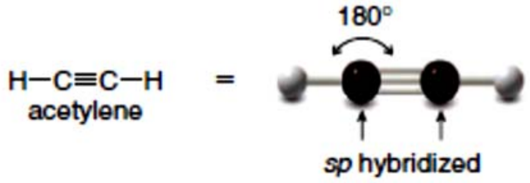
Alkynes

Introduction

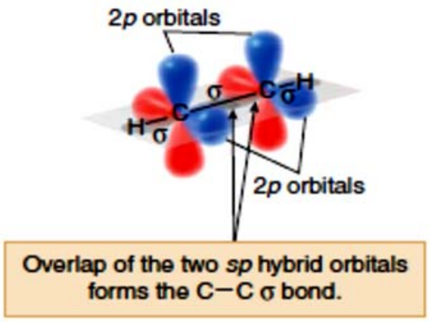
Molecules of alkyne series of hydrocarbon are characterized by having two adjacent carbon atoms joined to one another by a triple bond. The carbon-carbon triple bond is unsaturated and highly reactive toward the reagents that double bonds react with.

The general formula is $\mathbf{C_nH_{2n-2}}$.

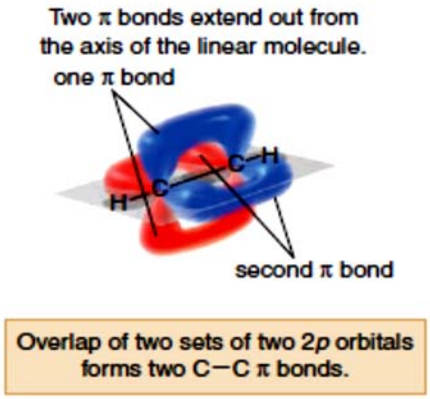
Each carbon of a triple bond is ***sp*** hybridized and **linear,** and all bond angles are **180°C**



The triple bond of an alkyne consists of one σ bond and two π bonds.

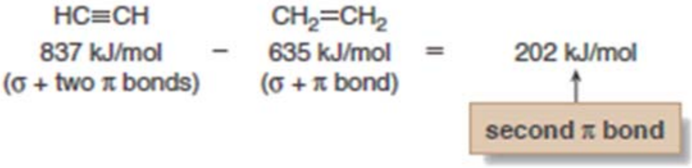


Overlap of the two *sp* hybrid orbitals forms the C−C σ bond.



Overlap of two sets of two 2*p* orbitals forms two C−C π bonds.

Bond dissociation energies of the C – C bonds in ethylene (one σ and one π bond) and acetylene (one σ and two π bonds) can be used to estimate the strength of the second π bond of the triple bond.



- Both π bonds of a C – C triple bond are weaker than a C – C σ bond, making them much more easily broken. As a result, alkynes undergo many addition reactions.

- Alkynes are more polarizable than alkenes because the electrons in their π bonds are more loosely held.

$HC \equiv CH$	Ethyne (acetylene)
$HC \equiv CCH_3$	Propyne
$HC \equiv CCH_2CH_3$	1-Butyne
$HC \equiv C(CH_2)_2CH_3$	1-Pentyne
$HC \equiv C(CH_2)_3CH_3$	1-Hexyne
$HC \equiv C(CH_2)_4CH_3$	1-Heptyne
$HC \equiv C(CH_2)_5CH_3$	1-Octyne
$HC \equiv C(CH_2)_6CH_3$	1-Nonyne
$HC \equiv C(CH_2)_7CH_3$	1-Decyne

Nomenclature

The alkynes are named according to two systems. In one, they are considered to be derived from acetylene by replacement of one or both hydrogen atoms by alkyl group.

$H-C\equiv C-C_2H_5$	**(Ethylacetylene) 1-Butyne**
$CH_3-C\equiv C-CH_3$	**(Dimethylacetylene) 2-Butyne**
$CH_3-C\equiv C-CH(CH_3)_2$	**(Isopropylmethylacetylene) 4-Methyl-2-pentyne**

For more complicated alkyne the IUPAC names are used. The rules are exactly as for the alkenes, except that the ending **-yne** is used in place of **–ene**.

$HC\equiv CCH_2CH_3$

1-Butyne

$CH_3C\equiv CCH_3$

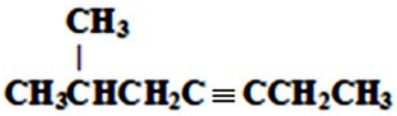
2-Butyne

$CH_3C\equiv CCH_2CH_3$

2-Pentyne

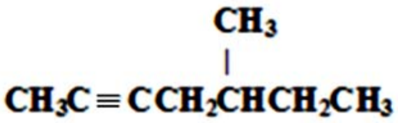
$CH_3CH=CHCH_2C\equiv CH$

4-Hexen-1-yne



$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2C\equiv CCH_2CH_3$

6-Methyl-3-heptyne



$CH_3C\equiv CCH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_3$

5-Methyl-2-heptyne

Physical Properties of Alkynes

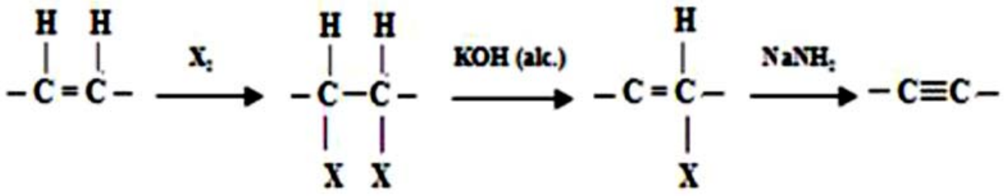
Being compounds of low polarity, the alkynes have physical properties that are essentially the same as those of the alkanes and alkenes. They are insoluble in water but quite soluble in the usual organic solvents of low polarity: ether, benzene, and carbon tetrachloride. They are less dense than water. Their boiling points show the usual increase with increasing carbon number, and the usual effects of chain branching; they are very nearly the same as the boiling points of alkanes and alkenes with the same carbon skeletons.

