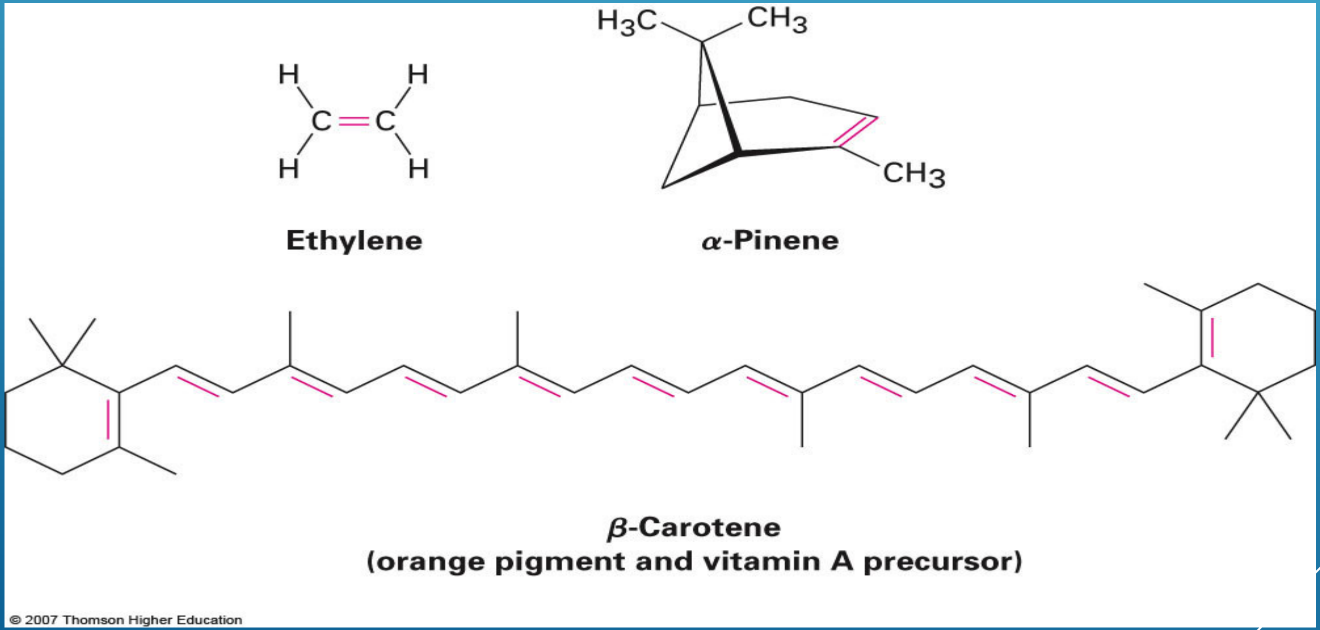
ALKENES AND ALKYNES

ALKENES

- Alkenes are hydrocarbons containing a carbon-carbon double bond,C=C.
- Alkenes have a general formula C_nH_{2n} (unsaturated compounds).
- Alkenes are also called as Olefins.
- Includes many naturally occurring materials.
- Flavors, fragrances, vitamins.



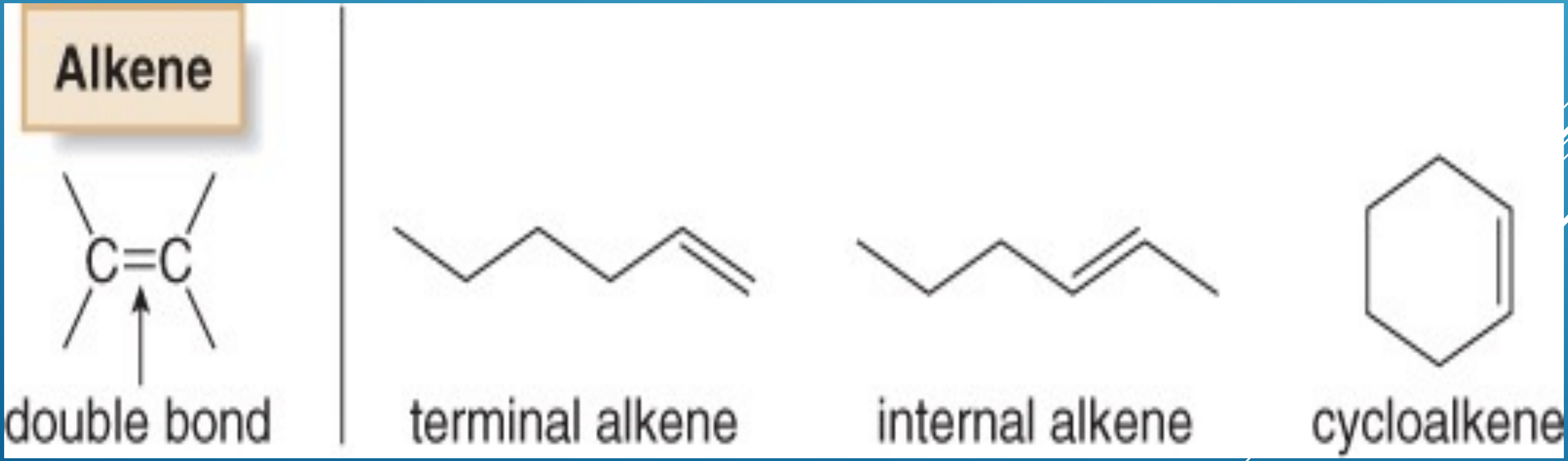
Ethylene

α-Pinene

β-Carotene
(orange pigment and vitamin A precursor)

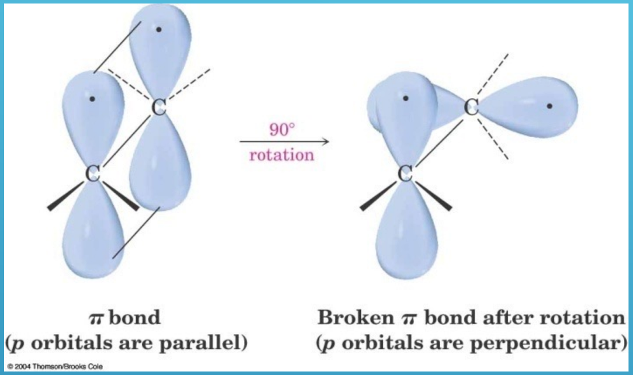
INTRODUCTION—STRUCTURE AND BONDING

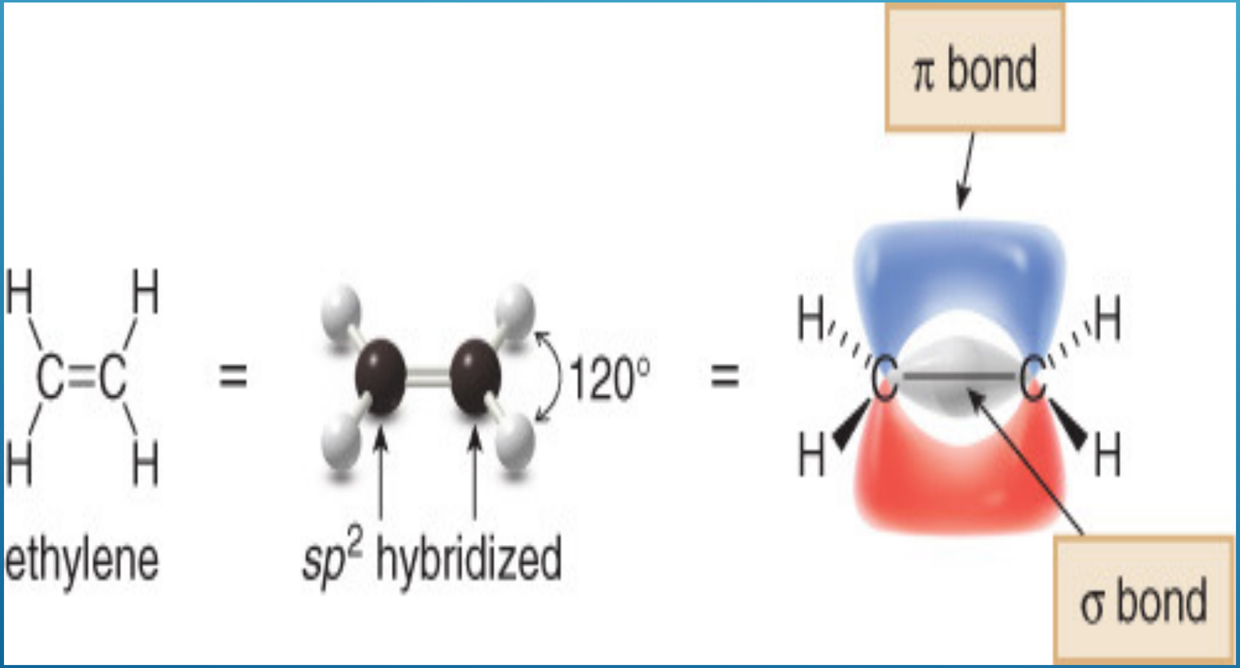
- Terminal alkenes have the double bond at the end of the carbon chain.
- Internal alkenes have at least one carbon atom bonded to each end of the double bond.
- Cycloalkenes contain a double bond in a ring.



STRUCTURE AND BONDING

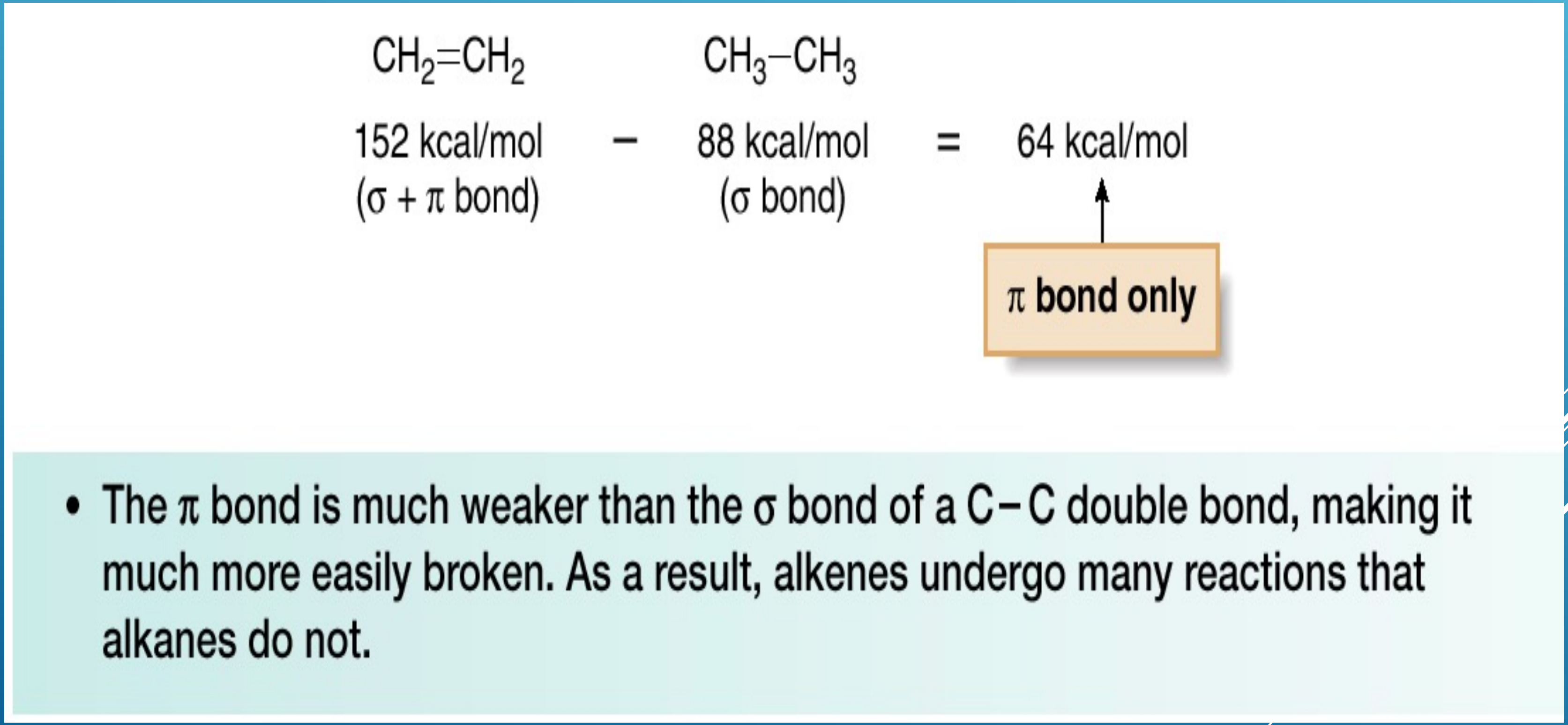
- Recall that the double bond consists of a σ bond and a π bond.
- Each carbon is sp^2 hybridized and trigonal planar, with bond angles of approximately 120°.





STRUCTURE AND BONDING

Bond dissociation energies of the C—C bonds in ethane (a σ bond only) and ethylene (one σ and one π bond) can be used to estimate the strength of the component of the double bond.



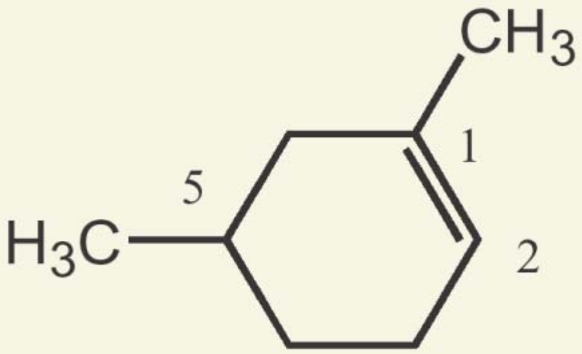
$CH_2{=}CH_2$		$CH_3{-}CH_3$		
152 kcal/mol (σ + π bond)	−	88 kcal/mol (σ bond)	=	64 kcal/mol

π bond only

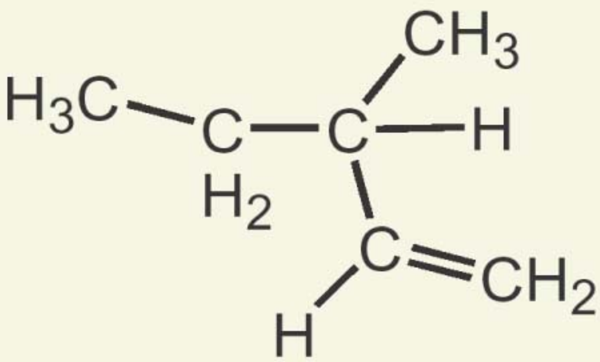
- The π bond is much weaker than the σ bond of a C−C double bond, making it much more easily broken. As a result, alkenes undergo many reactions that alkanes do not.

NOMENCLATURE OF ALKENES

- Find longest continuous carbon chain for root.
- Use the suffix - en- to show the presence of a C-C double bond.
- Number carbons in chain so that double bond carbons have lowest possible numbers.
- Rings have “cyclo” prefix - the double bond must be numbered 1,2.

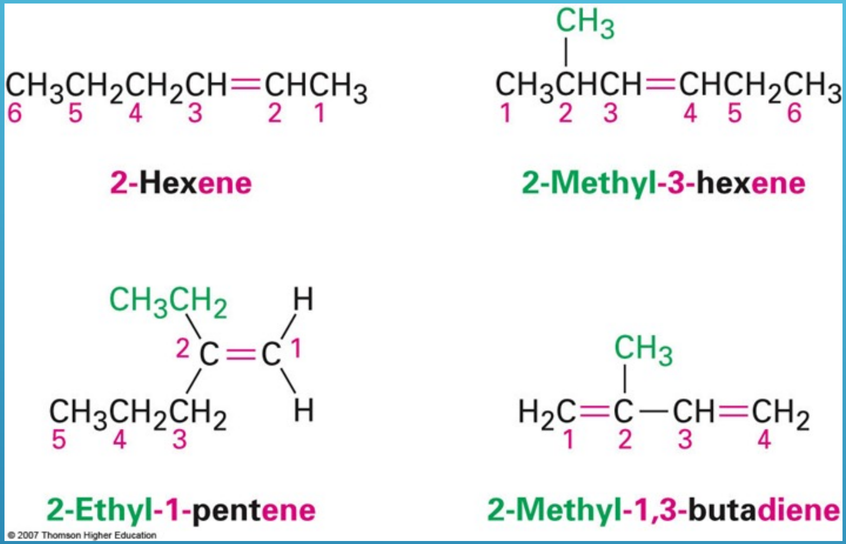


1,5-Dimethyl-cyclohexene



3-Methyl-1-pentene

EXAMPLES

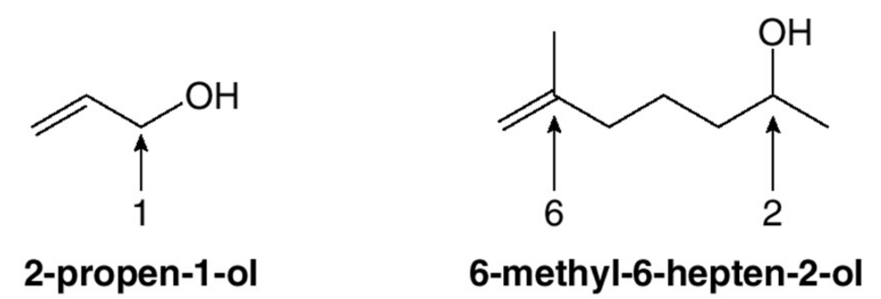


2-Hexene

2-Methyl-3-hexene

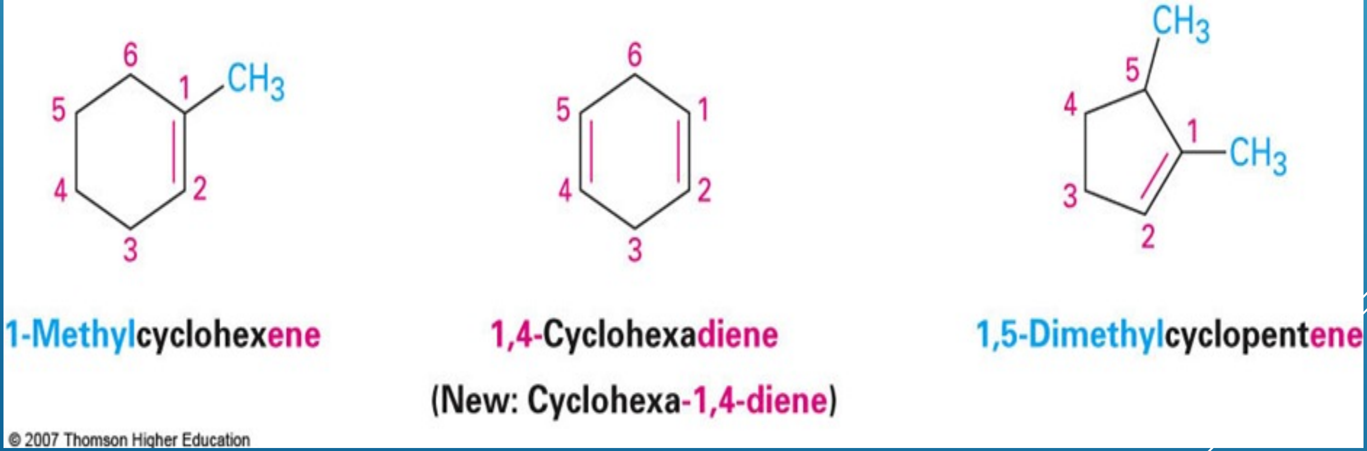
2-Ethyl-1-pentene

2-Methyl-1,3-butadiene



2-propen-1-ol

6-methyl-6-hepten-2-ol



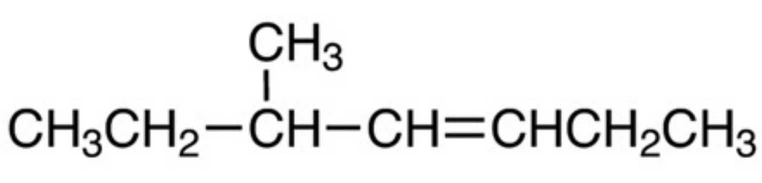
1-Methylcyclohexene

1,4-Cyclohexadiene

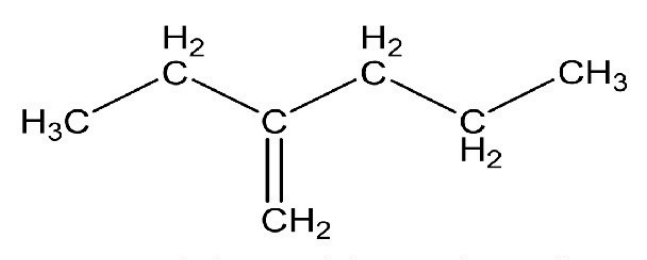
(New: Cyclohexa-1,4-diene)

