Organic Chemistry

1st year students

Lecture No. 5

Ahmed Mohamad Jawad

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Out line

- **1- Dienes:**
- Introduction of diene
- Nomenclature of diene
- Preparation of diene
- Reaction of diene
- **2- Alkyne**
- Introduction of Alkyne
- Nomenclature of Alkyne
- Physical properties of alkyne
- Preparation of Alkyne
- Reaction of Alkyne

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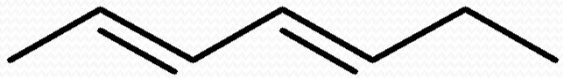
Introduction of diene

- **Dienes are simply alkenes that contain two carbon-carbon double bonds.**
- Dienes are divided into two major important classes according to the arrangement of the double bonds
- 1-Conjugated :

  Double bonds that alternate with single bonds are said to be conjugated.



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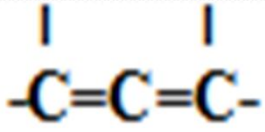
Introduction of diene

- 2-Isolated
- double bonds that are separated by more than one single bond are said to be isolated
- Less stable than conjugated

- 3-Cumulated :
- contains **cumulated double** bonds
- Least one stable .



Cumulated double bonds: allenes

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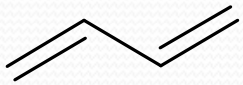
Nomenclature of diene

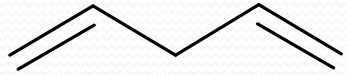
- Dienes are named by the IUPAC system in the same way as alkenes , except that the ending **diene** is used, with two numbers to indicate the position of the two double bonds.

$H_2C{=}C{=}CH_2$

1,2-propa**diene**



1,3-buta**diene**



1,4-penta**diene**

- This system is easily extended to compounds containing any number of double bonds.

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

1,3,5-Hexatriene

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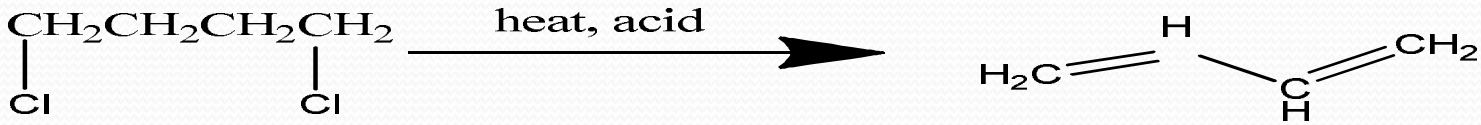
Preparation of diene

- 1- by acid catalyzed double dehydration

- 2- By dehydrogenation of dihalides:



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Reactions of Dienes

- In general terms, dienes undergo electrophilic addition reactions in a similar approach of alkenes
- **Conjugated dienes** undergo addition but the proximity of the conjugated **C=C** influences the reactions.
- Isolated dienes react just like alkenes

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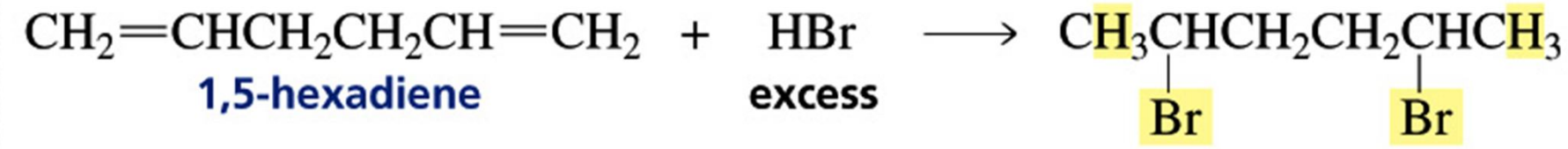
Electrophilic Addition Reactions of Isolated Dienes

- Reaction of 1,5-hexadiene with excess HBr adds HBr independently to each double bond
- Markovnikov's Rule is followed



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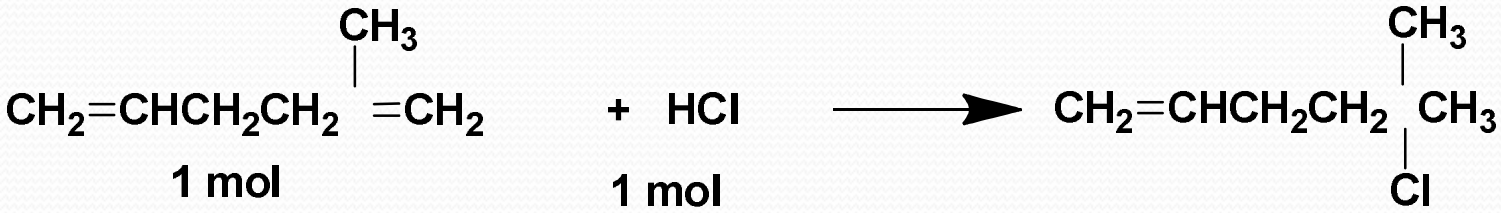
Electrophilic Addition Reactions of Isolated Dienes

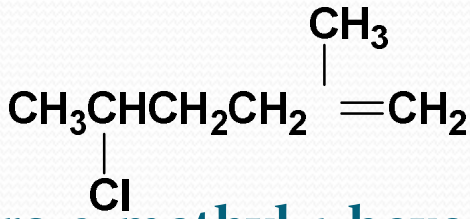


2-methyl-1,5-hexadiene

5-chloro-5-methyl-1-hexene

major product

+



5-chloro-2-methyl-1-hexene

minor product

If there is only enough electrophile to add to one double bond, a mixture of products will be obtained

