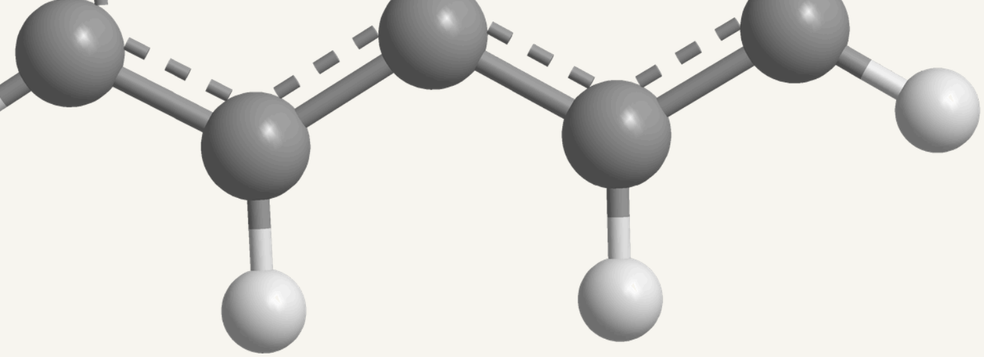
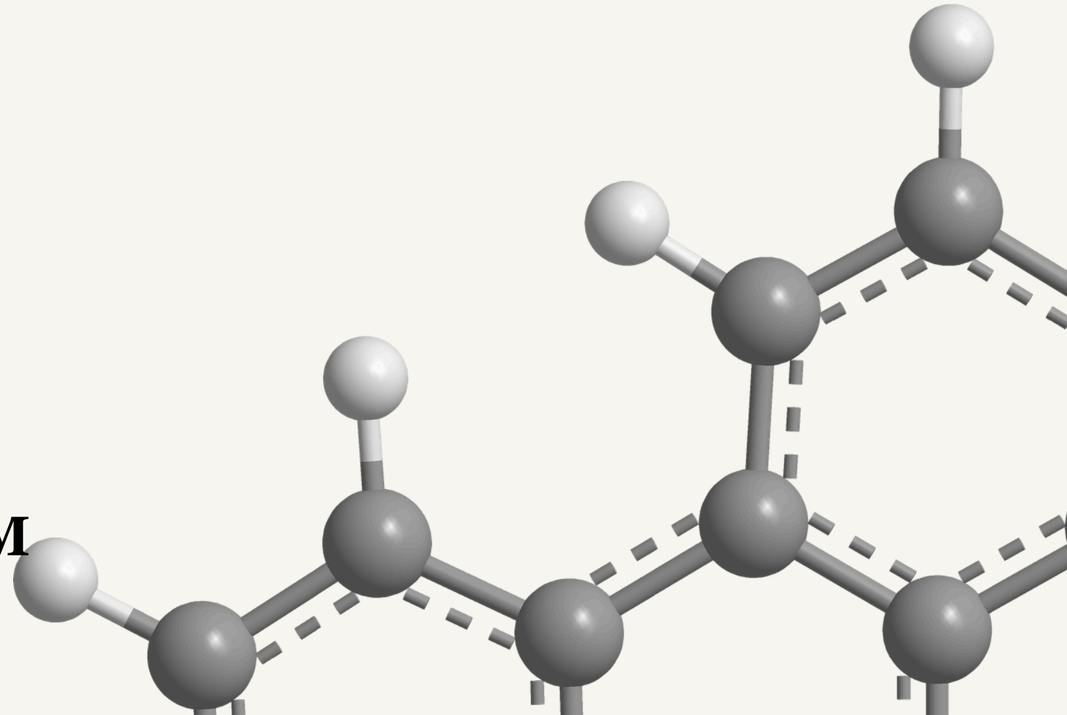


lector 9

Alkynes: isomerism, nomenclature, extraction and chemical properties.