Acetylene, $HC\equiv CH$, is a colorless gas with an ethereal odor that burns in oxygen to form CO_2 and H_2O. The combustion of acetylene releases more energy per mole of product formed than other hydrocarbons, it burns with a very hot flame, making it an excellent fuel for welding

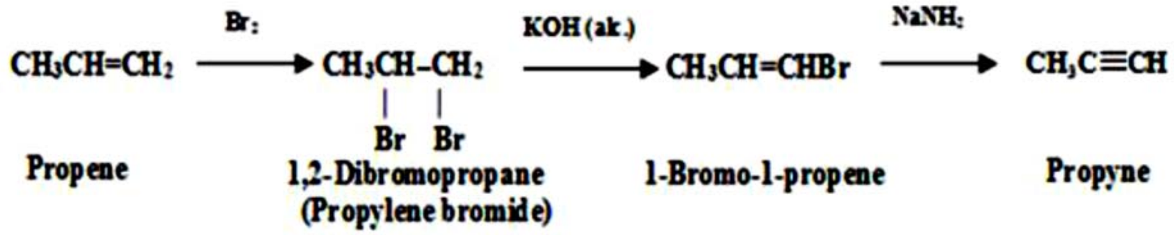
Preparation of Alkynes

1- Dehydrohalogenation of alkyl halides

A carbon-carbon triple bond is formed in the same way as a double bond: elimination of atoms or groups from two adjacent carbons.



$$-\overset{H}{\underset{}{C}}=\overset{H}{C}- \xrightarrow{X_2} -\underset{X}{\overset{H}{C}}-\underset{X}{\overset{H}{C}}- \xrightarrow{\text{KOH (alc.)}} -C=\underset{X}{\overset{H}{C}}- \xrightarrow{NaNH_2} -C\equiv C-$$



$$CH_3CH=CH_2 \xrightarrow{Br_2} CH_3\underset{Br}{CH}-\underset{Br}{CH_2} \xrightarrow{\text{KOH (alc.)}} CH_3CH=CHBr \xrightarrow{NaNH_2} CH_3C\equiv CH$$

Propene; 1,2-Dibromopropane (Propylene bromide); 1-Bromo-1-propene; Propyne

2- Reaction of metal acetylides with alkyl halides

Lithium or sodium acetylides can react with primary alkyl halides. The alkyl group becomes attached to the triply bonded carbon, and a new, larger alkyne has been generated.

$$-C\equiv C-H \xrightarrow{LiNH_2} -C\equiv C{:}^{-}Li^{+} + \underset{\text{R must be 1°}}{RX} \longrightarrow -C\equiv C-R+LiX$$

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

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

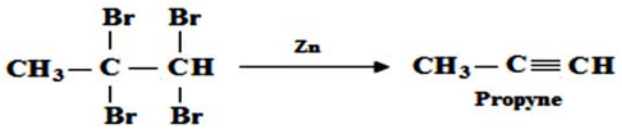
$$CH_3(CH_2)_4C\equiv C\text{-}Li + CH_3(CH_2)_3CH_2Cl \longrightarrow CH_3(CH_2)_4C\equiv C-CH_2(CH_2)_3CH_3$$

Lithium n-pentylacetylide **n-Pentyl chloride** **6-Dodecyne**

3- Dehalogenation of tetrahalides

Alkynes can be prepared by dehalogenation of tetrahalides.

$$-\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}- + 2Zn \longrightarrow -C\equiv C- + 2ZnX_2$$



$$CH_3-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{CH}} \xrightarrow{Zn} CH_3-C\equiv CH$$

Propyne

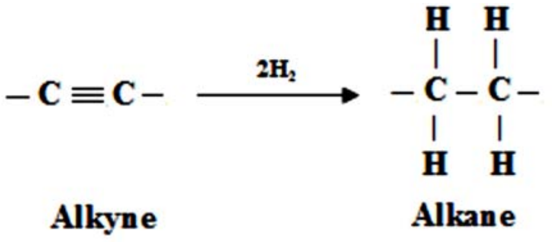
Reactions of Alkynes

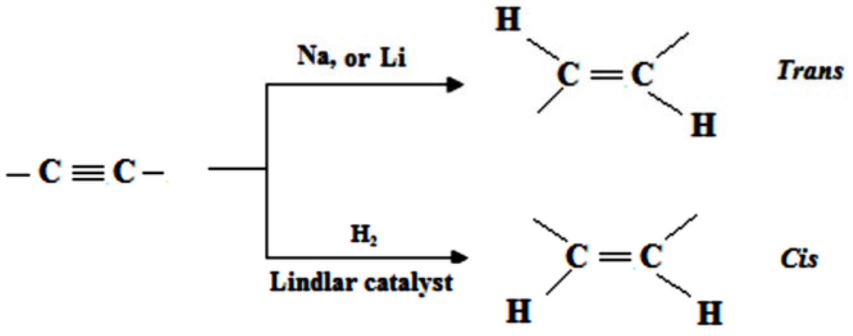
The carbon-carbon triple bond –C≡C– consists of one σ-bond and two weaker π-bonds, so it is not surprising that addition reactions are a characteristic feature of this functional group. Despite its high formal unsaturation, the triple bond dose not usually react so vigorously as a carbon-carbon double bond, as in alkenes, and it is therefore sometimes possible to stop the addition reaction after the uptake of 1 mol of reactant, rather than 2 mol which would be possible in principle.

(Addition Reactions)

1- Addition of hydrogen

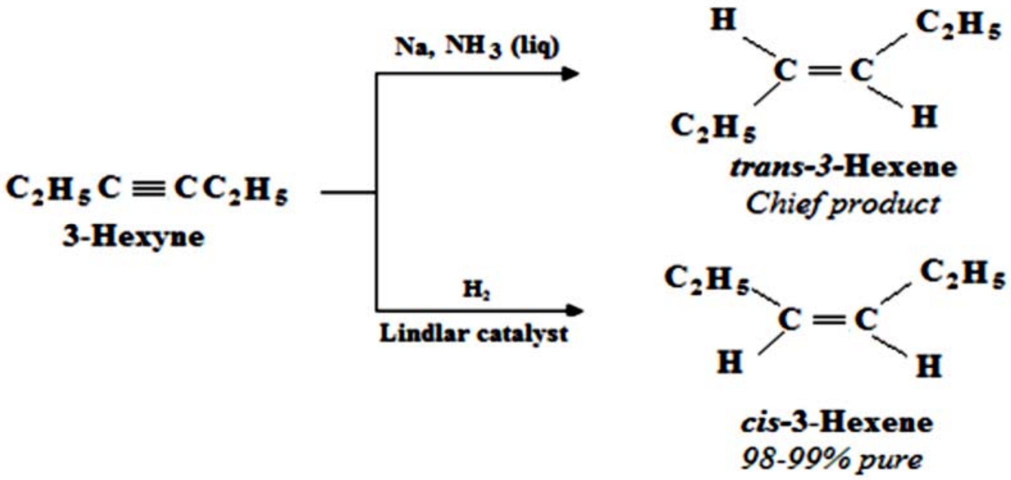
As would be expected, alkynes can be hydrogenated catalytically, taking up 2 mol of hydrogen per mol of alkyne to form the corresponding saturated molecule. Careful control of the hydrogenation can stop the reaction at the alkene stage.