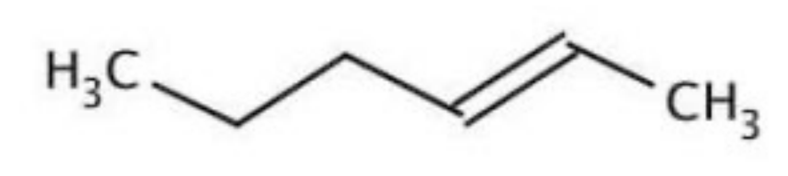
1,5-Dimethylcyclopentene

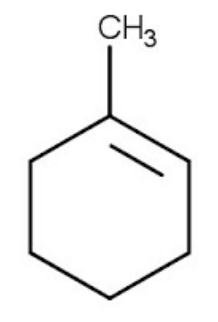
$CH_3CH_2CH_2CH{=}CHCH_3$

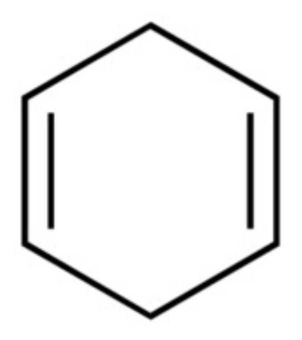


$CH_3CH_2-\overset{\overset{CH_3}{|}}{CH}-CH{=}CHCH_2CH_3$

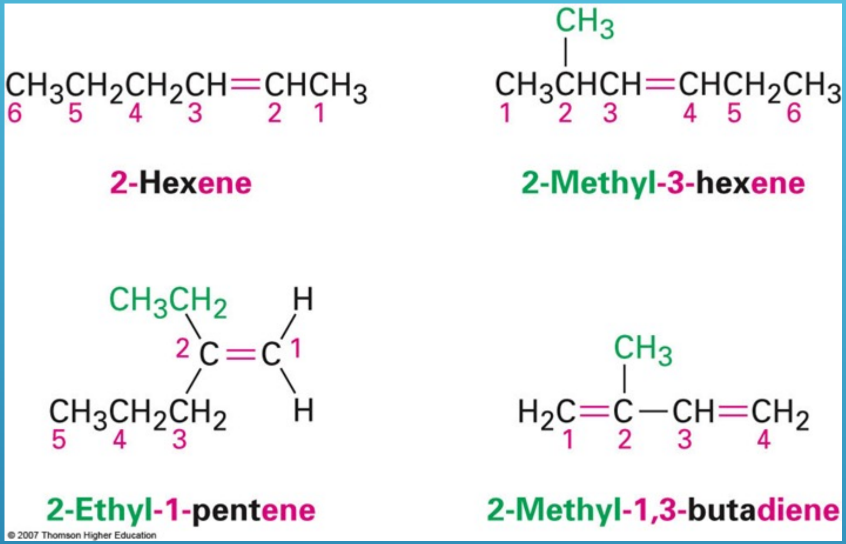








EXAMPLES

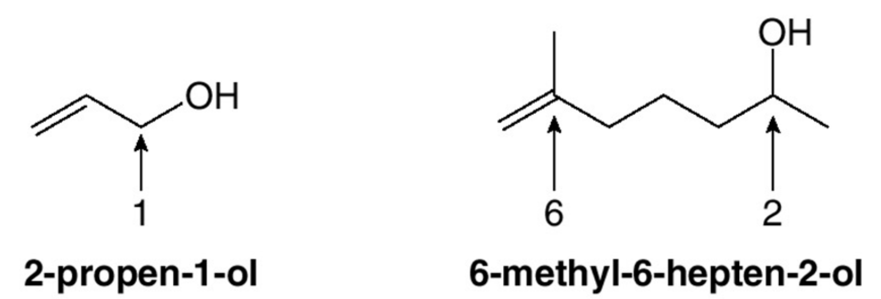


2-Hexene

2-Methyl-3-hexene

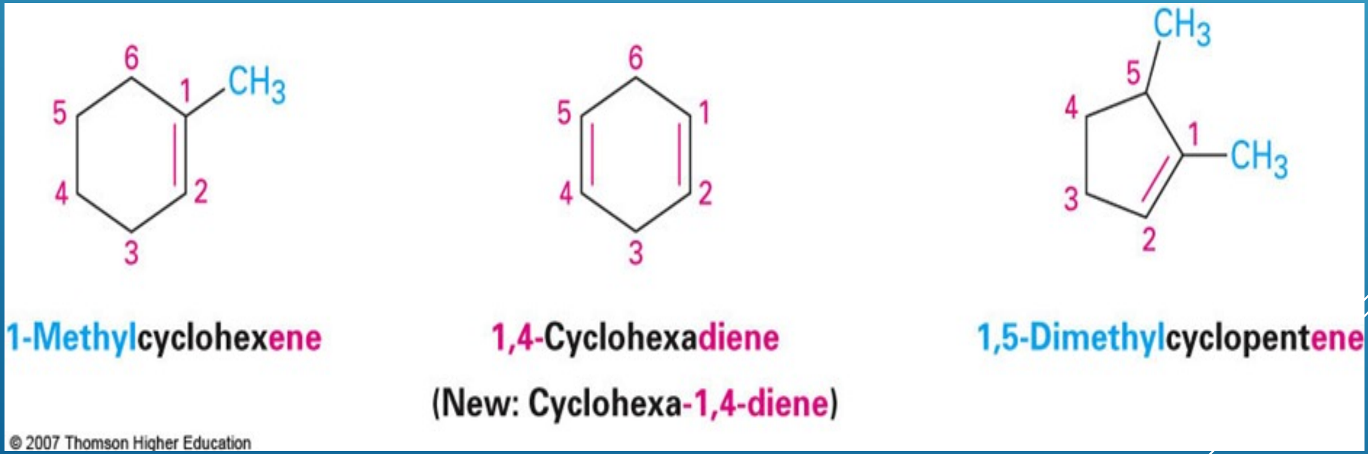
2-Ethyl-1-pentene

2-Methyl-1,3-butadiene



2-propen-1-ol

6-methyl-6-hepten-2-ol



1-Methylcyclohexene

1,4-Cyclohexadiene

(New: Cyclohexa-1,4-diene)

1,5-Dimethylcyclopentene

COMMON NAMES OF ALKENES

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

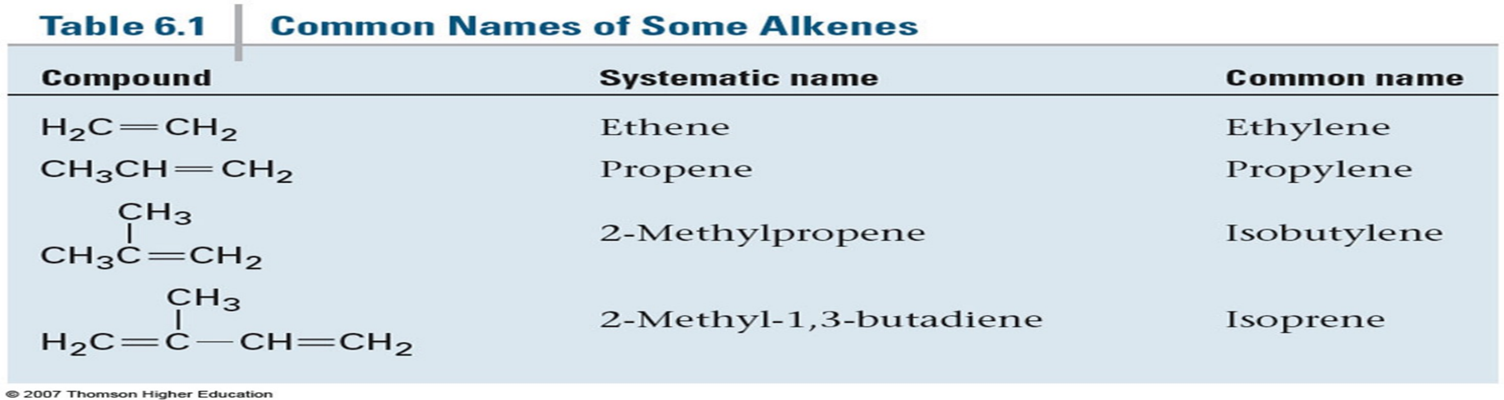
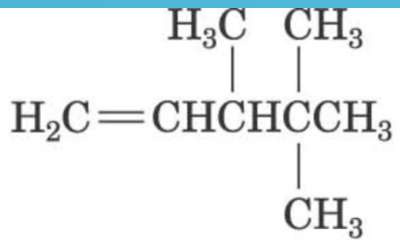


Table 6.1 **Common Names of Some Alkenes**

Compound	Systematic name	Common name
$H_2C{=}CH_2$	Ethene	Ethylene
$CH_3CH{=}CH_2$	Propene	Propylene
$CH_3\overset{CH_3}{\overset{\vert}{C}}{=}CH_2$	2-Methylpropene	Isobutylene
$H_2C{=}\overset{CH_3}{\overset{\vert}{C}}{-}CH{=}CH_2$	2-Methyl-1,3-butadiene	Isoprene

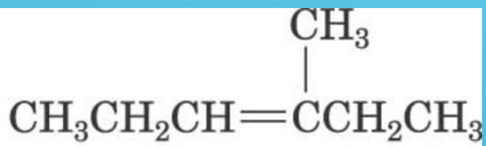
GIVE THE IUPAC NAMES OF THE FOLLOWING:

(a)



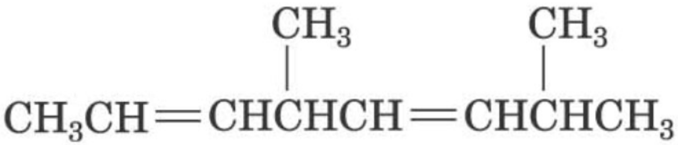
$H_2C{=}CH\overset{\displaystyle H_3C}{\overset{|}{C}}H\overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle CH_3}{|}}{C}}}CH_3$

(b)



$CH_3CH_2CH{=}\overset{\displaystyle CH_3}{\overset{|}{C}}CH_2CH_3$

(c)



$CH_3CH{=}CH\overset{\displaystyle CH_3}{\overset{|}{C}}HCH{=}CH\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_3$

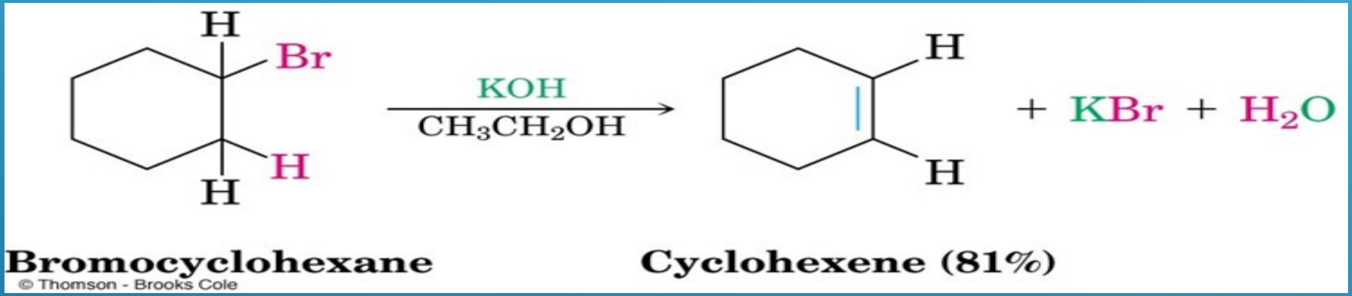
DRAW STRUCTURES CORRESPONDING TO THE FOLLOWING IUPAC NAMES:

- 2-Methyl-1,5-hexadiene
- 3-Ethyl-2,2-dimethyl-3-heptene
- 2,3,3-Trimethyl-1,4,6-octatriene
- 3,4-Diisopropyl-2,5-dimethyl-3-hexene
- 4-tert-Butyl-2-methylheptane

PREPARATION OF ALKENES

- The preparation of alkenes involves elimination reaction.
- Alkenes are commonly made by

1. Elimination of HX from alkyl halide (dehydrohalogenation)
2. Uses heat and alc.KOH.
3. elimination of H-OH from an alcohol (dehydration) require strong acids (sulfuric acid, 50 ºC).



Bromocyclohexane

Cyclohexene (81%)

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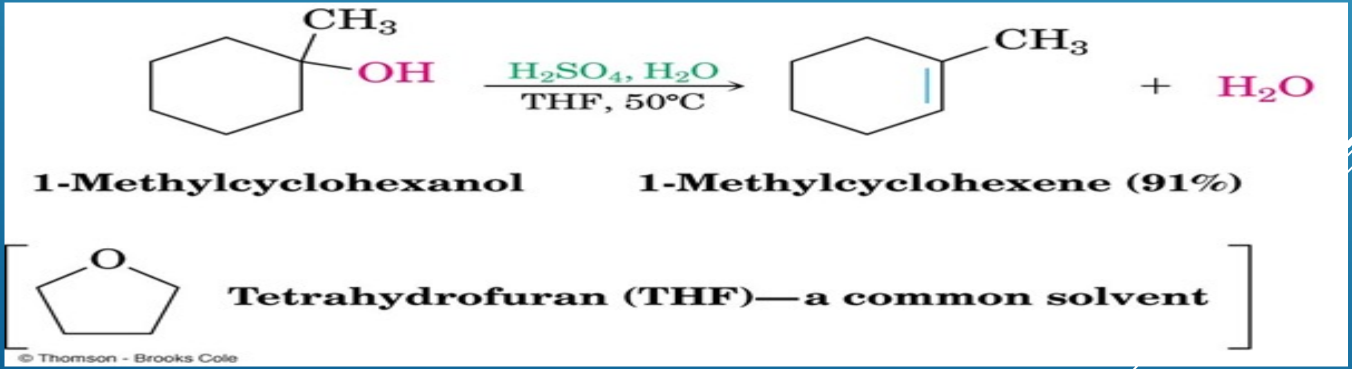

1-Methylcyclohexanol

1-Methylcyclohexene (91%)

Tetrahydrofuran (THF)—a common solvent

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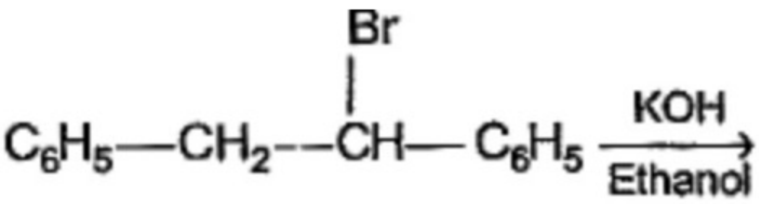
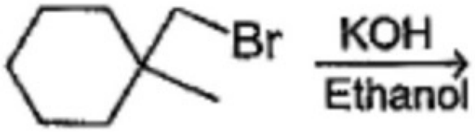
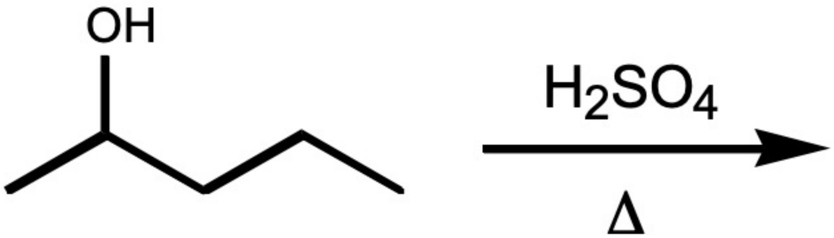
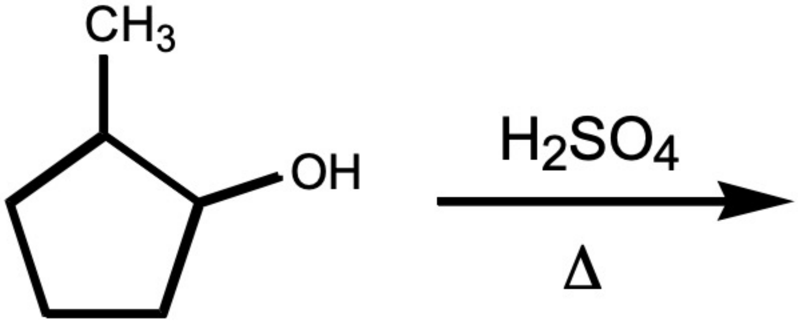
$$C_6H_5-CH_2-CH_2-CH_2-Br \xrightarrow[\text{Ethanol}]{\text{KOH}}$$



$$C_6H_5-CH_2-\overset{\overset{\displaystyle Br}{|}}{C}H-C_6H_5 \xrightarrow[\text{Ethanol}]{\text{KOH}}$$

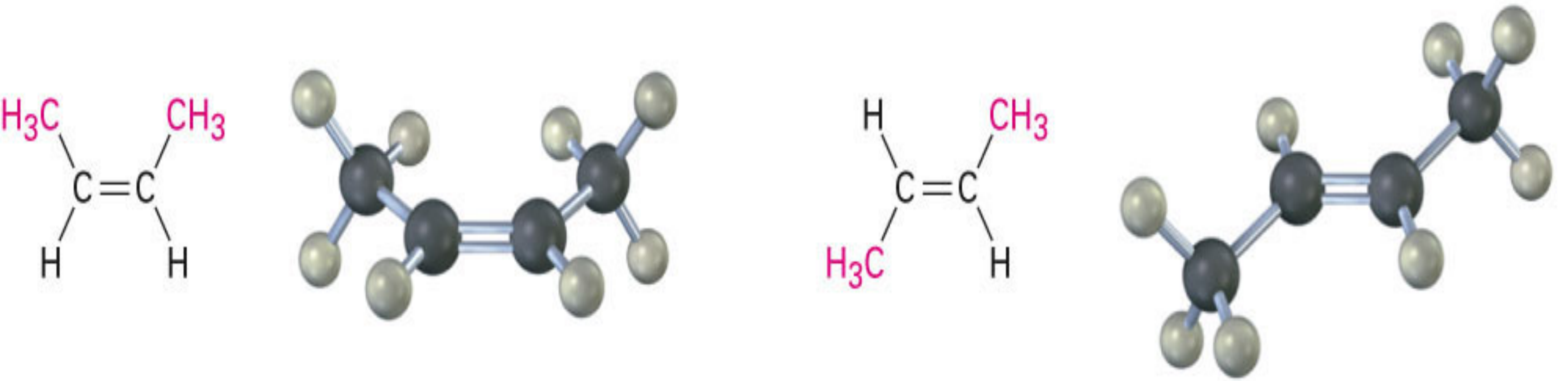






CIS-TRANS ISOMERS

- Because of restricted rotation about a C-C double bond, groups on adjacent carbons are either *cis* or *trans* to each other.
- cis isomer - two similar groups on same side of the double bond.
- trans isomer - similar groups on opposite sides .
- Each carbon must have two different groups for these isomers to occur.