Lecture: PhD, acc. professor: Kudaibergenova B.M



Aim and Objectives

Aim

To study the structure, isomerism, nomenclature, preparation and chemical properties of alkynes, and their significance in organic chemistry and industry.

Objectives

1. Define alkynes and their general formula
2. Explain bonding in the C≡C bond
3. Identify types of isomerism
4. Apply IUPAC naming rules
5. Study preparation methods
6. Study addition, oxidation and combustion
7. Explain acidity of terminal alkynes
8. Identify industrial applications

> Alkynes are the starting point for many industrial syntheses. Understanding their bonding explains why they react differently from alkanes and alkenes, and how chemists use them to build larger molecules.

Introduction to Alkynes

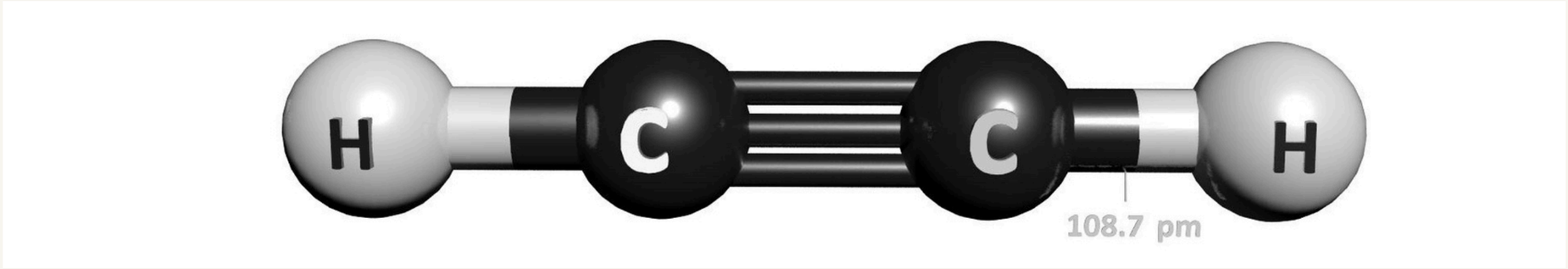
Unsaturated hydrocarbons with at least one C≡C bond.

$$C_nH_{2n-2} \quad (n \geq 2)$$

- sp-hybridized triple-bonded carbons
- Linear geometry, bond angle 180°
- Two π bonds: addition reactions

Name	Formula	Structure
Ethyne	C_2H_2	HC≡CH
Propyne	C_3H_4	CH_3–C≡CH
But-1-yne	C_4H_6	CH_3CH_2–C≡CH
But-2-yne	C_4H_6	CH_3–C≡C–CH_3

The name comes from the suffix -yne. Each triple bond removes four hydrogens compared with the alkane, so the formula is C_nH_{2n-2}. Ethyne (acetylene) is the simplest and most important member of the series.