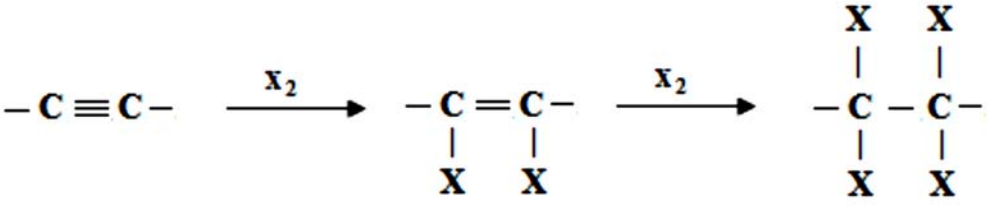
$$CH_3\text{-}C\equiv C\text{-}CH_3 \xrightarrow{2H_2,\ Ni} CH_3CH_2CH_2CH_3$$

2-Butyne **_n_-Butane**

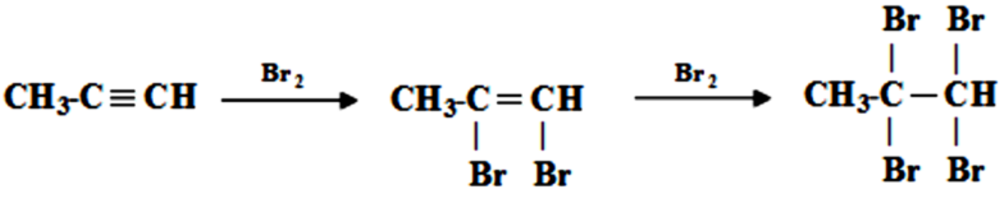


2- Addition of halogen

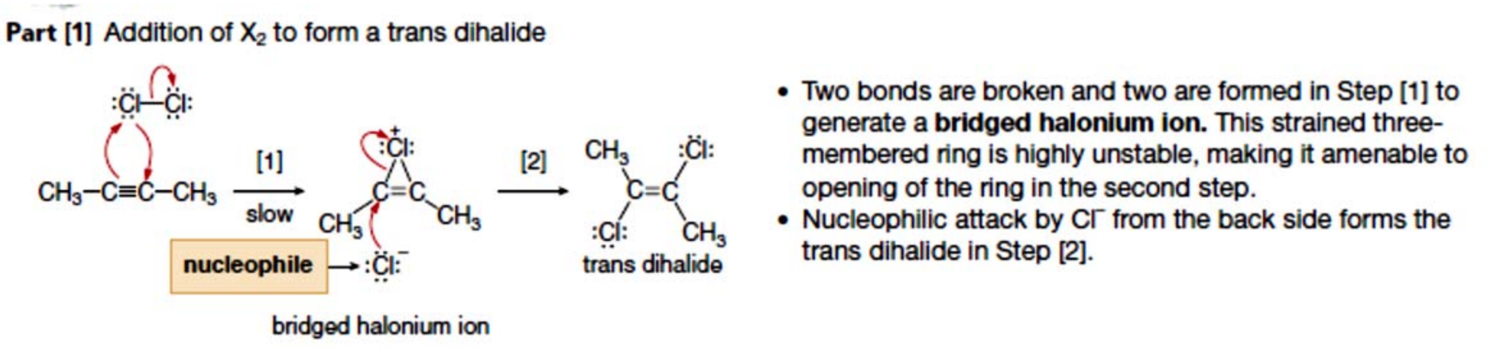
Alkynes can react with chlorine and bromine to yield tetrahaloalkanes. A dihaloalkene is an intermediate.



$X_2 = Cl_2, Br_2$



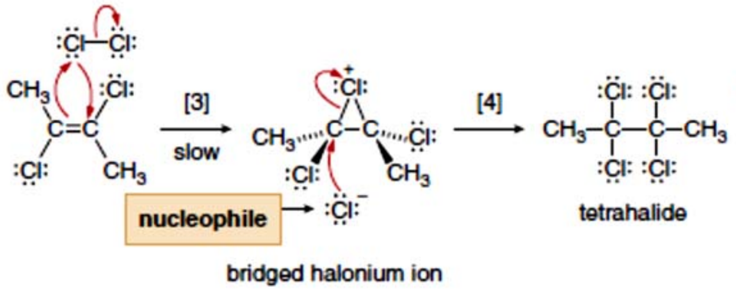
Mechanism: Addition of X_2 to an Alkyne—Halogenation



Part [1] Addition of X_2 to form a trans dihalide

- Two bonds are broken and two are formed in Step [1] to generate a **bridged halonium ion.** This strained three-membered ring is highly unstable, making it amenable to opening of the ring in the second step.
- Nucleophilic attack by Cl^- from the back side forms the trans dihalide in Step [2].

Part [2] Addition of X_2 to form a tetrahalide

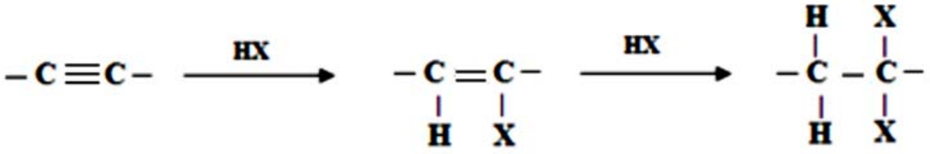


bridged halonium ion

- **Electrophilic addition** of Cl^+ in Step [3] forms the bridged halonium ion ring, which is opened with Cl^- to form the tetrahalide in Step [4].

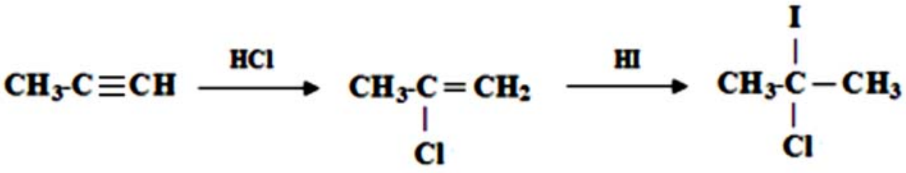
3- Addition of hydrogen halides

Alkynes also react with hydrogen halides to form alkyl halides. Addition of acids like hydrogen halides is electrophilic addition, and it appears to follow the same mechanism with alkynes as with alkenes: via an intermediate carbocation. The difference is that here the intermediate is a *vinylic cation*.

