



Chapter 3

Alkenes and Alkynes

3.1 Definition and Classification :

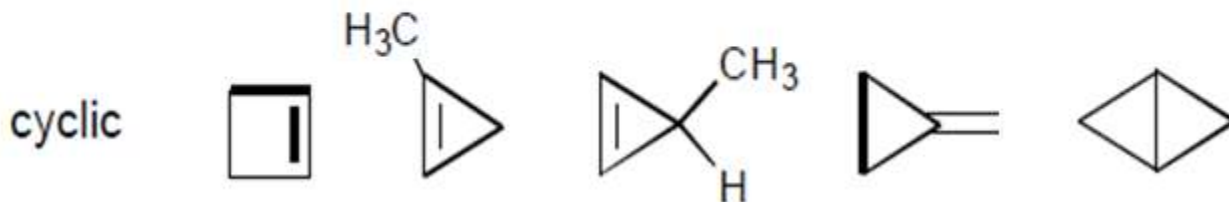
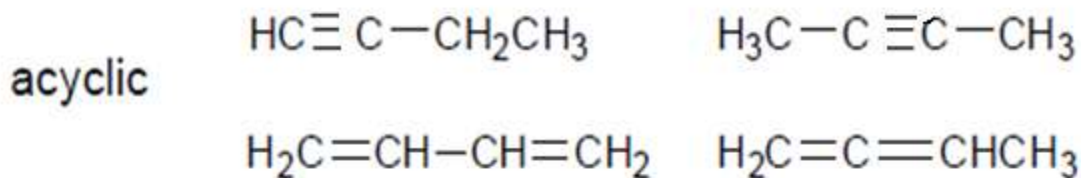
- **Alkenes** : hydrocarbons with one or more ($\text{C}=\text{C}$) bonds.
General Formula : $\text{C}_n \text{H}_{2n}$ (Simplest is ethylene C_2H_4)
(same as cycloalkanes)
 - **Alkynes** : hydrocarbons containing one or more ($\text{C}\equiv\text{C}$) bonds.
General Formula : $\text{C}_n \text{H}_{2n-2}$ (Simplest is acetylene C_2H_2)
(same as cycloalkenes)
- Both **unsaturated** : contain fewer H atoms than alkanes ($\text{C}_n\text{H}_{2n+2}$).

More than one C=C bond : **dienes** , **trienes** , **tetraenes** , **Polyenes**

Polyenes : in carrots (β -carotene), tomatoes (lycopene),etc.

PROBLEM 3.1 : Draw all structural possibilities for **C₄H₆**
(9 compounds : 4 acyclic + 5 cyclic)

C₄H₆ corresponds to C_nH_{2n-2}. The possibilities are :
one triple bond, two double bonds,
one double bond and one ring, or two rings



Two or more multiple bonds in same molecule can be:

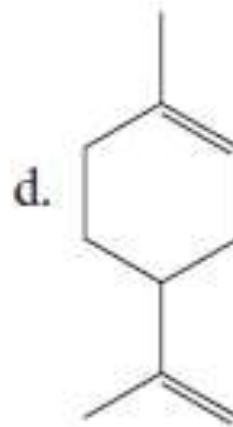
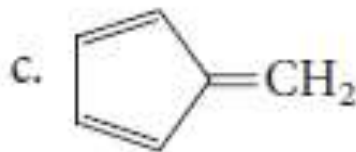
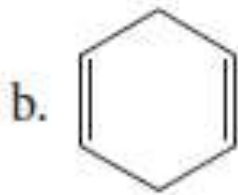
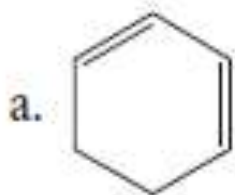


cumulated

conjugated

nonconjugated (isolated)

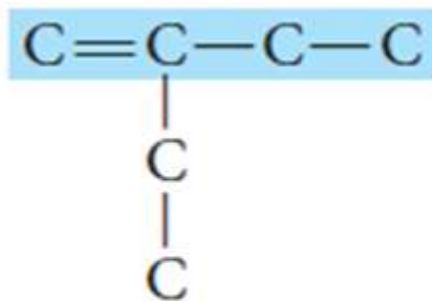
PROBLEM 3.2 Which of the following compounds have conjugated multiple bonds?



3.2 Nomenclature :

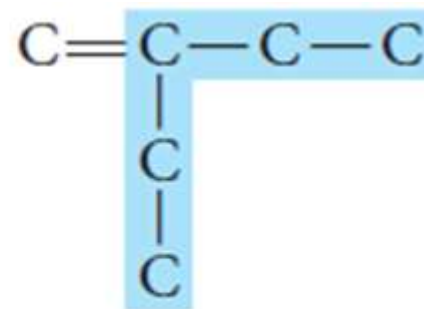
1. Ending for (C=C) bond : (**-ene**)
2. Ending if two or more (C=C) present : (**-diene, -triene,.....**)
3. Ending for (C≡C) bond : (**-yne**)
4. Ending if two or more (C≡C) present : (**-diyne,**)
5. Ending if a (C=C) + (C≡C) are present : (**-enyne**)
6. Longest chain must **include all** (C=C) and (C≡C) bonds present (for example in dienes, diynes, or enynes)

Example:



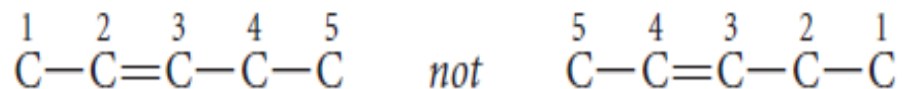
named as: **substituted butene**

not



not as pentene or pentane

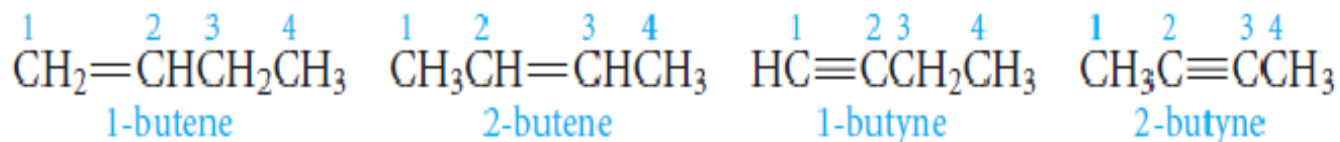
7. Numbering from the end **nearest to the multiple bond**.

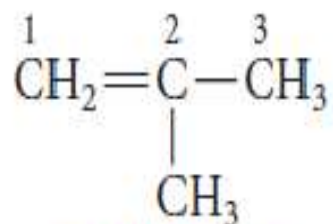


8. If the multiple bond is **equidistant** from both ends, start from the end **nearest to a branch** (or substituent).

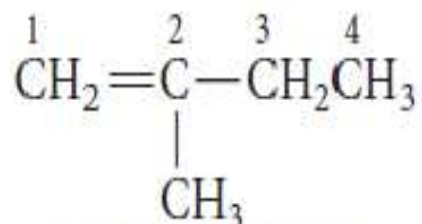


9. Position of multiple bond indicated by the **lower numbered carbon**.

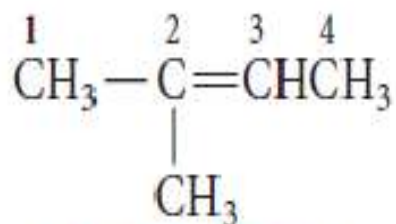




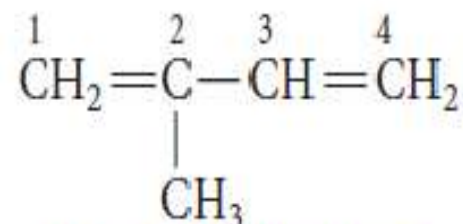
methylpropene
(isobutylene)



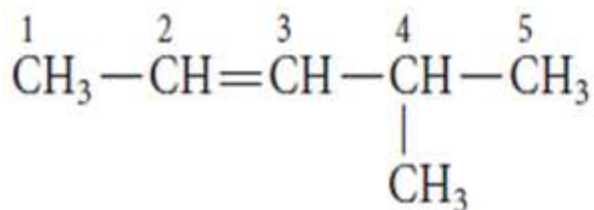
2-methyl-1-butene



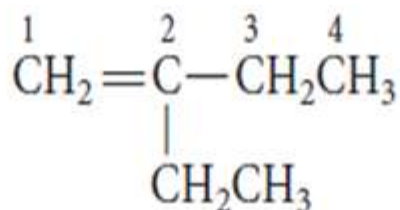
2-methyl-2-butene



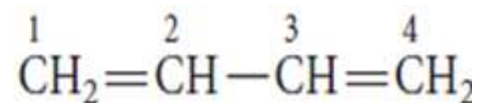
2-methyl-1,3-butadiene
(isoprene)



4-methyl-2-pentene
Not 2-methyl-3-pentene



2-ethyl-1-butene



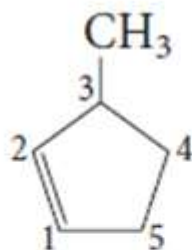
1,3-butadiene

Cycloalkenes :



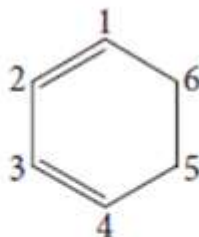
cyclopentene

No number

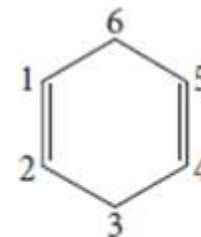


3-methylcyclopentene

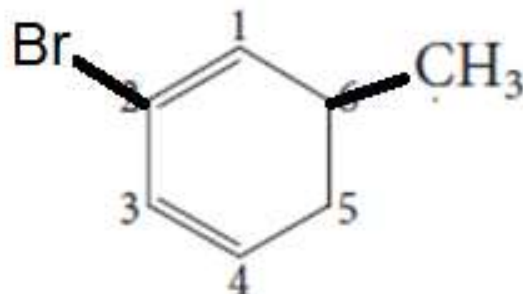
Not 5-methylcyclopentene
or 1-methyl-2-cyclopentene



1,3-cyclohexadiene

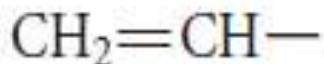


1,4-cyclohexadiene



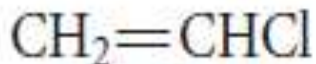
2-Bromo-6-methyl-1,3-cyclohexadiene

Common names of special groups:



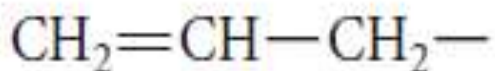
vinyl

(ethenyl)



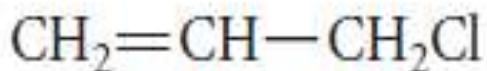
vinyl chloride

(chloroethene)



allyl

(2-propenyl)



allyl chloride

(3-chloropropene)

PROBLEM 3.4

Write structural formulas for the following:

a. 1,4-dichloro-2-pentene

b. 3-hexyne

c. 1,2-diethylcyclobutene

d. 2-bromo-1,3-pentadiene

3.3 Some Facts About (C—C) Bonds

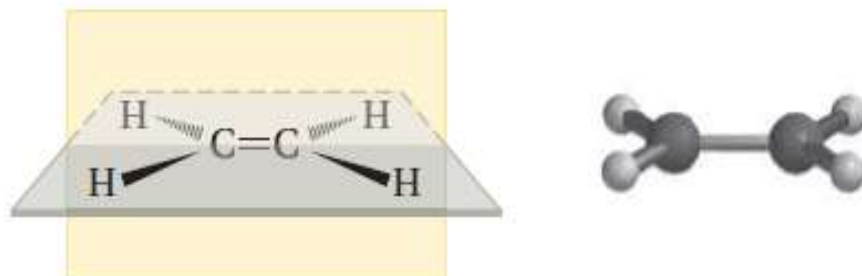
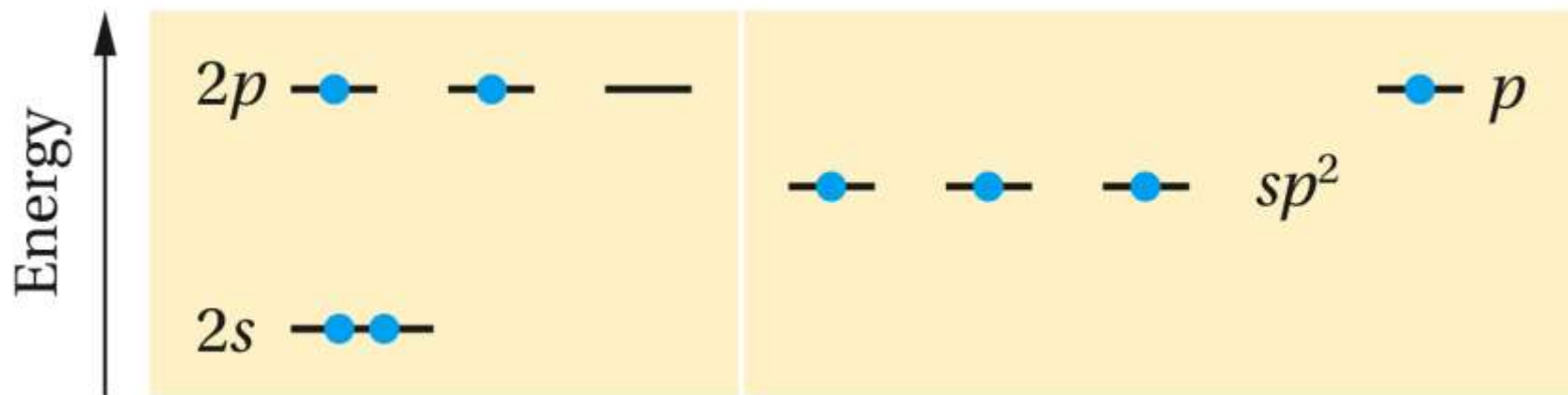