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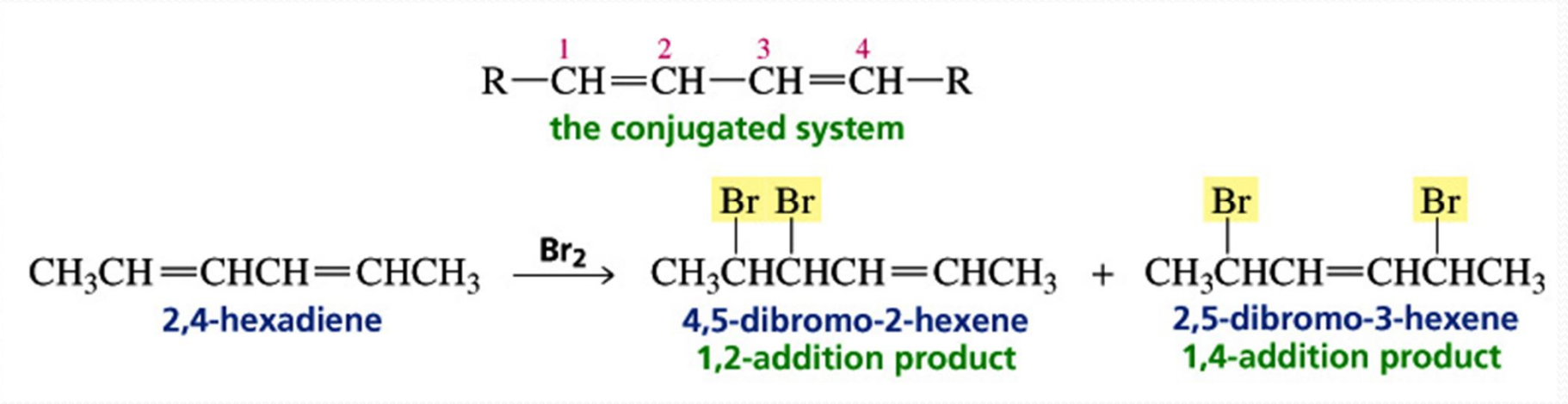
Electrophilic Addition Reactions of Conjugated Dienes

- Conjugated dienes can give both 1,2- and 1,4- addition products



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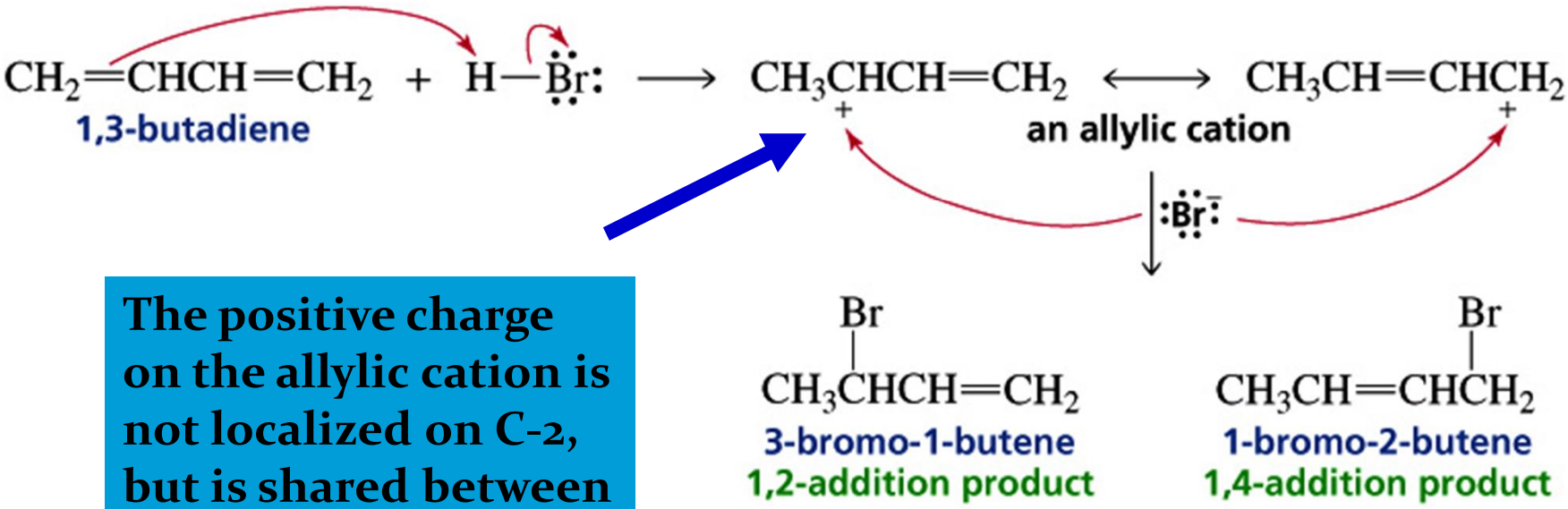
Mechanism of Addition of HBr to Conjugated Dienes

mechanism for the reaction of 1,3-butadiene with HBr



The positive charge on the allylic cation is not localized on C-2, but is shared between C-2 and C-4

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Introduction of Alkyne

- Alkynes contain a triple bond.
- General formula is C_nH_{2n-2}.
- Some reactions similar to the reactions of alkenes, like addition and oxidation.
- Some reactions are specific to alkynes.