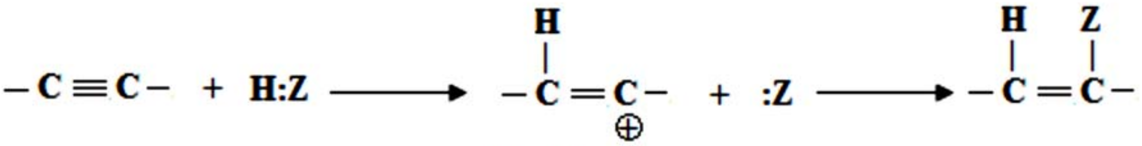


$$-C\equiv C- \xrightarrow{HX} -\underset{H}{C}=\underset{X}{C}- \xrightarrow{HX} -\overset{H}{\underset{H}{C}}-\overset{X}{\underset{X}{C}}-$$

HX = HCl, HBr, HI



$$CH_3-C\equiv CH \xrightarrow{HCl} CH_3-\underset{Cl}{C}=CH_2 \xrightarrow{HI} CH_3-\overset{I}{\underset{Cl}{C}}-CH_3$$

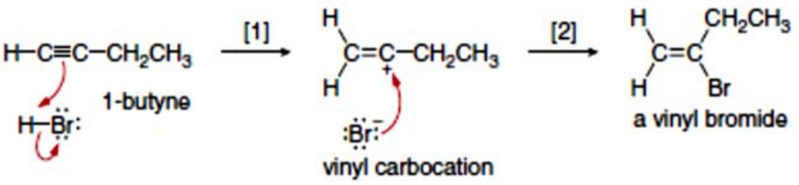


$$-C\equiv C- \;+\; H{:}Z \longrightarrow -\overset{H}{C}=\underset{\oplus}{C}- \;+\; {:}Z \longrightarrow -\overset{H}{C}=\overset{Z}{C}-$$

A vinylic cation

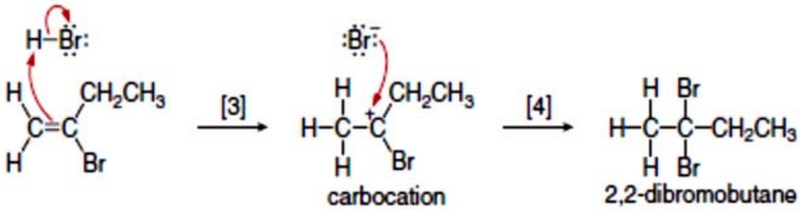
Mechanism: Electrophilic Addition of HX to an Alkyne.

Part [1] Addition of HBr to form a vinyl halide



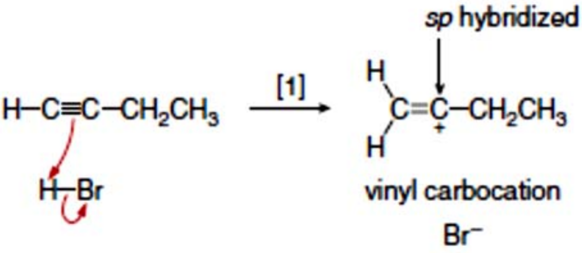
- The π bond attacks the H atom of HBr to form a new C−H bond, generating a **vinyl carbocation.** Addition follows Markovnikov's rule: H^+ adds to the less substituted carbon atom to form the **more substituted, more stable carbocation.** Nucleophilic attack of Br^- then forms a vinyl bromide; one mole of HBr has now been added.

Part [2] Addition of HBr to form a geminal dihalide



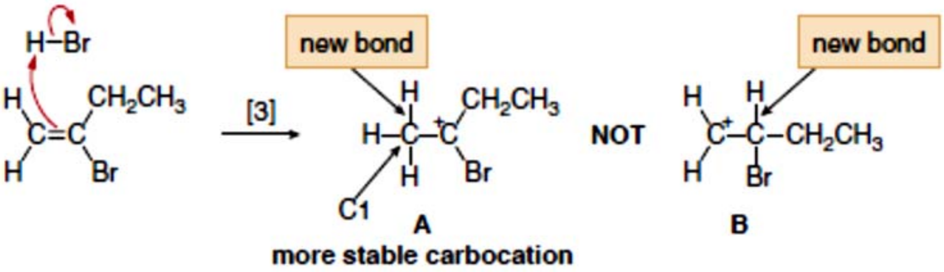
- **The second addition of HBr occurs in the same two-step manner.** Addition of H^+ to the π bond of the vinyl bromide generates a carbocation. Nucleophilic attack of Br^- then forms a geminal dibromide (2,2-dibromobutane), and two moles of HBr have now been added.

Electrophilic addition of HX to an alkyne ***slower*** than electrophilic addition of HX to an alkene, even though alkynes are more polarizable and have more loosely held π electrons than alkenes.



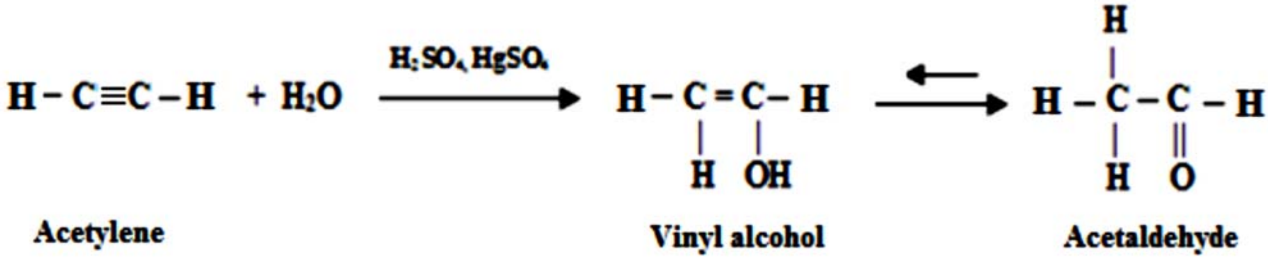
This unstable carbocation slows the first step, **making an alkyne less reactive than an alkene towards HX.**

Markovnikov addition in Step [3] places the H on the terminal carbon to form the more substituted carbocation A, rather than the less substituted carbocation B.



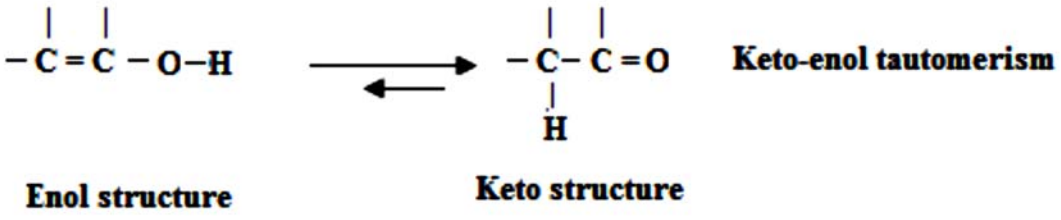
4- Addition of water (hydration)

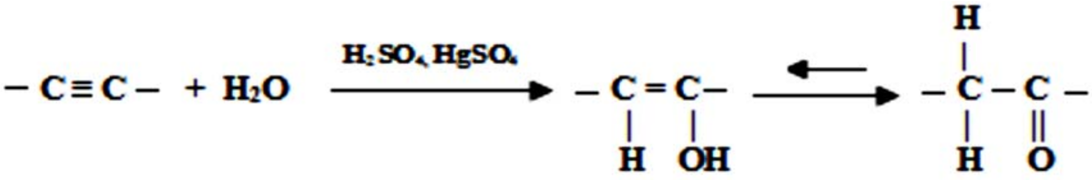
In the presence of dilute sulphuric acid and a mercury (II) sulphate catalyst at about 60°C, water adds across a triple bond and alkyne is said to be hydrated.



