Alkynes: Molecular and Structural Formulas

The **alkynes** comprise 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_nH_{2n--2}, where *n* equals any integer greater than one.

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

$$H-C\equiv C-H$$

In longer alkyne chains, the additional carbon atoms are attached to each other by single covalent bonds. Each carbon atom is also attached to sufficient hydrogen atoms to produce a total of four single covalent bonds about itself. In alkynes of four or more carbon atoms, the triple bond can be located in different positions along the chain, leading to the formation of structural isomers. For example, the alkyne of molecular formula C_4H_6 has two isomers,

$$HC\equiv C-CH_2CH_3 \quad \text{and} \quad CH_3-C\equiv C-CH_3$$

Although alkynes possess restricted rotation due to the triple bond, they do not have stereoisomers like the alkenes because the bonding in a carbon-carbon triple bond is *sp* hybridized. In *sp* hybridization, the maximum separation between the hybridized orbitals is 180°, so the molecule is linear. Thus, the substituents on triple-bonded carbons are positioned in a straight line, and stereoisomers are impossible

Alkynes: Nomenclature

Although some common alkyne names, such as acetylene, are still found in many textbooks, the International Union of Pure and Applied Chemistry (IUPAC) nomenclature is required for journal articles. The rules for alkynes in this system are identical with those for alkenes, except for the ending. The following rules summarize alkyne nomenclature.

1. Identify the longest continuous chain of carbon atoms that contains the carbon-carbon triple bond. The parent name of the alkyne comes from the IUPAC name for the alkane of the same number of carbon atoms, except the - *ane* ending is changed to - *yne* to signify the presence of a triple bond. Thus, if the longest continuous chain of carbon atoms containing a triple bond has five atoms, the compound is **pentyne.**

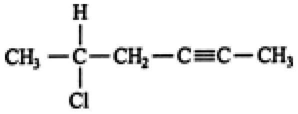
2. Number the carbon atoms of the longest continuous chain, starting at the end closest to the triple bond. Thus,

$$CH_3-CH_2-C\equiv C-CH_3$$

3. is numbered from right to left, placing the triple bond between the second and third carbon atoms of the chain. (Numbering the chain from left to right incorrectly places the triple bond between the third and fourth carbons of the chain.)

4. The position of the triple bond is indicated by placing the lower of the pair of numbers assigned to the triple-bonded carbon atoms in front of the name of the alkyne. Thus the compound shown in rule 2 is 2-pentyne.

5. The location and name of any substituent atom or group is indicated. For example, the compound



$$CH_3-\underset{\displaystyle Cl}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}-CH_2-C\equiv C-CH_3$$

6. is 5-chloro-2-hexyne

Alkynes: Physical Properties

The physical properties of alkynes are very similar to those of the alkenes. Alkynes are generally nonpolar molecules with little solubility in polar solvents, such as water. Solubility in nonpolar solvents, such as ether and acetone, is extensive. Like the alkanes and alkenes, alkynes of four or fewer carbon atoms tend to be gases.

Substituted alkynes have small dipole moments due to differences in electronegativity between the triple-bonded carbon atoms, which are *sp* hybridized, and the single-bonded carbon atoms, which are sp^3 hybridized. The *sp*-hybridized carbon atom, which possesses more *s* character than the sp^3-hybridized carbon atom, is more electronegative in character. The resulting asymmetrical electron distribution in the bond between such carbon atoms results in the generation of a dipole moment

Alkynes: Acidity

Alkynes of the general structure

$$R-C\equiv C-H$$

are referred to as **terminal alkynes.** These types of alkynes are weakly acidic. Exposure to a strong base, such as sodium amide, produces an acid-base reaction.

$$\underset{\text{alkyne}}{R-C\equiv C-H} + \underset{\text{amide ion}}{NH_2^-} \rightleftharpoons \underset{\text{acetylide ion}}{R-C\equiv C^-} + \underset{\text{ammonia}}{NH_3}$$

The acidity of a terminal alkyne is due to the high level of *s* character in the *sp* hybrid orbital, which bonds with the *s* orbital of the hydrogen atom to form a single covalent bond. The high level of *s* character in an *sp*-hybridized carbon causes the overlap region of the σ bond to shift much closer to the carbon atom. This polarizes the bond, causing the hydrogen atom to become slightly positive. This slight positive charge makes the hydrogen atom a weak proton, which can be removed by a strong base.

In the case of alkanes and alkenes, the *s* character in the hybridized carbon bonds is less, resulting in fewer electronegative carbon atoms and a corresponding lesser shift toward those atoms in the overlap region of the σ bond. The location of the overlap region makes the corresponding hydrogen atoms less electron deficient and thus less acidic. In reality, the hydrogen atoms bonded to alkanes and alkenes can be removed as protons, but much stronger nonaqueous bases are necessary.