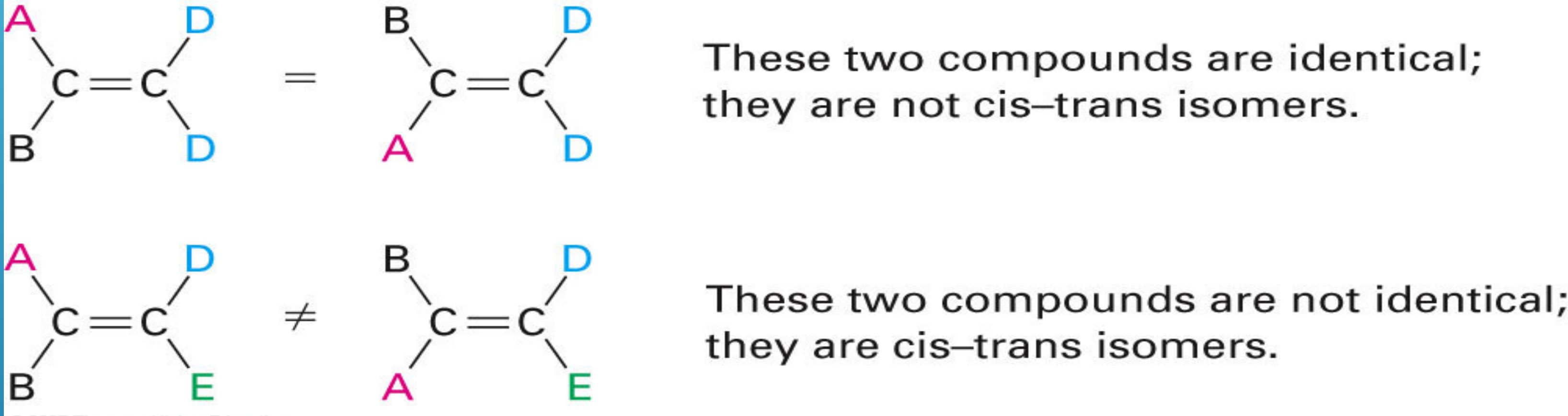


cis-2-Butene

trans-2-Butene

CIS-TRANS ISOMERS

- The cis-trans system: configuration is determined by the orientation of atoms of the main chain.
- Cis-trans isomers require that end groups must differ in pairs.



These two compounds are identical; they are not cis–trans isomers.

These two compounds are not identical; they are cis–trans isomers.

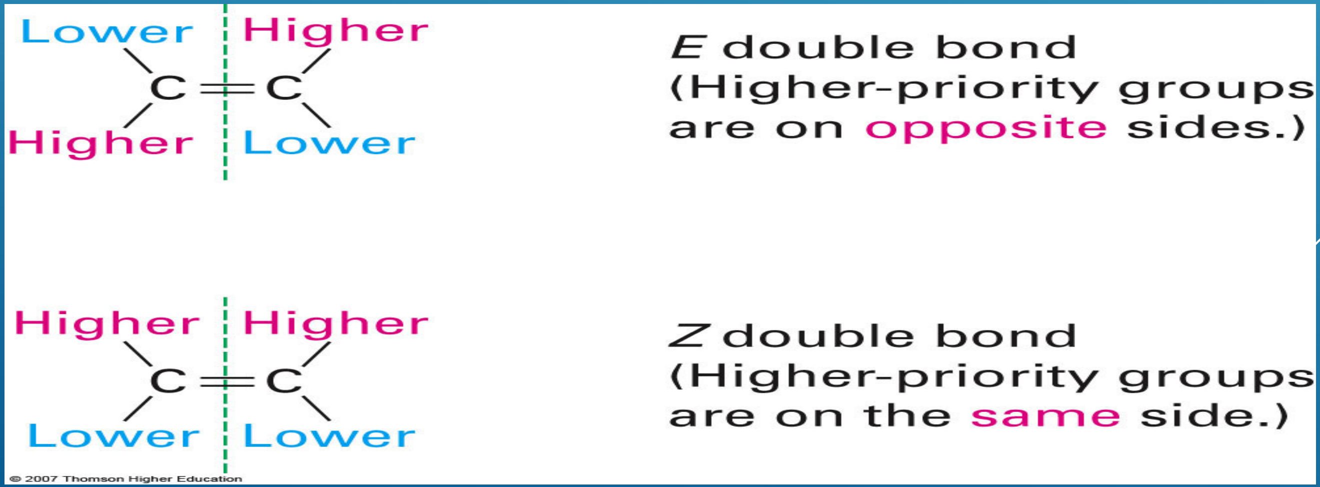
1.Which of the following can exist as cis–trans isomers?

$CH_3CH=CH_2$

$CH_3CH_2CH=CHCH_3$

SEQUENCE RULES: THE *E,Z* DESIGNATION

- Cis, trans nomenclature only works for disubstituted double bonds.
- E/Z Nomenclature for 3 or 4 substituents.
- Priority rules of Cahn, Ingold, and Prelog.
- Compare where higher priority groups are with respect to bond and designate as prefix.
- E -entgegen, opposite sides.
- Z - zusammen, together on the same side.



E double bond
(Higher-priority groups are on opposite sides.)

Z double bond
(Higher-priority groups are on the same side.)

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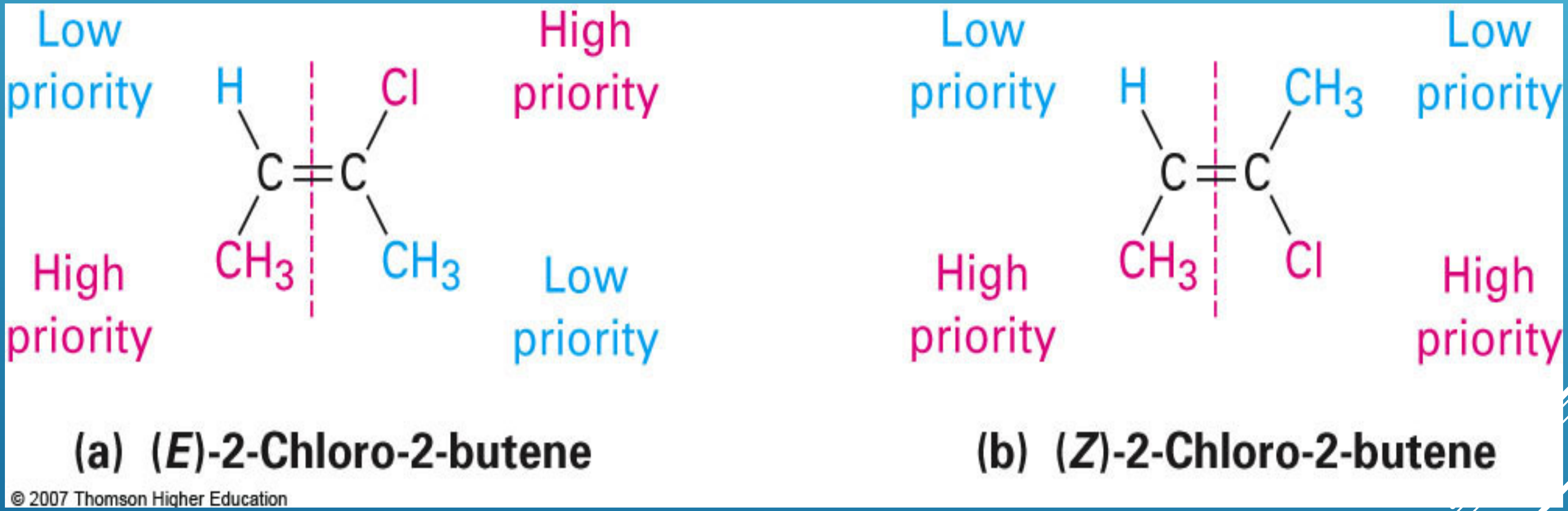
RANKING PRIORITIES: CAHN-INGOLD-PRELOG RULES

- Must rank atoms that are connected at comparison point.
- Higher atomic number gets higher priority.
- Br > Cl > S > P > O > N > C > H

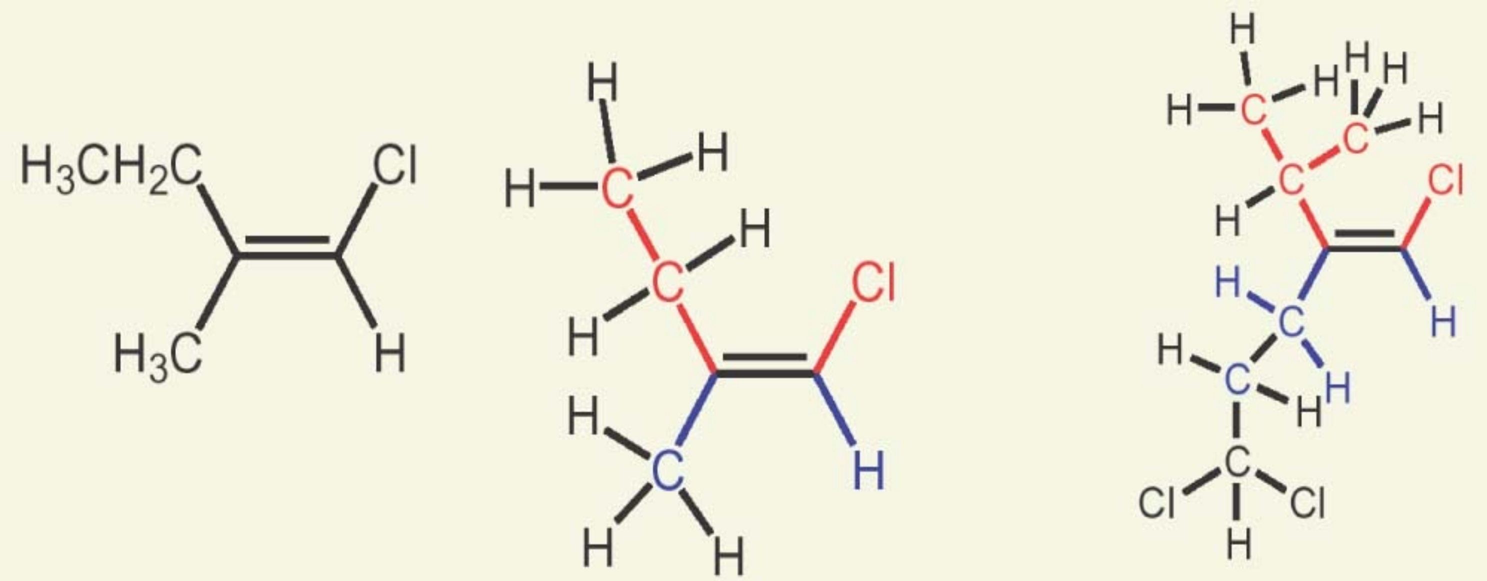


(a) (*E*)-2-Chloro-2-butene

(b) (*Z*)-2-Chloro-2-butene

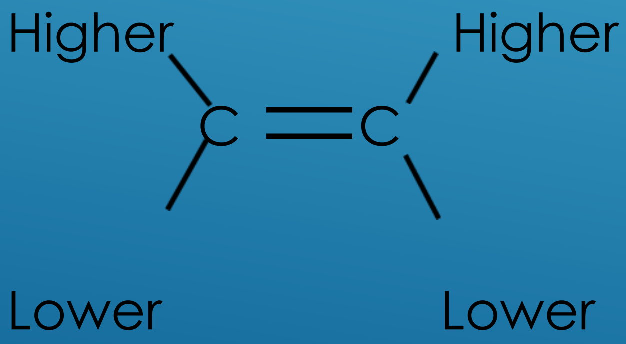
COMPARISON

- If atomic numbers are the same, compare at next connection point at same distance.
- Compare until something has higher atomic number.
- Do not combine – always compare.

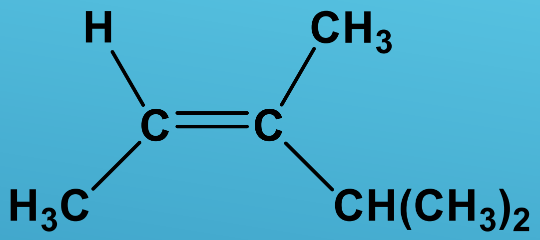


E,Z CONFIGURATION

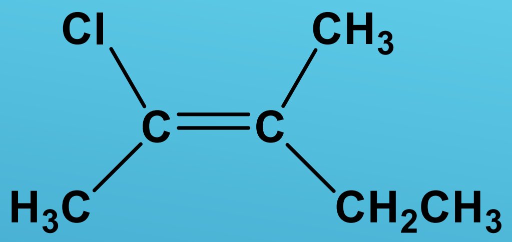
- The E,Z uses priority rules:
- If groups of higher priority are on the same side, configuration is Z (German, zusammen).
- If groups of higher priority are on opposite sides, configuration is E (German, entgegen).



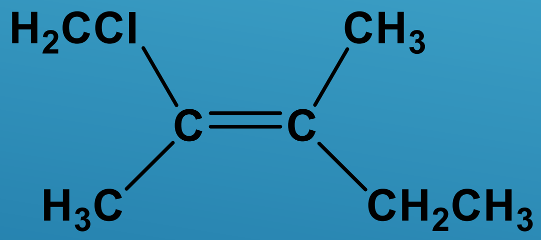
EXAMPLES



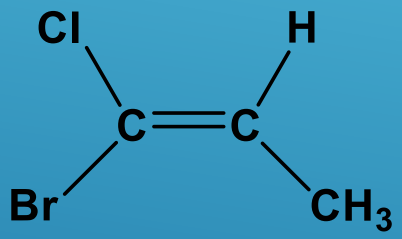
(Z)-4,5-dimethyl hexene



(E)-4-chloro-2- pentene

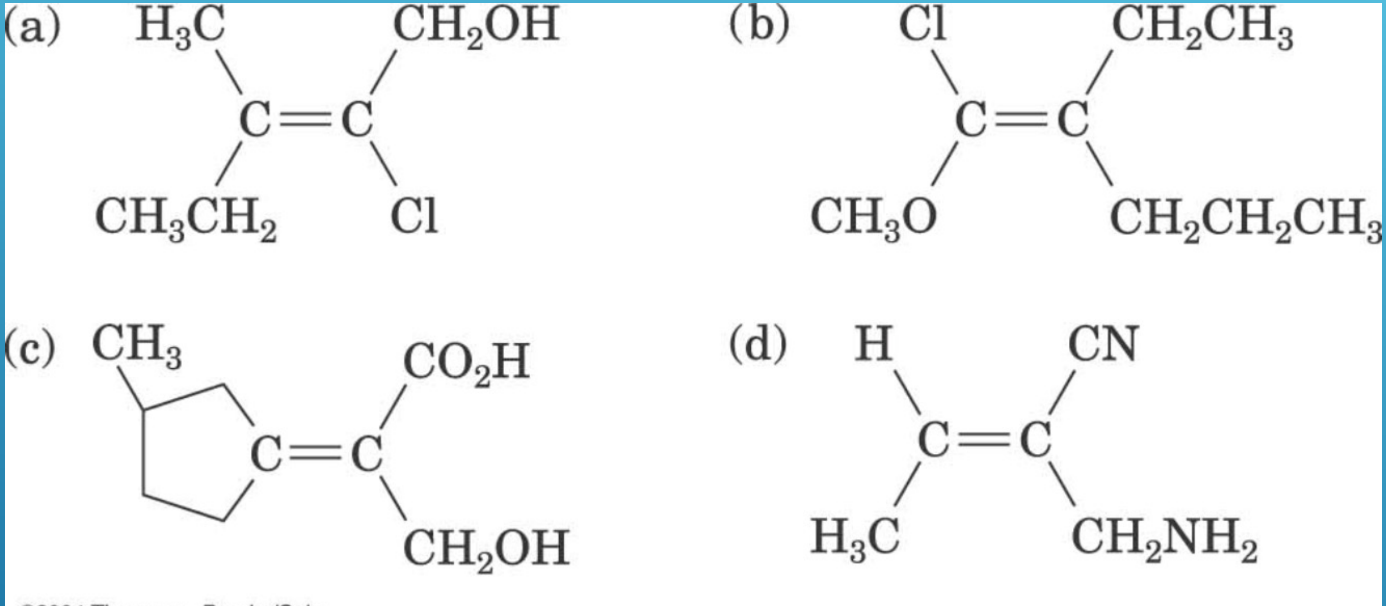


(E)-1-chloro-2,3-dimethyl-2-pentene



(Z)-1-chloro-1-bromo-1-propene

ASSIGN E OR Z CONFIGURATION TO THE FOLLOWING ALKENES:



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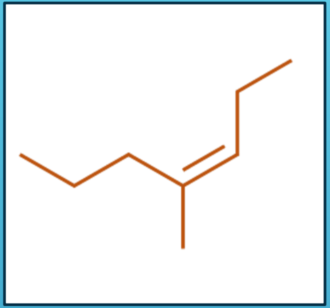
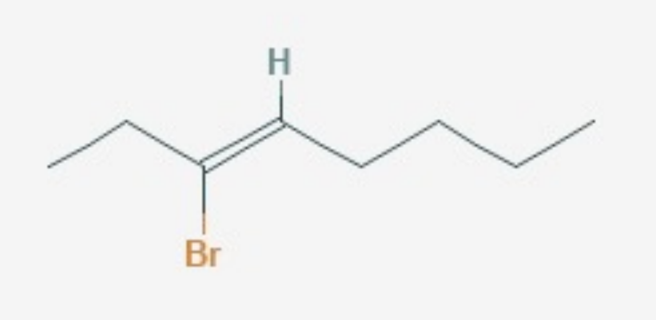


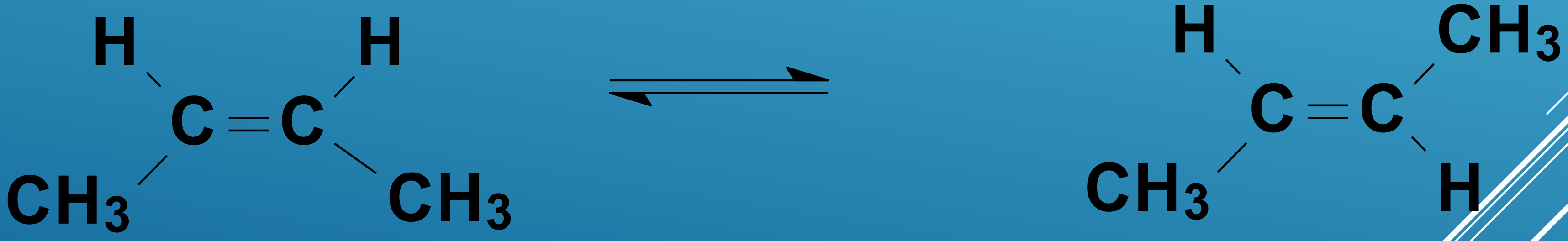

H
Br

STABILITY OF ALKENES

- Cis alkenes are less stable than trans alkenes.
- This is due to steric (spatial) strain between the two bulky substituents on the same side of the double bond.
- Less stable isomer is higher in energy.