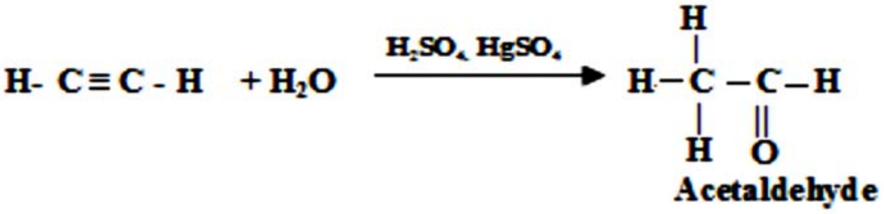
If hydration of acetylene followed the same pattern as hydration of alkenes, we would expect addition of H- and –OH to the triple bond to yield *vinyl alcohol*. But all attempts to prepare vinyl alcohol result, like hydration of acetylene, in the formation of acetaldehyde.

A structure with –OH attached to doubly bonded carbon is called **enol** (*-ene* for the carbon-carbon double bond, *-ol* for *alcohol*). It is almost always true that when we try to make a compound with the enol structure, we obtain instead a compound with **keto** structure (one that contains a C=O group). There is an equilibrium between the two structures, but it generally lies very much in favor of the keto form.

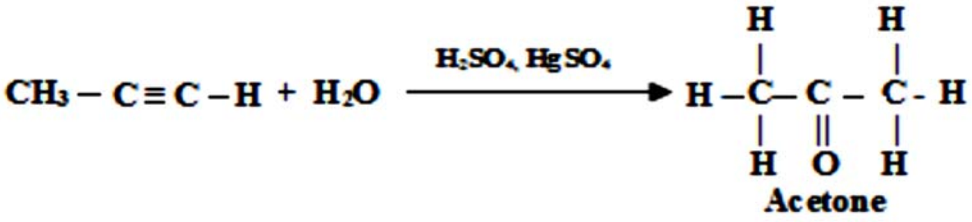




$$-C\equiv C- + H_2O \xrightarrow{H_2SO_4,\ HgSO_4} -\underset{H}{\underset{|}{C}}=\underset{OH}{\underset{|}{C}}- \rightleftharpoons -\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\underset{O}{\underset{\|}{C}}-$$



$$H-C\equiv C-H + H_2O \xrightarrow{H_2SO_4,\ HgSO_4} H-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\underset{O}{\underset{\|}{C}}-H$$



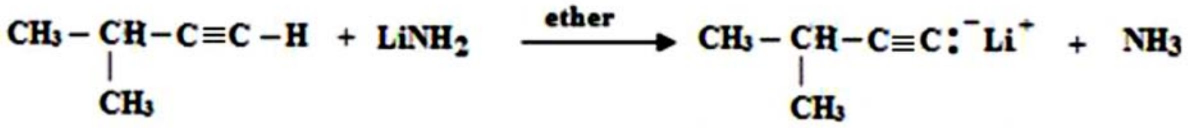
$$CH_3-C\equiv C-H + H_2O \xrightarrow{H_2SO_4,\ HgSO_4} H-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\underset{O}{\underset{\|}{C}}-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-H$$

(Reaction as Acid)

$$-C\equiv C-H + \text{base} \longrightarrow -C\equiv C\colon^{-}$$

5- Formation of metal acetylides

Hydrogen attached to triply bonded carbon, as in acetylene or any alkyne with the triple bond at the end of the chain (RC≡C-H), shows appreciable acidity. So, when a terminal triple bond is treated with an alkylmagnesium halide or an alkyllithium, the alkane is displaced from its salt, and the metal acetylide is obtained.



$$CH_3-\underset{\displaystyle CH_3}{CH}-C\equiv C-H + LiNH_2 \xrightarrow{ether} CH_3-\underset{\displaystyle CH_3}{CH}-C\equiv C:^{-}Li^{+} + NH_3$$

Lithium isopropylacetylide

$$CH_3-C\equiv C-H + n\text{-}BuLi \longrightarrow CH_3C\equiv C^{-}Li^{+} + n\text{-}BuH$$

Lithium methyacetylide

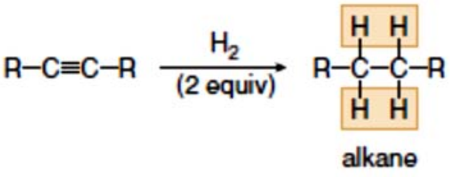
$$HC\equiv CH + C_2H_5MgBr \longrightarrow HC\equiv CMgBr + C_2H_6$$

Ethynylmagnesium bromide

6- Reduction of Alkynes:

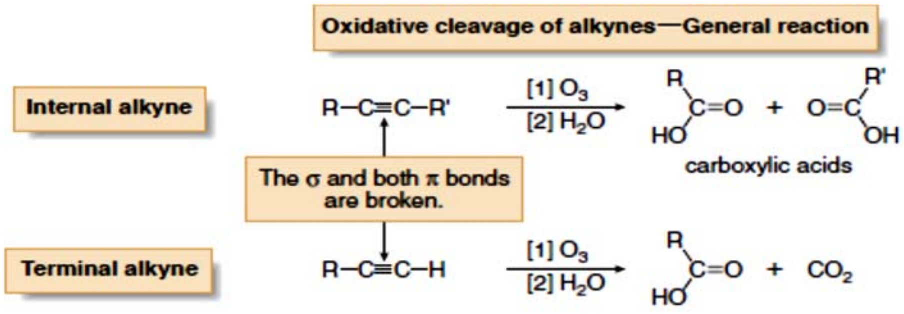
Reduction of an alkyne adds H_2 to one or both of the π bonds.

- **Adding two equivalents of H_2 forms an alkane.**



7- Ozonolysis:

Alkynes also undergo oxidative cleavage of the σ bond and both π bonds of the triple bond. Internal alkynes are oxidized to **carboxylic acids (RCOOH),** whereas terminal alkynes afford carboxylic acids and **CO_2** from the *sp* hybridized C – H bond.