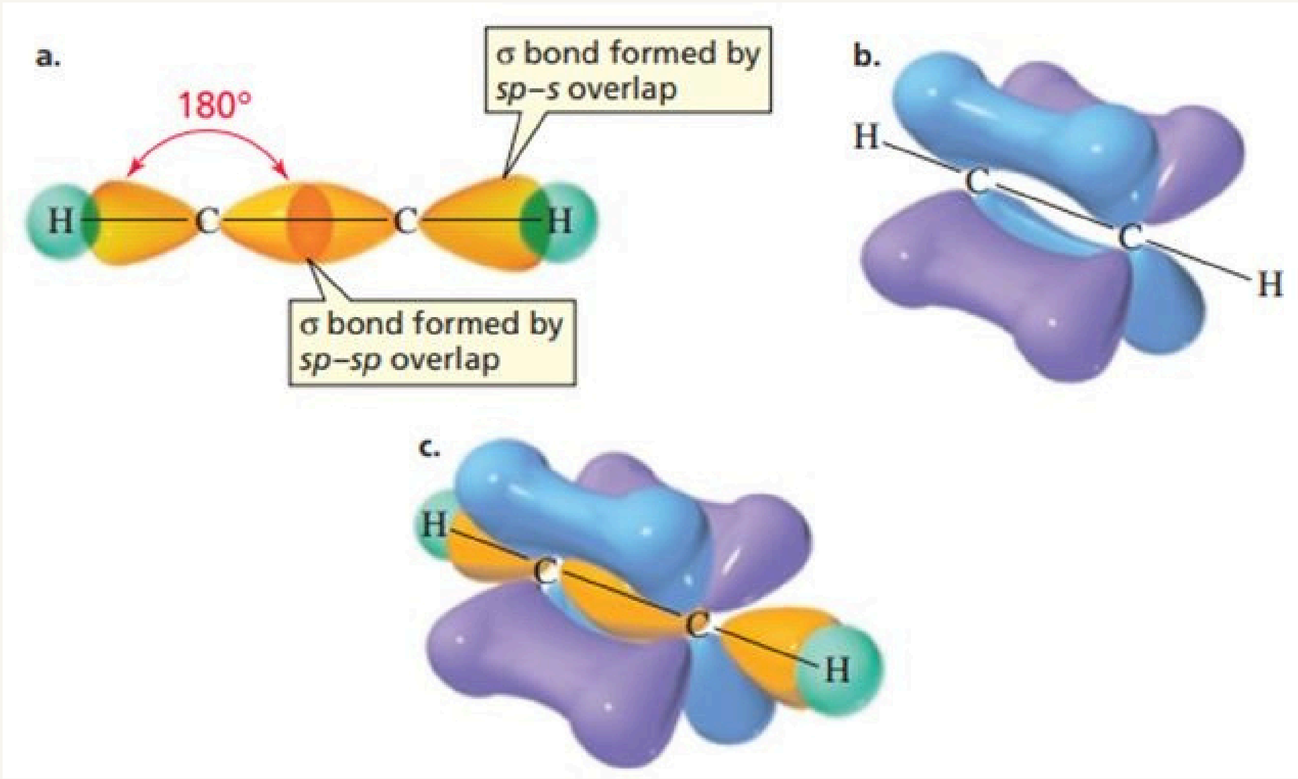


Structure and Bonding

- One σ bond: overlap of sp hybrid orbitals
- Two π bonds: sideways overlap of p orbitals
- Shorter and stronger overall than C–C and C=C
- 50% s-character of sp carbon raises the acidity of terminal alkynes

$$H–C\equiv C–H$$

Ethyne



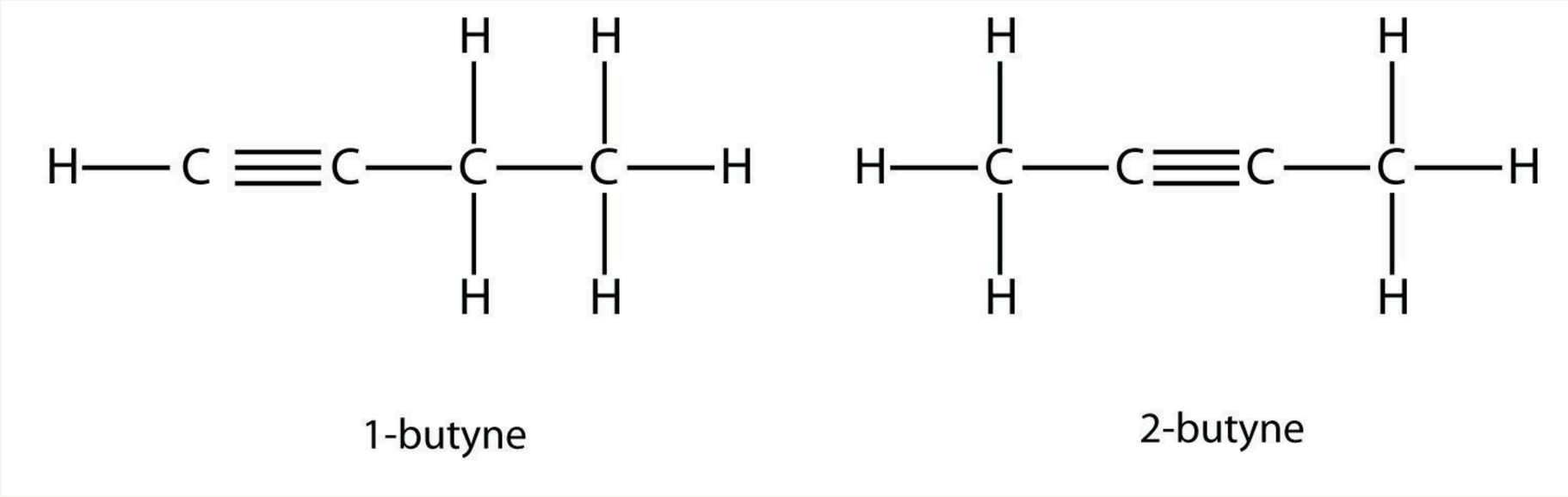
The two π bonds lie in perpendicular planes around the C–C axis and form a cylinder of electron density. This electron-rich region attracts electrophiles, which is why addition is the typical reaction. The C≡C bond length is about 120 pm.

