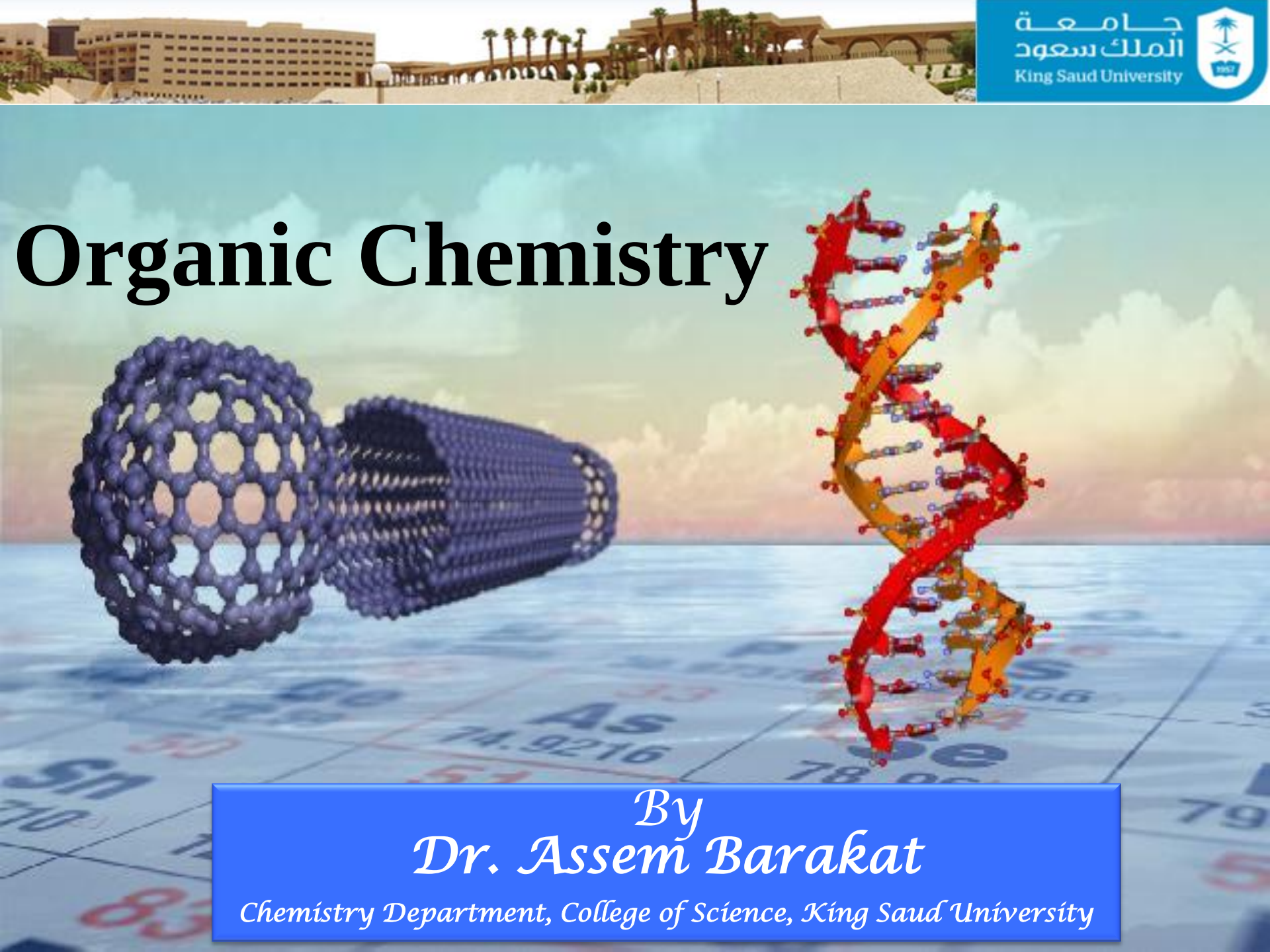

Organic Chemistry

By
Dr. Assem Barakat
Chemistry Department, College of Science, King Saud University

Chapter 3

Alkenes and Alkyne

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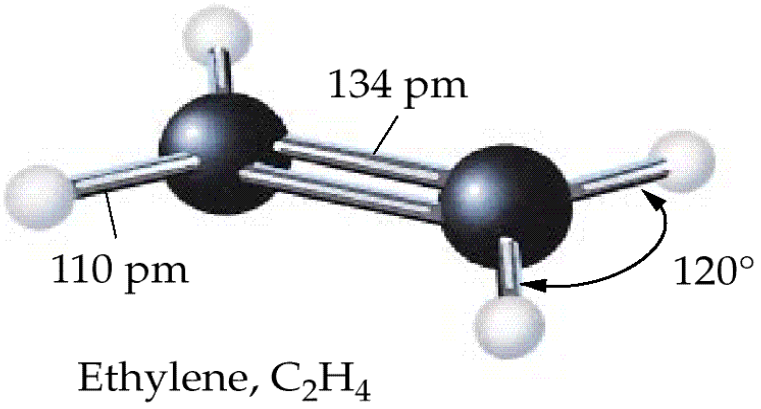
Alkenes and Cycolalkenes

C_nH_{2n}



Ethylene, C_2H_4

Ethylene

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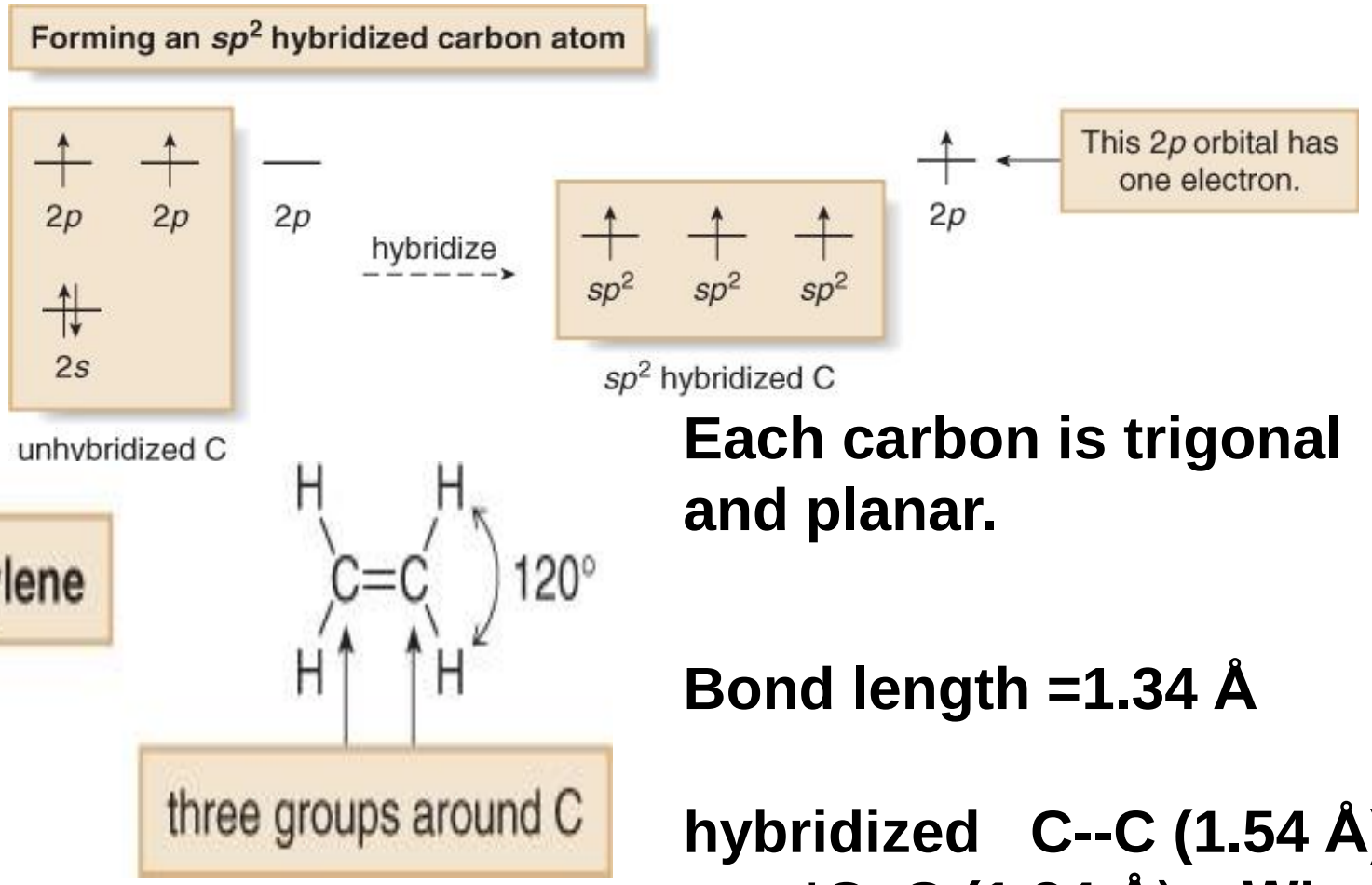
SP^2 Hibridization:



Each carbon is trigonal and planar.

Bond length =1.34 Å

hybridized C--C (1.54 Å) < *C=C (1.34 Å) Why?

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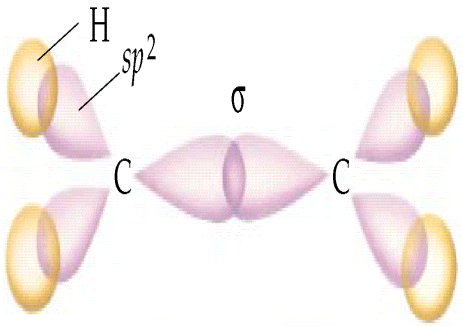
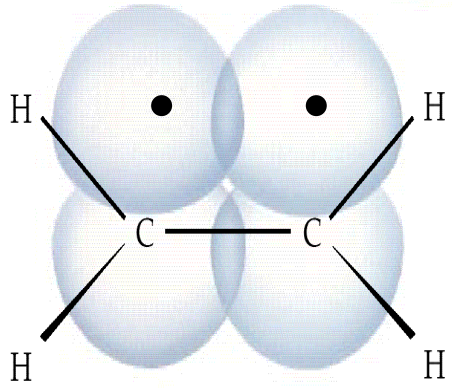
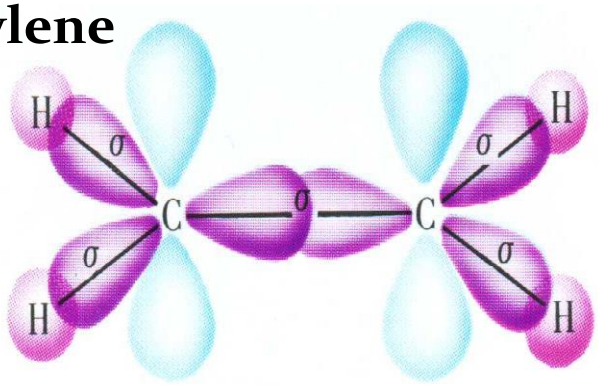
σ bond = end-to-end overlap of the sp^2 hybridized orbital



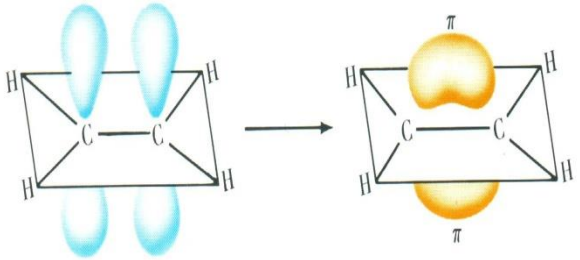


π bond = side-by-side overlap of the unhybridized p-orbitals

Sigma (σ) Bonding in Ethylene



Pi (π) Bonding in Ethylene
π is weaker than δ



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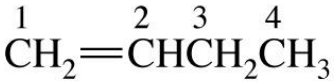
♦ Nomenclature of Alkenes and Cycloalkenes

➔ **Alkenes are named by finding the longest chain containing the double bond and changing the name of the corresponding parent alkane from -ane to -ene**

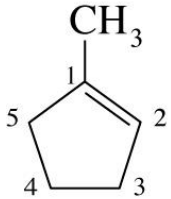
➔ **The compound is numbered to give one of the alkene carbons the lowest number**



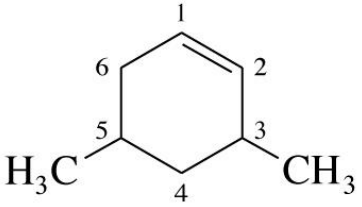
1-Butene
(*not* 3-butene)

2-Hexene
(*not* 4-hexene)

➔ **The double bond of a cylcoalkene must be in position 1 and 2**



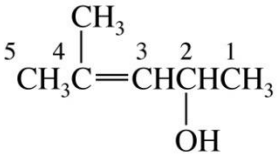
1-Methylcyclopentene
(*not* 2-methylcyclopentene)



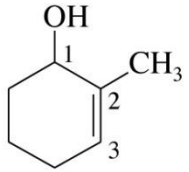
3,5-Dimethylcyclohexene
(*not* 4,6-dimethylcyclohexene)

➔ **Compounds with double bonds and alcohol hydroxyl groups are called alkenols**

- **The hydroxyl is the group with higher priority and must be given the lowest possible number**

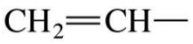


4-Methyl-3-penten-2-ol or 4-methylpent-3-en-2-ol



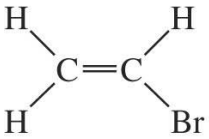
2-Methyl-2-cyclohexen-1-ol or 2-methylcyclohex-2-en-1-ol

➔ **Two groups which contain double bonds are the vinyl and the allyl groups**

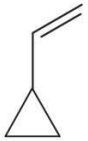


The vinyl group

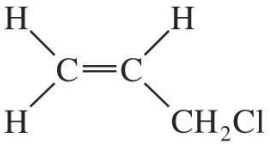
The allyl group



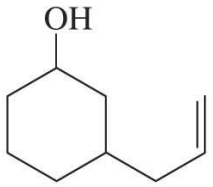
Bromoethene or vinyl bromide (common)



Ethenylcyclopropane or vinylcyclopropane



3-Chloropropene or allyl chloride (common)

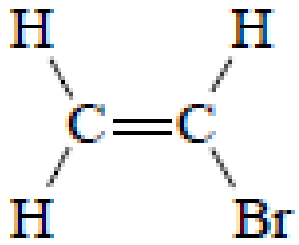


3-(Prop-2-en-1-yl)cyclohexanol or 3-allylcyclohexanol

The vinyl group and the allyl group.