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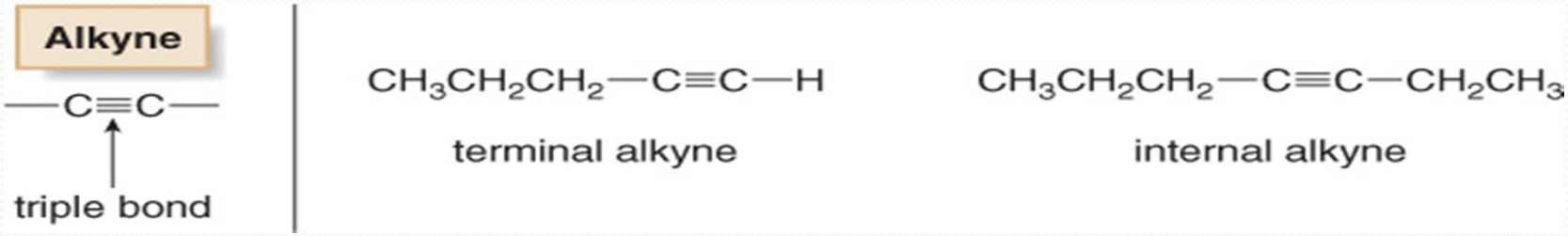
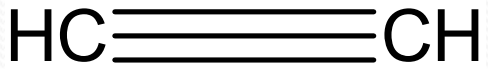
Introduction of Alkyne

- Alkynes: Molecular And Structural Formulae
- The **alkynes** containing a series of carbon and hydrogen based compounds that contain at least one triple bond. This group of compounds is a homologous series with the general molecular formula of **C*n* H2*n*—2**
- The alkyne triple bond is containing of one σ and two 2 π covalent bonds, the triple bond can be terminal or internal.



- 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:



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Nomenclature of Alkyne

- Find the longest chain containing the triple bond.
- Change -*ane* ending to -*yne*.
- Number the chain, starting at the end closest to the triple bond.
- Give branches or other substituents a number to locate their position.

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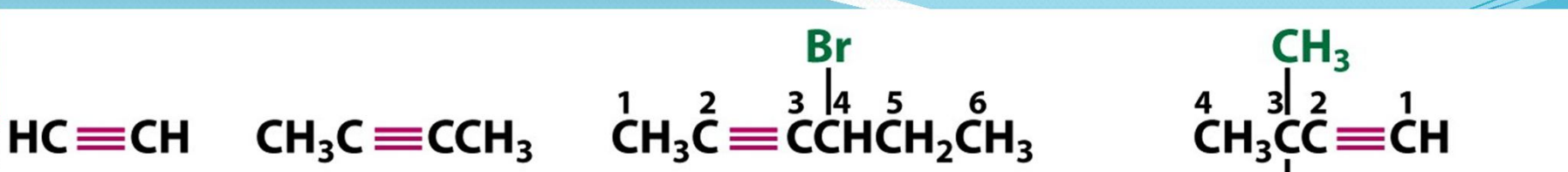
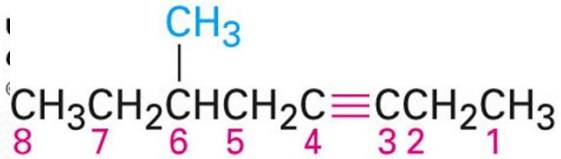
Ethyne

2-Butyne

4-Bromo-2-hexyne

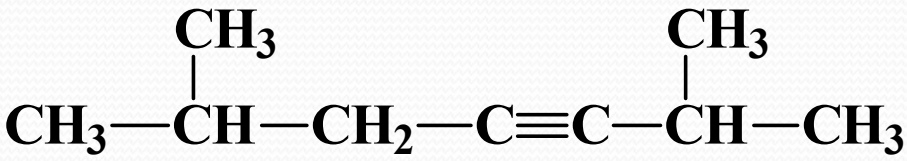


3,3-Dimethyl-1-butyne



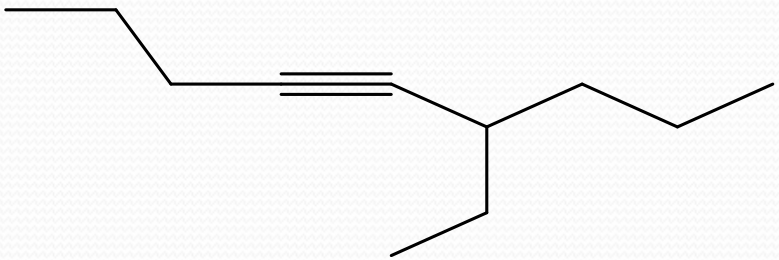
6-Methyl-3-octyne

Propyne

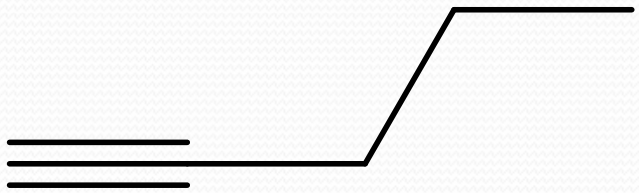


2,6-Dimethyl-3-heptyne

5-bromo-2-pentyne



6-Ethyl-4-nonyne



Pentyne

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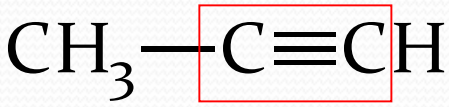
Common Nomenclature