Order of stability:

tetrasubstituted > trisubstituted > disubstituted > monosusbtituted.

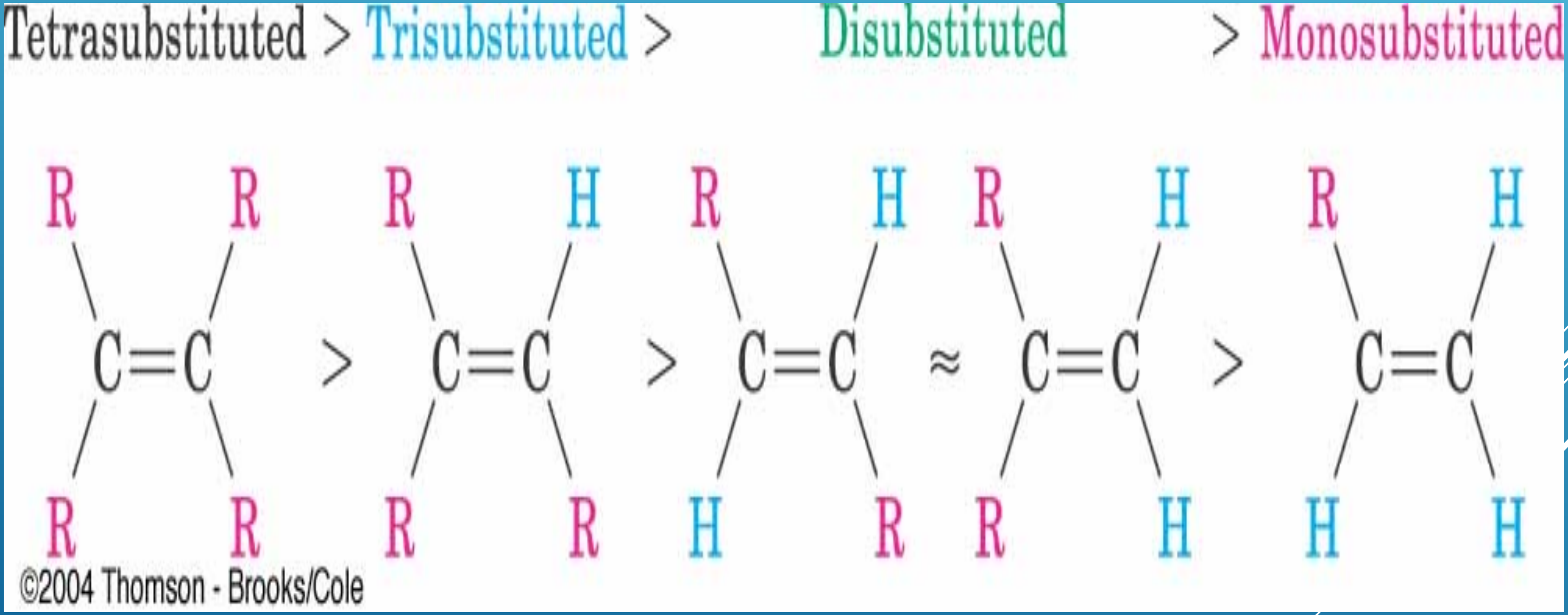


Cis 24%

Trans 76%

AS A GENERAL RULE, ALKENES FOLLOW THE STABILITY ORDER:

- This order of stability is due to:
- hyper conjugation.
- bond strength.



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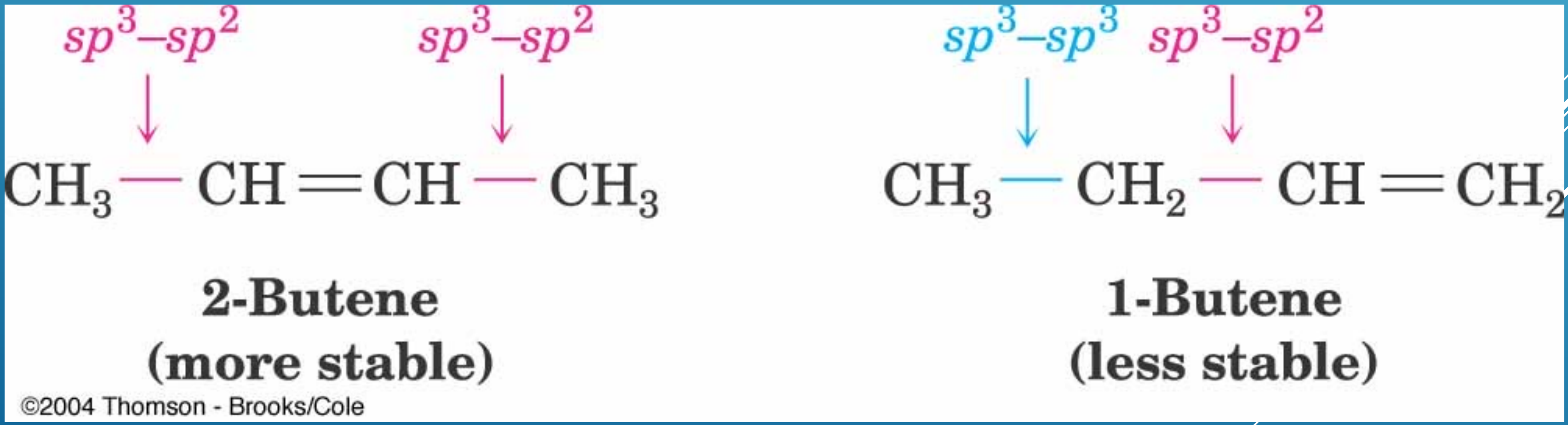
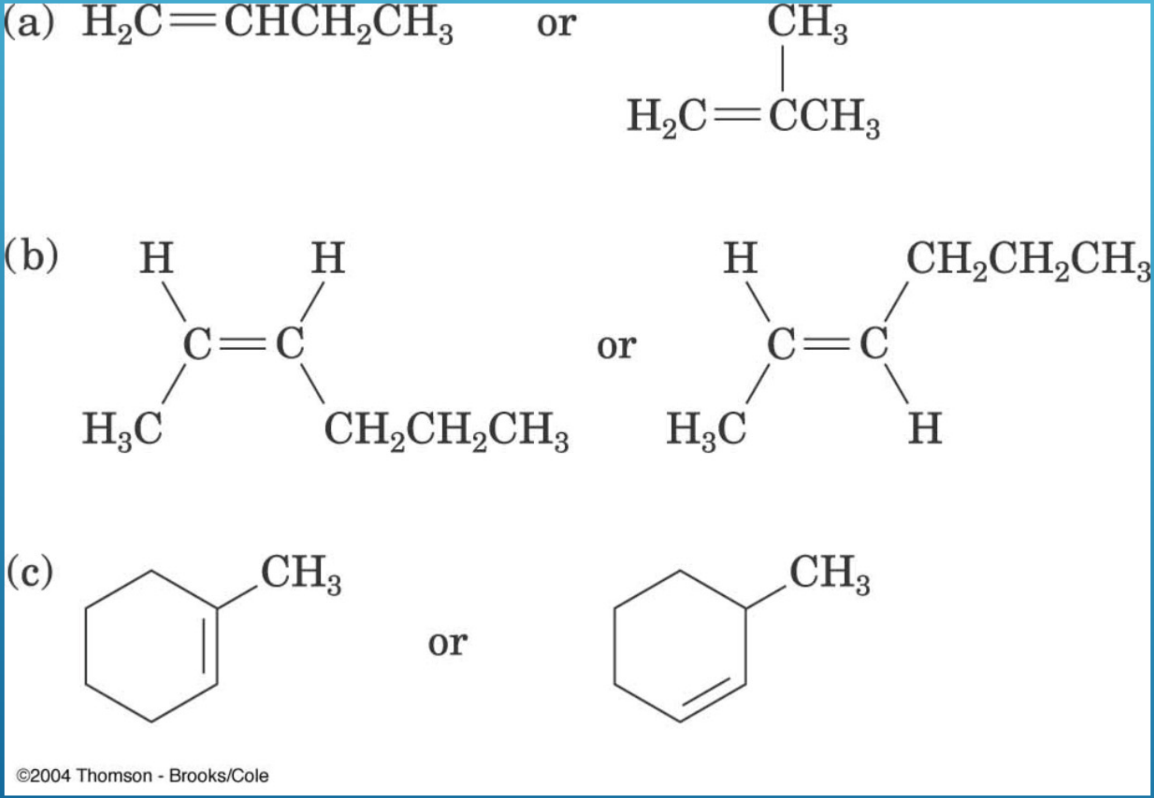
BOND STRENGTH

- Bond strength can also explain the order of stability.
- sp^3–sp^2 bond is slightly stronger than sp^3–sp^3.
- More highly substituted alkenes always have a higher ratio of sp^2-sp^3 bonds to sp^3-sp^3 bonds than less highly substituted alkenes and thus are more stable.



WHICH COMPOUND IN EACH OF THE FOLLOWING PAIRS IS MORE STABLE?



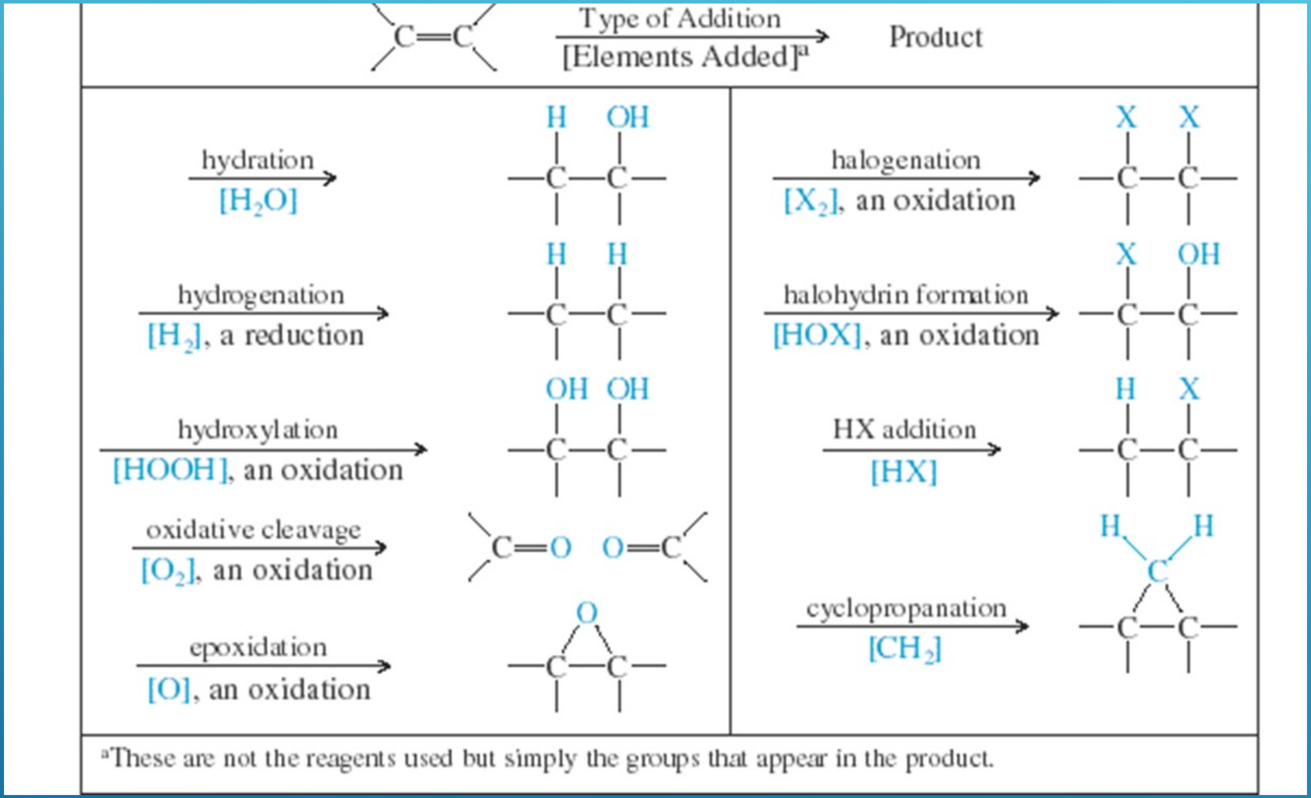
REACTIVITY OF ALKENES

- The pi bond of an alkene is weak an hence loosely held.
- The electrophiles attract to the pi electrons.
- A carbocation reaction intermediate is formed.
- Then the nucleophile adds to the carbocation.
- Therefore, alkenes undergo electrophilic addition reactions and the double bond breaks to form a single bond.
- Alkenes undergo different types of addition reactions to form different products.

Note: Electrophile: Electron-poor. Eg: NO_2^+, Br^+, NH_4^+.

Nucleophile: Electron-rich. Eg: CN^-, Cl^-,OH^-.

TYPES OF ADDITION REACTIONS



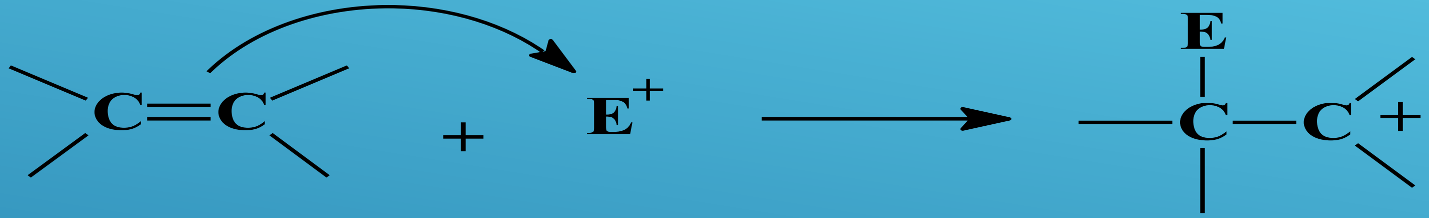
Type of Addition	[Elements Added][a]
hydration	[H_2O]
hydrogenation	[H_2], a reduction
hydroxylation	[HOOH], an oxidation
oxidative cleavage	[O_2], an oxidation
epoxidation	[O], an oxidation
halogenation	[X_2], an oxidation
halohydrin formation	[HOX], an oxidation
HX addition	[HX]
cyclopropanation	[CH_2]

Product

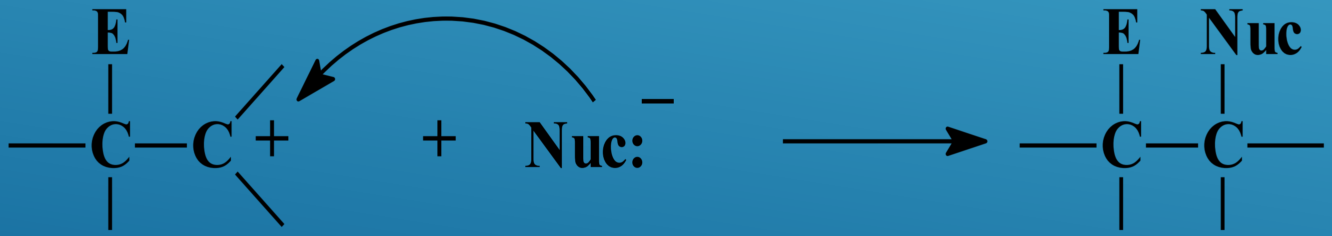
[a] These are not the reagents used but simply the groups that appear in the product.

ELECTROPHILLIC ADDITION

Step 1: Pi (π) electrons attack the electrophile



Step 2: Nucleophile attacks the carbocation.