Dienes

Introduction

Dienes are simply alkenes that contain two carbon-carbon double bonds. They therefore have essentially the same properties as the alkenes we have already studied. For certain of the dienes, these alkene properties are modified in important ways; we shall focus our attention on these modifications.

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

$CH_2=CH-CH=CH_2$

1,3-Butadiene

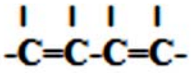
$CH_2=CH-CH_2-CH=CH_2$

1,4-Pentadiene

$CH_2=CH-CH=CH-CH=CH_2$

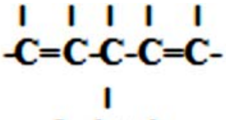
1,3,5-Hexatriene

Dienes are divided into two important classes according to the arrangement of the double bonds. Double bonds that alternate with single bonds are said to be conjugated; double bonds that are separated by more than one single bond are said to be isolated.



$-C=C-C=C-$

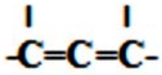
Conjugated double bonds



$-C=C-C-C=C-$

Isolated double bonds

A third class of dienes, of increasing interest to organic chemists, contain cumulated double bonds; these compounds are known as allenes;

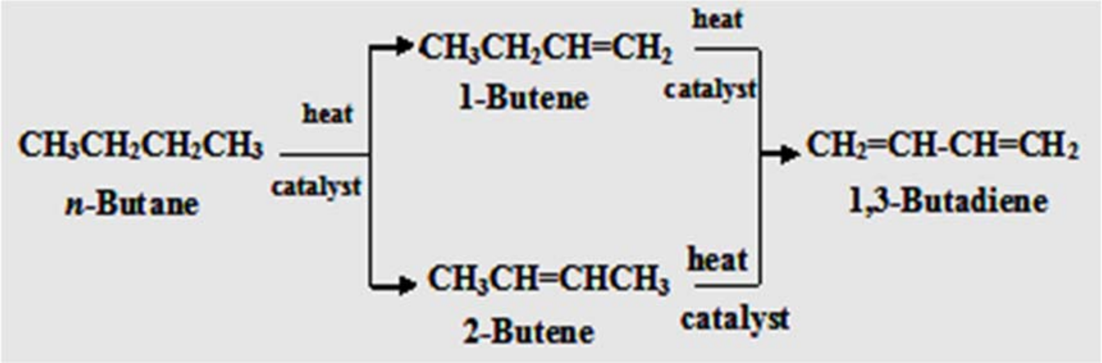


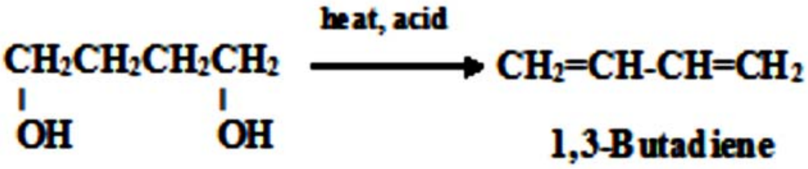
$-C=C=C-$

Cumulated double bonds: allenes

Preparation and Properties of Dienes

Dienes are usually prepared by adaptations of the methods used to make simple alkenes. For example, the most important diene, 1,3-butadiene (used to make synthetic rubber), has been made by cracking process, or by dehydration of an alcohol containing two –OH groups:



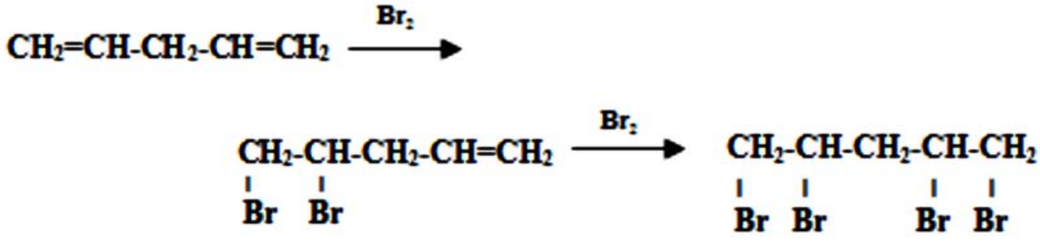


The chemical properties of a diene depend upon the arrangement of its double bonds. Isolated double bonds exert little effect on each other, and hence each reacts as though it were the only double bond in the molecule. Except for the consumption of larger amounts of reagents, then, the chemical properties of the non-conjugated dienes are identical with those of the simple alkenes.

Conjugated dienes differ from simple alkenes in three ways: (a) they are more stable, (b) they undergo 1,4-addition, and (c) toward free radical addition, they are more reactive.

Electrophilic Addition to Conjugated dienes, 1,4-Addition

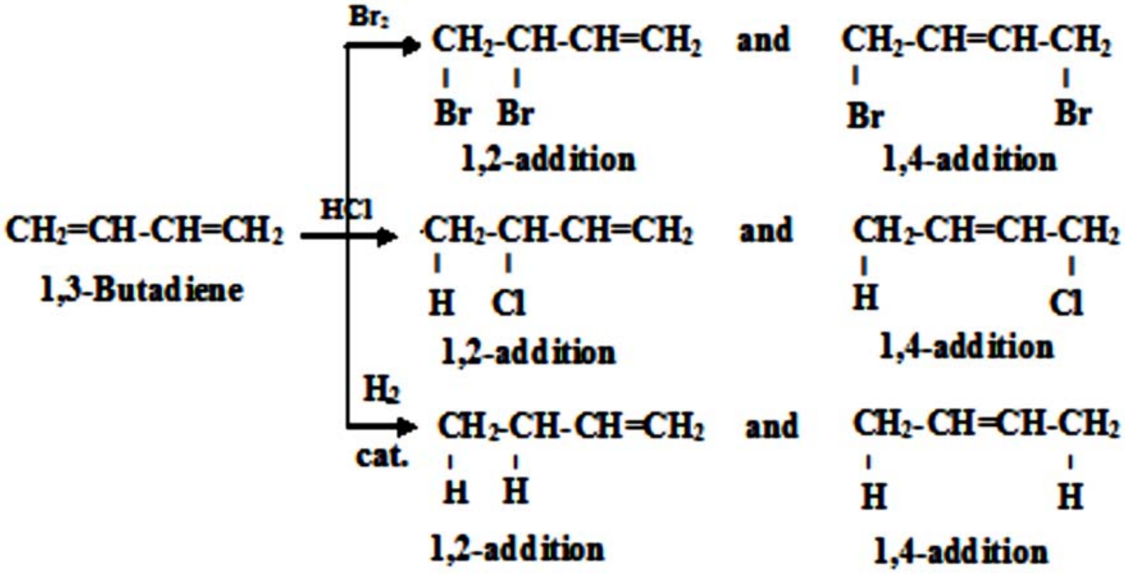
When 1,4-Pentadiene is treated with bromine under conditions that favor formation of the dihalide, there is obtained the expected product, 4,5-dibromo-1-pentene. Addition of more bromine yield the 1,2,4,5-tetrabromopentane.



$$CH_2{=}CH{-}CH_2{-}CH{=}CH_2 \xrightarrow{Br_2} \underset{Br}{CH_2}{-}\underset{Br}{CH}{-}CH_2{-}CH{=}CH_2 \xrightarrow{Br_2} \underset{Br}{CH_2}{-}\underset{Br}{CH}{-}CH_2{-}\underset{Br}{CH}{-}\underset{Br}{CH_2}$$

This is typical of the behavior of dienes containing isolated double bonds: the double bonds react independently, as though they were in different molecules.