Acetylene

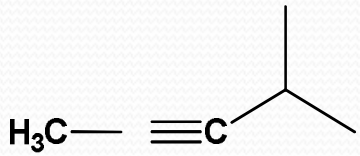
Methylacetylene

Dimethylacetylene

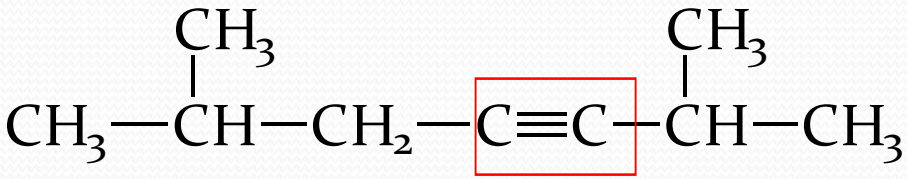
Ethylmethylacetylene



Methyl acetylene
(terminal alkyne)



Isopropylmethylacetylene



Isobutyl isopropyl acetylene
(internal alkyne)

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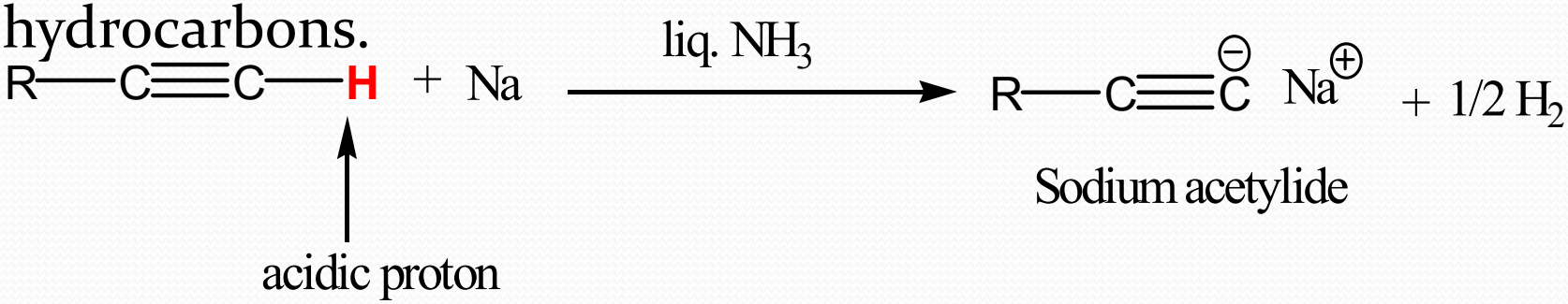
Physical Properties of Alkyne

- 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.



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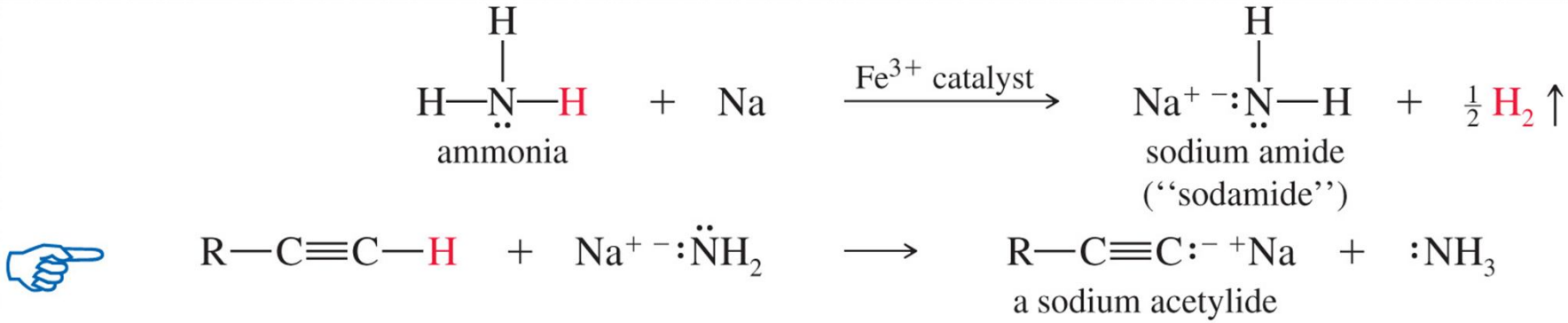
Physical Properties of Alkyne

Formation of Acetylide Ions

H^+ can be removed from a terminal alkyne by sodium amide, $NaNH_2$



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The acetylide ion is a strong nucleophile that can easily do addition and substitution reactions

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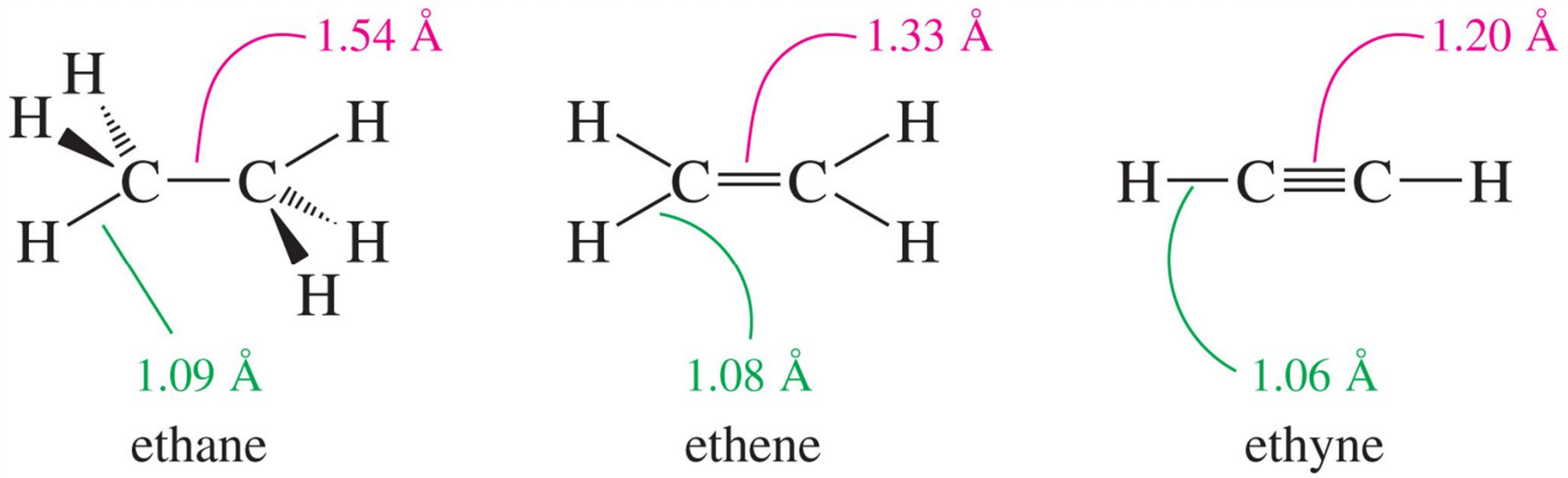
Physical Properties of Alkyne