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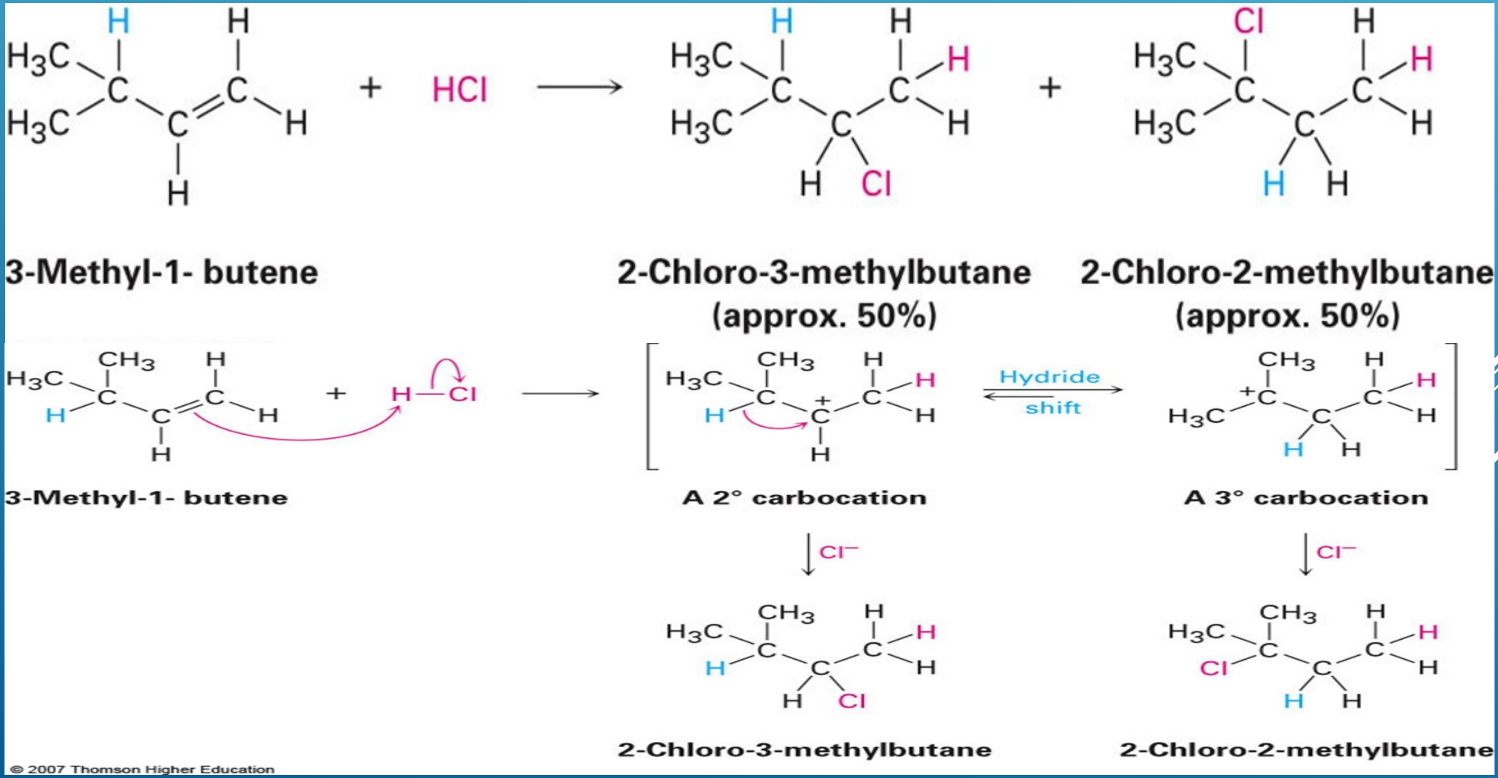
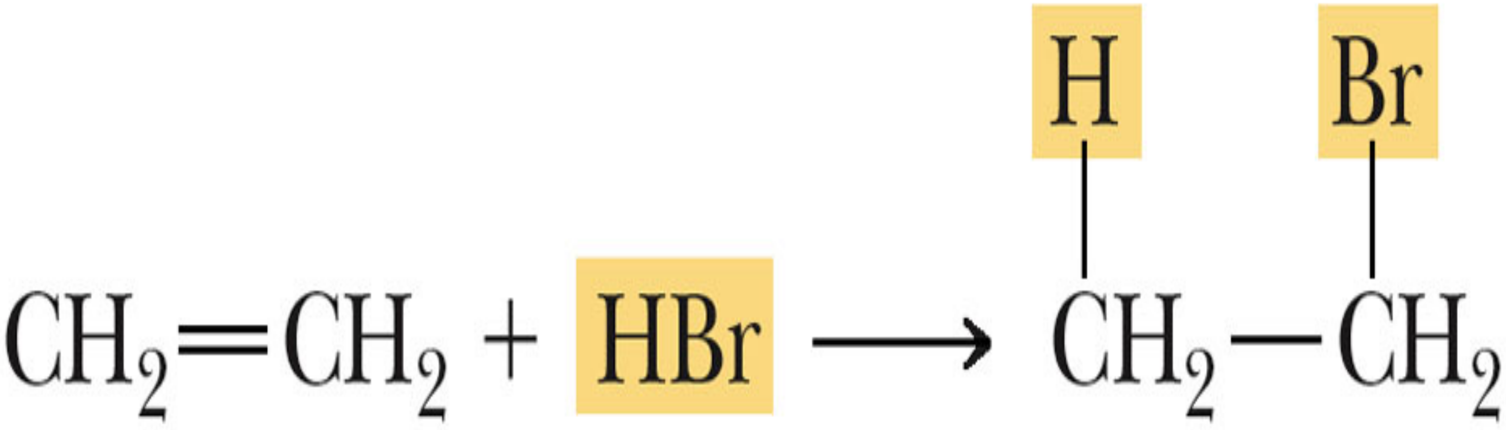
MECHANISM OF ELECTROPHILIC ADDITION:

- Attack on electrophile (such as HBr) by a π bond of alkene (nucleophile)
- This produces carbocation and bromide ion
- Carbocation is an electrophile, reacting with nucleophilic bromide ion.



ELECTROPHILIC ADDITION OF HX TO ETHENE

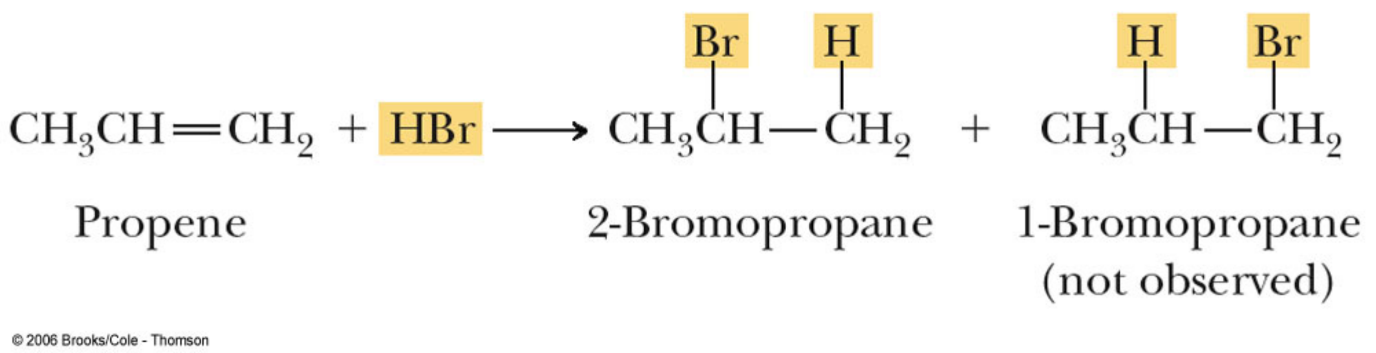


$$CH_2{=}CH_2 + HBr \longrightarrow \overset{H}{CH_2}{-}\overset{Br}{CH_2}$$

Ethylene

Bromoethane
(Ethyl bromide)

REGIOSELECTIVITY (ORIENTATION)



$$\mathrm{CH_3CH{=}CH_2} + \mathrm{HBr} \longrightarrow \mathrm{CH_3}\overset{\mathrm{Br}}{\overset{|}{\mathrm{C}}}\mathrm{H}-\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}\mathrm{H_2} + \mathrm{CH_3}\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}\mathrm{H}-\overset{\mathrm{Br}}{\overset{|}{\mathrm{C}}}\mathrm{H_2}$$

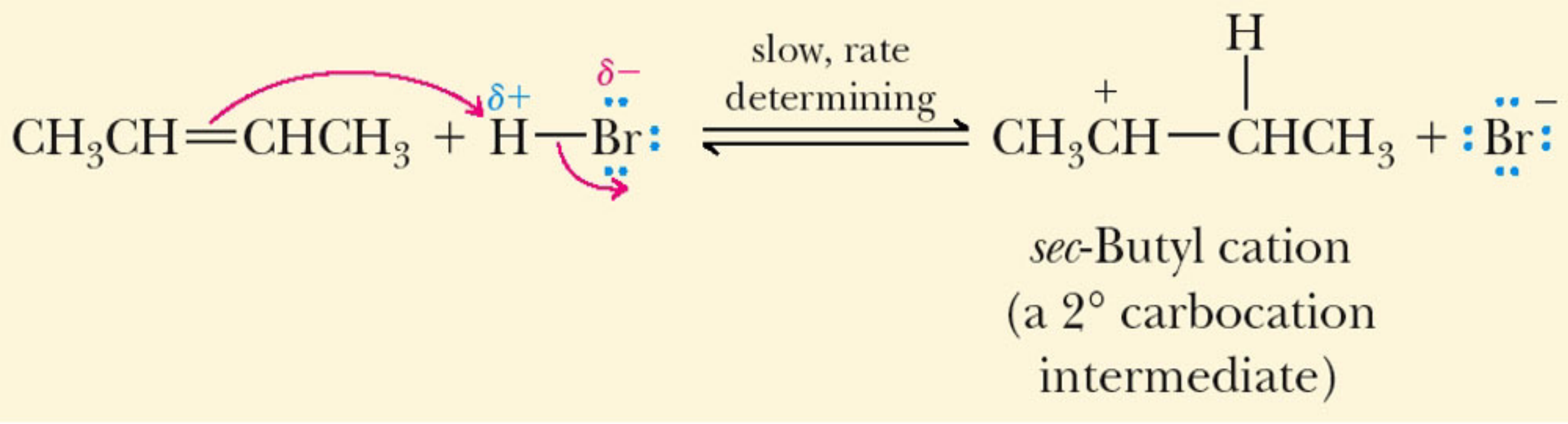
Propene

2-Bromopropane

1-Bromopropane
(not observed)

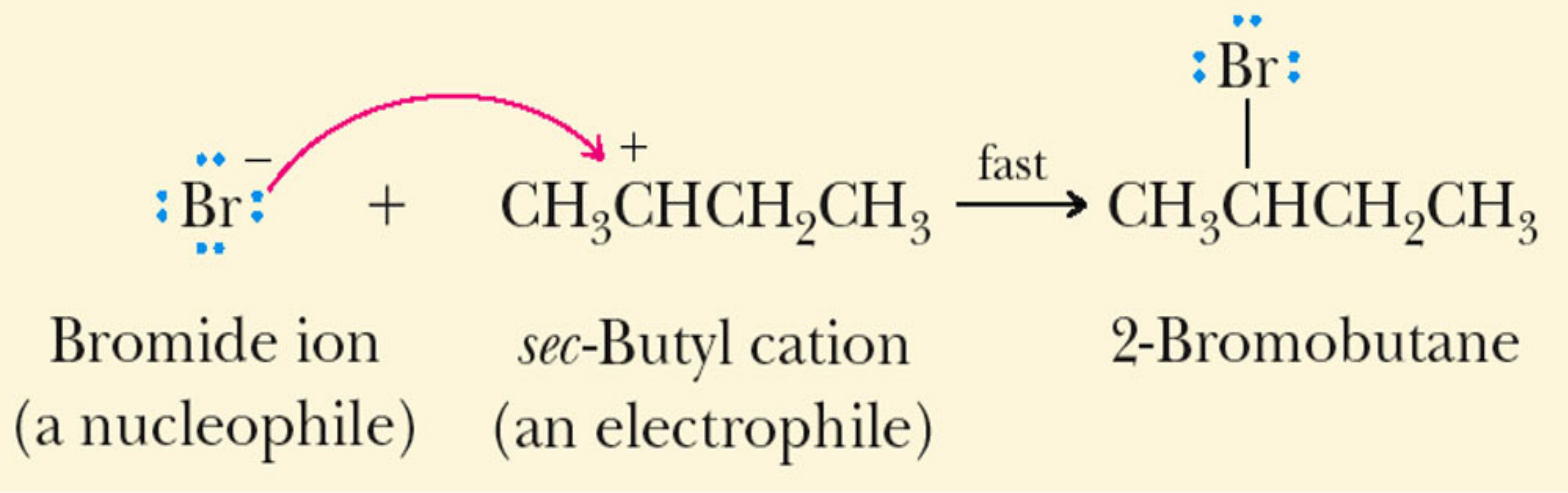
The incoming hydrogen attaches to the carbon with the greater number of hydrogen's. This is **regioselectivity**. It is called **Markovnikov** orientation.

MECHANISM:



$$CH_3CH{=}CHCH_3 + \overset{\delta+}{H}-\overset{\delta-}{\ddot{Br}}: \xrightleftharpoons{\text{slow, rate determining}} CH_3\overset{+}{C}H-\overset{\overset{H}{|}}{C}HCH_3 + :\ddot{Br}:^-$$

sec-Butyl cation
(a 2° carbocation
intermediate)



$$:\ddot{Br}:^- + CH_3\overset{+}{C}HCH_2CH_3 \xrightarrow{\text{fast}} CH_3\overset{\overset{:\ddot{Br}:}{|}}{C}HCH_2CH_3$$

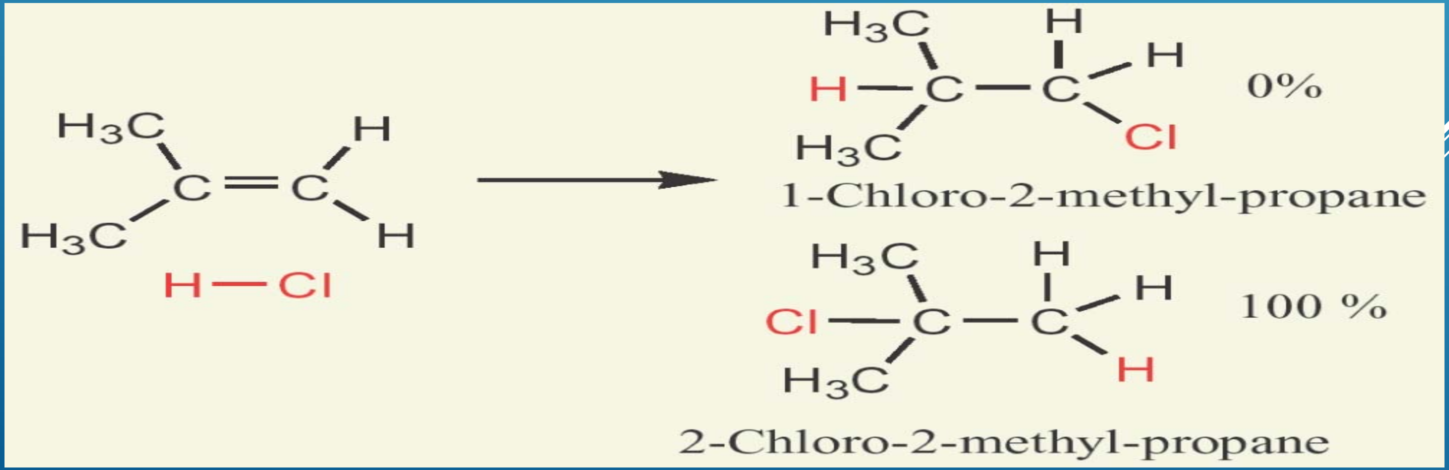
Bromide ion
(a nucleophile)

sec-Butyl cation
(an electrophile)

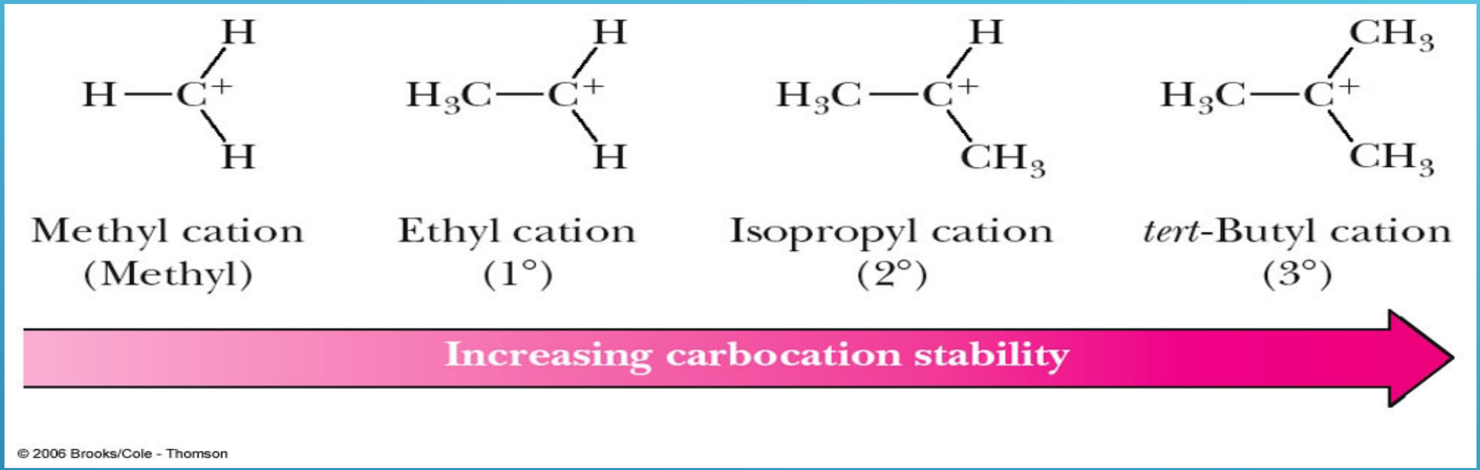
2-Bromobutane

MARKOVNIKOV'S RULE:

- In an unsymmetrical alkene, HX reagents can add in two different ways, but one way may be preferred over the other.
- If one orientation predominates, the reaction is **regiospecific.**
- Markovnikov observed in the 19th century that in the addition of HX to alkene, the H attaches to the carbon with the most H's and X attaches to the other end (to the one with the most alkyl substituents).
  - This is **Markovnikov's rule.**



ENERGY OF CARBOCATION'S AND MARKOVNIKOV'S RULE:



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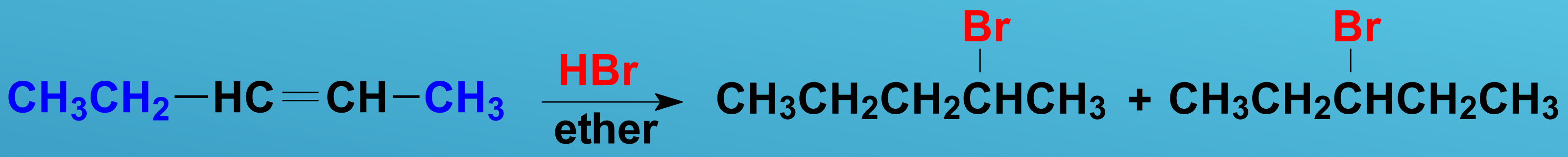
- More stable carbocation forms faster
- Tertiary cations and associated transition states are more stable than primary cations

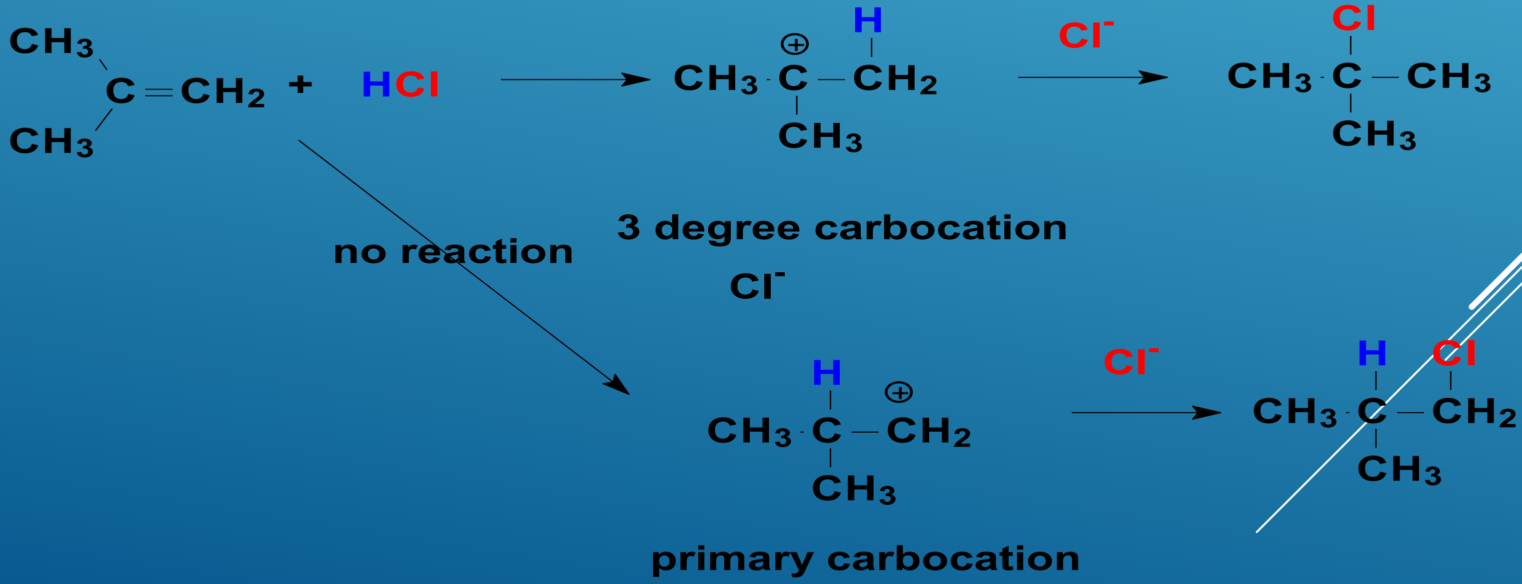
MARKOVNIKOV'S RULE

- When both ends of the double bond have the same degree of substitution, a mixture of products results.