Isomerism of Alkynes

Same molecular formula, different arrangement of atoms.

Type	Example
Position	But-1-yne and but-2-yne (C_4H_6)
Chain	Pent-1-yne and 3-methylbut-1-yne (C_5H_8)
Functional group (ring–chain)	But-1-yne and buta-1,3-diene (C_4H_6)

Position isomerism starts at C_4, because ethyne and propyne have only one possible position for the triple bond. Alkynes show no cis–trans isomerism at the triple bond, since the geometry around it is linear.



Nomenclature of Alkynes

1. Select the longest chain containing the triple bond
2. Number from the end nearest the triple bond
3. Replace -ane with -yne
4. Give the position of the triple bond
5. Name and number substituents
6. Write the full name

Structure	IUPAC name
HC≡CH	Ethyne
CH_3–C≡CH	Propyne
HC≡C–CH_2–CH_3	But-1-yne
CH_3–C≡C–CH_3	But-2-yne
HC≡C–CH(CH_3)–CH_3	3-Methylbut-1-yne

> If a molecule has both a double and a triple bond, number the chain to give the lowest locants to the multiple bonds together; on a tie, the double bond gets the lower number. Example: HC≡C–CH_2–CH=CH_2 is pent-1-en-4-yne.

Naming and Drawing Alkynes

Prefix	Name	Structure
Eth-	Ethyne	H-C≡C-H
Prop-	Propyne	H-C≡C-CH_2-H
But-	1-Butyne	H-C≡C-CH_2-CH_2-H
Pent-	1-Pentyne	H-C≡C-CH_2-CH_2-CH_2-H
Hex-	1-Hexyne	H-C≡C-CH_2-CH_2-CH_2-CH_2-H
Hept-	1-Heptyne	H-C≡C-CH_2-CH_2-CH_2-CH_2-CH_2-H
Oct-	1-Octyne	H-C≡C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-H

Physical Properties

- Small alkynes are gases at room temperature
- Larger ones are liquids or solids
- Poorly soluble in water
- Dissolve in organic solvents
- Boiling points rise with molecular mass
- Less dense than water

Acetylene, C_2H_2

Colourless, highly flammable gas. Burns in oxygen with a very hot flame; used in welding and synthesis.

Alkynes are slightly more polar than alkenes because an sp carbon is more electronegative, so their boiling points are a little higher than those of alkenes with the same number of carbons. The main intermolecular forces are weak London dispersion forces.