TABLE 3.1 Comparison of C—C and C=C Bonds

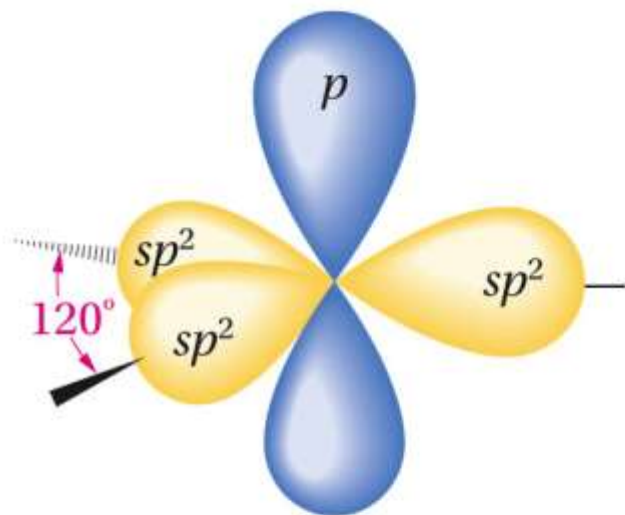
Property	C—C	C=C
1. Number of atoms attached to a carbon	4 (tetrahedral)	3 (trigonal)
2. Rotation	relatively free	restricted
3. Geometry	many conformations are possible; staggered is preferred	planar
4. Bond angle	109.5°	120°
5. Bond length	1.54 Å	1.34 Å

3.4 Orbital Model of the Double Bond:

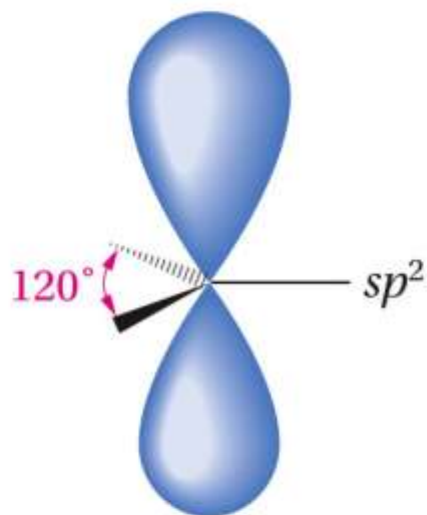


Atomic orbitals
of carbon

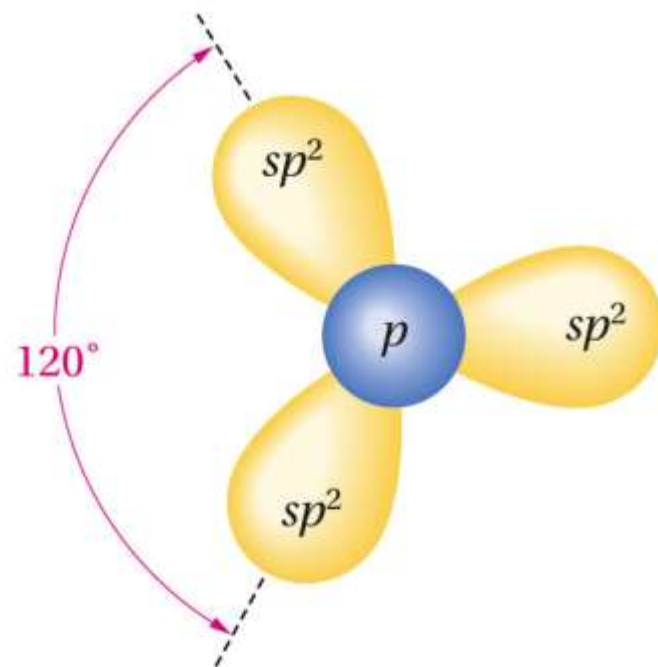
The $2s$ and two $2p$ orbitals
are combined to form three
hybrid sp^2 orbitals, leaving
one electron still in a p
orbital.



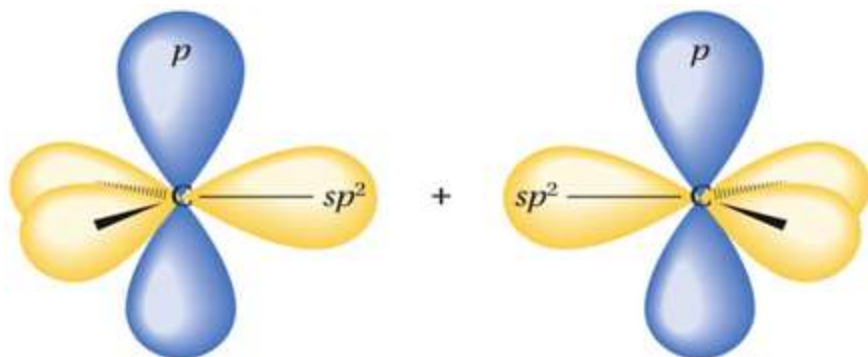
side view



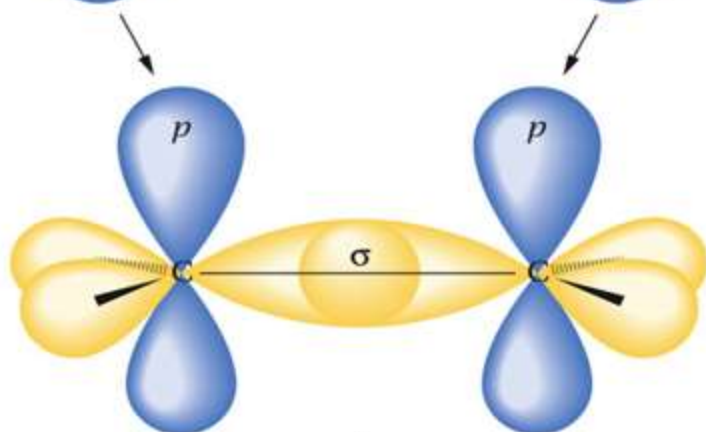
side view with
the sp^2 orbitals
represented by lines



top view

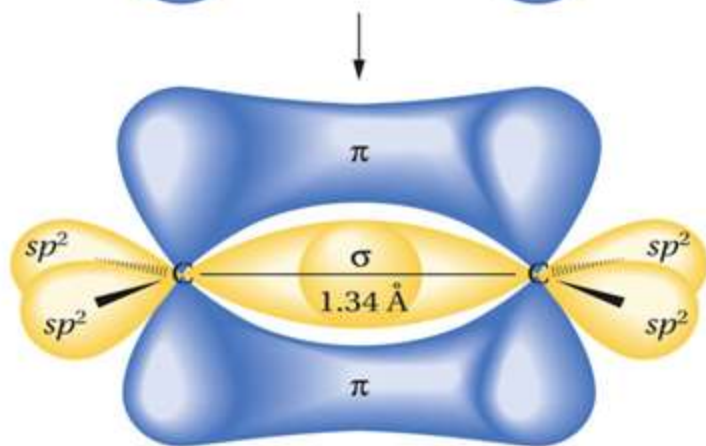


two sp^2 -hybridized carbons with p orbitals parallel



the σ bond is formed by two electrons in overlapping sp^2 orbitals

sp^2 - sp^2 overlap

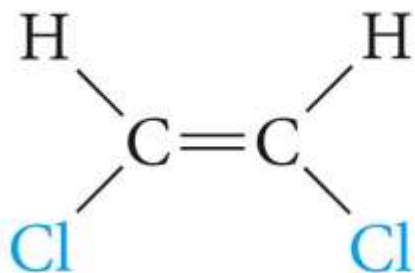


the π bond is formed by two electrons in overlapping parallel p orbitals

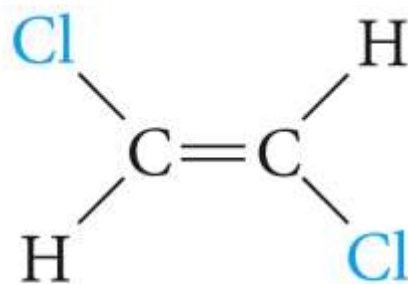
p - p overlap

3.5 *Cis-Trans* Isomerism in Alkenes :

Because rotation at (C=C) bonds is restricted, *cis-trans* isomerism (geometric isomerism) is possible in some alkenes.



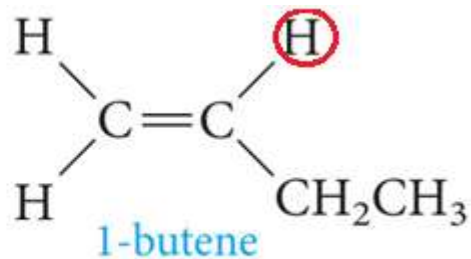
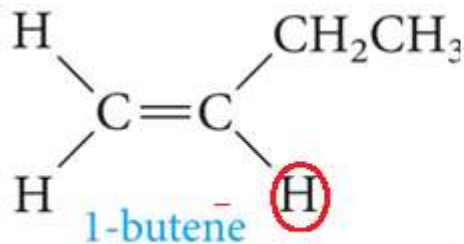
cis-1,2-dichloroethene
bp 60°C, mp -80°C



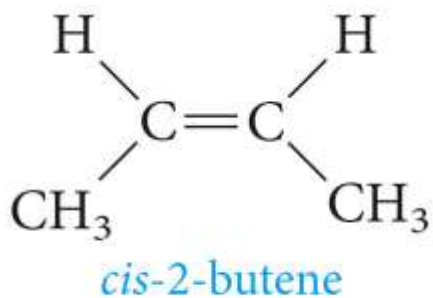
trans-1,2-dichloroethene
bp 47°C, mp -50°C

Can Alkynes show *cis-trans* isomerism?
Why?