- **Bond Lengths**
- Triple bonds are shorter than double or single bonds because of the two pi overlapping orbitals .



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Physical Properties of Alkyne

- Acidity of Alkynes
- Terminal alkynes, are more acidic than other hydrocarbons due to the higher *s* character of the *sp* hybridized carbon.
- Terminal alkynes can be deprotonated quantitatively with strong bases such as sodium amide ($^{-}NH_2$).
- Hydroxide and alkoxide bases are not strong enough to deprotonate the alkyne quantitatively.

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Preparation of Alkynes

- ***1- Dehydrohalogenation Reaction***
- Removal of two molecules of HX from a vicinal or geminal dihalide produces an alkyne.
- First step (-HX) is easy, forms vinyl halide.
- Second step, removal of HX from the vinyl halide requires very strong base and high temperatures.

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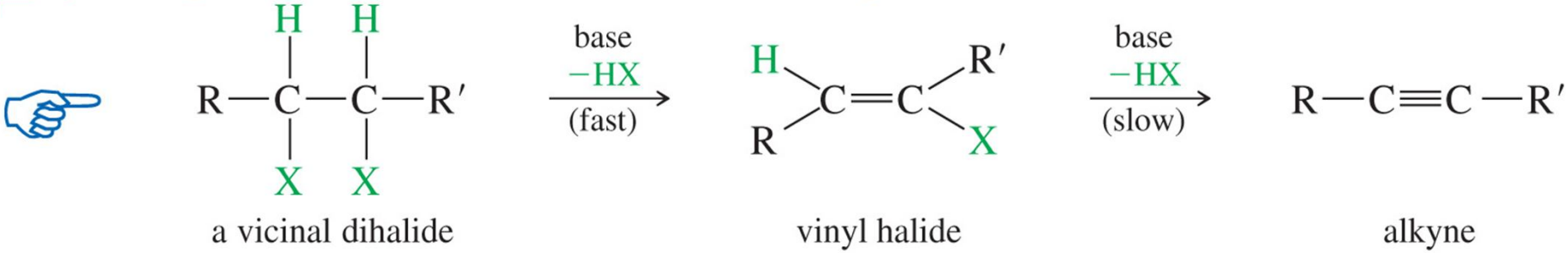
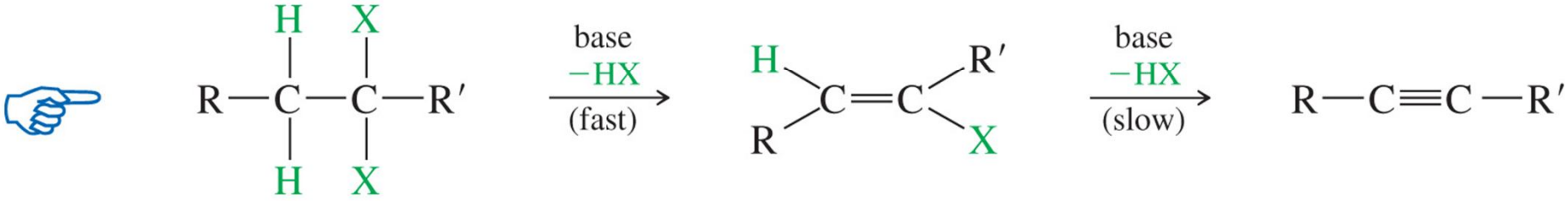
Preparation of Alkynes



a vicinal dihalide — vinyl halide — alkyne



a geminal dihalide — vinyl halide — alkyne

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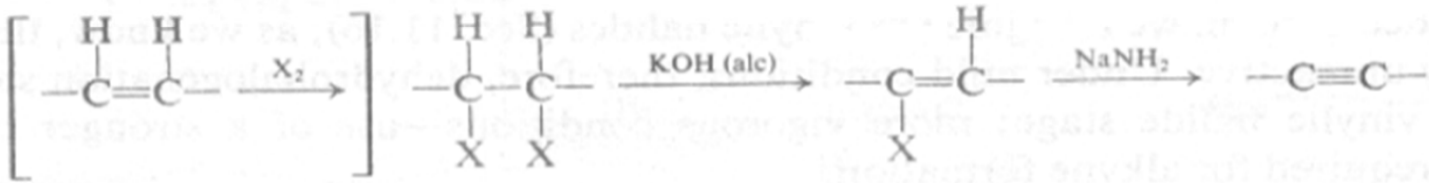
1. Dehydrohalogenation of alkyl dihalides.