When 1,3-butadiene is treated with bromine under similar conditions, there is obtained not only the expected 3,4-dibromo-1-butene, but also 1,4-dibromo-2-butene. Treatment with HCl yields not only 3-chloro-1-butene, but also 1-chloro-2-butene. Hydrogenation yields not only 1-butene but also 2-butene.



$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{Br_2} \underset{Br}{CH_2}{-}\underset{Br}{CH}{-}CH{=}CH_2 \text{ and } \underset{Br}{CH_2}{-}CH{=}CH{-}\underset{Br}{CH_2}$$

$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{HCl} \underset{H}{CH_2}{-}\underset{Cl}{CH}{-}CH{=}CH_2 \text{ and } \underset{H}{CH_2}{-}CH{=}CH{-}\underset{Cl}{CH_2}$$

$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[cat.]{H_2} \underset{H}{CH_2}{-}\underset{H}{CH}{-}CH{=}CH_2 \text{ and } \underset{H}{CH_2}{-}CH{=}CH{-}\underset{H}{CH_2}$$

Study of many conjugated dienes and many reagents shows that such behavior is typical: in addition to conjugated dienes, a reagent may attach itself not only to a pair of adjacent carbons (1,2-addition), but also to the carbons at the two ends of the conjugated system (1,4-addition). Very often the 1,4-addition product is the major one.

Free-Radical Addition to Conjugated Dienes: Orientation

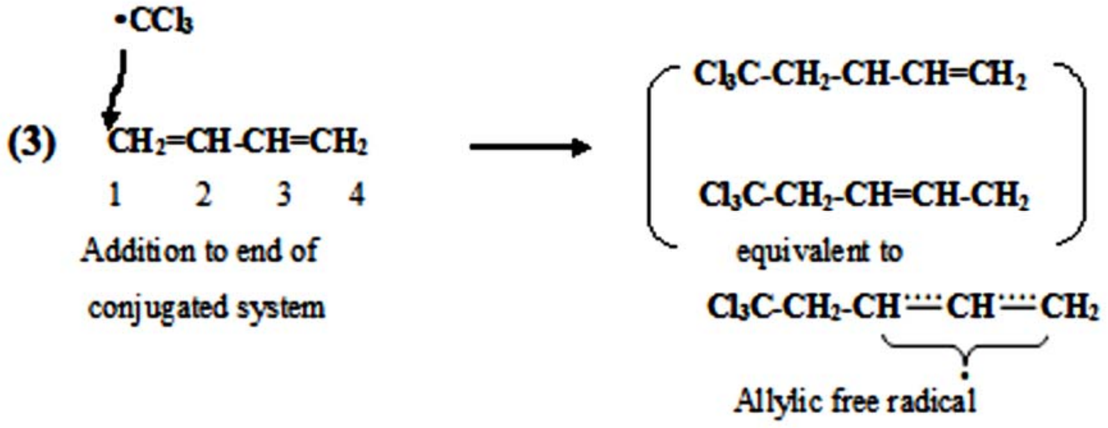
Like other alkenes, conjugated dienes undergo addition not only by electrophilic reagents but also by free radical. In free-radical addition, conjugated dienes show two special features: they undergo 1,4-addition as well as 1,2-addition, and they are much more reactive than ordinary alkenes. We can account for both features, orientation and reactivity, by examining the structure of the intermediate free radical.

Let us take, as an example, addition of, $BrCCl_3$ to 1,3-butadiene in the presence of a peroxide. The peroxide decomposes (step 1) to yield a free radical, which abstracts bromine from $BrCCl_3$ (step 2) to generate a CCl_3 radical.

$$(1) \quad \text{Peroxide} \longrightarrow \text{Rad}\cdot$$

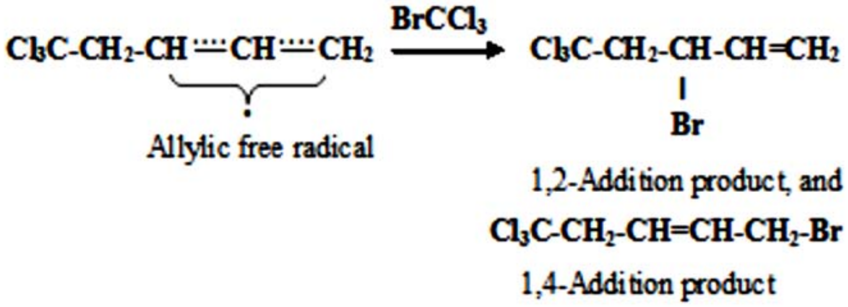
$$(2) \quad \text{Rad}\cdot + BrCCl_3 \longrightarrow \text{Rad-Br} + \cdot CCl_3$$

The $\cdot CCl_3$ radical thus formed adds to the butadiene (step 3). Addition to one of the ends of the conjugated system is the preferred reaction, since this yields a resonance-stabilized allyl free radical.



The allyl free radical then abstracts bromine from a molecule of BrCCl3 (step 4) to complete the addition, and in doing so forms a new $\cdot CCl_3$ radical which can carry on the chain. In step (4) bromine can become attached to either C-2 or C-4 to yield either the 1,2- or 1,4-product.