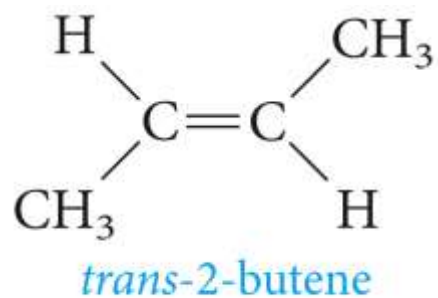
Are cis-trans isomers possible for 1-butene and 2-butene?



identical

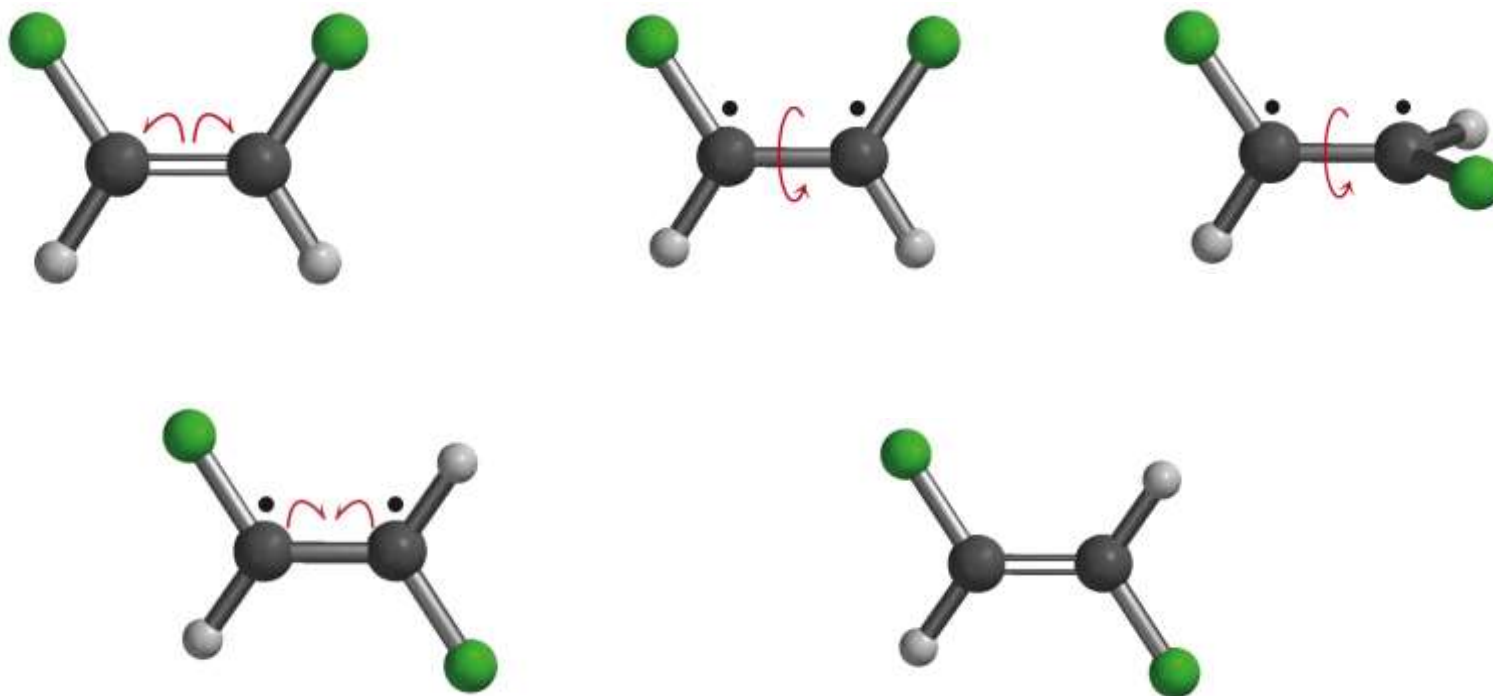


bp 3.7°C , mp -139°C



bp 0.3°C , mp -106°C

Geometric isomers of alkenes can interconvert **only** by breaking the π -bond to allow rotation.

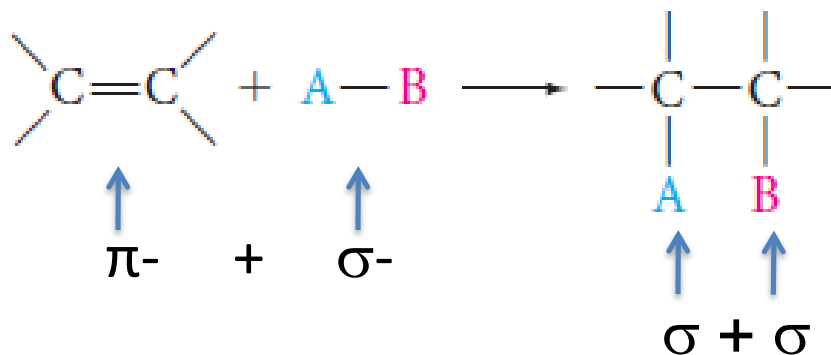


3.6 Addition and Substitution Reactions :

Substitution : (example : halogenation of alkanes)



Addition : (example : reactions with alkanes and alkynes)



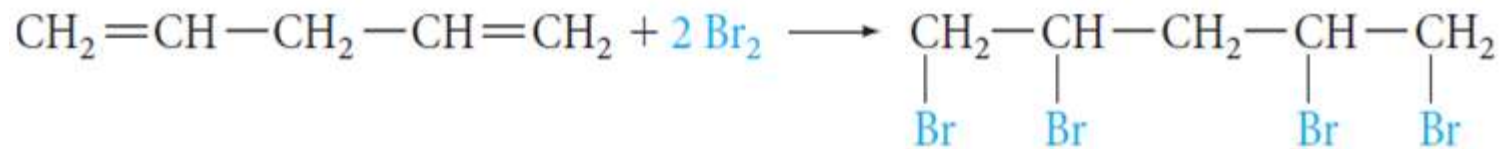
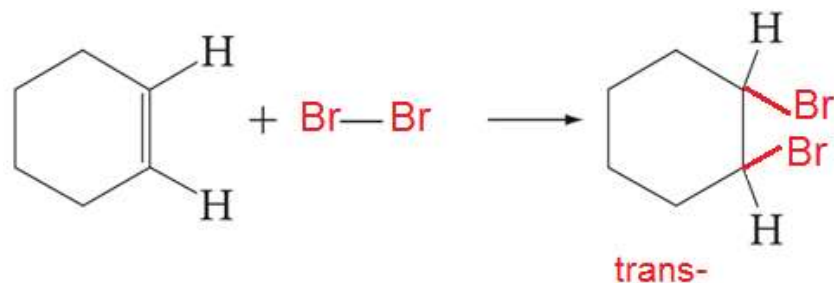
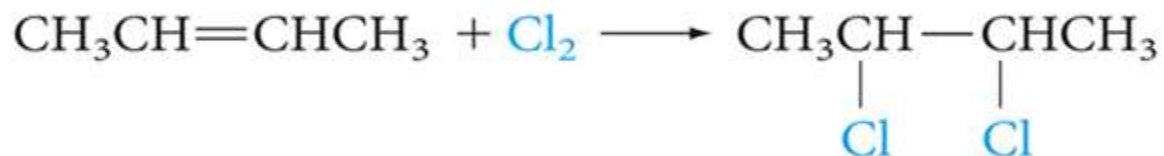
bonds broken :

Bonds formed:

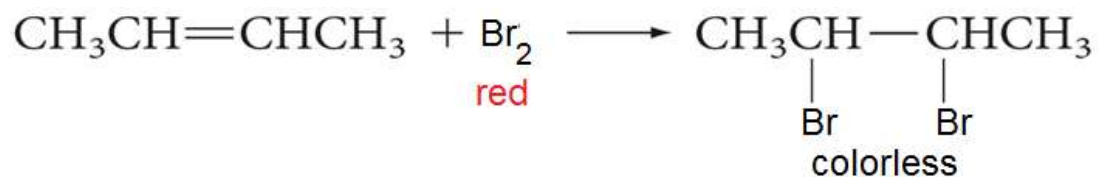
Because σ -bonds are stronger than π -bonds, reaction is favorable.

3.7 Polar Addition Reactions :

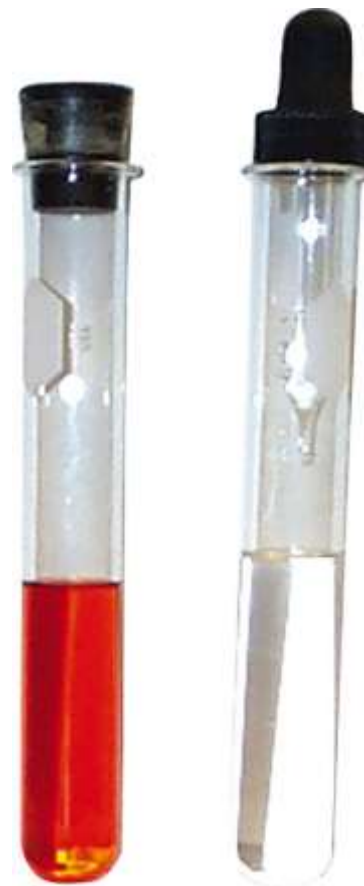
3.7-a Addition of Halogen:



Bromine/ CCl₄ as a test for **unsaturation**:
(positive with alkenes and alkynes)



Positive test : bromine red color is discharged
(red → colorless) →

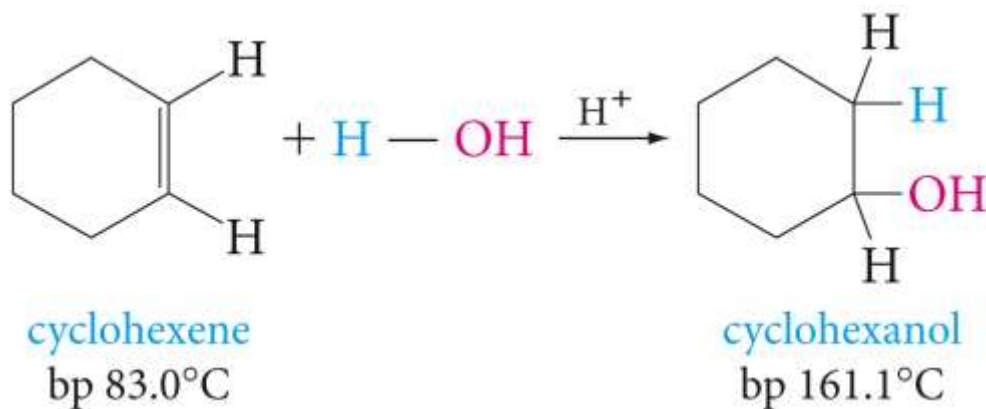
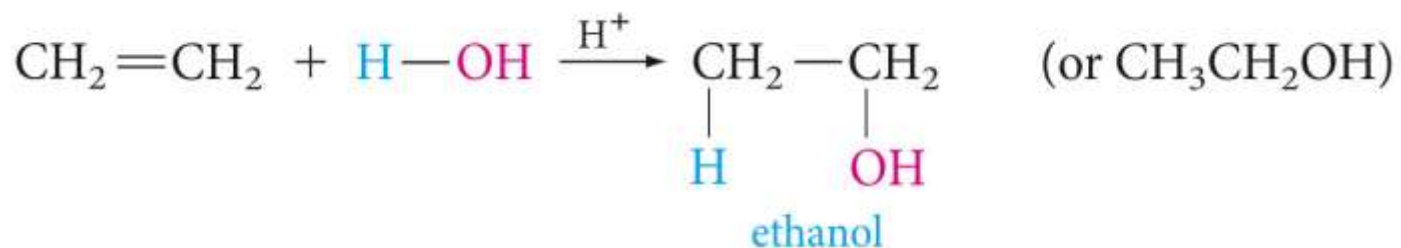


PROBLEM 3.8: Write an equation for the reaction of bromine with

- a. propene b. 4-methylcyclohexene c. 2-butyne

3.7-b Addition of Water (Hydration) :