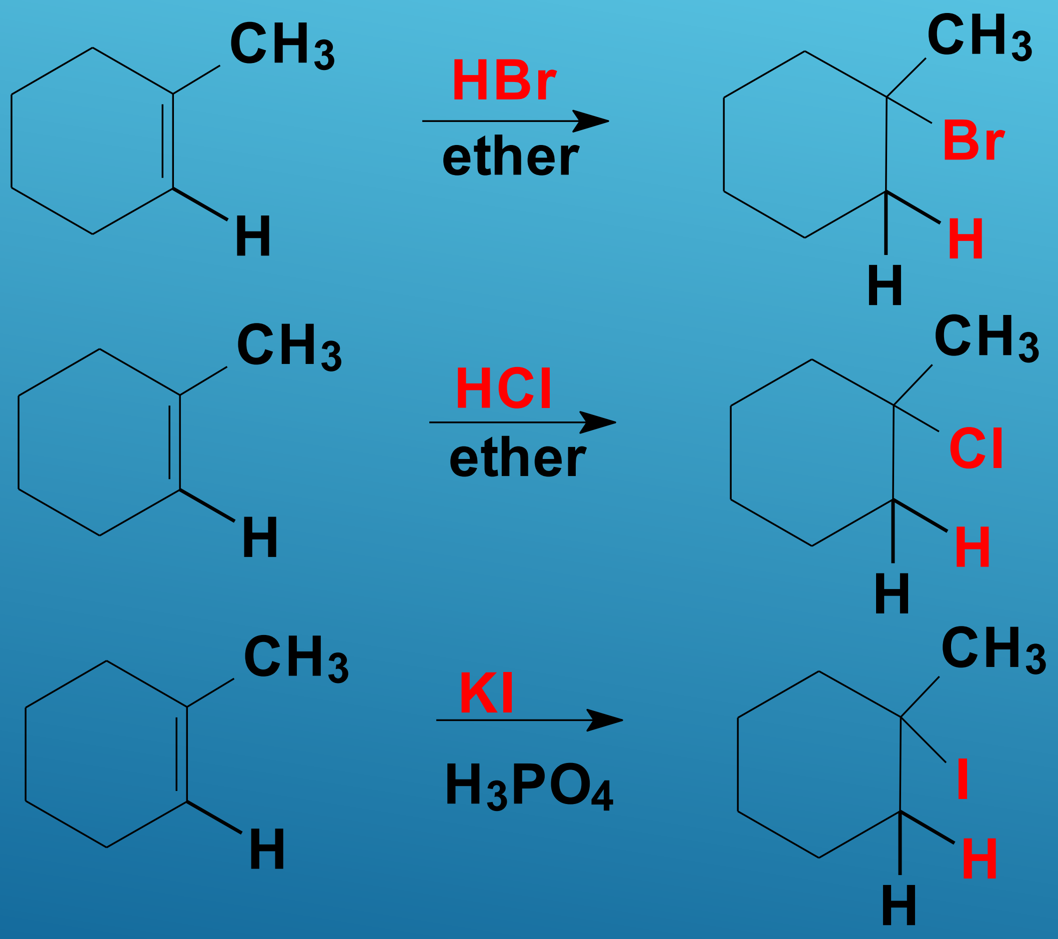


$$CH_3CH_2-HC=CH-CH_3 \xrightarrow[\text{ether}]{HBr} CH_3CH_2CH_2\overset{Br}{CH}CH_3 + CH_3CH_2\overset{Br}{CH}CH_2CH_3$$

- When the double bonds have differ by degree of substitution.



ADDITIONAL EXAMPLES



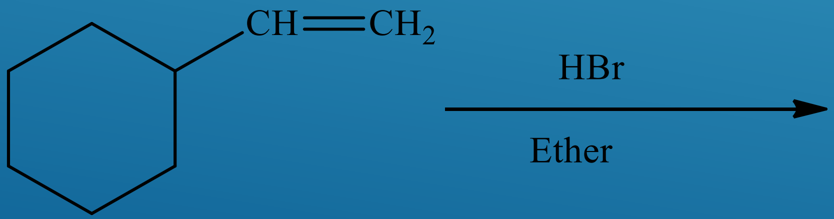
PRACTICE PROBLEMS

1. $(CH_3)_2C{=}CH_2 \xrightarrow{HBr}$

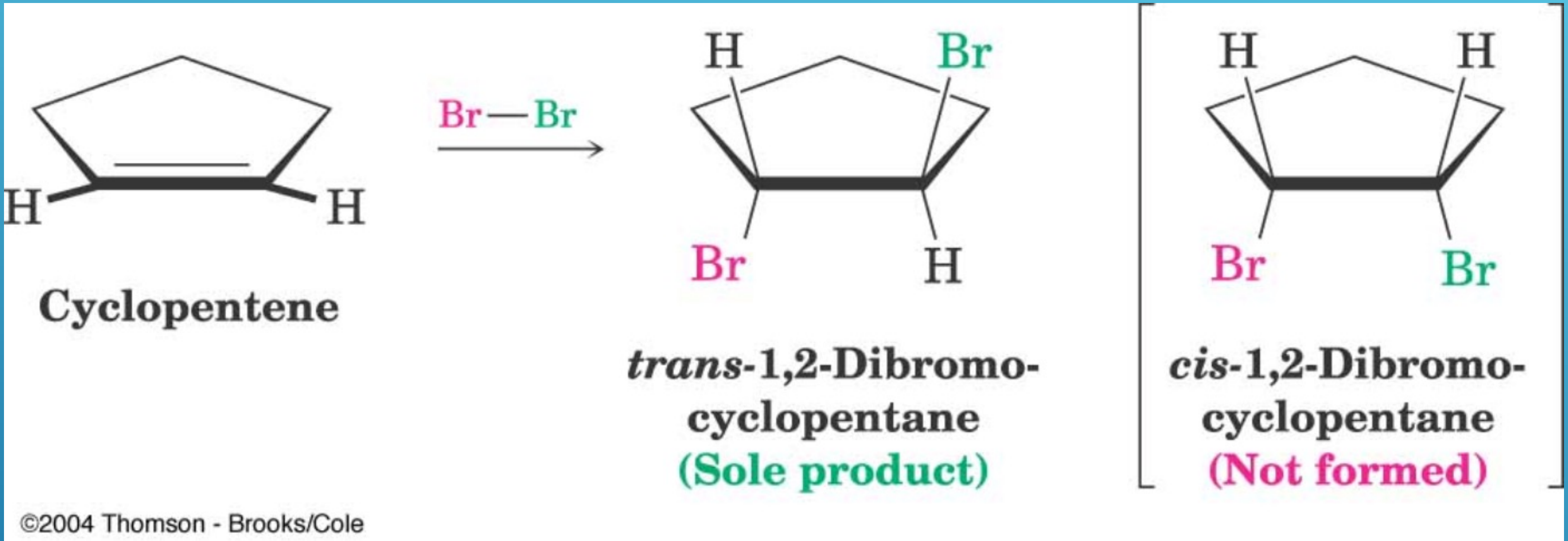
2. The reaction of pent-2-ene with HCl results in the formation of ______________ and ______________.

3. $CH_3CH_2CH_2CH{=}CH_2 \xrightarrow[\text{Ether}]{HI}$

4.



ADDITION REACTION OF BROMINE TO ALKENES



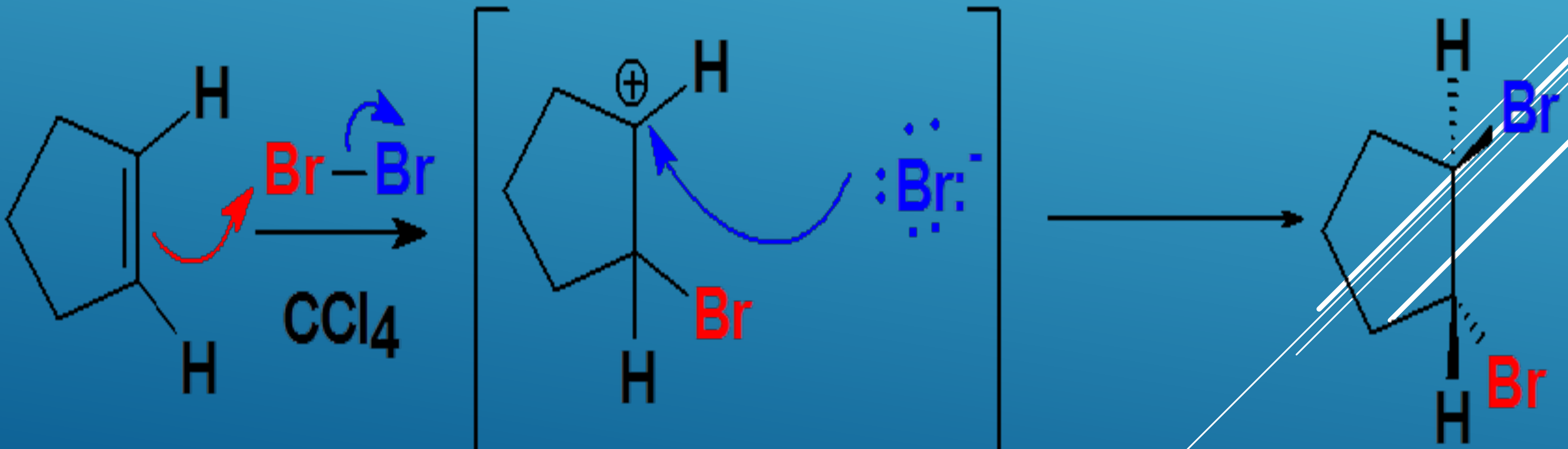
Cyclopentene

***trans*-1,2-Dibromocyclopentane**
(Sole product)

***cis*-1,2-Dibromocyclopentane**
(Not formed)

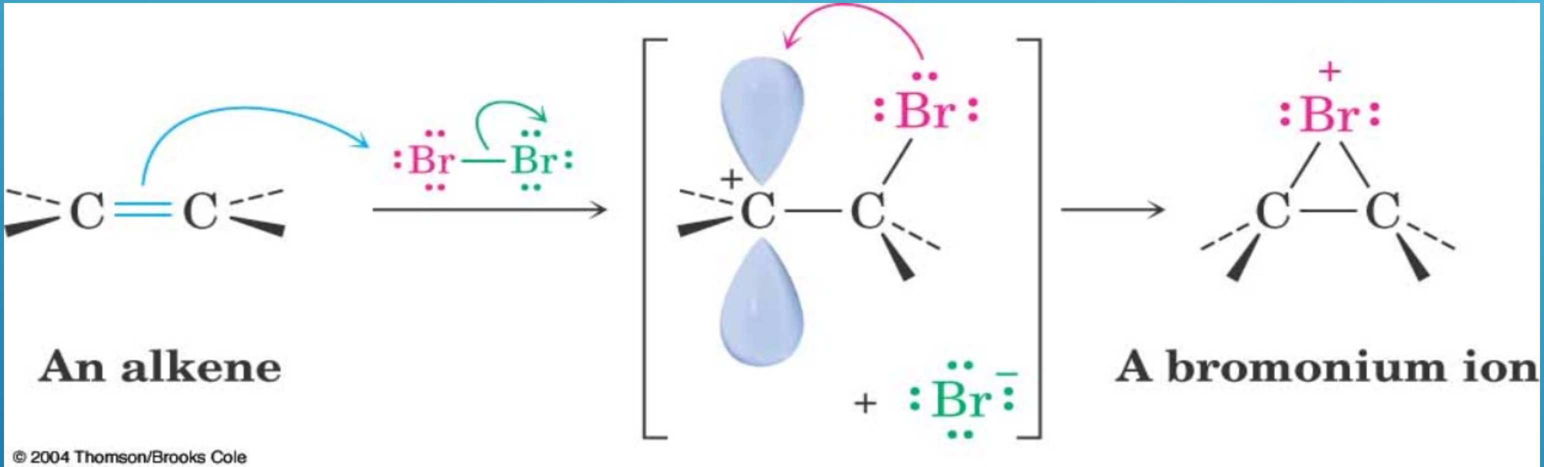
MECHANISM OF BROMINATION OF ALKENES

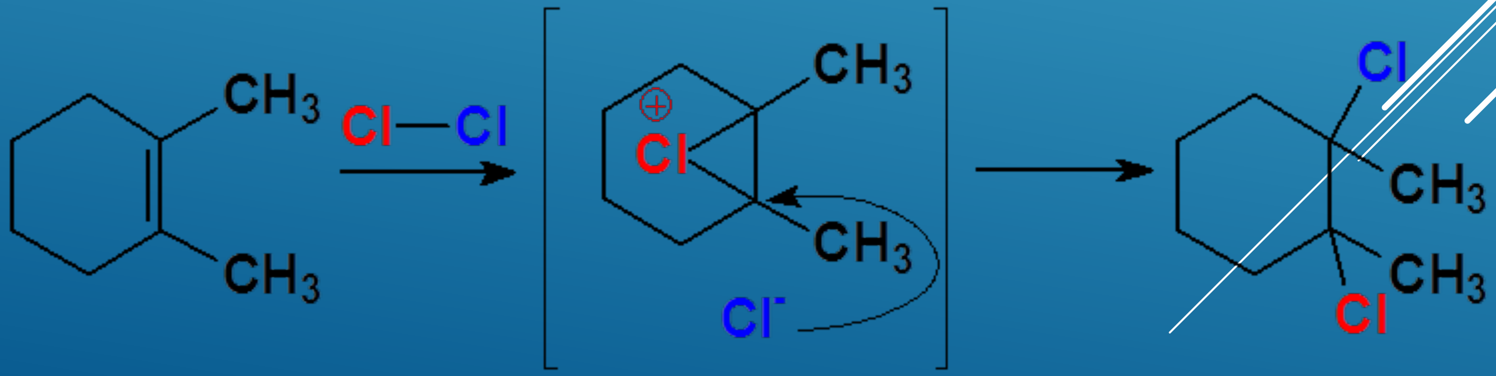
- Electrophilic addition of bromine to give a cation is followed by cyclization to give a bromonium ion.
- This bromonium ion is a reactive electrophile and bromide ion is a good nucleophile.
- Only the trans product is formed.



HALONIUM ION

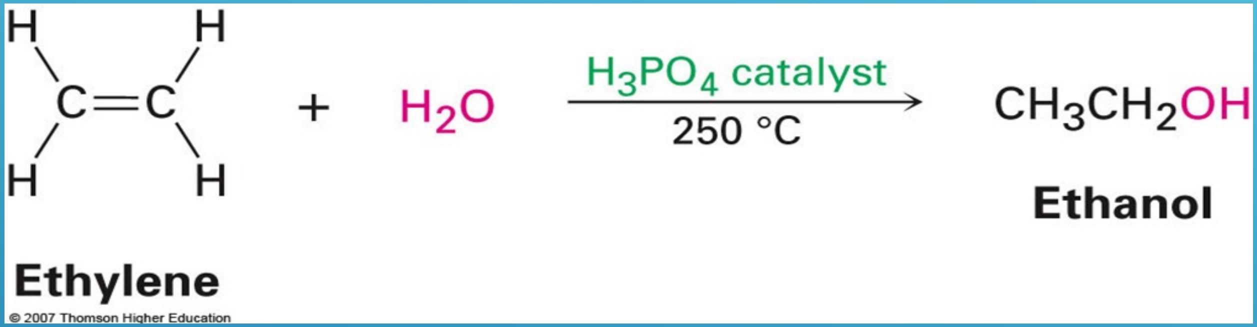
Halogenation reaction of alkenes give only trans-productwith anti stereochemistry, means, that the two bromine atoms come from directions approximately 180˚ apart.





ADDITION OF H_2O TO ALKENES

Hydration of an alkene is the addition of H-OH to to give an alcohol.