$H_2C{=}CH{-}$

The vinyl group

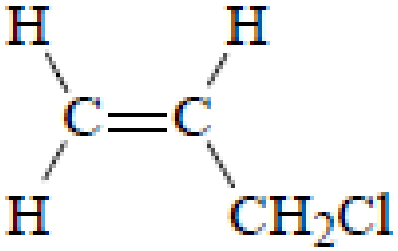


Bromoethene or

vinyl bromide (common)

$H_2C{=}CHCH_2{-}$

The allyl group



3-Chloropropene or

allyl chloride (common)

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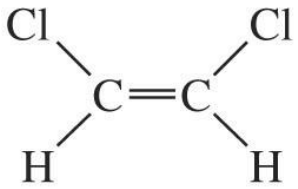
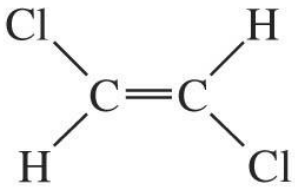
➔ **If two identical groups occur on the same side of the double bond the compound is cis**

➔ **If they are on opposite sides the compound is trans**



***cis*-1,2-Dichloroethene**



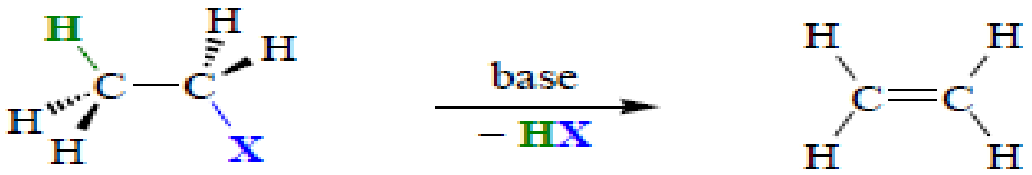
***trans*-1,2-Dichloroethene**

➔ **Several alkenes have common names which are recognized by IUPAC**

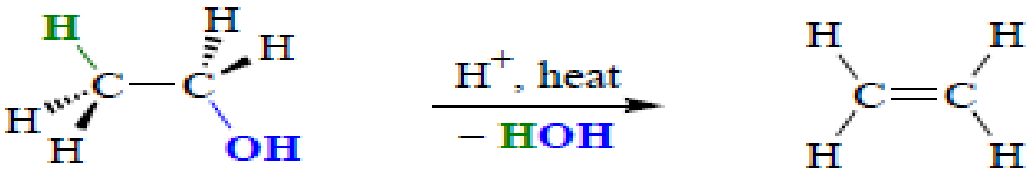
	$CH_2=CH_2$	$CH_3CH=CH_2$	$CH_3-\overset{CH_3}{\overset{\vert}{C}}=CH_2$
IUPAC:	**Ethene**	**Propene**	**2-Methylpropene**
Common:	**Ethylene**	**Propylene**	**Isobutylene**

SYNTHESIS OF ALKENES VIA ELIMINATION REACTIONS

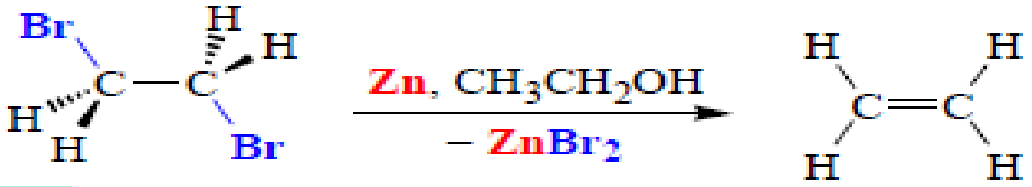
1. **Dehydrohalogenation of Alkyl Halides**



2. **Dehydration of Alcohols**



3. **Debromination of *vic*-Dibromides**



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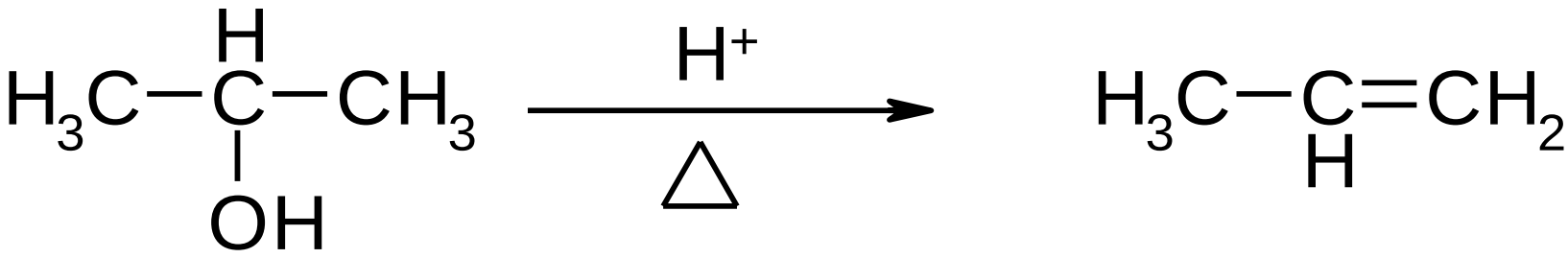
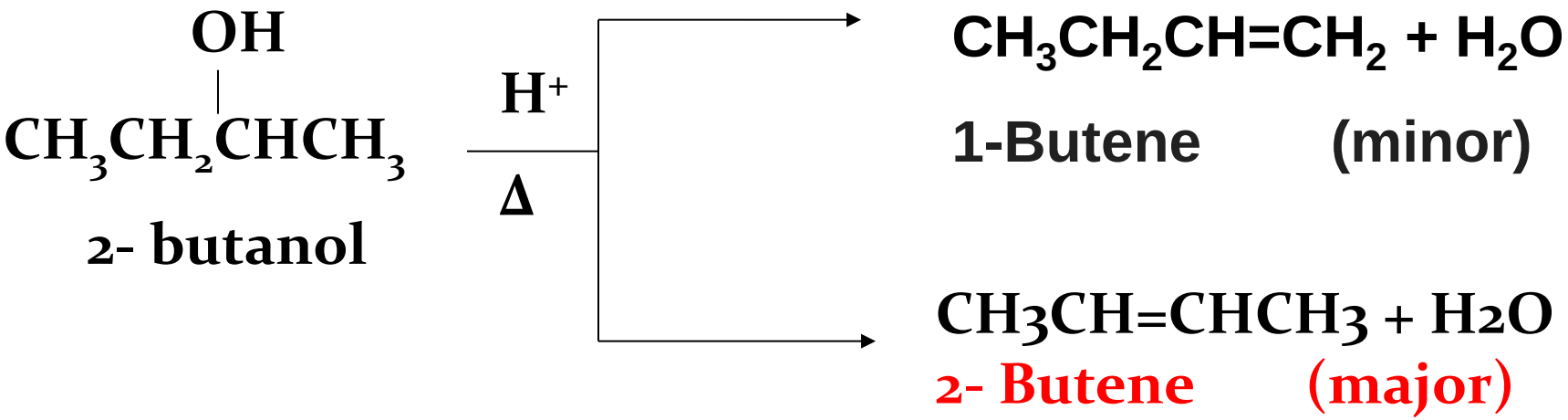
1) Dehydration of alcohols

Mineral acids (H_2SO_4, H_3PO_4)
General equation:



2-Propanol Propene

Saytzeff's Rule



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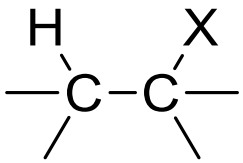
(2) Dehydrohalogenation of alkyl halides

General equation:



$$+ \quad KOH \xrightarrow{EtOH} CH_2{=}CH_2 + KX + H_2O$$

i) $CH_3{-}CHH{-}CHBr{-}CHH_2 + KOH \xrightarrow[\Delta]{EtOH} CH_3CH{=}CH{-}CH_2 +$