In presence of acid catalyst, water adds to alkenes to form alcohols

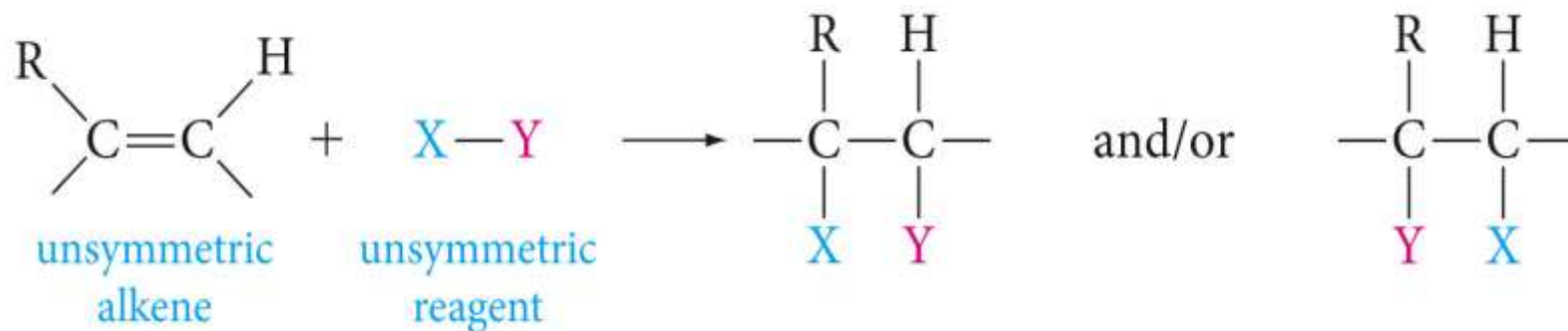


3.8 Addition of Unsymmetric Reagents to Unsymmetric Alkenes (Markovnikov's Rule) :

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

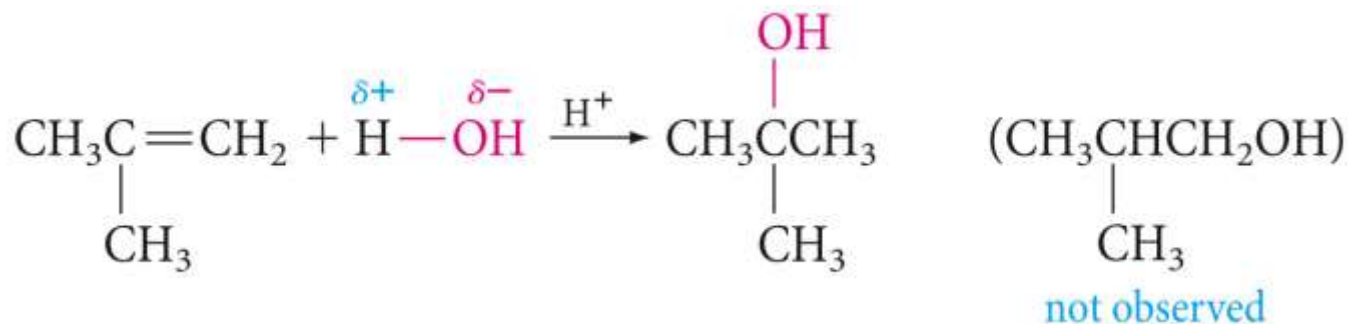
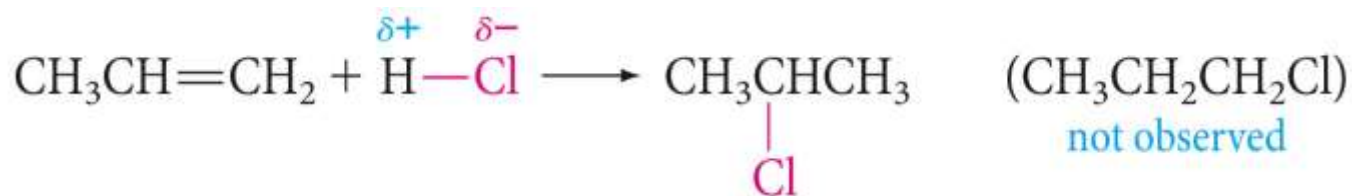
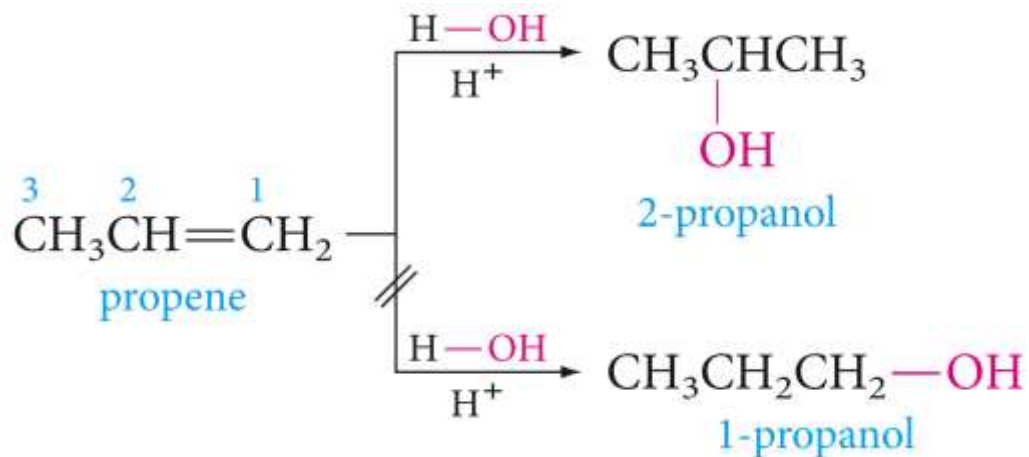
	Symmetric	Unsymmetric
Reagents	$\begin{array}{c} \text{Br} - - \text{Br} \\ \\ \text{Cl} - - \text{Cl} \\ \\ \text{H} - - \text{H} \end{array}$	$\begin{array}{c} \text{H} - - \text{Br} \\ \\ \text{H} - - \text{OH} \\ \\ \text{H} - - \text{OSO}_3\text{H} \end{array}$
Alkenes	$\begin{array}{c} \text{CH}_2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

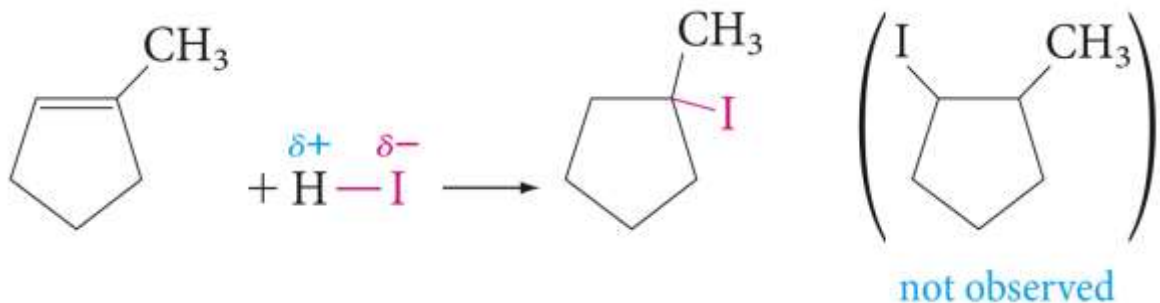
Two isomeric products can be formed (**regioisomers**) :



Reaction which gives only one of them is called **regiospecific**.

If it gives one of them as major product it is **regioselective**.





Markovnikov's Rule :

When **Unsymmetric** reagent adds to **Unsymmetric** alkene, the **positive** part of reagent bonds to the carbon that has **more hydrogens**.

PROBLEM 3.11

Use Markovnikov's Rule to predict which regioisomer predominates in each of the following reactions:

- 1-pentene + HBr
- 2-methyl-2-hexene + H_2O (H^+ catalyst)

3.9 Mechanism of Electrophilic Addition :

The C=C bond has weak π - bond and π - electrons are more exposed to be attacked by electron-poor reagents than σ - electrons.

So the C=C bond acts as e-donor to e-poor reagents (**Electrophiles**).

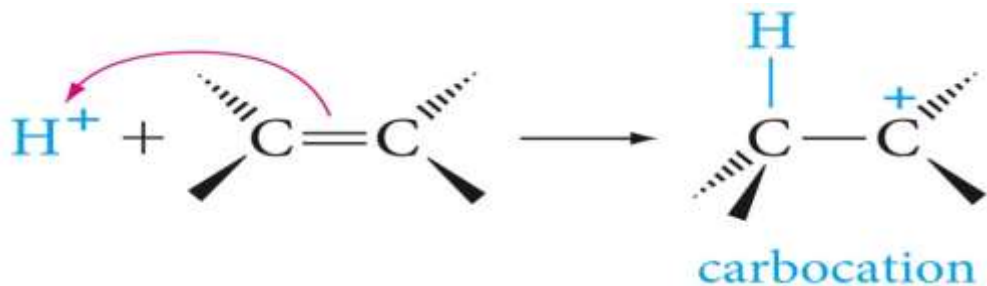
Electrophiles: electron-poor reagents, e-acceptors.

Nucleophiles: electron-rich reagents, e-donors

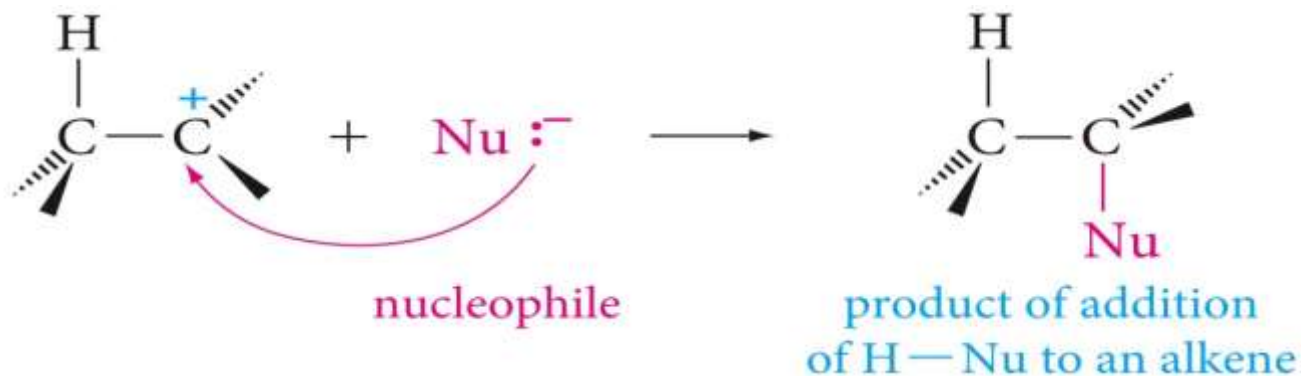


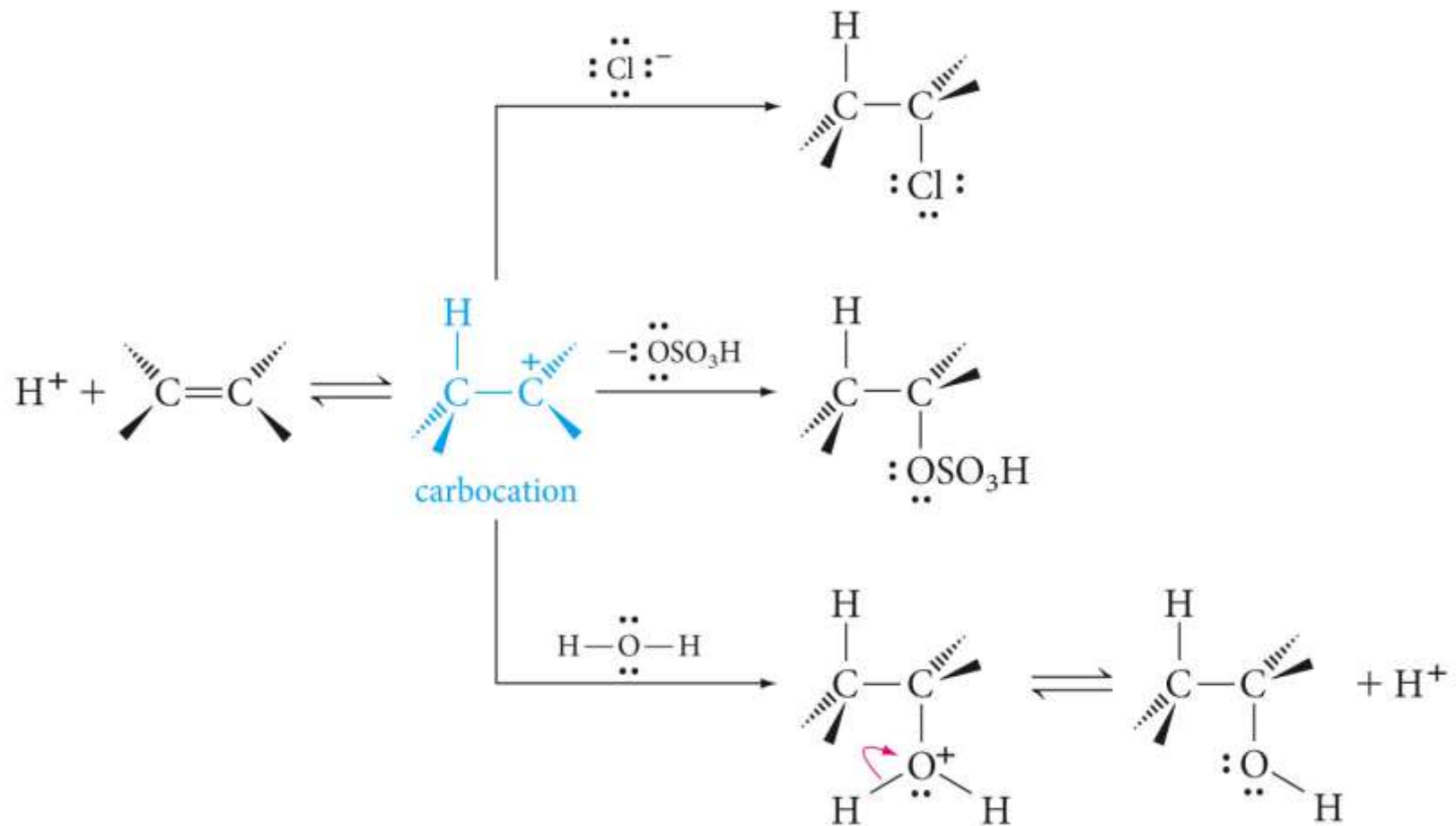
Electrophilic Addition to Alkenes (mechanism):