The reaction that forms the acetylide ion is reversible. Thus, the base may not form an acid of greater strength than the starting alkyne by acceptance of the proton, or the newly formed conjugate acid will reprotonate the acetylide ion. The fact that stronger acids are capable of reprotonating the acetylide ion can be seen in its reaction with water.

$$R-C\equiv C^- + H_2O \longrightarrow R-C\equiv C-H + OH^-$$

⊞ Stereochemistry
⊞ Conjugated Dienes
⊞ Summary of Preparations
⊞ Summary of Reactions

CliffsNotes Poll

Test your knowledge: In psychology, what is the term given to when there is an improved performance due to the presence of others?

○ Social facilitation

○ Group polarization

○ Social loafing

○ Groupthink

Vote View Results

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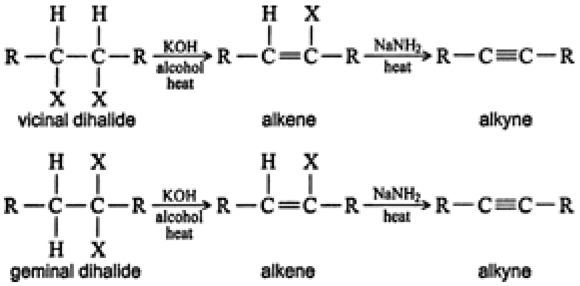
Alkynes: Preparations

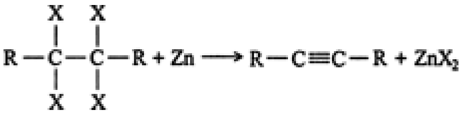
The preparations of alkynes are very similar to those of the alkenes. The main preparative reactions involve the elimination of groups or ions from molecules, resulting in the formation of π bonds.

Dehydrohalogenation. The loss of a hydrogen atom and a halogen atom from adjacent alkane carbon atoms leads to the formation of an alkene. The loss of additional hydrogen and halogen atoms from the double-bonded carbon atoms leads to alkyne formation. The halogen atoms may be located on the same carbon (a **geminal dihalide**) or on adjacent carbons (a **vicinal dihalide**).



During the second dehydrohalogenation step, certain conditions are necessary, namely high temperatures and an extremely strong basic solution.

Dehalogenation. Vicinal tetrahaloalkanes can be dehalogenated with zinc metal in an organometallic reaction to form alkynes.

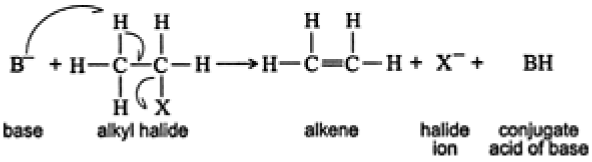


$$R-\overset{X}{\underset{X}{C}}-\overset{X}{\underset{X}{C}}-R + Zn \longrightarrow R-C\equiv C-R + ZnX_2$$

Substitution. Larger alkynes can be generated by reacting an alkyl halide with an acetylide ion, which is generated from a shorter alkyne.

$$R-C\equiv C^- + R'X \longrightarrow R-C\equiv C-R'$$

Because acetylide ions are bases, elimination reactions can occur, leading to the formation of an alkene from the alkyl halide. Because substitution and elimination reactions proceed through the formation of a common intermediate, these two types of reactions always occur simultaneously.



Ethyne (acetylene) preparation. Ethyne, which is commonly called **acetylene**, is the simplest alkyne. Historically, it was prepared by reacting calcium carbide with water.

$$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + HC\equiv CH$$

Today, ethyne is normally prepared by the pyrolysis of methane. In this procedure, a stream of methane gas is briefly heated to 1500°C in an airless chamber. Air must be excluded from the reaction or oxidation (combustion) will occur.

$$CH_4 \xrightarrow[0.1\ s]{1500°C} H-C\equiv C-H + H_2$$

Groupthink

Vote View Results

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Alkynes: Addition Reactions

The principal reaction of the alkynes is addition across the triple bond to form alkanes. These addition reactions are analogous to those of the alkenes.

Hydrogenation. Alkynes undergo catalytic hydrogenation with the same catalysts used in alkene hydrogenation: platinum, palladium, nickel, and rhodium. Hydrogenation proceeds in a stepwise fashion, forming an alkene first, which undergoes further hydrogenation to an alkane.