Major

$CH_3{-}CH_2{-}CH{=}CH_2$

Minor

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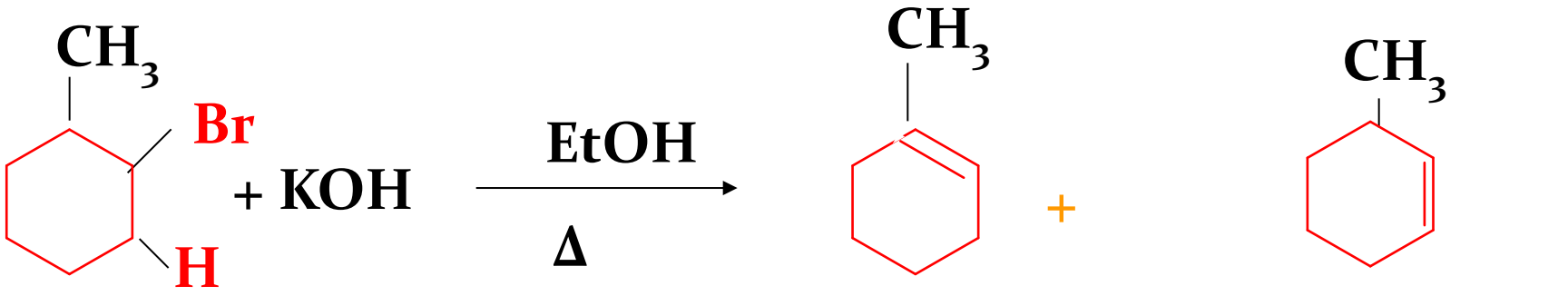

1-methyl cyclohexene

Major

3 methyl cyclohexene

Minor

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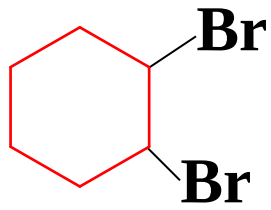
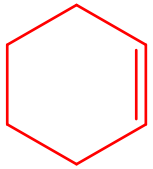
(3) Vicinal dihalides

General equation:

$$\text{-CX – CX-} + \text{Zn} \xrightarrow[\Delta]{\text{Methanol}} \text{-C=C-} + \text{Zn X}_2$$

i) By Zn in acetic acid

i) 

$+ \text{Zn} \xrightarrow{CH_3COOH}$  $+ \text{NaBr} + \text{I}_2$

ii) By NaI in acetone

ii) $\text{H}_3\text{C–CHBr–CH}_2\text{Br} + \text{NaI} \xrightarrow{\text{Acetone}} \text{H}_3\text{C-CH} = \text{CH}_2 + \text{I}_2 + \text{NaBr}$

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Reactions of alkenes

Electrophilic Addition Reaction

General equation:

$$H_2C{=}CH_2 + A\text{-}B \longrightarrow H_2A\text{-}C\text{-}C\text{-}H_2B$$

1]Addition of hydrogen:

i) $$H_2C{=}CH_2 + H_2 \xrightarrow[\text{Low pr.}]{\text{Pt / Ni}} H_2H\text{-}C\text{-}C\text{-}HH_2$$

ii) $$CH_3\text{-}CH{=}CH\text{-}CH_3 + H_2 \xrightarrow[\text{Low pr.}]{\text{Pt / Ni}} CH_3CHHCHHCH_3$$

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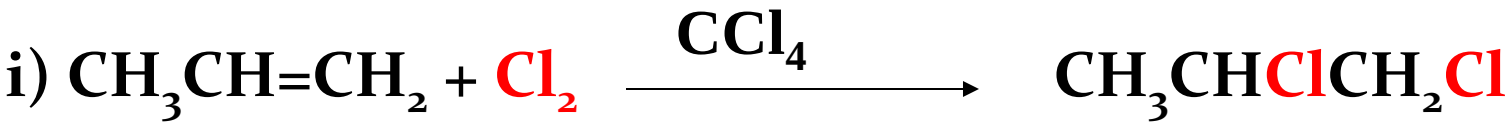
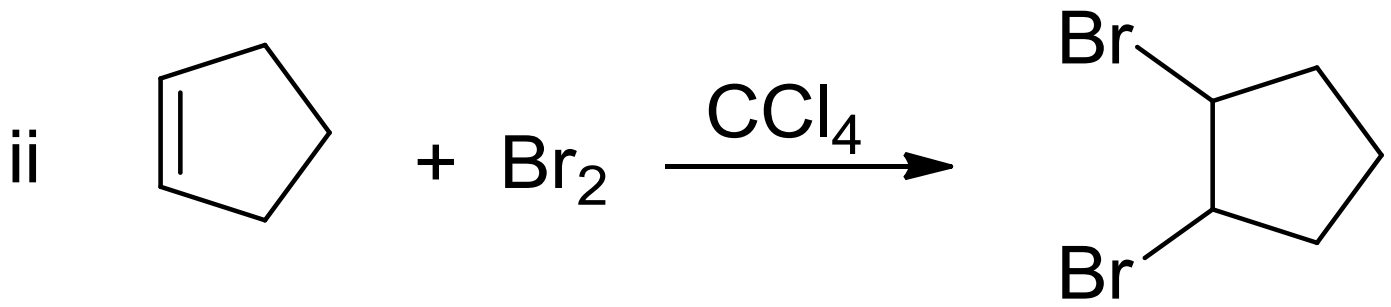
2] Addition of halogens (Halogenations):

General equation:





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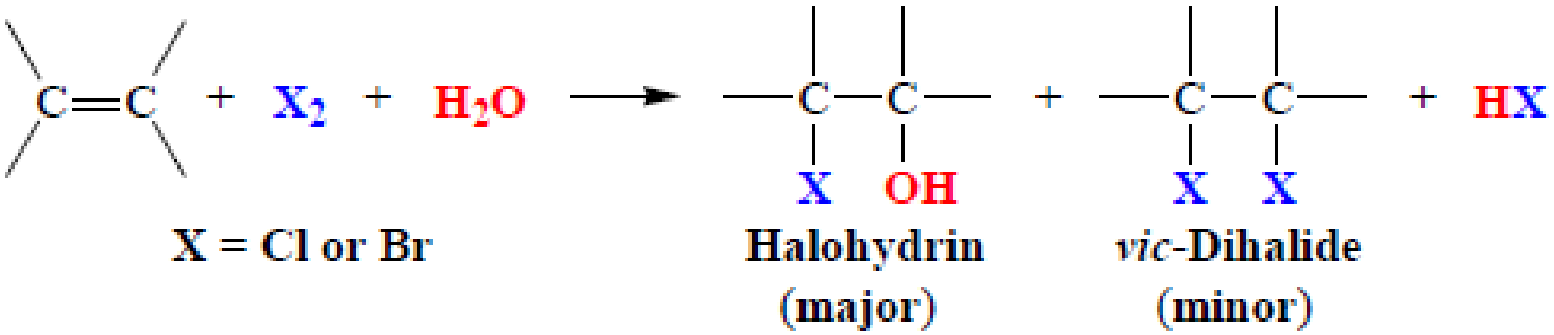
3] Addition of HOX (Halohydrin formation):



X = Cl or Br

Halohydrin (major)

vic-Dihalide (minor)

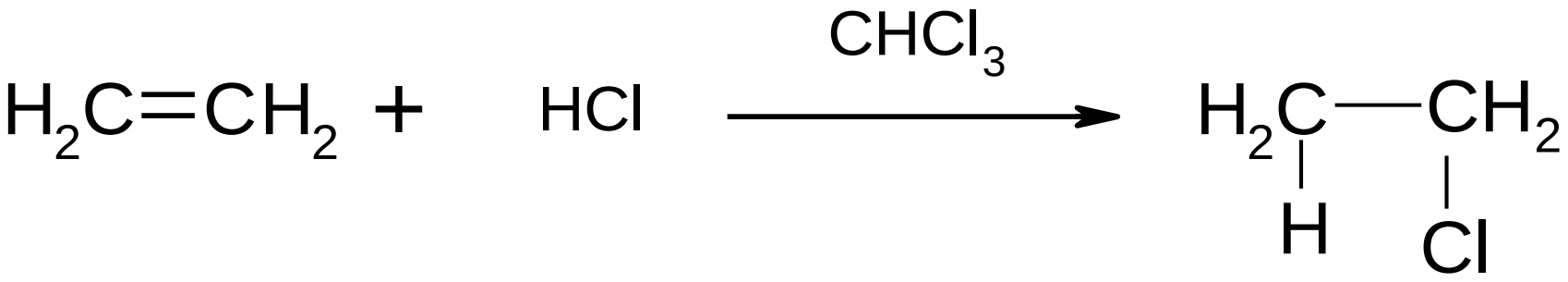
$CH_3CH=CH_2 + Cl_2, H_2O \longrightarrow CH_3CHOHCH_2Cl$