Step 1: The positive (**electrophilic**) part of reagent attacks the e-rich C=C bond forming an intermediate carbocation: (**π -bond broken, σ -bond forms**)



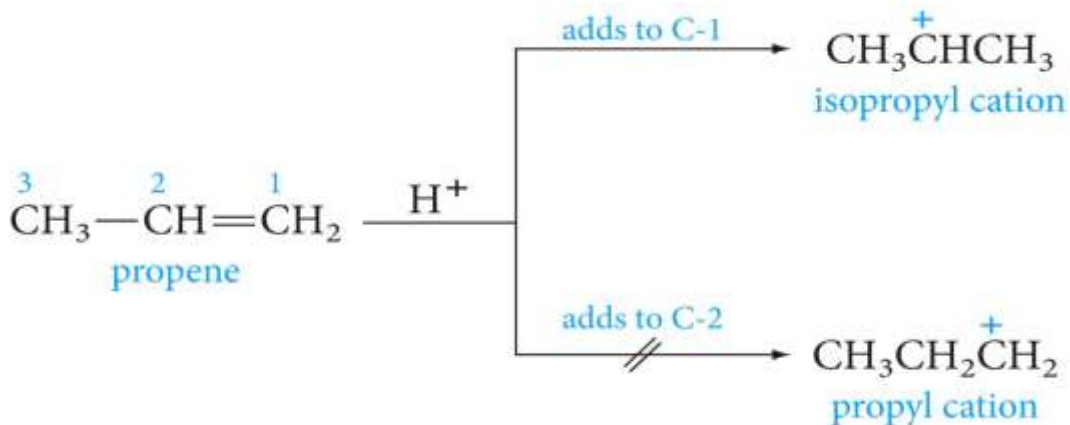
Step 2: The negative (**nucleophilic**) part of reagent adds to the +vely charged carbon of the carbocation: (**another σ -bond forms**)



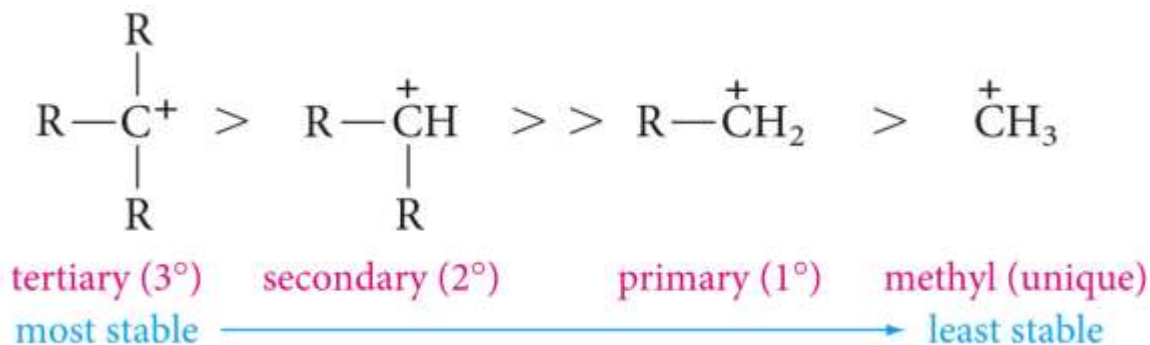


Since first step is attack by **Electrophile**, it is called **Electrophilic Addition**.

3.10 Markovnikov's Rule Explained:

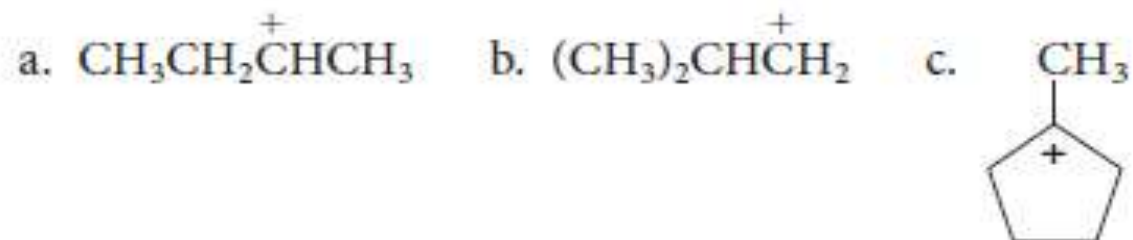


Stability of carbocations decreases in the following order:



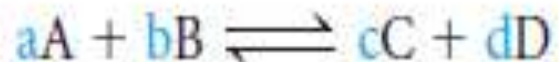
Markovnikov's Rule restated : Electrophilic addition of unsymmetric reagent to unsymmetric alkenes proceeds involves formation of the **most stable carbocation**.

PROBLEM 3.13 Classify each of the following carbocations as primary, secondary, or tertiary:



3.11 Reaction Equilibrium: What Makes a Reaction Go?

A chemical reaction can proceed in two directions.

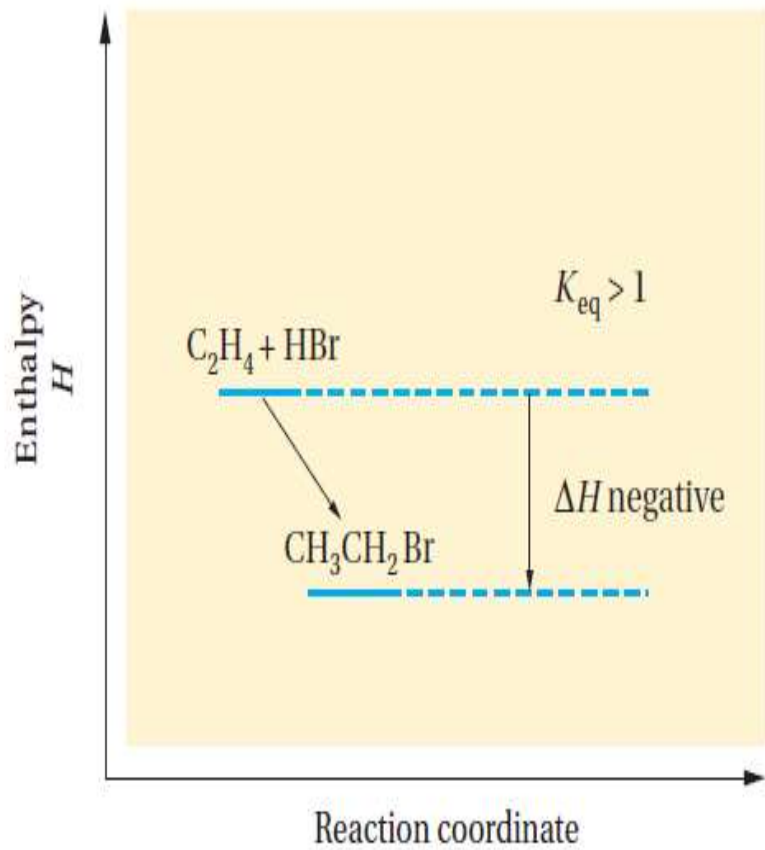


We describe the chemical equilibrium for the forward and backward reactions by the following equation:

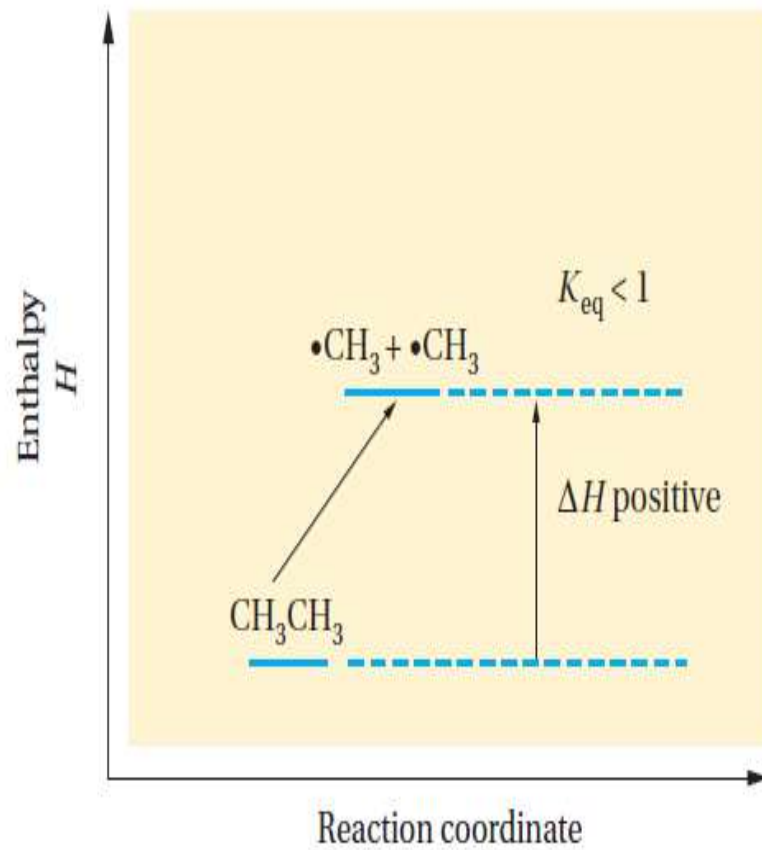
$$K_{\text{eq}} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- If K_{eq} is greater than 1, the formation of products C and D will be favored over the formation of reactants A and B.
- if K_{eq} is less than 1, the preferred direction for the reaction is from right to left.

- What determines whether a reaction will proceed to the right, toward products?
- A reaction will occur when the products are lower in energy (more stable) than the reactants. A reaction in which products are higher in energy than reactants will proceed to the left, toward reactants.
- When products are lower in energy than reactants, heat is given off in the course of the reaction. Such a reaction is ***exothermic***.
- On the other hand, heat must be added to ethane to produce two methyl radicals .This reaction is ***endothermic*** (takes in heat).



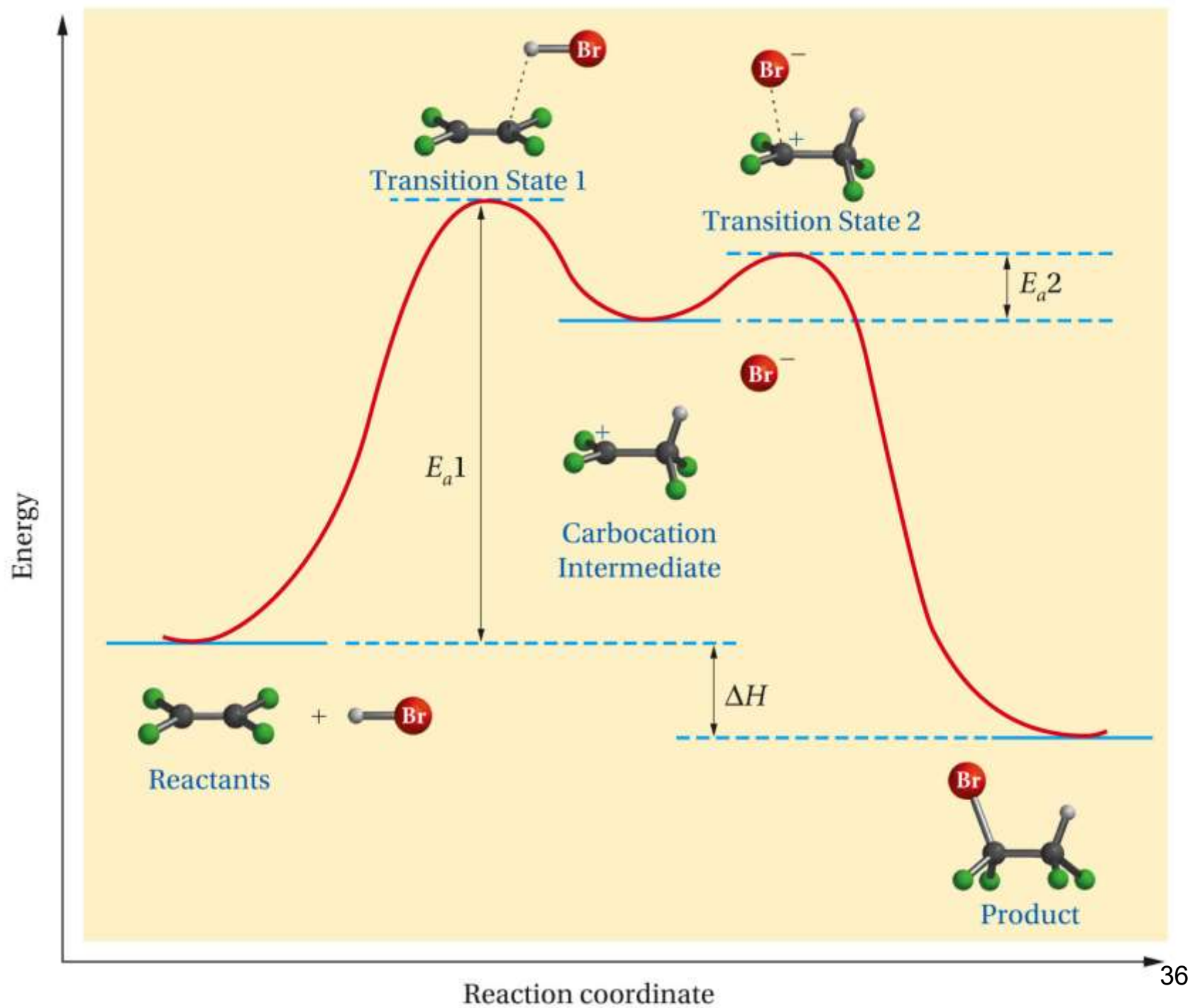
(a)