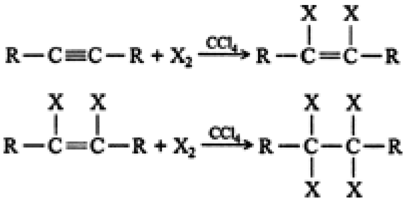
$$R{-}C{\equiv}C{-}R' \xrightarrow[Pt]{H_2} R{-}CH{=}CH{-}R' \xrightarrow[Pt]{H_2} R{-}CH_2{-}CH_2{-}R'$$

This reaction proceeds so smoothly that it is difficult, if not impossible, to stop the reaction at the alkene stage, although by using palladium or nickel for the catalyst, the reaction can be used to isolate some alkenes. Greater yields of alkenes are possible with the use of **poisoned catalysts.** One such catalyst, the **Lindlar catalyst**, is composed of finely divided palladium coated with quinoline and absorbed on calcium carbonate. This treatment makes the palladium less receptive to hydrogen, so fewer hydrogen atoms are available to react. When a catalyst is deactivated in such a manner, it is referred to as being **poisoned.**

The mechanism of alkyne hydrogenation is identical to that of the alkenes. Because the hydrogen is absorbed on the catalyst surface, it is supplied to the triple bond in a *syn* manner.

Alkynes can also be hydrogenated with sodium in liquid ammonia at low temperatures. This reaction is a chemical reduction rather than a catalytic reaction, so the hydrogen atoms are not attached to a surface, and they may approach an alkene from different directions, leading to the formation of *trans* alkenes.

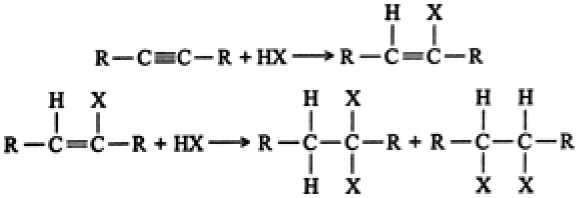
Halogenation. The addition of halogens to an alkyne proceeds in the same manner as halogen addition to alkenes. The halogen atoms add to an alkyne molecule in a stepwise fashion, leading to the formation of the corresponding alkene, which undergoes further reaction to a tetrahaloalkane.



$$R-C\equiv C-R + X_2 \xrightarrow{CCl_4} R-\overset{X}{C}=\overset{X}{C}-R$$
$$R-\overset{X}{C}=\overset{X}{C}-R + X_2 \xrightarrow{CCl_4} R-\overset{X}{\underset{X}{C}}-\overset{X}{\underset{X}{C}}-R$$

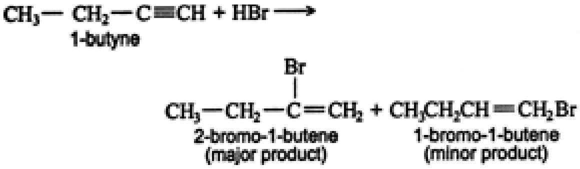
Unlike most hydrogenation reactions, it is possible to stop this reaction at the alkene stage by running it at temperatures slightly below 0°C.

Hydrohalogenation. Hydrogen halides react with alkynes in the same manner as they do with alkenes.



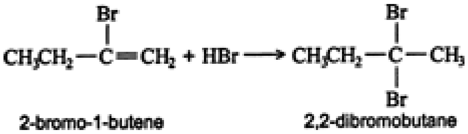
$$R-C\equiv C-R + HX \longrightarrow R-\overset{H}{C}=\overset{X}{C}-R$$
$$R-\overset{H}{C}=\overset{X}{C}-R + HX \longrightarrow R-\overset{H}{\underset{H}{C}}-\overset{X}{\underset{X}{C}}-R + R-\overset{H}{\underset{X}{C}}-\overset{H}{\underset{X}{C}}-R$$

Both steps in the above addition follow the Markovnikov rule. Thus, the addition of hydrogen bromide to 1-butyne gives 2-bromo-1-butene as the major product of the first step.



$$\underset{\text{1-butyne}}{CH_3-CH_2-C\equiv CH} + HBr \longrightarrow \underset{\substack{\text{2-bromo-1-butene}\\\text{(major product)}}}{CH_3-CH_2-\overset{Br}{C}=CH_2} + \underset{\substack{\text{1-bromo-1-butene}\\\text{(minor product)}}}{CH_3CH_2CH=CH_2Br}$$

The reaction of 2-bromo-1-butene in the second step gives 2,2-dibromobutane as the major product.



$$\underset{\text{2-bromo-1-butene}}{CH_3CH_2-\overset{Br}{C}=CH_2} + HBr \longrightarrow \underset{\text{2,2-dibromobutane}}{CH_3CH_2-\overset{Br}{\underset{Br}{C}}-CH_3}$$

Hydration. The addition of the elements of water across the triple bond of an alkyne leads to the formation of aldehydes and ketones. Water addition to terminal alkynes leads to the generation of **aldehydes**, while nonterminal alkynes and water generate **ketones.**