1-chloro-2-propanol

$CH_3CH=CH_2 + Br_2, H_2O \longrightarrow CH_3CHOHCH_2Br$

1-bromo-2-propanol

4] Hydrohalogenation



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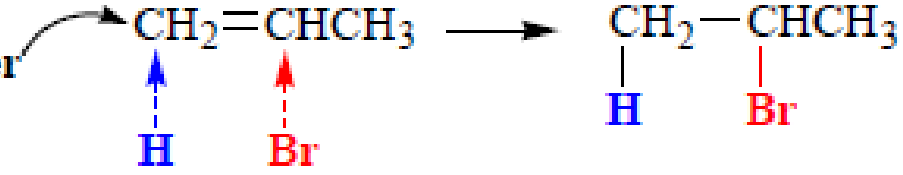
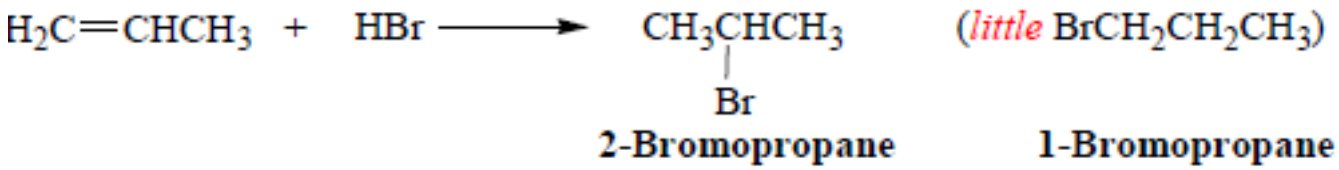
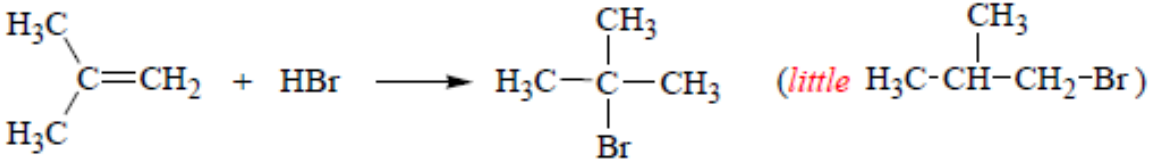
MARKOVNIKOV'S RULE

Carbon atom with the greater number of hydrogen atoms





2-Bromopropane 1-Bromopropane



2-Methylpropene (isobutylene) *tert*-Butyl bromide Isobutyl bromide

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5] ADDITION OF SULFURIC ACID

HA = [H_2SO_4 , (H_2O / H^+), HCl, HBr,]

General equation:

-C=C- +HA ⟶ -HC-CA-

a)Sulfuric acid (H_2SO_4= H-OSO_3H)

$H_2C=CH_2$ + H- OSO_3H ⟶ H_2H-C-$COSO_3HH_2$

$CH_3CH=CH_2$+ H_2SO_4 ⟶ CH_3CHOSO_3H-CH_2H

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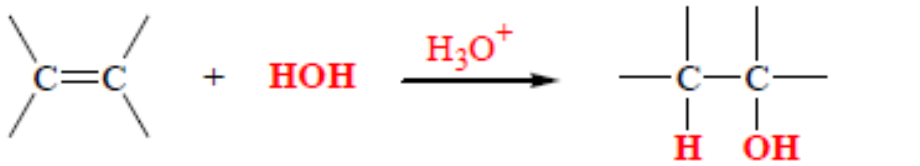
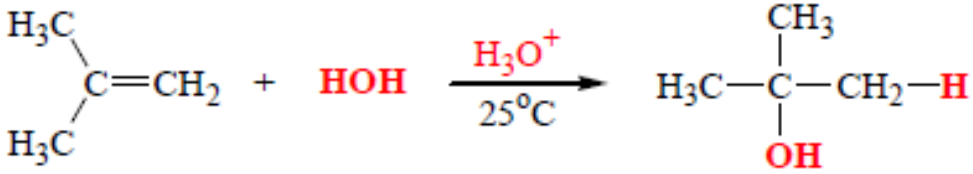
5] ADDITION OF WATER TO ALKENES: (ACID-CATALYZED HYDRATION)





2-Methylpropene (isobutylene)

***tert*-Butyl alcohol**

The addition of water to a double bond usually follows Markovnikov's rule.

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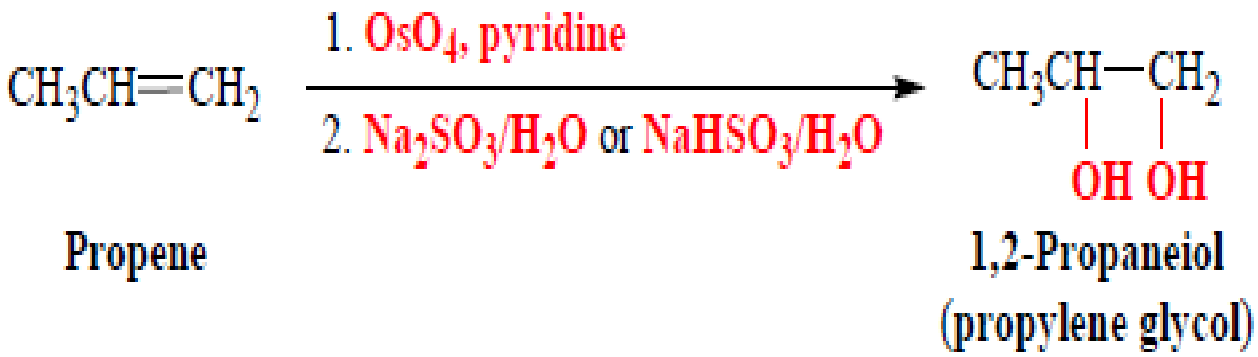
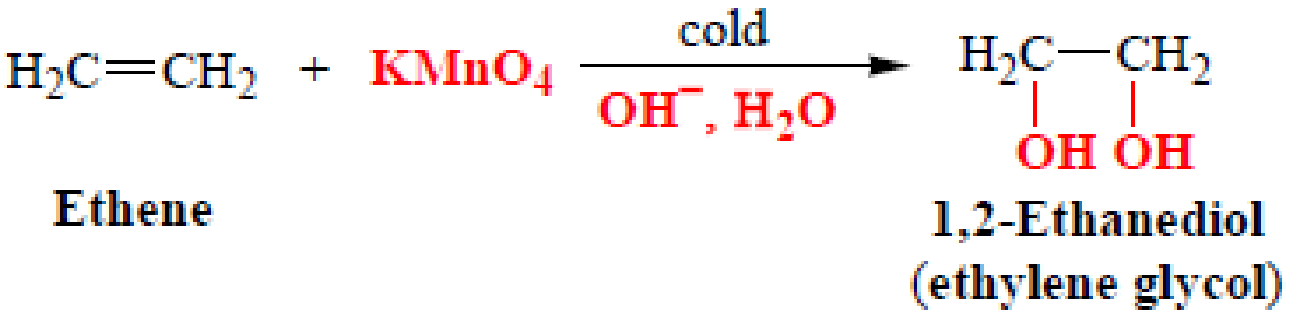
6] Oxidation:

Oxidizing Agents

- There are two main categories of oxidizing agents:
  1. Reagents that contain an oxygen-oxygen bond
  2. Reagents that contain metal-oxygen bonds
- Oxidizing agents containing an O—O bond include O_2, O_3 (ozone), H_2O_2 (hydrogen peroxide), $(CH_3)COOH$ (*tert*-butyl hydroperoxide), and peroxyacids.
- Peroxyacids (or peracids) have the general formula RCO_3H.
- $KMnO_4$ (potassium permanganate).
- OsO_4 (osmium tetroxide) and Ag_2O [silver(I) oxide].