Preparation of Alkynes

$$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$$

Hydrolysis of calcium carbide

$$CH_2Br{-}CH_2Br + 2NaNH_2 \rightarrow HC{\equiv}CH + 2NaBr + 2NH_3$$

Double dehydrohalogenation of dihalides

$$2CH_4 \rightarrow C_2H_2 + 3H_2 \quad \text{(high temperature)}$$

Industrial conversion of methane

Calcium carbide is made by heating lime with coke in an electric furnace. The dehydrohalogenation route needs a very strong base such as sodium amide, because the second elimination starts from a vinyl halide, which is less reactive.

Chemical Properties

$$HC{\equiv}CH + 2H_2 \rightarrow[(Ni)] CH_3CH_3$$

Two π bonds: addition occurs in two stages.

- Hydrogenation
- Halogenation
- Hydrohalogenation
- Hydration
- Oxidation
- Combustion
- Acid–base reactions of terminal alkynes

Alkynes are less reactive toward electrophiles than alkenes, even though they have more π electrons, because the intermediate vinyl cation is less stable. Additions to terminal alkynes generally follow Markovnikov’s rule.



Hydrogenation

$$CH_3C{\equiv}CCH_3 + 2H_2 \xrightarrow{(Ni)} CH_3CH_2CH_2CH_3$$

Complete: but-2-yne gives butane

$$CH_3C{\equiv}CCH_3 + H_2 \xrightarrow{(Lindlar)} \text{cis-}CH_3CH{=}CHCH_3$$

Partial: cis-alkene

$$CH_3C{\equiv}CCH_3 \xrightarrow{(Na/NH_3(l))} \text{trans-}CH_3CH{=}CHCH_3$$

Dissolving-metal reduction: trans-alkene

> Lindlar’s catalyst is palladium on calcium carbonate, poisoned with lead acetate and quinoline, which stops the reaction at the alkene stage. Hydrogen adds to the same face of the triple bond, giving the cis product; sodium in liquid ammonia adds hydrogen to opposite faces, giving the trans product.

Halogenation and Hydrohalogenation

Halogenation

$$HC{\equiv}CH + Br_2 \rightarrow BrCH{=}CHBr$$

One equivalent

$$HC{\equiv}CH + 2Br_2 \rightarrow CHBr_2CHBr_2$$

Excess bromine

Hydrohalogenation

$$CH_3C{\equiv}CH + HBr \rightarrow CH_3C(Br){=}CH_2$$

2-Bromoprop-1-ene

$$CH_3C(Br){=}CH_2 + HBr \rightarrow CH_3CBr_2CH_3$$

2,2-Dibromopropane

Halogen addition is usually anti, giving the trans dihaloalkene first. The second HBr adds so that both bromine atoms end up on the same carbon (Markovnikov addition), which is why 2,2-dibromopropane forms rather than 1,2-dibromopropane.

Hydration of Alkynes

Water adds across the triple bond with Hg^{2+} and H_2SO_4.