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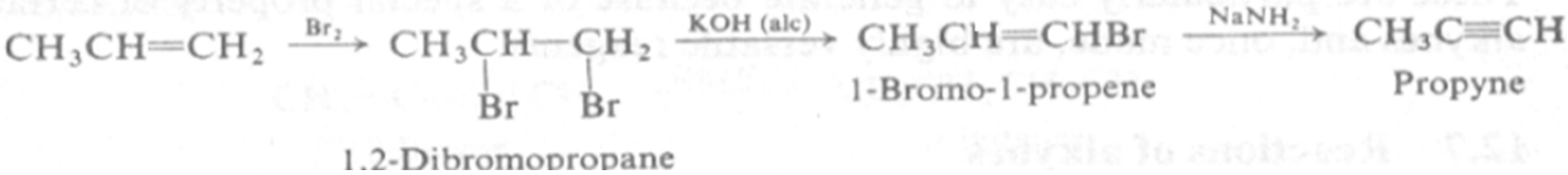

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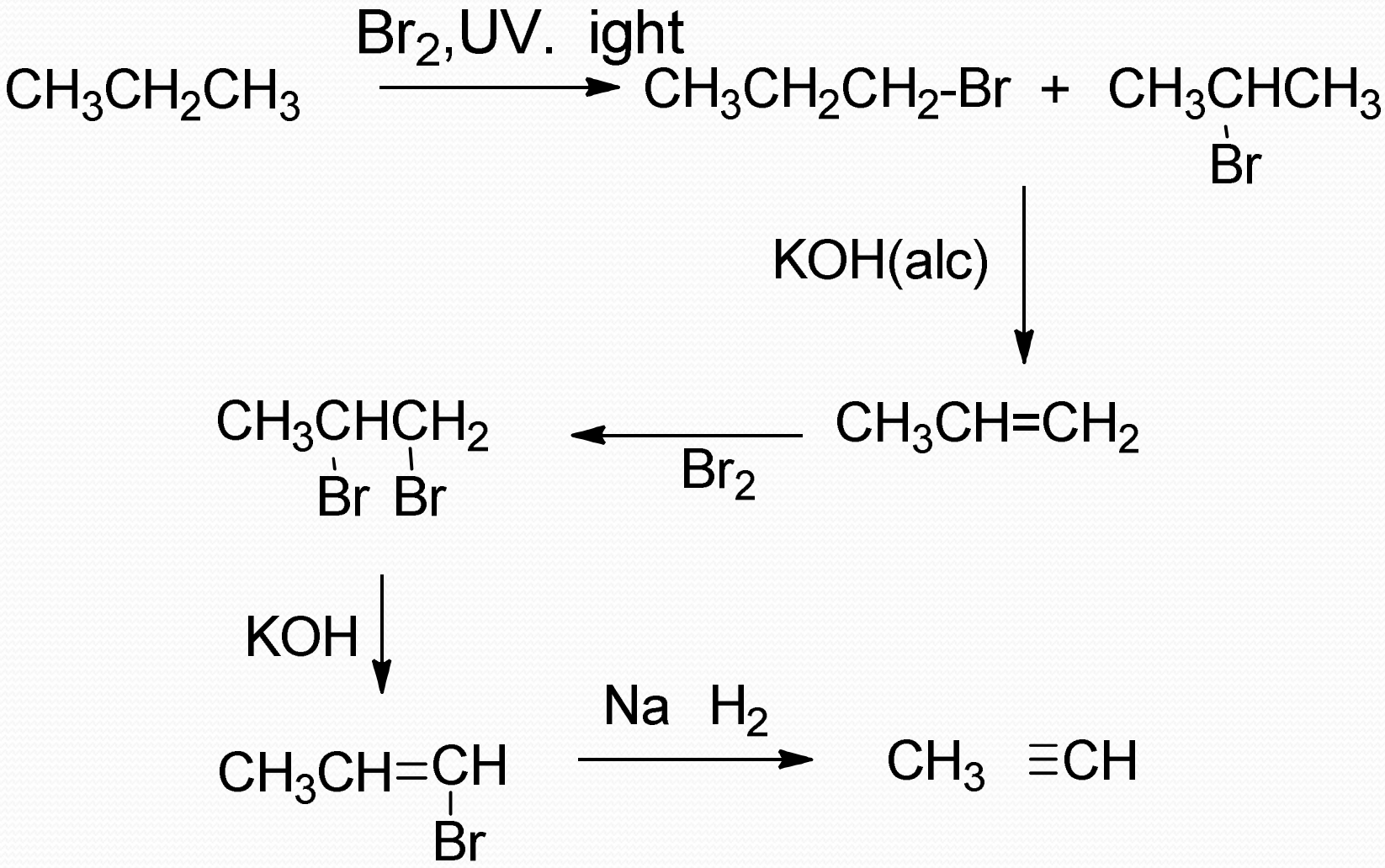
Preparation of Alkynes

Synthesis of propyne from propane



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Preparation of Alkynes

2-coupling of metal acetylides with 1°/CH_3 alkyl halides

$$R\text{-}C{\equiv}C^{-}Na^{+} + R'X \rightarrow R\text{-}C{\equiv}C\text{-}R' + NaX$$

2. Reaction of metal acetylides with primary alkyl halides. Discussed in Sec. 12.12.

$$\left[-C{\equiv}C-H \xrightarrow{LiNH_2}\right] -C{\equiv}C:^{-}Li^{+} + RX \longrightarrow -C{\equiv}C-R + LiX$$