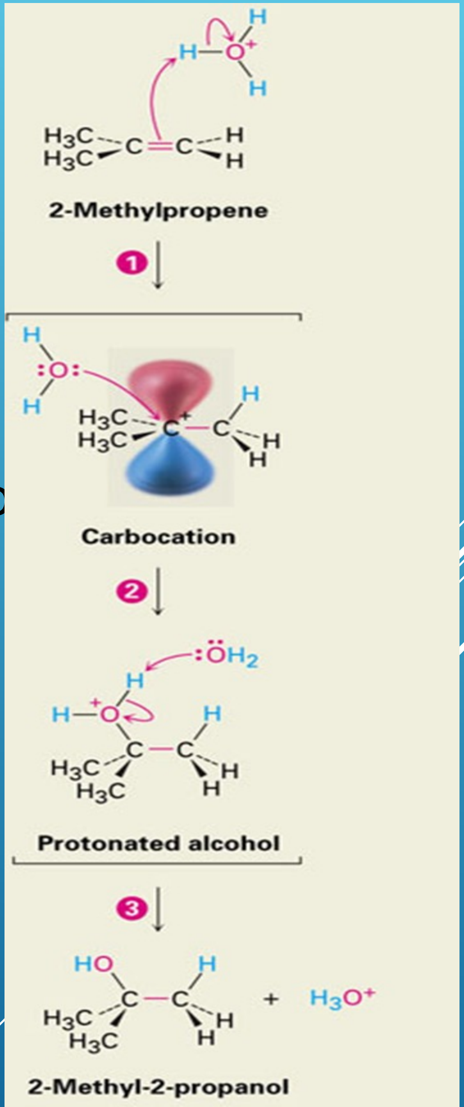


Mechanism:

Hydration reaction takes place by a mechanism similar to of HX addition.

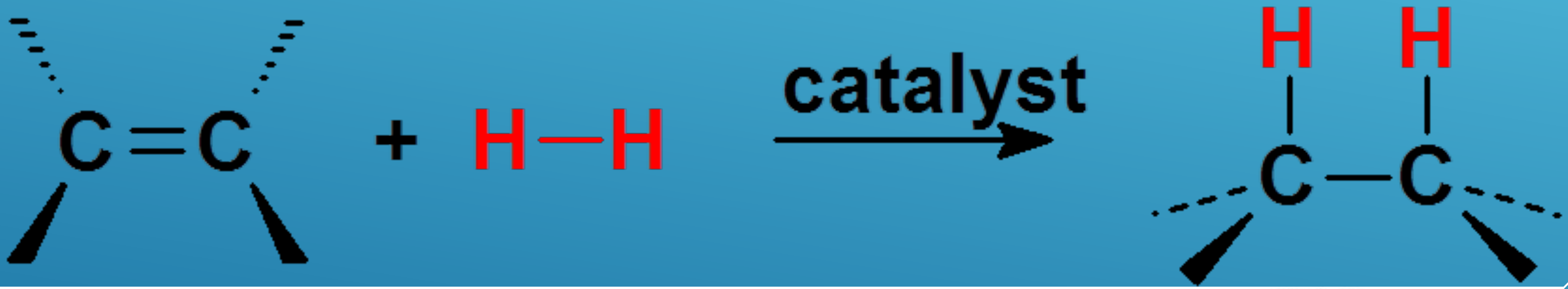
For unsymmetrical alkenes, it follows Markovnikov's rule a more highly substituted alcohol.

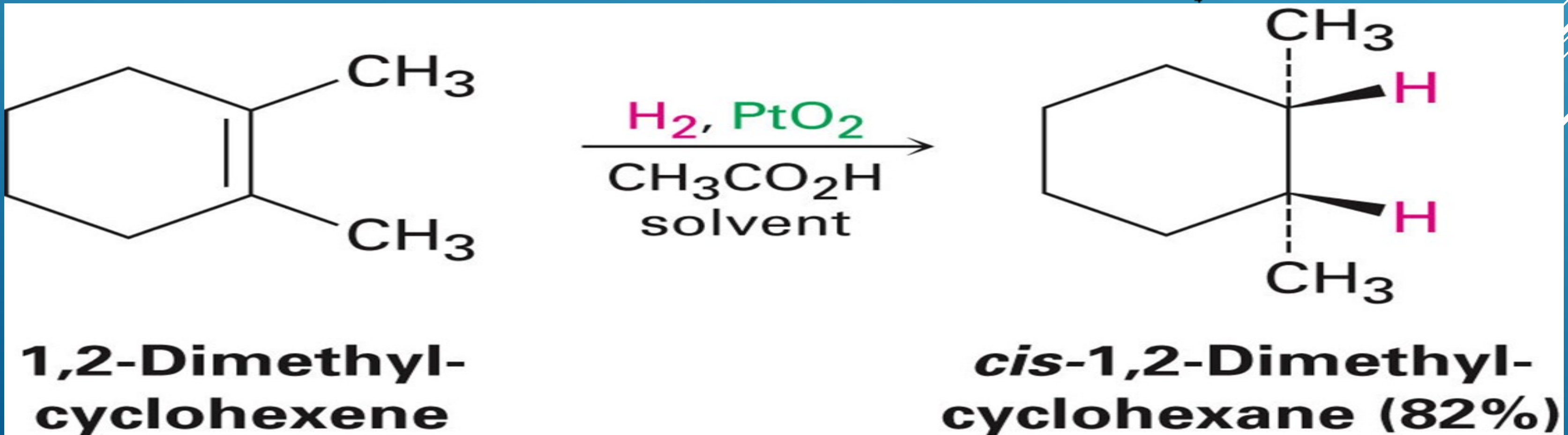
In the hydration of ethylene with aqueous acid (H_3PO_4) , ethyl alcohol is obtained as a product.



ADDITION OF H_2 TO ALKENES

- Catalytic hydrogenation of alkenes, in presence of palladium metal or Platinum(PtO_2) as a catalyst adds hydrogen's across the C=C bond in alkenes (also referred as Reduction reaction-addition of H_2).
- The reaction occurs with a syn stereochemistry, both the hydrogen's add to the double bond from the same side.



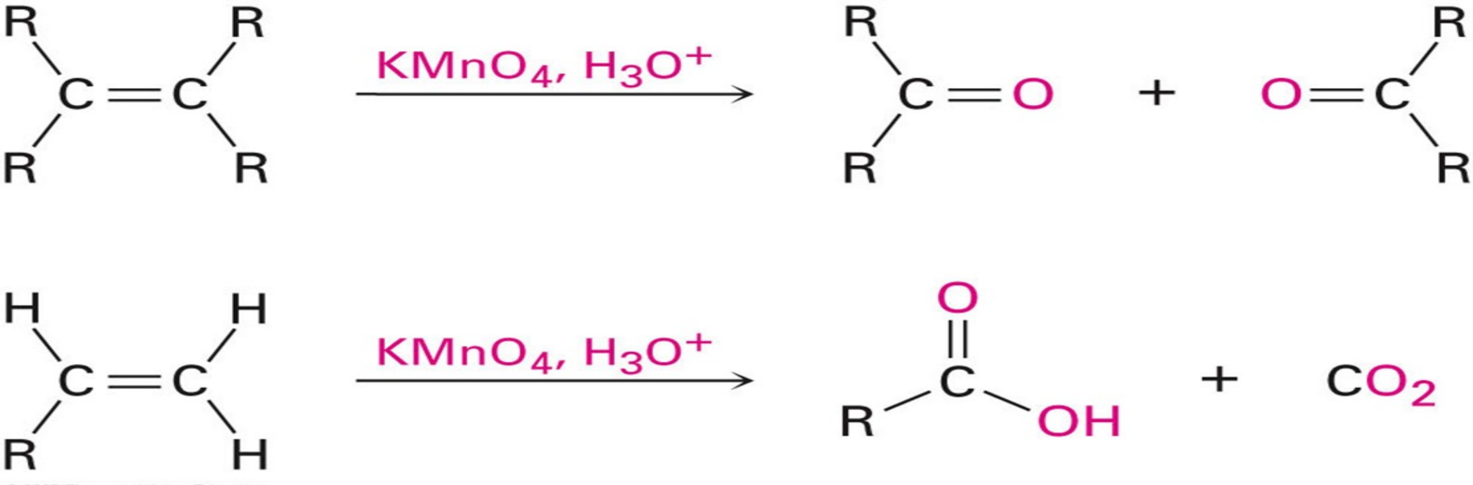


1,2-Dimethylcyclohexene

***cis*-1,2-Dimethylcyclohexane (82%)**

OXIDATION OF ALKENES

The reaction of an alkene with $KMnO_4$ in acidic solution results with the cleavage of double bond occurs and carbonyl containing products are obtained.



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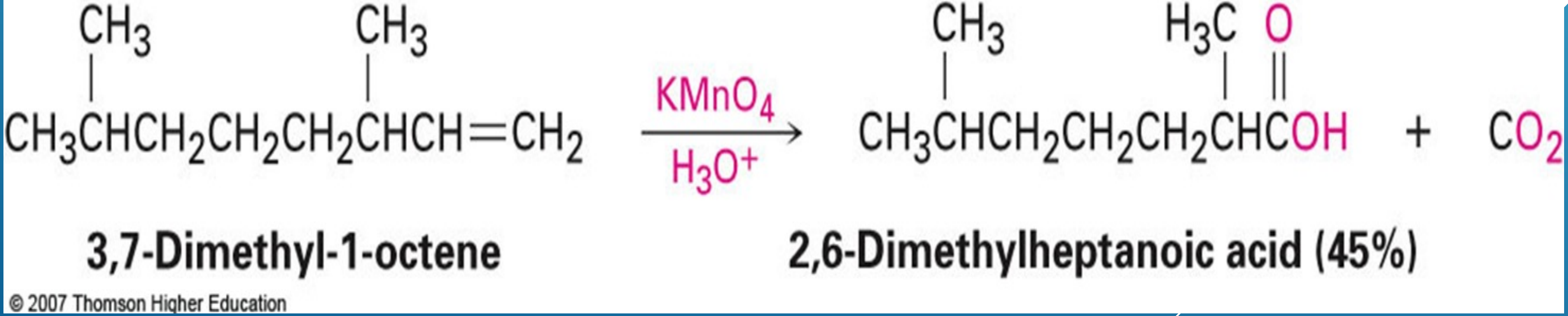

$$\mathrm{CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2CH_2CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}HCH{=}CH_2 \xrightarrow[H_3O^+]{KMnO_4} CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2CH_2CH_2\overset{\displaystyle H_3C}{\overset{|}{C}}H\overset{\displaystyle O}{\overset{\|}{C}}OH + CO_2}$$

3,7-Dimethyl-1-octene

2,6-Dimethylheptanoic acid (45%)

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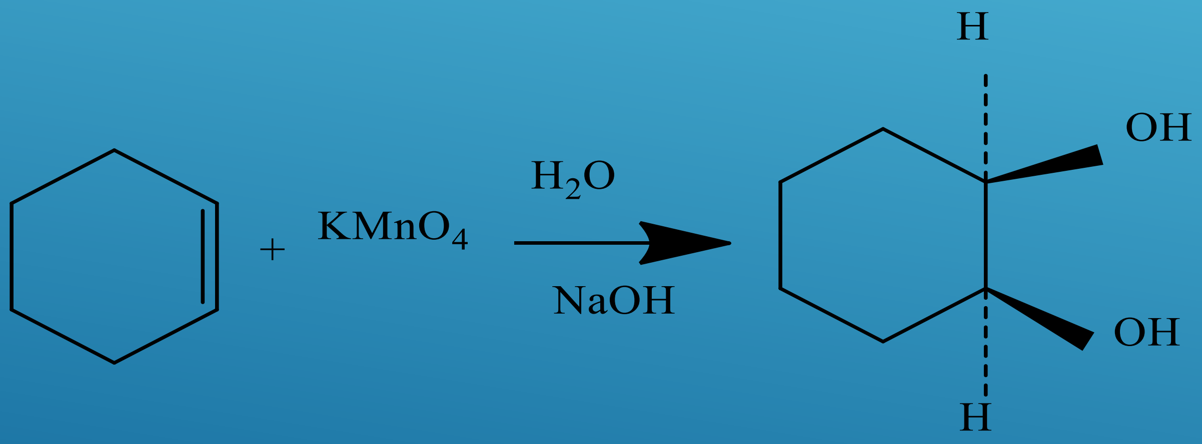
OXIDATION OF ALKENES

- Oxidation of alkenes is also as hydroxylation reaction.
- The reaction of an alkene with $KMnO_4$ in basic solution results with formation of 1,2-dialcohols or diols with a syn stereochemistry.

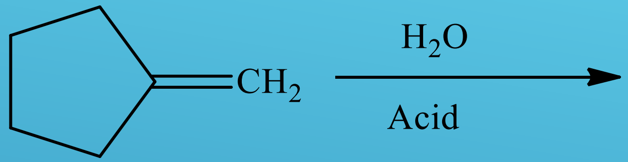


Cylohexene

cis-cyclohexane-1,2-diol

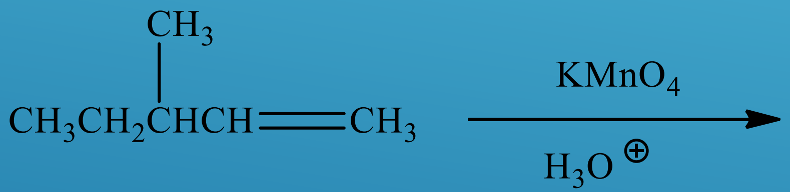
PRACTICE PROBLEMS

1.



2. What is the product obtained when 3,3-dimethylcyclopentene undergoes catalytic hydrogenation?

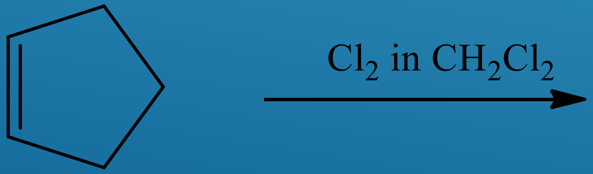
3.



$$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH{=}CH_3 \xrightarrow[H_3O^{\oplus}]{KMnO_4}$$

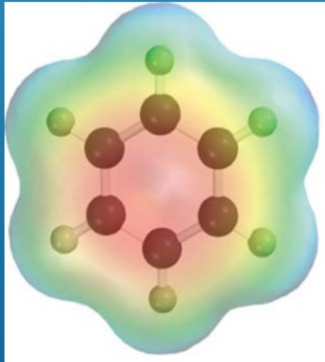
4.

5.



RESONANCE

- Some molecules are have structures that cannot be shown with a single representation.
- In these cases we draw structures that contribute to the final structure but which differ in the position of the π bond(s) or lone pairs.
- Such a structure is delocalized and to is represented by resonance forms.
- The resonance forms are connected by a double-headed arrow.



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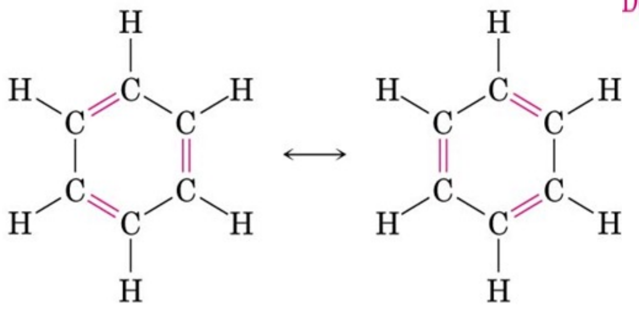
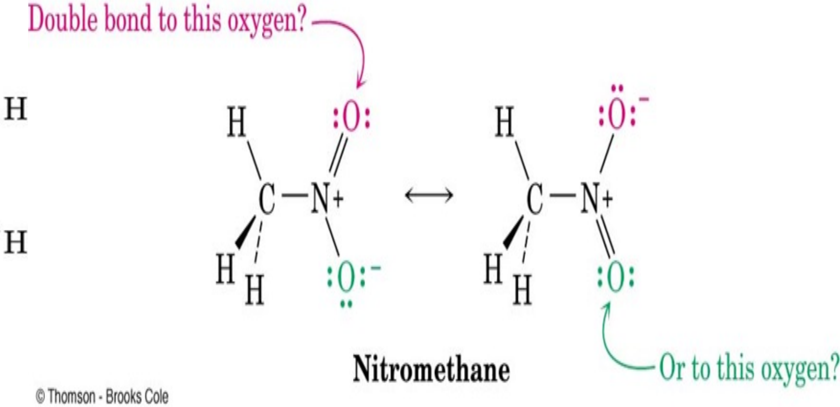


Benzene (two resonance forms)



Double bond to this oxygen?

Or to this oxygen?

Nitromethane

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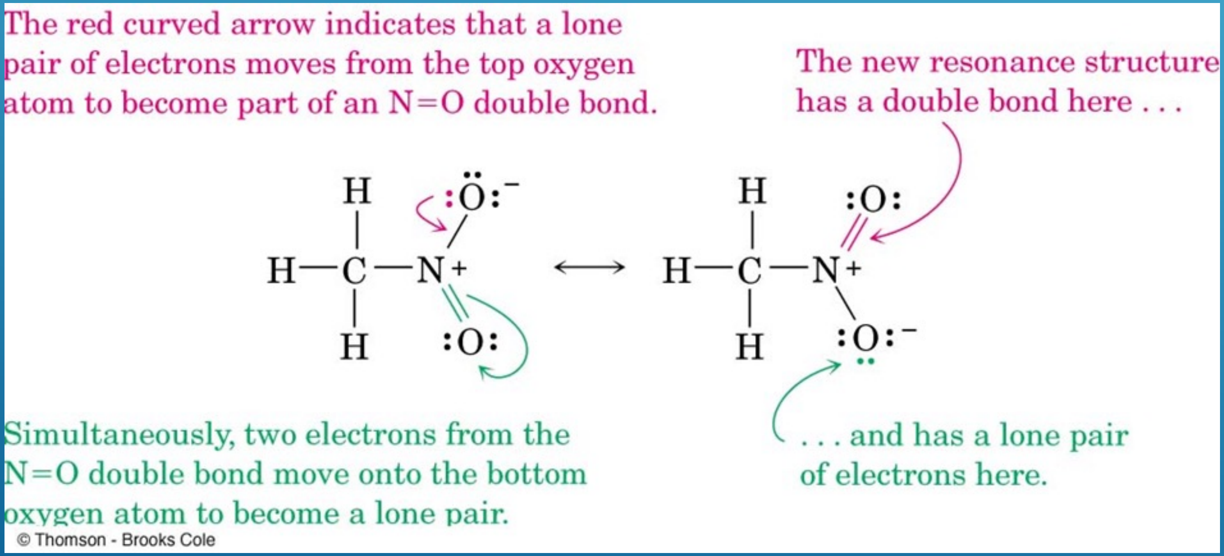
RESONANCE

- A curved arrow shows the flow of an electron pair.

The flow may be only:

- From an atom to an adjacent bond or
- From a bond to an adjacent atom or
- From a bond to an adjacent bond.



The red curved arrow indicates that a lone pair of electrons moves from the top oxygen atom to become part of an N=O double bond.

The new resonance structure has a double bond here . . .

Simultaneously, two electrons from the N=O double bond move onto the bottom oxygen atom to become a lone pair.