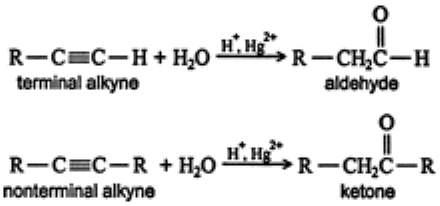
These products are produced by rearrangement of an unstable enol (vinyl alcohol) intermediate. The term "enol" comes from the *en* in "alkene" and *ol* in "alcohol," reflecting that one of the carbon atoms in vinyl alcohol has both a double bond (alkene) and an OH group (alcohol) attached to it. A vinyl group is

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

and a vinyl alcohol is

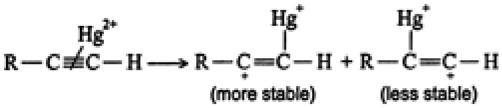
$$CH_2{=}CH{-}OH$$

Water adds across the triple bond of an alkyne via a carbocation mechanism. Dilute mineral acid and mercury(II) ions are needed for the reaction to occur.

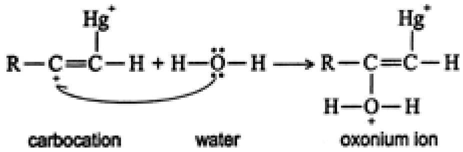


The first step of the mechanism is an acid-base reaction between the mercury(II) ion (Hg^{2+}) and the π system of the alkyne to form a π complex.

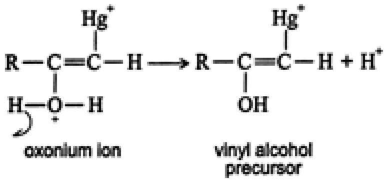
The π complex is converted into a single bond between one or the other of the carbons of the triple bond and the mercury (II) ion, with the resulting generation of a carbocation.



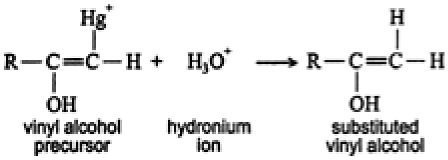
A molecule of water is attracted to the carbocation to form an oxonium ion.



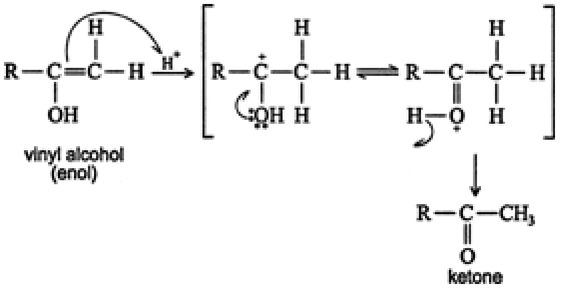
The oxonium ion loses a proton to stabilize itself.



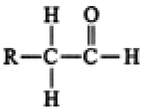
The vinyl alcohol precursor that results is converted into vinyl alcohol (enol) by reaction with a hydronium ion (H_3O^+).



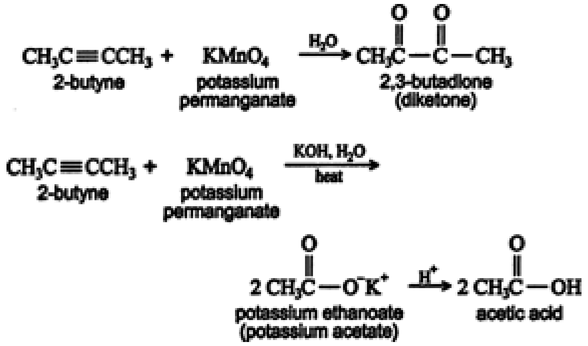
Vinyl alcohols (enols) are unstable intermediates, and they undergo rapid isomerization to form ketones. Such isomerization is called **keto-enol tautomerism.**



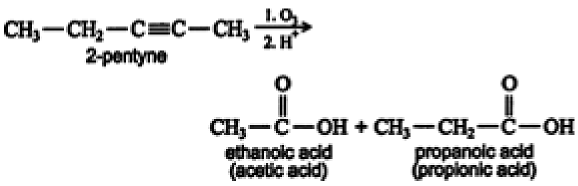
In a similar fashion, the less-stable intermediate generates an aldehyde.



Oxidation. Alkynes are oxidized by the same reagents that oxidize alkenes. Disubstituted alkynes react with potassium permanganate to yield vicinal diketones (Vic-diketones or 1,2-diketones) or, under more vigorous conditions, carboxylic acids.



Ozonolysis of an alkyne also leads to carboxylic acid formation.



Polymerization. Alkynes can be polymerized by both cationic and free-radical methods. The reactions and mechanisms are identical with those of the alkenes