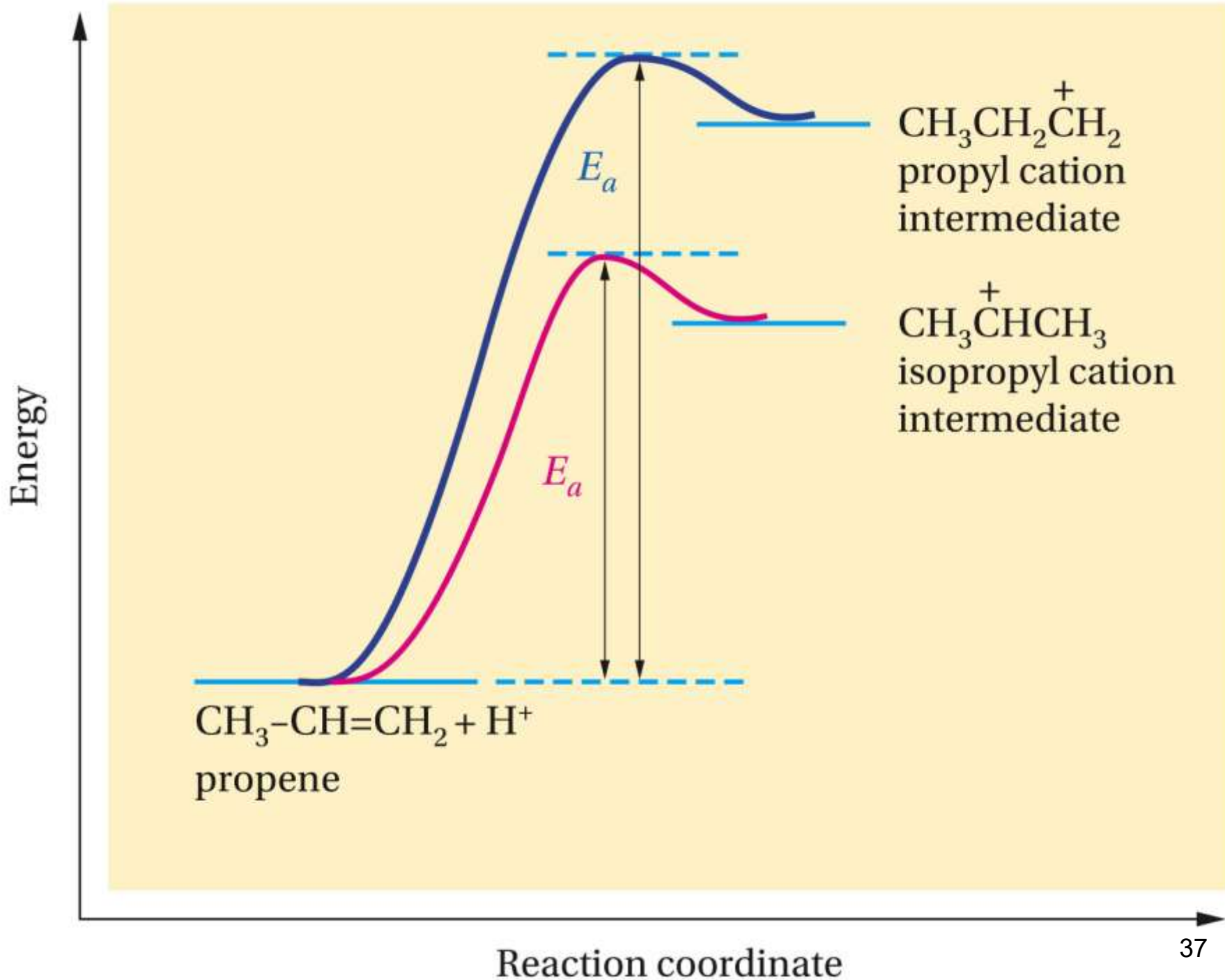


(b)

3.12 Reaction Rate: How Fast a Does Reaction Go?

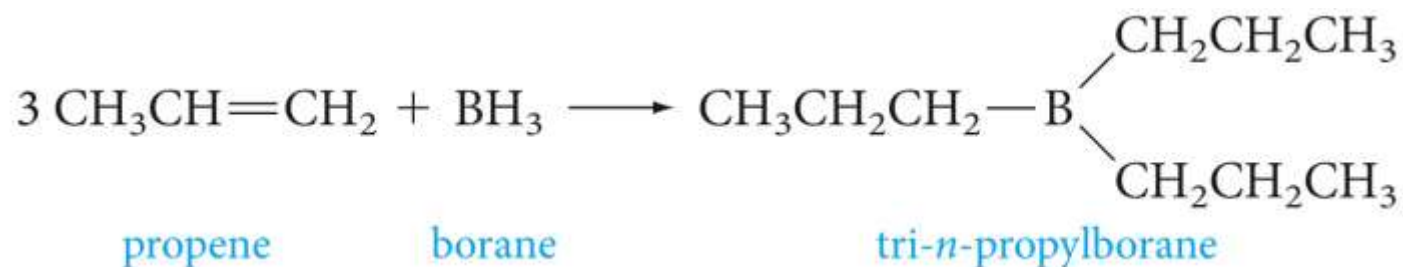
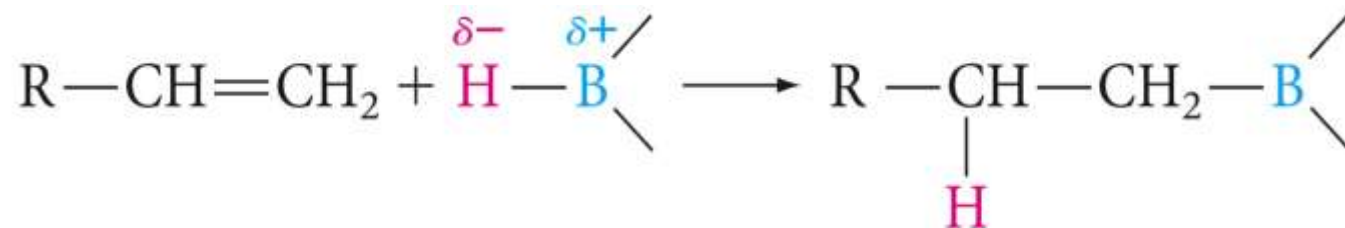
- A **reaction energy diagram** shows the changes in energy that occur in the course of a reaction.
- A **transition state** is a structure with maximum energy for a particular reaction step.
- **Activation energy**, E_a , is the difference in energy between reactants and the transition state, and the activation energy determines the **reaction rate**.



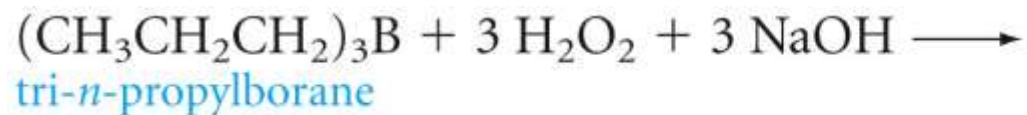


3.13 Hydroboration of Alkenes :

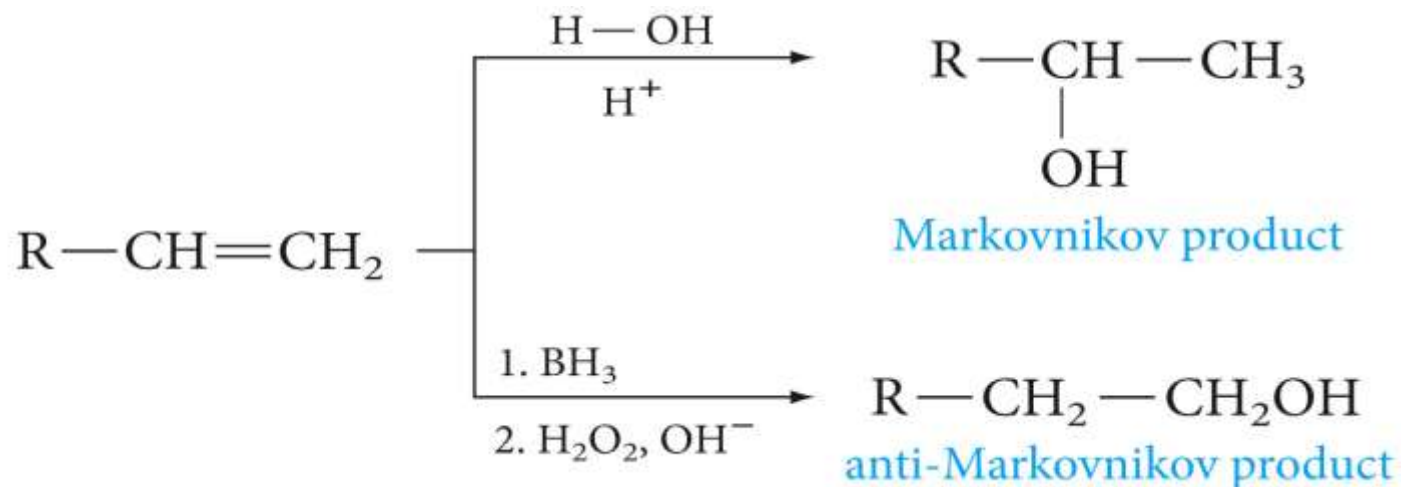
- Hydroboration involves addition of hydrogen–boron bond to alkenes.



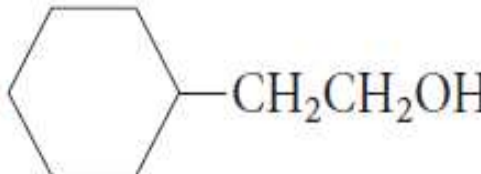
Hydroboration–oxidation gives alcohols that **cannot** be obtained by hydration of alkene (**Anti-Markovnikov's** Alcohols)



Anti-Markovnikov



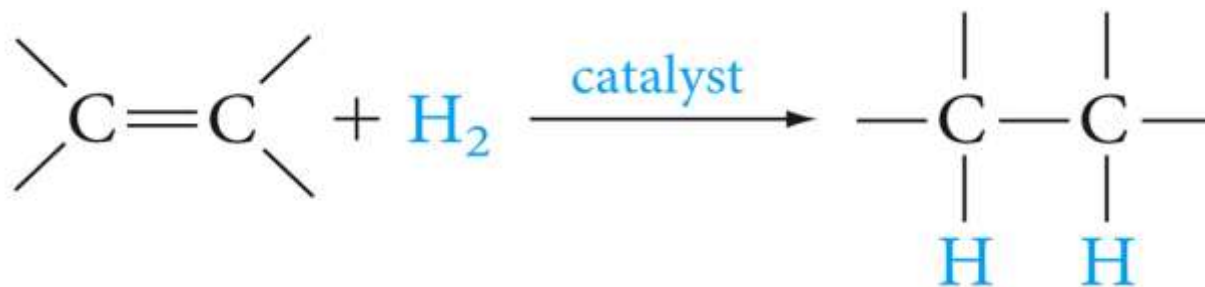
PROBLEM 3.20

What alkene is needed to obtain  via the hydroboration-oxidation sequence? What product would this alkene give with acid-catalyzed hydration?

via the hydroboration-oxidation sequence? What product would this alkene give with acid-catalyzed hydration?