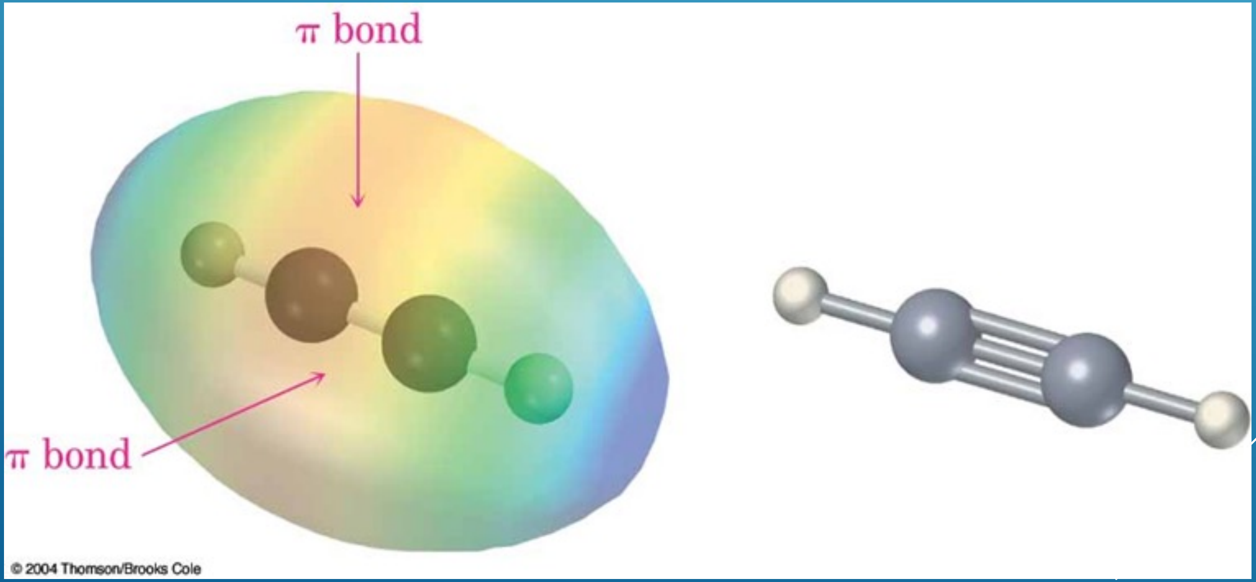
. . . and has a lone pair of electrons here.

ALKYNES

- Alkynes contain a triple bond.
- General formula is C_nH_{2n-2}.
- Two elements of unsaturation for each triple bond.
- Acetylene, the simplest alkyne is produced industrially from methane and steam at high temperature.
- Our study of alkynes provides an introduction to organic synthesis, the preparation of organic molecules from simpler organic molecules

BONDING AND STRUCTURE IN ALKYNES

- Carbon-carbon triple bond result from the overlap of two sp-hybridized carbon atoms and consists of one sp-sp σ bond and two p-p π bonds.
- The remaining sp orbitals form bonds to other atoms at 180º to C-C triple bond.
- The bond is shorter and stronger than single or double.
- Breaking a π bond in acetylene (HCCH) requires 318 kJ/mole (in ethylene it is 268 kJ/mole.



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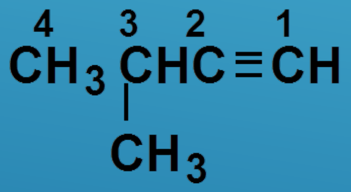
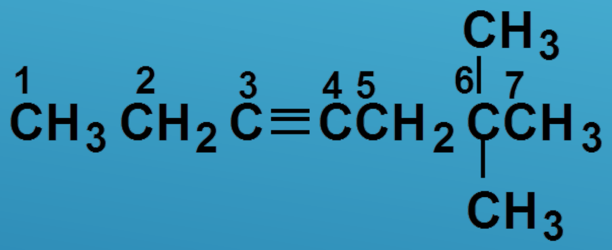
NOMENCLATURE OF ALKYNES

- General hydrocarbon rules apply with “-yne” as a suffix indicating an alkyne.
- Numbering of chain with triple bond is set so that the smallest number possible include the triple bond.



$\overset{4}{CH_3}\overset{3}{C}H(CH_3)\overset{2}{C}\equiv\overset{1}{C}H$

3-Methyl-1-butyne



$\overset{1}{CH_3}\overset{2}{C}H_2\overset{3}{C}\equiv\overset{4}{C}\overset{5}{C}H_2\overset{6}{C}(CH_3)_2\overset{7}{C}H_3$

6,6-Dimethyl-3-heptyne

	$CH_3C\equiv CH$	$CH_3C\equiv CCH_3$	$CH_2{=}CHC\equiv CH$
IUPAC:	Propyne	2-Butyne	1-Buten-3-yne
Common:	Methylacetylene	Dimethylacetylene	Vinylacetylene

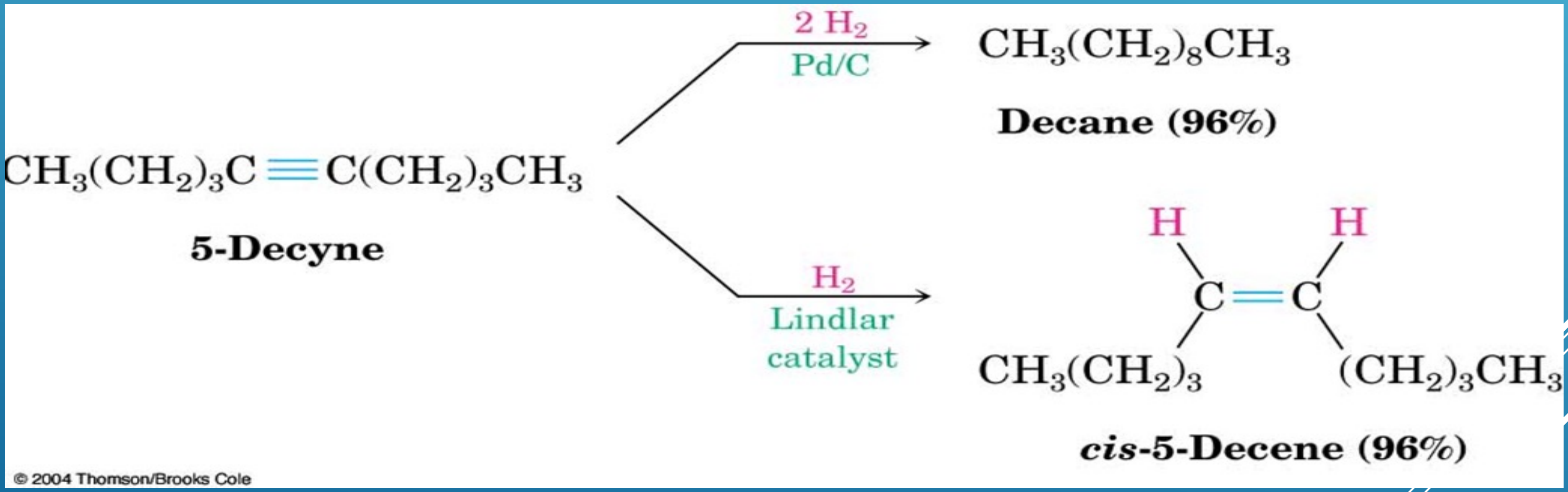
REACTIONS OF ALKYNES

Addition of H_2: the addition of hydrogen to alkynes in presence of palladium metal /carbon converts alkyne into an alkane

$$CH_3(CH_2)_3\equiv C(CH_2)_2CH_3 \xrightarrow[Pd/C]{2H_2} CH_3(CH_2)_3CH_2-CH_2(CH_2)_2CH_3$$

Addition of H_2 using chemically deactivated palladium on calcium carbonate as a catalyst (the Lindlar's catalyst) produces a cis alkene.

The two hydrogen's add syn (from the same side of the triple bond).



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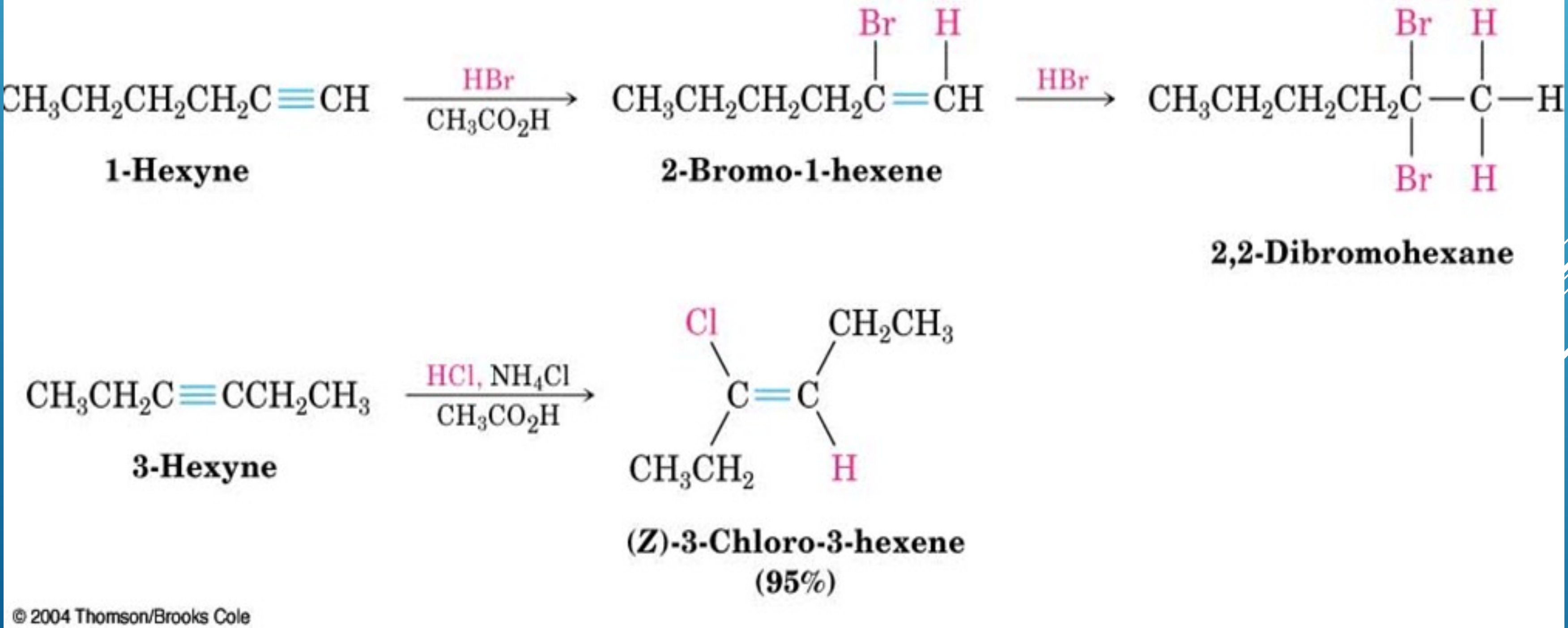
ADDITION OF HX

- Addition of 1 equivalent of HX yield a vinylic halide(an alkene).
- But with excess of HX alkynes leads to the formation of a dihalide product.
- The regioselectivity in the addition of monosubstituted alkynes follows Markovnikov's rule.



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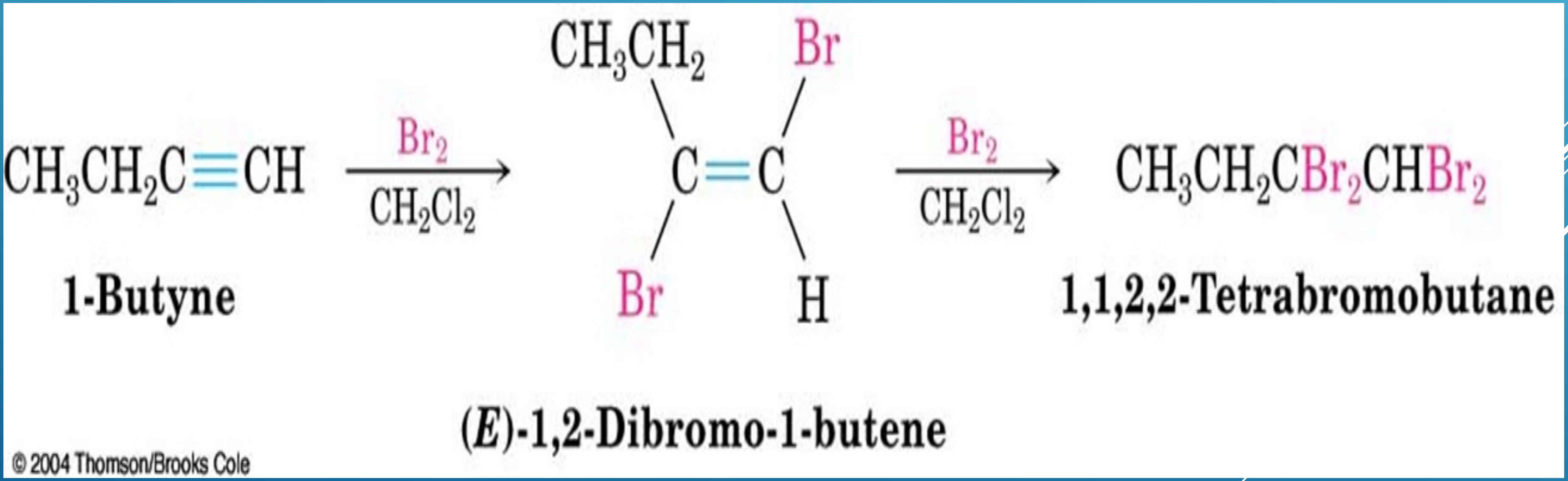
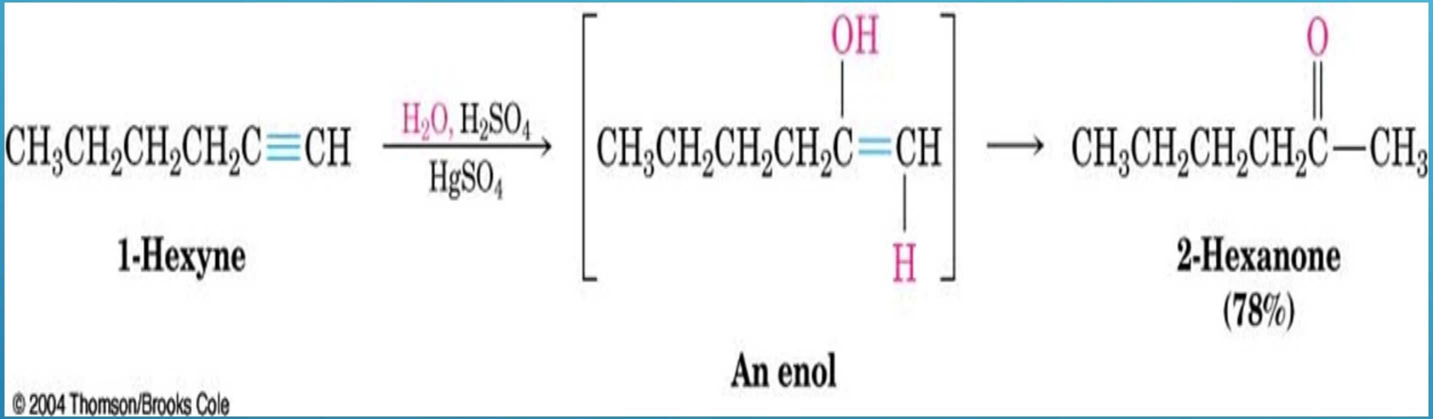
ADDITION OF HALOGENS (X_2)

- Initial addition gives trans intermediate (anti stereochemistry).
- Product with excess reagent is tetrahalide.
- Alkynes react with halogens in presence of CH_2Cl_2 /CCl_4



ADDITION OF H_2O

- Addition of H-OH as in alkenes.
- Mercury (II) catalyzes Markovinikov’s oriented addition.



$$CH_3CH_2CH_2CH_2C{\equiv}CH \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4} \left[CH_3CH_2CH_2CH_2\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C{=}CH}} \right] \longrightarrow CH_3CH_2CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$$

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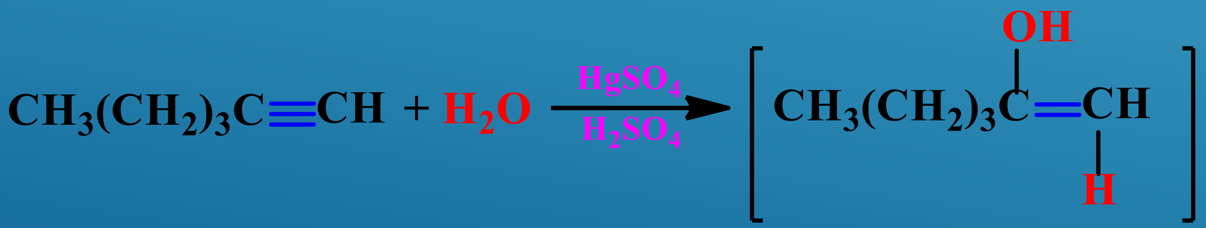


$$CH_3(CH_2)_3C{\equiv}CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} \left[CH_3(CH_2)_3\overset{\overset{\displaystyle OH}{|}}{C}{=}\underset{\underset{\displaystyle H}{|}}{CH} \right]$$

1-Hexyne

4-Hydroxy-1-Hexene (enol)

FORMATION OF ACETYLIDE ANIONS

- The difference between alkenes and alkynes is that terminal alkynes (R-C≡C-H) are weakly acidic, with $pK_a \approx 25$.
- When a terminal alkyne is treated with a strong base such as sodium amide, $NaNH_2$, the terminal hydrogen is removed and an acetylide anion is formed.

$$R—C\equiv C—H \;+\; NaNH_2 \longrightarrow R—C\equiv C{:}^{-}Na^{+} \;+ {:}NH_3$$

Eg: $HC\equiv CH \;+ NaNH_2 \longrightarrow HC\equiv C^{-}Na^{+} \;+ RCH_2Br$

$$\downarrow$$

(A terminal alkene) $HC\equiv CCH_2R$

QUESTIONS

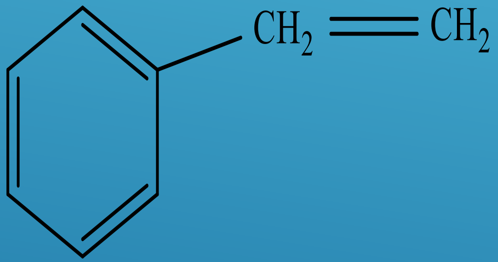
1. Predict the products for the following reactions on hex-1-yne.

a. With 2 equivalent HBr

b. H_2, Lindlar's catalyst.

c. 1 mol Br_2 in CH_2Cl_2.

2. Predict the reactions of styrene.



a. H_2/Pd

b. HBr

c. $KMnO_4/NaOH,H_2O$