R + oxidation ($KMnO_4$,H_2O_2, OsO_4) ⟶ Di-alcohol





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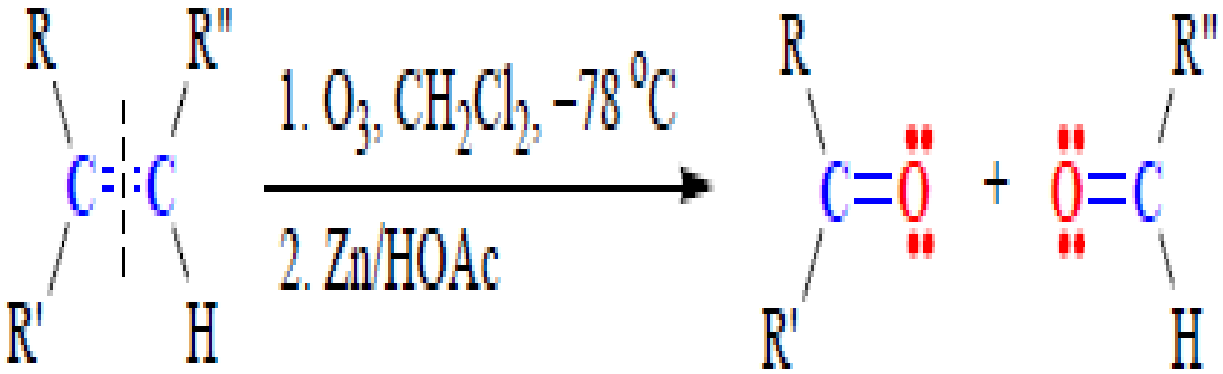
7] Ozonolysis:

Alkene + O_3 ⟶ ozonoid + H_2O ⟶ Aldehyde + Ketone



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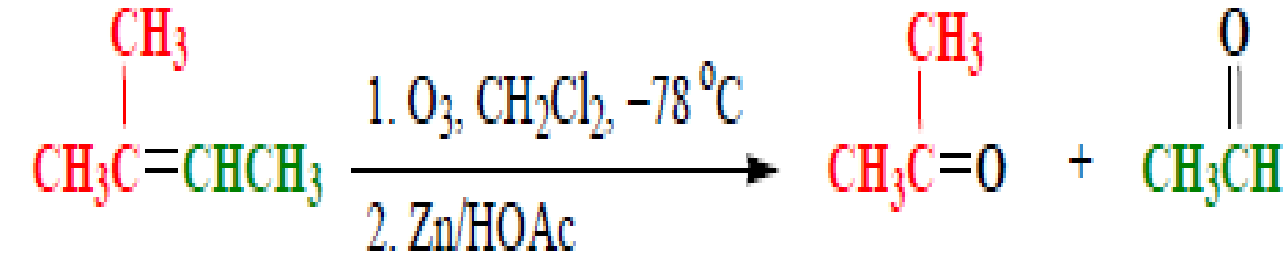
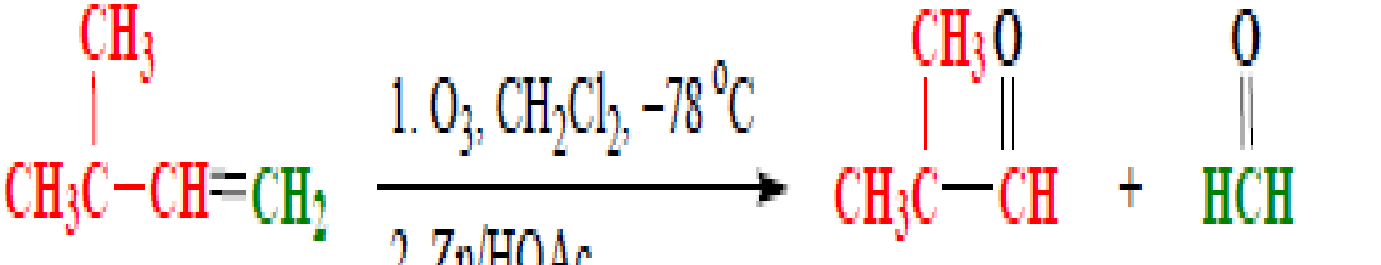


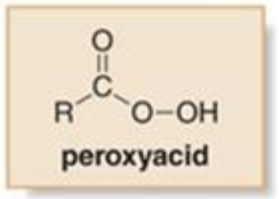
2-Methyl-2-butene Acetone Acetaldehyde



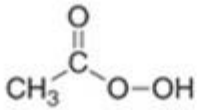
3-Methyl-1-butene Isobutyraldehyde Formaldehyed

8] EPOXIDTION OF ALKENES:

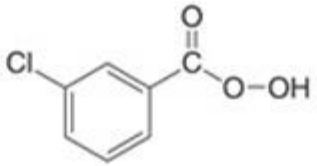
Common peroxyacids



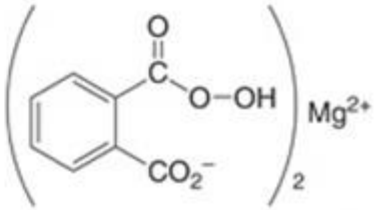
peroxyacid



peroxyacetic acid



meta-chloroperoxybenzoic acid
mCPBA



magnesium monoperoxyphthalate
MMPP

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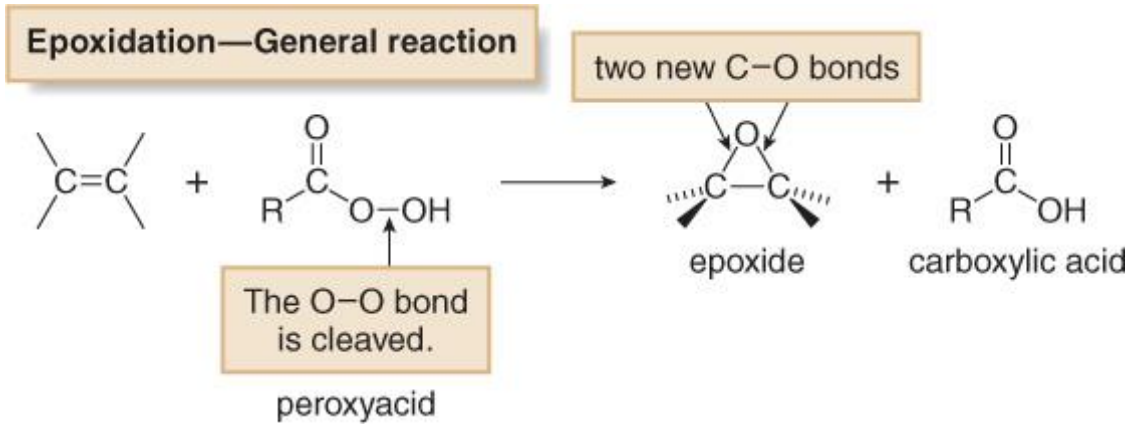