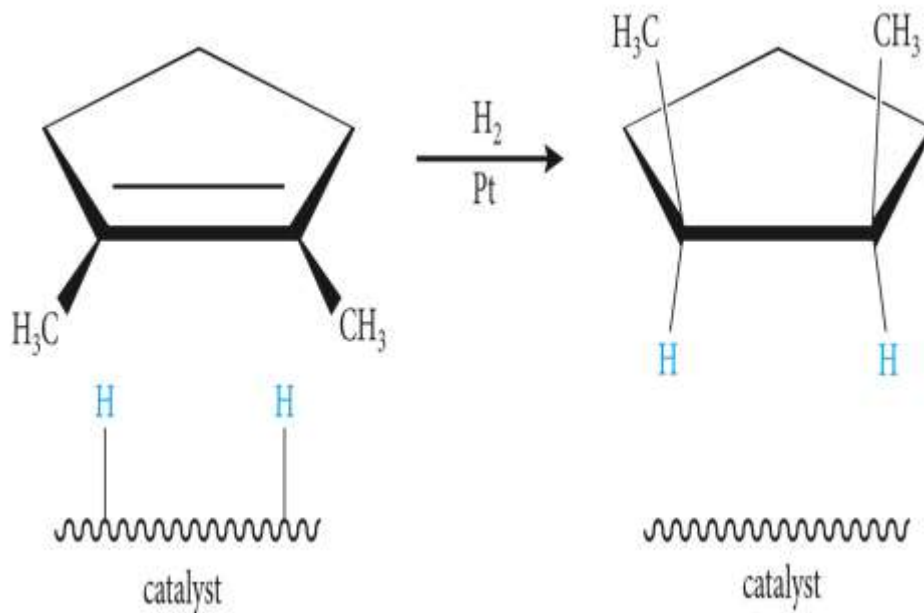
3.14 Addition of Hydrogen (hydrogenation) :

- Hydrogen adds to alkenes in the presence of metal catalyst.



- **Catalyst** : finely divided **nickel, platinum, or palladium**.
- Both H atoms add to **same face** of C=C bond (**cis**-addition).

- **Example:** 1,2-dimethylcyclopentene gives **cis**-1,2-dimethylcyclopentane.



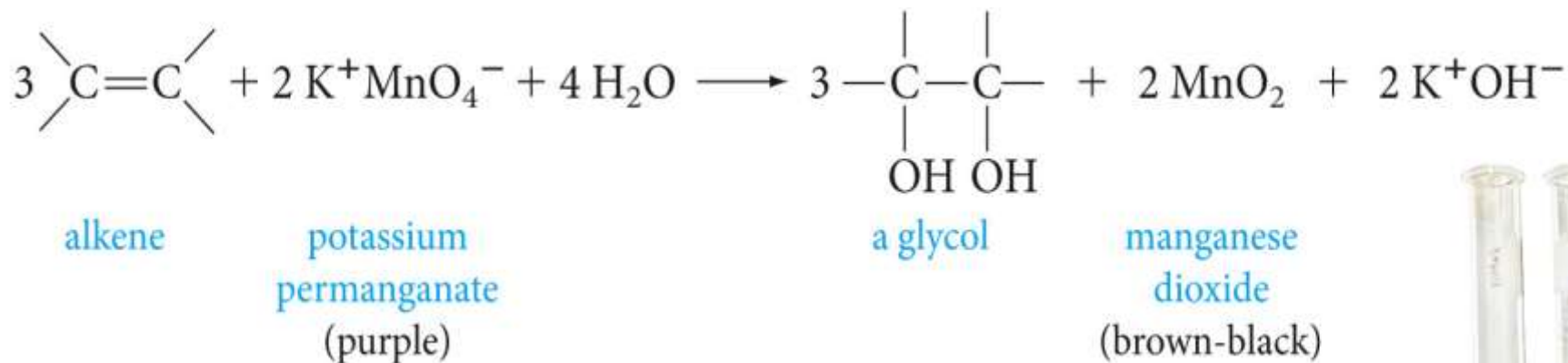
PROBLEM 3.21 Write an equation for the catalytic hydrogenation of

- 2-methyl-2-pentene
- 4-methylcyclopentene
- 3-methylcyclohexene
- vinylcyclobutane

3.17 Oxidation of Alkenes :

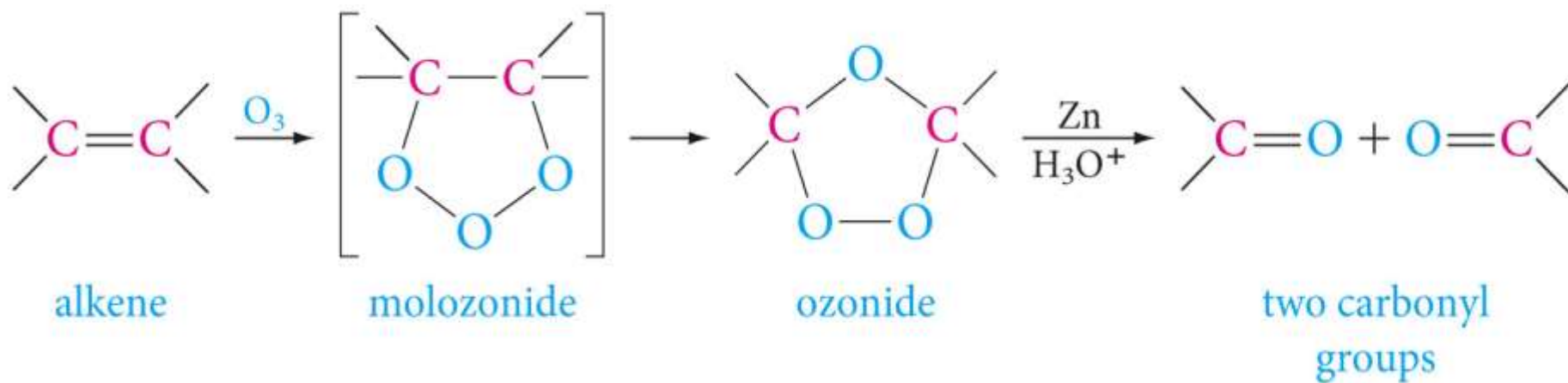
Alkenes are more easily oxidized than alkanes by oxidizing agents. Reactions useful as chemical tests for unsaturation.

3.17 a Oxidation with Permanganate (product : **cis** – diol)

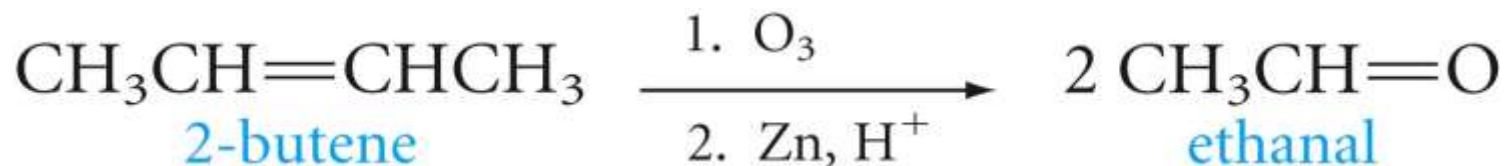
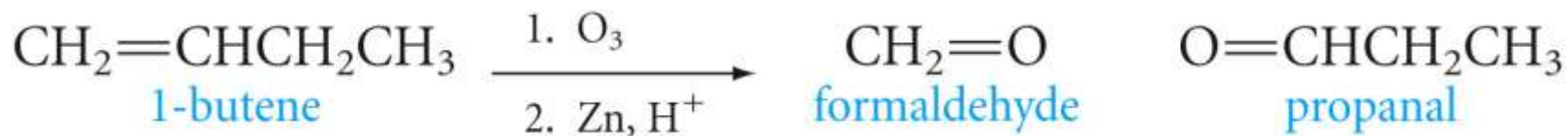


3.17b Ozonolysis :

Alkenes react rapidly with ozone (O_3)

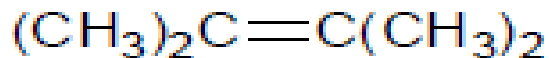


The ($C=C$) bond is cleaved and gives two ($C=O$) bonds

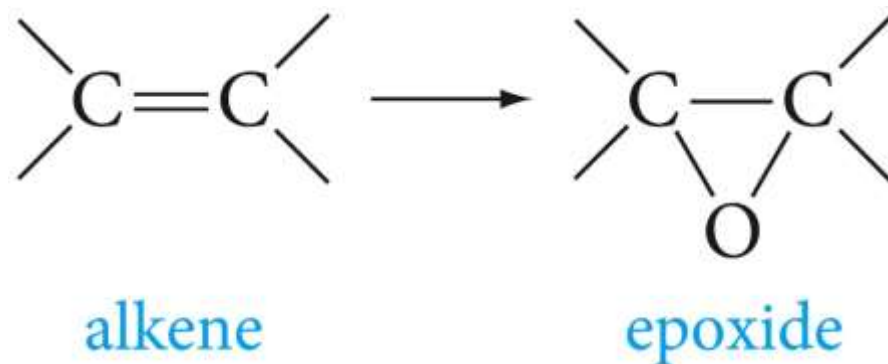


PROBLEM 3.28

Which alkene will give only acetone, $(\text{CH}_3)_2\text{C}=\text{O}$, as the ozonolysis product?



3.17 c Other Alkene Oxidations :



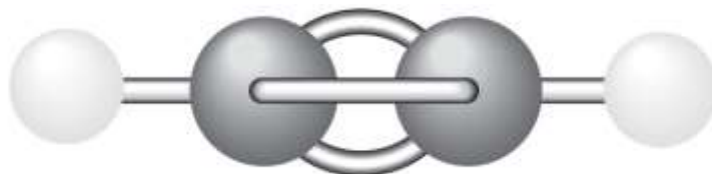
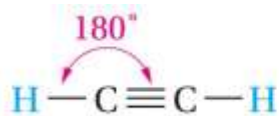
Alkynes

3.18 Some Facts About Triple Bond :

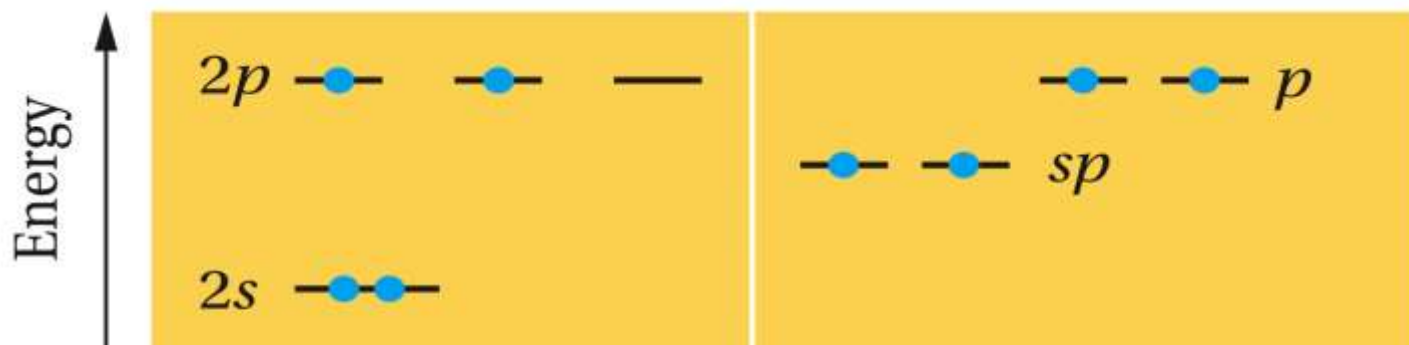
Bond angle = 180°

Bond distance = 1.21 \AA (shorter than $\text{C}=\text{C}$: 1.34 \AA), electrons **closer** to the atoms

Geometry : linear, no cis–trans isomerism,
no rotation about triple bond,
no conformations