(4)



$$\underbrace{Cl_3C\text{-}CH_2\text{-}CH\cdots CH\cdots CH_2}_{\text{Allylic free radical}} \xrightarrow{BrCCl_3} \underset{\displaystyle Br}{Cl_3C\text{-}CH_2\text{-}CH}\text{-}CH=CH_2$$

1,2-Addition product, and

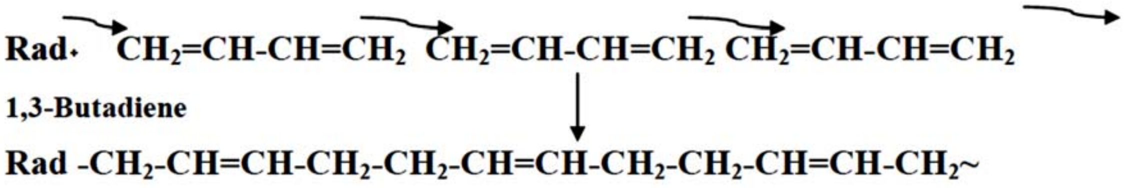
$$Cl_3C\text{-}CH_2\text{-}CH=CH\text{-}CH_2\text{-}Br$$

1,4-Addition product

Free-radical Polymerization of Dienes: Rubber and Rubber Substitutes

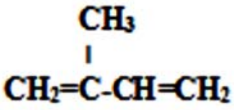
Like substituted ethylenes, conjugated dienes, too, undergo free-radical polymerization. From 1,3-butadiene, for example, there is obtained a polymer whose structure indicates that 1,4-addition occurs predominantly:

$$\underset{\textbf{1,3-Butadiene}}{CH_2=CH\text{-}CH=CH_2} \qquad \underset{\textbf{Polybutadiene}}{[\text{-}CH_2\text{-}CH=CH\text{-}CH_2\text{-}]_n}$$



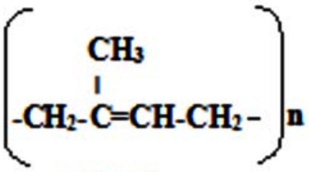
Such a polymer differs from the polymer of simple alkenes in one of very important way: each unit still contains one double bond.

Natural rubber has a structure that strongly resembles these synthetic polydienes. We could consider it to be a polymer of the conjugated diene 2-methyl-1,3-butadiene, **isoprene.**



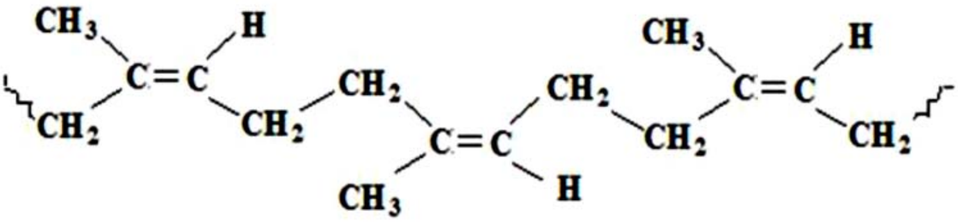
$$CH_2=\overset{\displaystyle CH_3}{C}\text{-}CH=CH_2$$

Isoprene



$$\left(\text{-}CH_2\text{-}\overset{\displaystyle CH_3}{C}=CH\text{-}CH_2\text{-}\right)_n$$

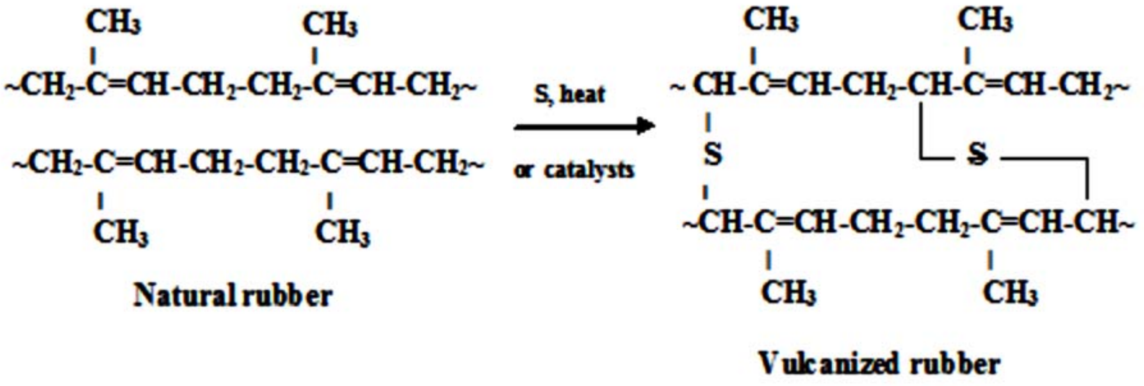
***cis*-Polyisoprene**
Natural rubber



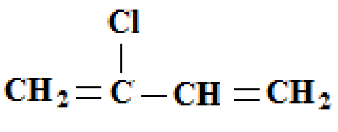
Natural rubber

All-cis configuration

The double bonds in the rubber molecule are highly important, since apparently by providing reactive allylic hydrogens, they permit vulcanization, the formation of sulfur bridges between different chains. These cross-links make the rubber harder and stronger, and do away with the tackiness of the untreated rubber.

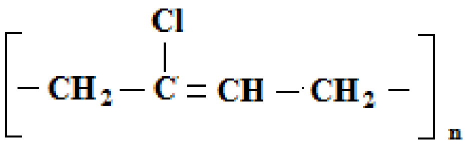


Polymerization of dienes to form substitutes for rubber was the forerunner of the enormous present-day plastics industry. Polychloroprene (Neoprene, Duprene) was the first commercially successful rubber substitute in the United States.



$$CH_2=\overset{\overset{Cl}{|}}{C}-CH=CH_2$$

Chloroprene



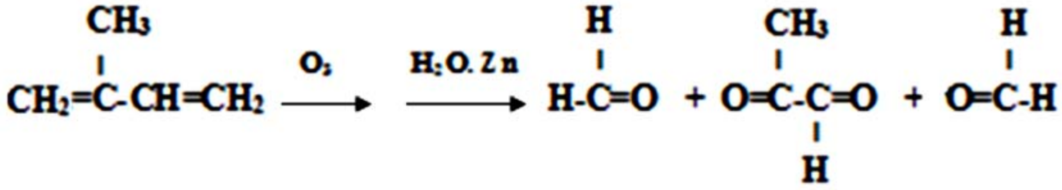
$$\left[-CH_2-\overset{\overset{Cl}{|}}{C}=CH-CH_2-\right]_n$$

Polychloroprene

Analysis of Dienes

Dienes respond to characterization tests in the same way as alkenes, they decolorize bromine in carbon tetrachloride without evolution of hydrogen bromide, and they decolorize cold, neutral, dilute permanganate; they are not oxidized by chromic anhydride. They are, however, more unsaturated than alkenes.

Ozonolysis of dienes yields aldehydes and ketones, including double-ended ones containing two C=O groups per molecule. For example:



$$CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}CH{=}CH_2 \xrightarrow{O_3} \xrightarrow{H_2O.Zn} H{-}\overset{\overset{H}{|}}{C}{=}O + O{=}\overset{\overset{CH_3}{|}}{C}{-}\underset{\underset{H}{|}}{C}{=}O + O{=}\overset{\overset{H}{|}}{C}{-}H$$