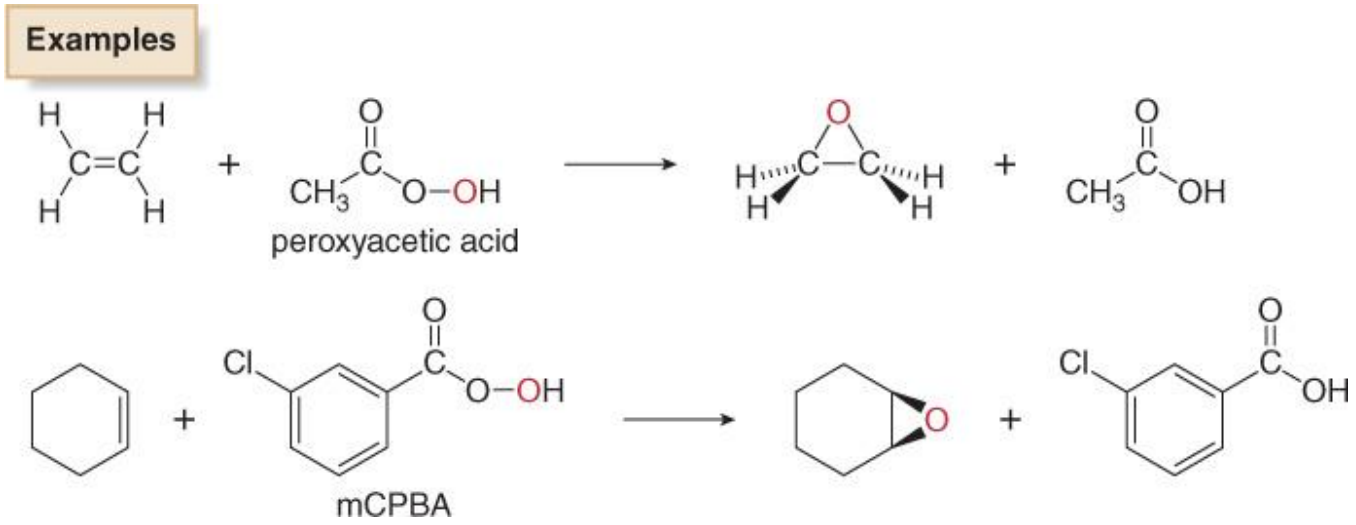

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Unsaturated Hydrocarbons II: Alkynes

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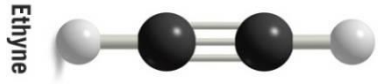
Alkynes: Molecular and Structural Formulas

- General molecular formula C_nH_{2n-2}
- The alkyne triple bond is composed of one σ and two π covalent bonds.
- The simplest alkyne, ethyne (also known as acetylene), has two carbon atoms and the molecular formula of C_2H_2. The structural formula for ethyne is:



Common Nomenclature

$HC\equiv CH$

Acetylene

- **Derived from acetylene**

$HC\equiv C\text{-}CH_3$

Methylacetylene

$CH_3\text{-}C\equiv C\text{-}CH_3$

Dimethylacetylene

$CH_3\text{-}C\equiv C\text{-}CH_2CH_3$

Ethylmethylacetylene

IUPAC Nomenclature

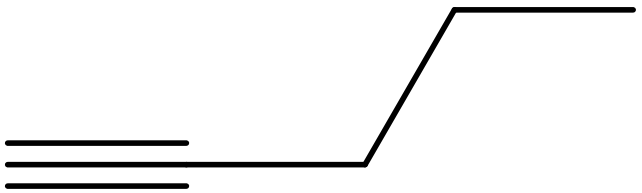
1. Identify the longest continuous chain of carbon atoms that contains the carbon-carbon triple bond. Put the ending – *yne*
2. Number the carbon atoms of the longest continuous chain, starting at the end closest to the triple bond.
3. The location and name of any substituent atom or group is indicated.

$CH_3—C\equiv CH$

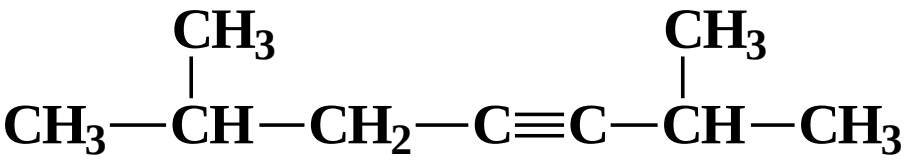
Propyne

$CH_3—C\equiv C—CH_2—CH_2—Br$

5-bromo-2-pentyne

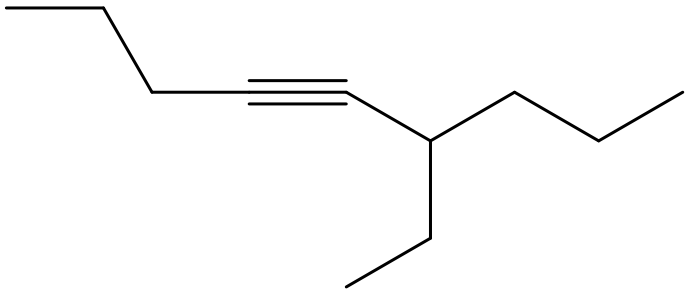


Pentyne



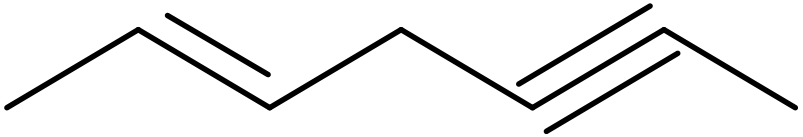
IUPAC :2,6-Dimethyl-3-heptyne

Common:Isobutylisopropylacetylene



6-Ethyl-4-nonyne

- <u>If there is a compound that contains both a double and a triple bond:</u>
- 1) Choose the chain that contains both bonds even if it is not the longest chain.
- 2) Start numbering the chain from the side nearer to the double bond.
- 3) Omit the letter (e) at the end of (ene)
- 4) End the name with the ending (yne) preceded with the number indicating the position of the triple bond.



Hept-2-en-5-yne

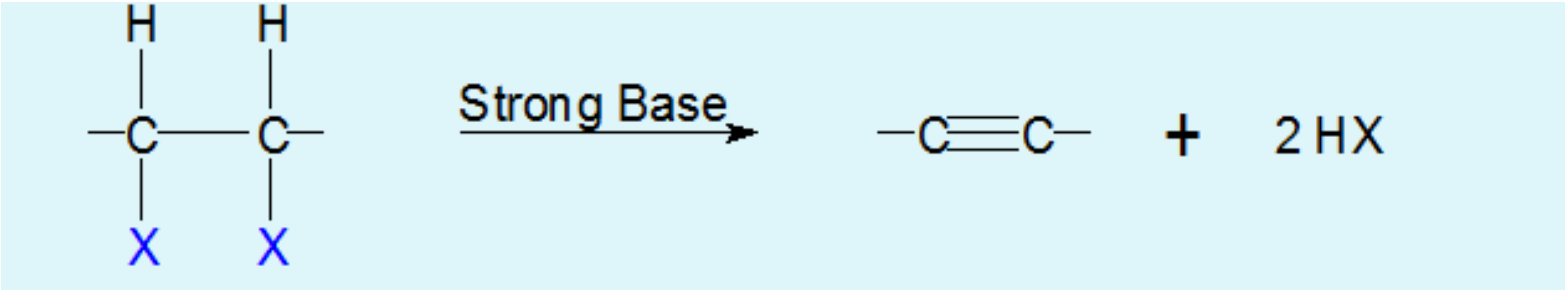
or 2-Hepten-5-yne

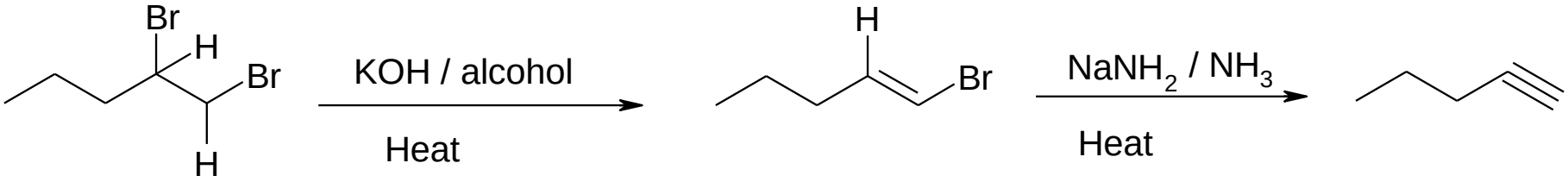
Physical Properties

- Nonpolar, insoluble in water.
- Soluble in most organic solvents.
- Boiling points similar to alkane of same size.
- Less dense than water.
- Up to 4 carbons, gas at room temperature.
- Terminal alkynes, R-C≡C-H, are more acidic than other hydrocarbons.

