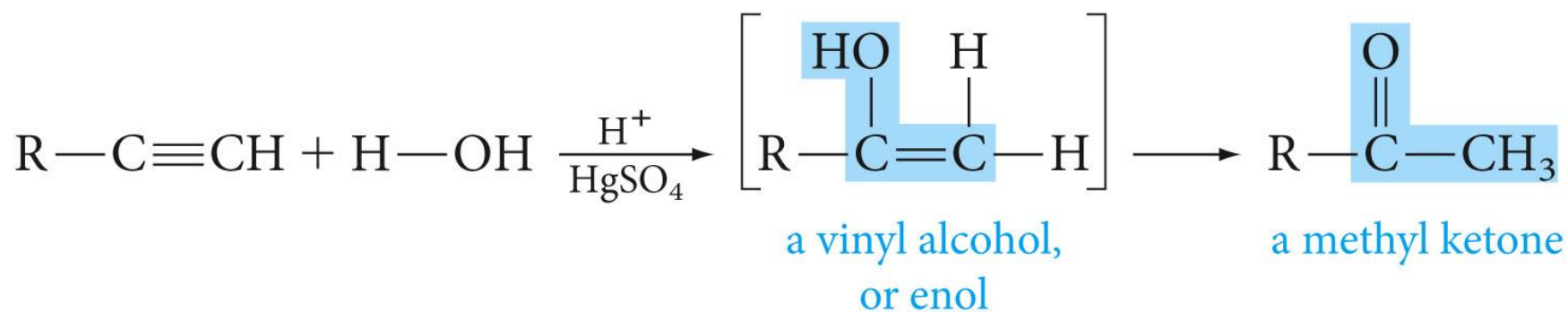
Alkynes: Reactions

Markovnikov's rule is followed for asymmetric alkynes, $R-C\equiv C-H$



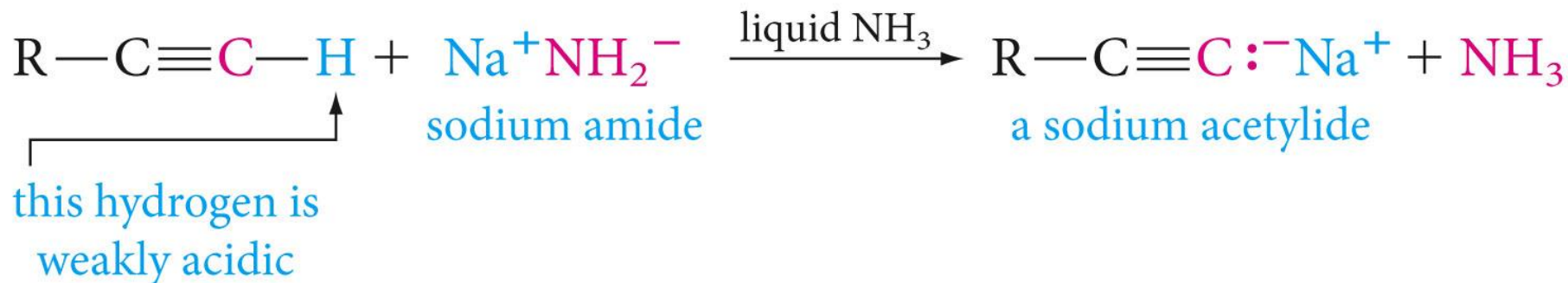
Alkynes: Reactions

Hydration: requires an additional mercury (Hg^{2+}) catalyst. The initial product, an enol, rearranges rapidly to form a ketone, i.e.



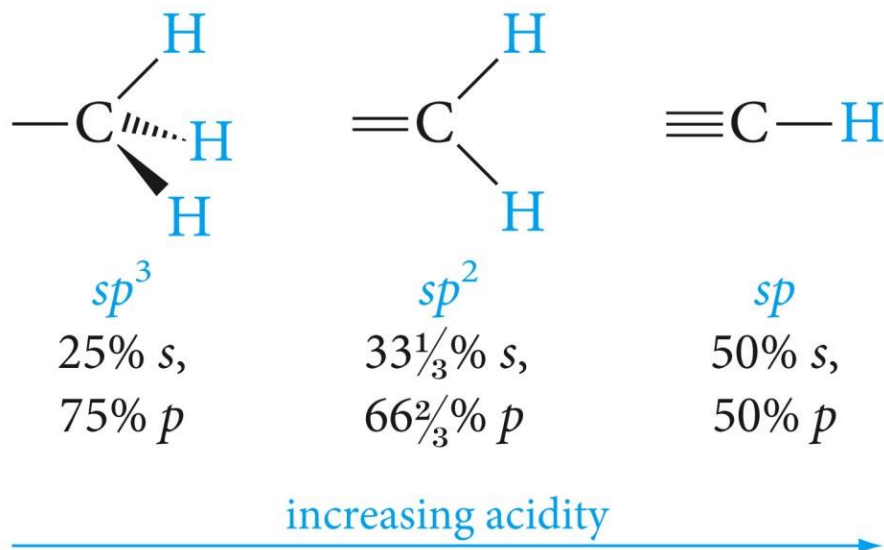
Alkynes: Acidity

The alkyne proton is quite acidic for a hydrocarbon with a pK_a of ~ 25 . This means it can be removed by strong bases such as sodium amide (made by adding metallic sodium to ammonia).



Alkynes: Acidity

The reason for the high acidity is the hybridization of the C atom in an alkyne. As the hybridization becomes more s like the acidity increases.



This is very important as it is one of the few ways to generate a carbon nucleophile!