R *must be* 1°

Examples:

$$HC{\equiv}C:^{-}Li^{+} + CH_3CH_2CH_2CH_2Br \longrightarrow HC{\equiv}C-CH_2CH_2CH_2CH_3$$

Lithium acetylide — *n*-Butyl bromide — 1-Hexyne (*n*-Butylacetylene)

CONTINUED

$$CH_3CH_2-C{\equiv}C:^{-}\ {}^{+}Na + H_3C-I \longrightarrow CH_3CH_2-C{\equiv}C-CH_3 + NaI$$

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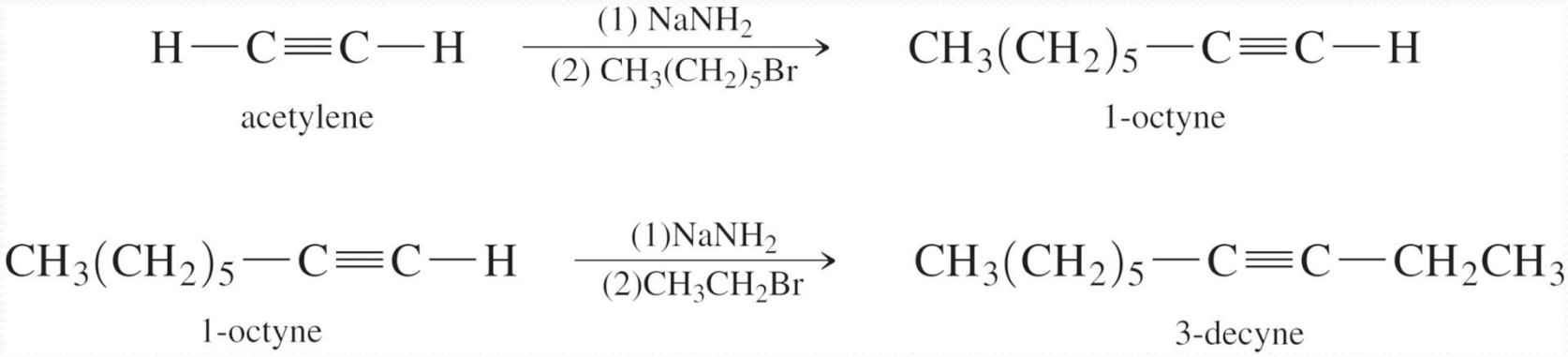

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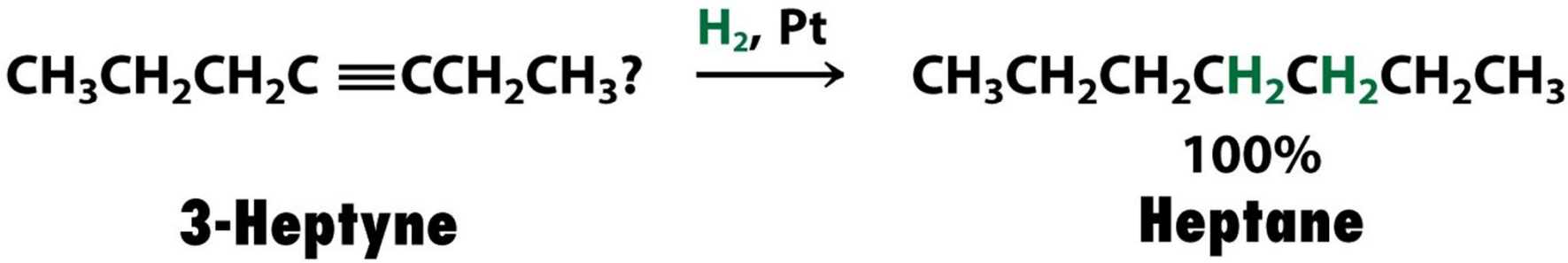
Reaction of alkyne

1-***Catalytic Hydrogenation of Alkynes***

Addition of H_2 over a metal catalyst (such as palladium on carbon, Pd/C) converts alkynes to alkanes (complete reduction)

- A catalyst such as Pd, Pt, or Ni needs to be used for the reaction to occur.

Complete Hydrogenation of Alkynes



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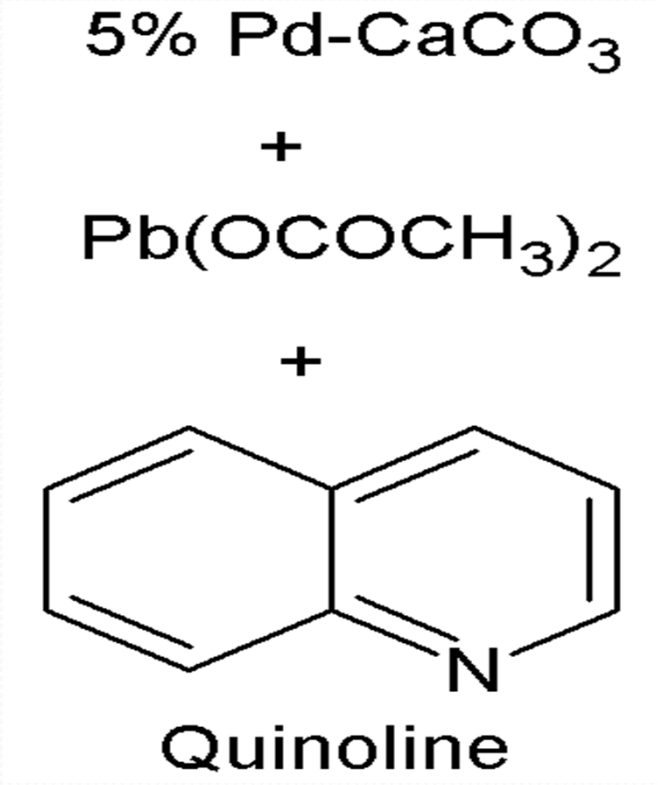
Reaction of alkyne