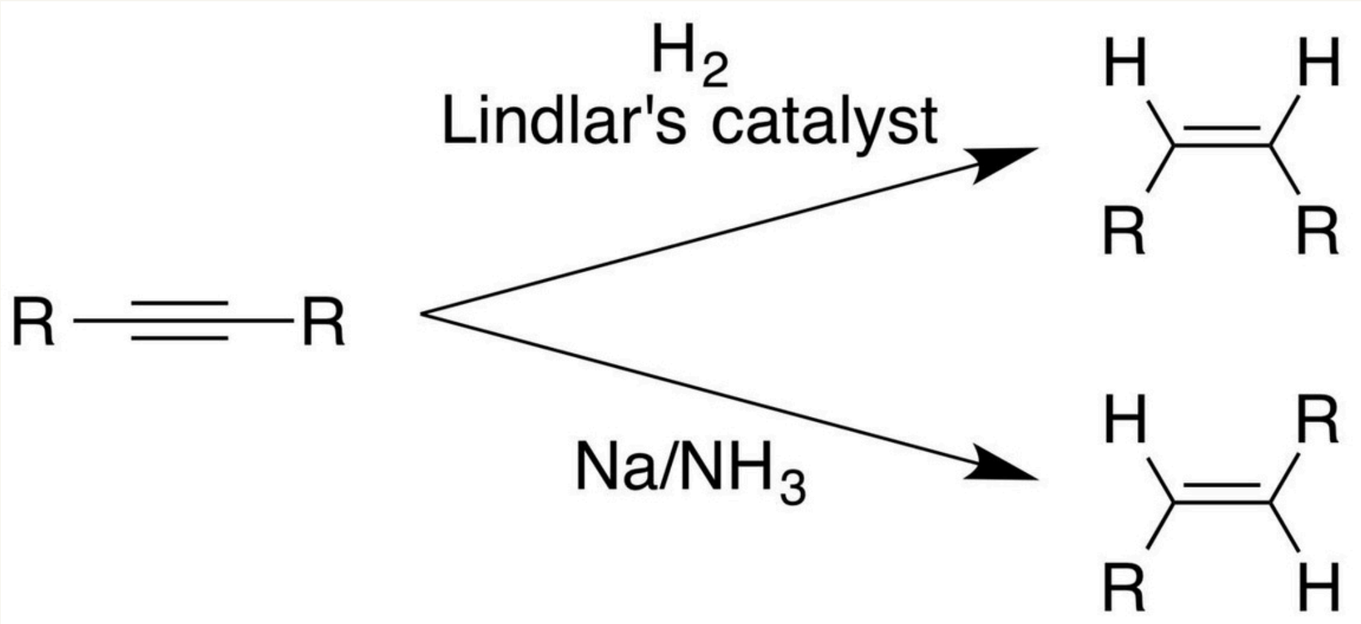
1. Water adds to C≡C
2. An enol forms
3. Keto–enol tautomerization
4. A carbonyl compound results

$$HC{\equiv}CH + H_2O \rightarrow (HgSO_4/H_2SO_4)\ CH_3CHO$$

Acetaldehyde from ethyne

$$CH_2{=}CHOH \rightarrow CH_3CHO$$

Enol intermediate to final product



Hydration of terminal alkynes follows Markovnikov’s rule, so propyne gives propanone (acetone), not an aldehyde. Ethyne is the only alkyne that gives an aldehyde, acetaldehyde. The enol intermediate is unstable and rapidly converts to the keto form.

Oxidation and Combustion

Oxidation

Strong oxidants cleave internal alkynes to carboxylic acids.

$$CH_3C{\equiv}CCH_3 + 3[O] + H_2O \rightarrow 2CH_3COOH$$

But-2-yne gives acetic acid

Combustion

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$$

Very hot flame: welding and metal cutting

Hot, concentrated $KMnO_4$ or ozonolysis followed by water also cleaves the triple bond to carboxylic acids; the CH end of a terminal alkyne becomes CO_2. Burning ethyne releases about 1300 kJ per mole, and the oxyacetylene flame reaches roughly 3000 °C.

Acidity and Applications

Terminal alkynes

The H on an sp carbon is more acidic than H on sp^2 or sp^3 carbon.

$$RC{\equiv}CH + NaNH_2 \rightarrow RC{\equiv}CNa + NH_3$$

Acetylide ions are useful nucleophiles

Applications

- Oxyacetylene welding and cutting
- Organic intermediates
- Carbon–carbon bond formation
- Specialized chemicals
- Research on new compounds

The pKa of a terminal alkyne is about 25, compared with about 44 for alkenes and about 50 for alkanes. Sodium amide is strong enough to remove this proton; hydroxide is not. Acetylide ions react with primary alkyl halides to lengthen the carbon chain.

Conclusion

- Triple bond: one σ and two π bonds
- Position, chain and functional-group isomerism
- IUPAC naming with the suffix -yne
- Prepared by double dehydrohalogenation and industrial routes
- Characteristic reactions: addition across C≡C
- Terminal alkynes are weakly acidic
- Wide use in synthesis and industry

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