Preparation of alkynes

1. Dehydrohalogenation of alkyl dihalides





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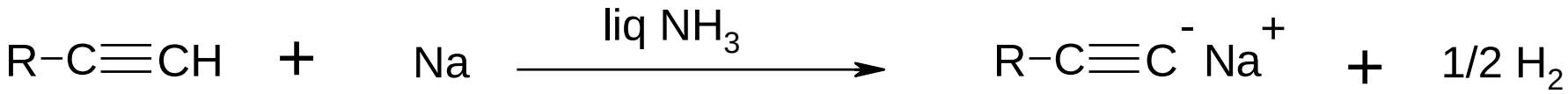
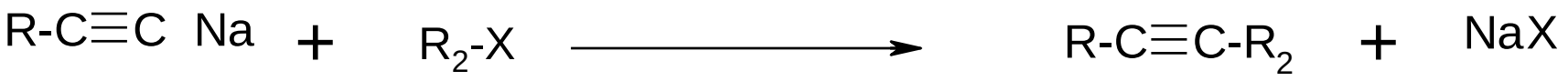
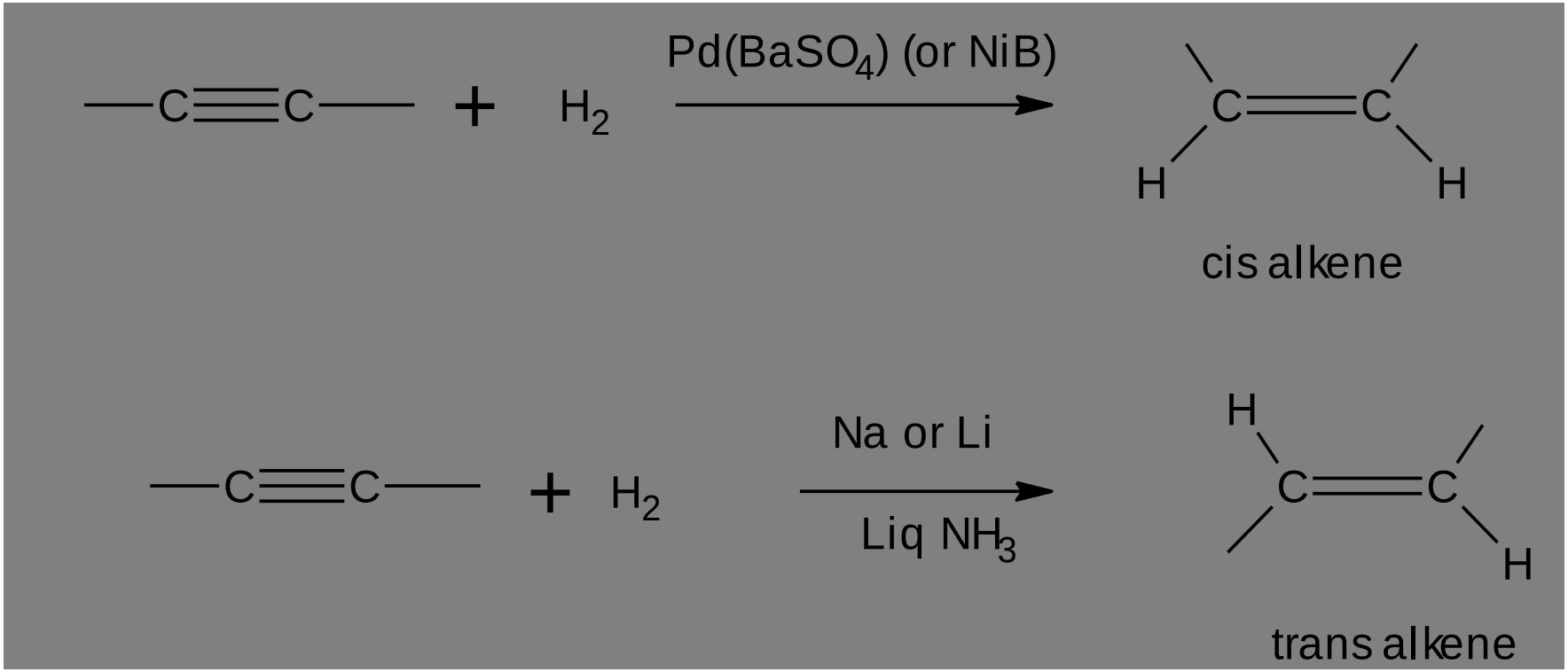
2. Reaction of sodium Acetylide with Primary Alkyl Halides



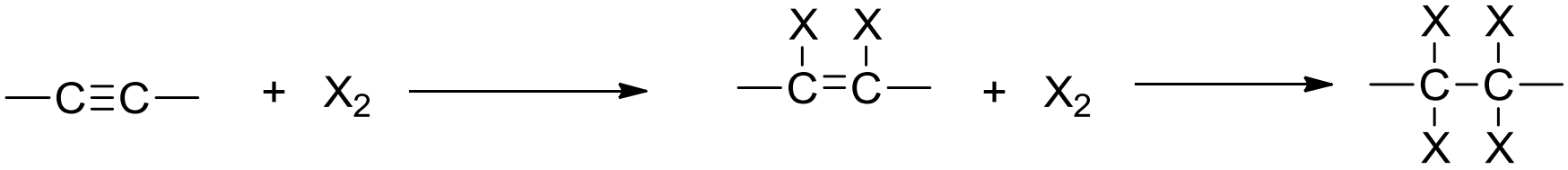


Reactions of alkynes
Electrophilic Addition Reaction

1. Addition of hydrogen



2. Addition of halogen



X = Br , Cl

Dihalide

Tetrahalide

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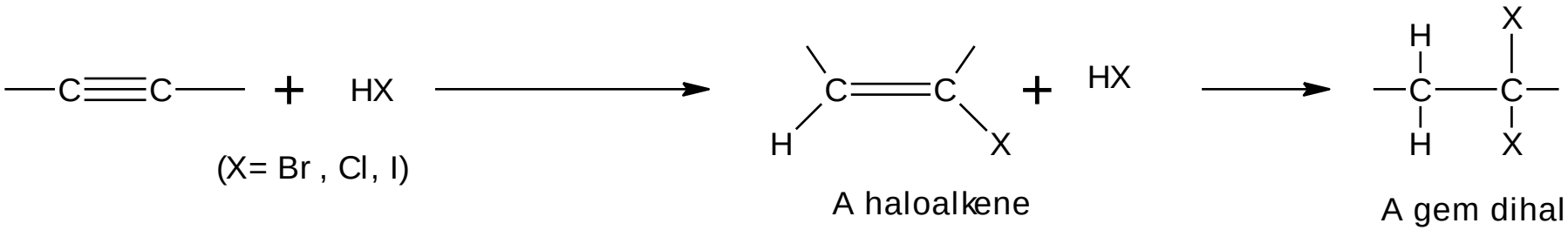
3. Addition of hydrogen halide



4- Addition of water : Hydration