- ***2- Hydrogenation with Lindlar's Catalyst***



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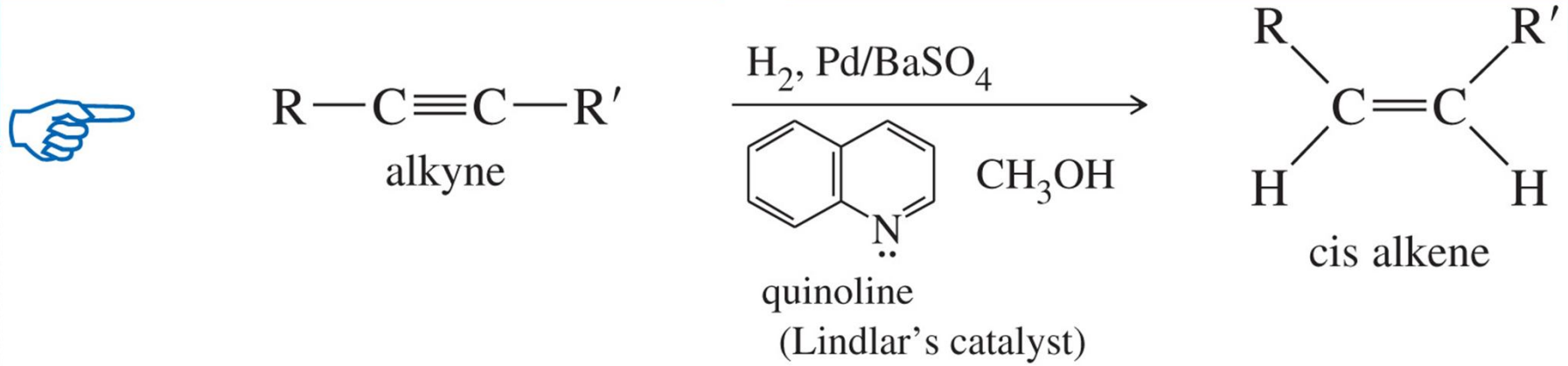

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- The catalyst used for the hydrogenation reaction is partially deactivated (poisoned), the reaction can be stopped after the addition of only one mole of hydrogen.

- The catalyst used is commonly known as Lindlar's catalyst and it is composed of powdered barium sulfate, coated with palladium poisoned with quinoline.
- The reaction produces alkenes with cis stereochemistry.

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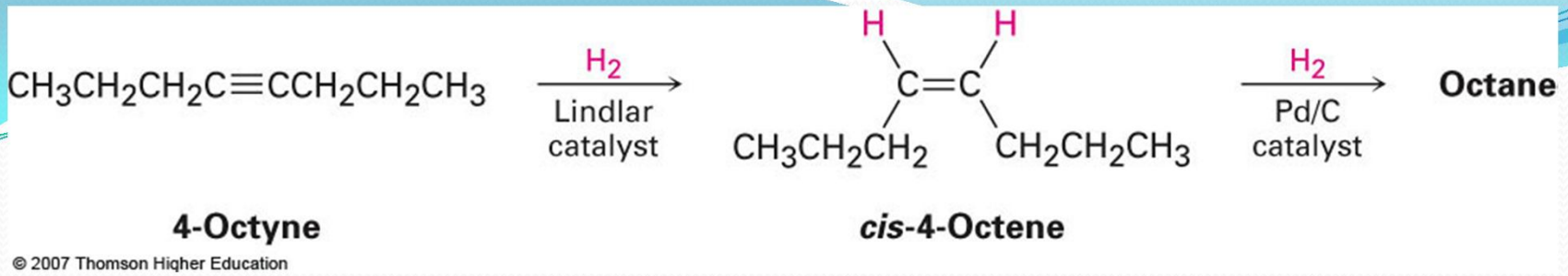

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Hydrogenation with Lindlar Catalyst

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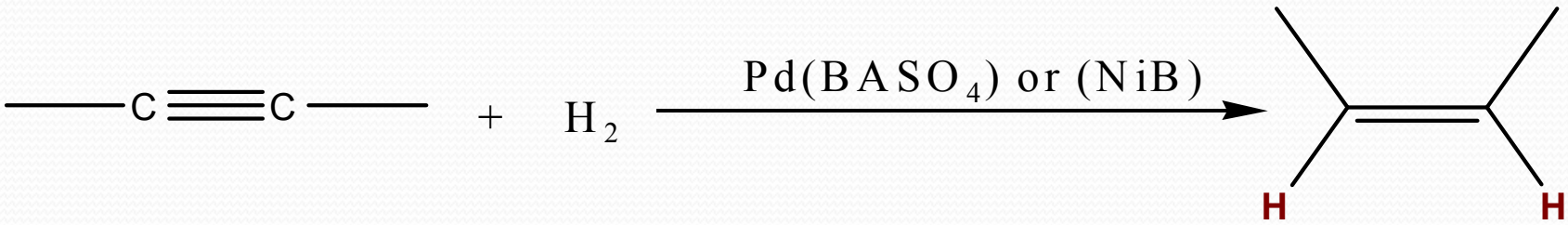

Cis- alkene

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