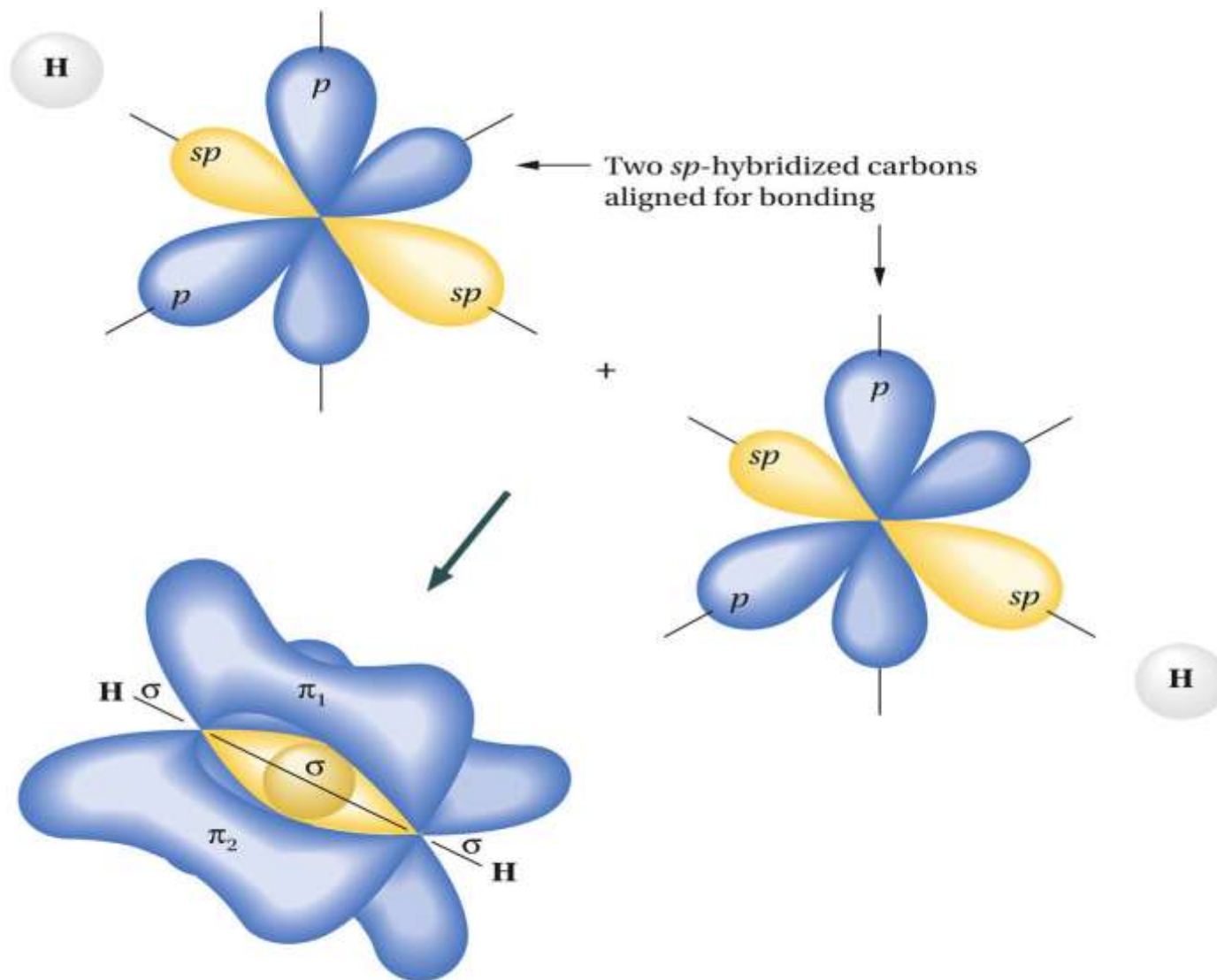


3.19 The Orbital Model of a Triple Bond :



Atomic orbitals
of carbon

The 2s and one 2p
orbital are combined to
form two hybrid *sp*
orbitals, leaving one
electron in each of two
p orbitals.



The resulting carbon-carbon triple bond, with a hydrogen atom attached to each remaining sp bond. (The orbitals involved in the C—H bonds are omitted for clarity.)

3.20 Addition Reactions of Alkynes :

Like alkenes, they undergo **Electrophilic Addition** reactions.

But alkynes **are less reactive** than alkenes (slower reaction) .

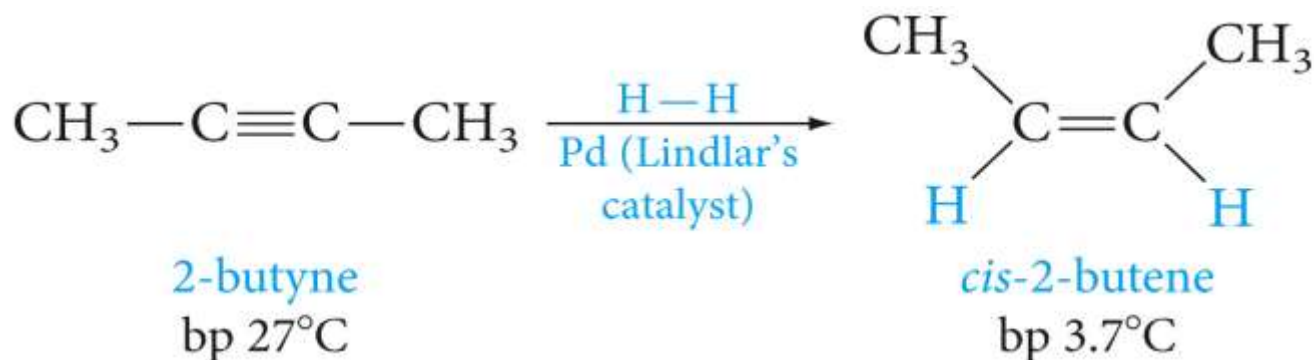
Some reactions require an additional catalyst (example : hydration)



Trans- addition of halogens

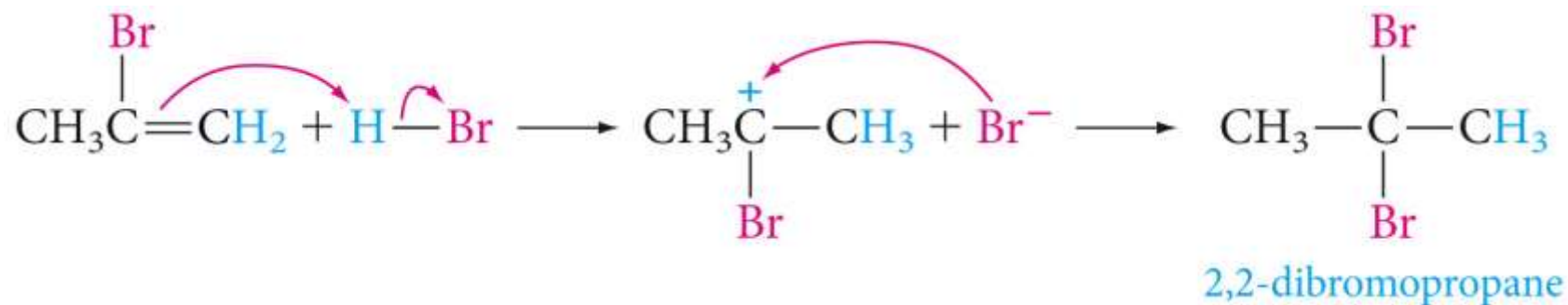
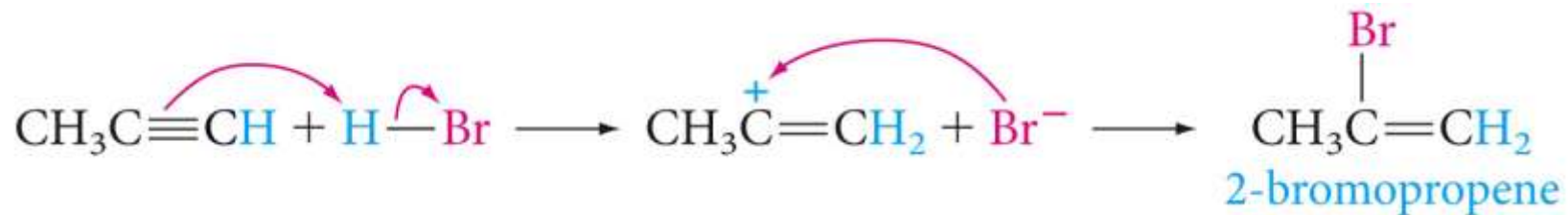
With **Ni** or **Pd** catalyst, alkynes are hydrogenated to **alkanes**.

Special Pd-catalyst (**Lindlar's catalyst**) only 1 mole H₂ adds to give **cis-alkene**

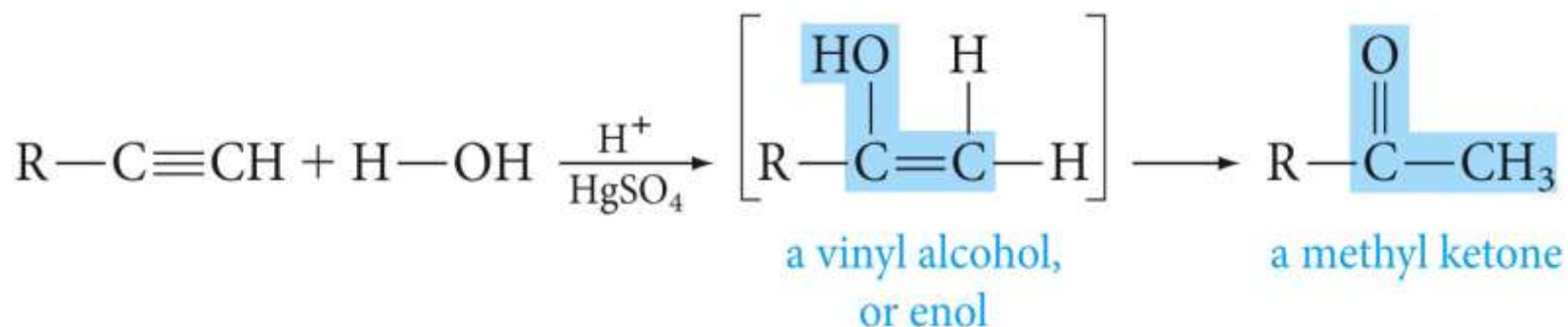


trans-alkene can be obtained by hydrogenation with **Na in NH₃**

Unsymmetric alkynes + unsymmetric reagents : **Markovnikov's Rule** applies



Addition of water requires acid and mercuric ion catalyst. Product is ketone. Acetylene (R = H), gives acetaldehyde.

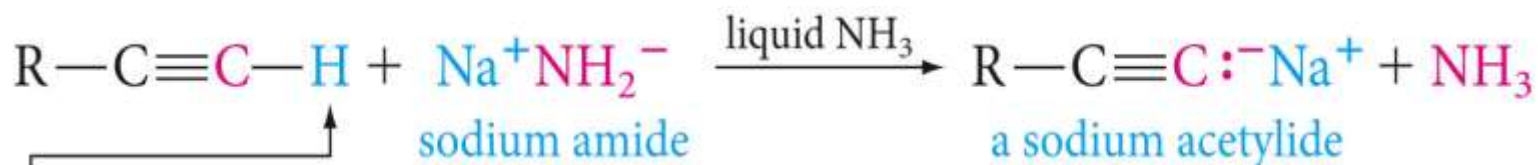


PROBLEM 3.29 Write equations for the following reactions:

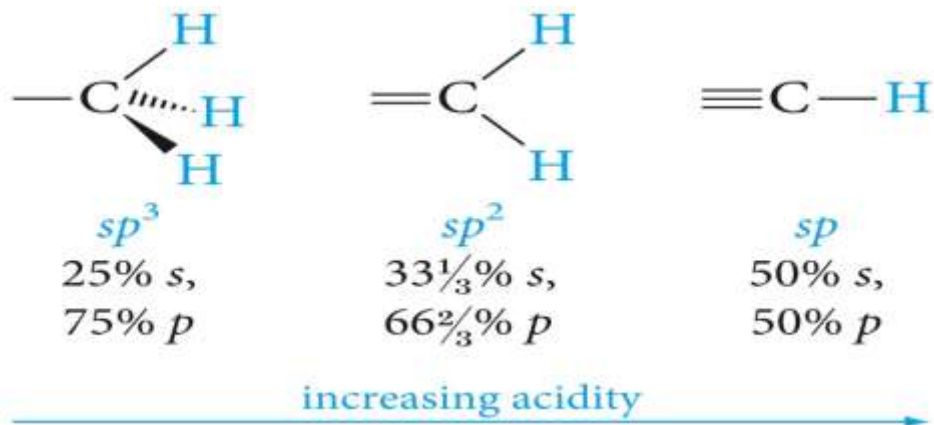
- | | |
|---|--|
| a. $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH} + \text{Br}_2$ (1 mole) | c. 1-hexyne + HBr (1 and 2 moles) |
| b. $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CCH}_3 + \text{Cl}_2$ (2 moles) | d. 1-butyne + H_2O (Hg^{2+} , H^+) |

3.21 Acidity of Alkynes :

H atom on triple bond is weakly acidic and can be removed by a very strong base (such as Sodium amide) to give acetylides.



this hydrogen is weakly acidic



As s-character increases, acidity of the attached hydrogens increases.