1. Nomenclature of unsaturated hydrocarbons
2. Polymerization
3. Reactions of the alkenes (table)
4. Reactions of the alkynes (table)

TEST - Alkenes, alkadienes and alkynes. Polymerization

- Give the names
- Write the structural formula
- Write all isomeric compounds
- The processes explanation

1. NOMENCLATURE OF UNSATURATED HYDROCARBONS

ALKENE NOMENCLATURE

We give alkenes IUPAC names by replacing the **-ane** ending of the corresponding alkane with **-ene**. The two simplest alkenes are ethene and propene. Both are also well known by their common names ethylene and propylene.

$H_2C{=}CH_2$
IUPAC name: **ethene**
Common name: ethylene

$CH_3CH{=}CH_2$
IUPAC name: **propene**
Common name: propylene

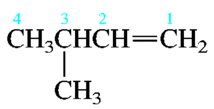
Ethylene is an acceptable synonym for ethene in the IUPAC system. Propylene, isobutylene, and other common names ending in **-ylene** are not acceptable IUPAC names.

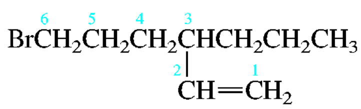
1. The longest continuous chain that includes the double bond forms the base name of the alkene.
2. Chain is numbered in the direction that gives the doubly bonded carbons their lower numbers.
3. The locant (or numerical position) of only one of the doubly bonded carbons is specified in the name; it is understood that the other doubly bonded carbon must follow in sequence.

$\overset{1}{H_2C}{=}\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H_3$
1-Butene
(not 1,2-butene)

$\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H{=}\overset{2}{C}H\overset{1}{C}H_3$
2-Hexene
(not 4-hexene)

4. Carbon-carbon double bonds take precedence over alkyl groups and halogens in determining the main carbon chain and the direction in which it is numbered.

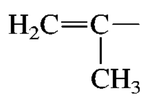
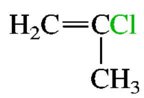

3-Methyl-1-butene
(not 2-methyl-3-butene)


6-Bromo-3-propyl-1-hexene
(longest chain that contains double bond is six carbons)

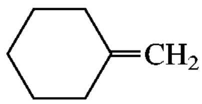
5. The common names of certain frequently encountered alkyl groups, such as isopropyl and tert-butyl, are acceptable in the IUPAC system. Three alkenyl groups--vinyl, allyl, and isopropenyl--are treated the same way:

$H_2C{=}CH{-}$ as in $H_2C{=}CHCl$
Vinyl — Vinyl chloride

$H_2C{=}CHCH_2{-}$ as in $H_2C{=}CHCH_2OH$
Allyl — Allyl alcohol

 as in 
Isopropenyl — Isopropenyl chloride

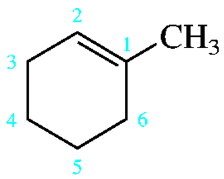
6. When a CH_2 group is doubly bonded to a ring, the prefix methylene is added to the name of the ring:



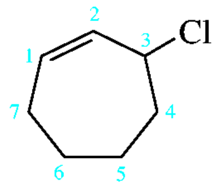
Methylenecyclohexane

7. Cycloalkenes and their derivatives are named by adapting cycloalkane terminology to the principles of alkene nomenclature:

Cyclopentene



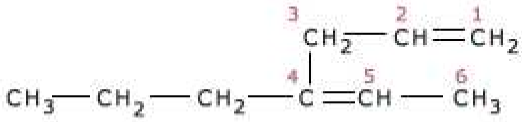
1-Methylcyclohexene



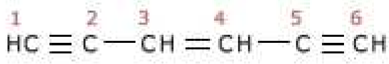
3-Chlorocycloheptene
(not 1-chloro-2-cycloheptene)

No locants are needed in the absence of substituents; it is understood that the double bond connects C-1 and C 2. Substituted cycloalkenes are numbered beginning with the double bond, proceeding through it, and continuing in sequence around the ring. The direction is chosen so as to give the lower of two possible numbers to the substituent.

Here are some more examples:

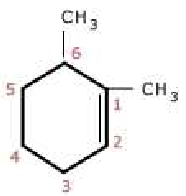


4 - Propyl - hexa - 1, 4 - diene

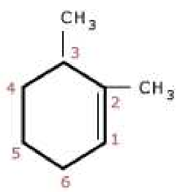


Hex - 3 - ene - 1, 5 - diyne
('e' of ene is not dropped)

In case of cyclic alkenes, the position of double bond is always given the number 1.

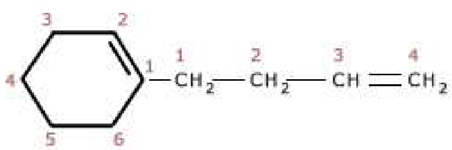


1, 6 - Dimethyl cyclohex - 1 - ene
(correct)

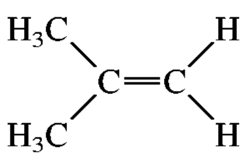


2, 3 - Dimethyl cyclohex - 1 - ene
(Wrong)

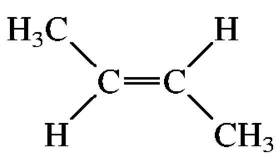
The name of the compound cannot be 2,3 – Dimethyl cyclohex – 1 – enebecause of lowest set rule. compare the set (1,6) with (2,3), the former is correct because 1 is lower than 2.



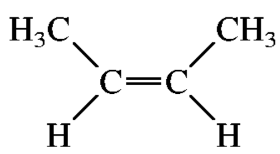
1 - (3 -butenyl) cyclohex - 1 - ene



2-Methylpropene



trans-2-Butene



cis-2-Butene

2. POLYMERIZATION

In their polymerization, many individual alkene molecules combine to give a high-molecular-weight product. Among the methods for alkene polymerization, *cationic polymerization, coordination polymerization, and free-radical polymerization* are the most important.

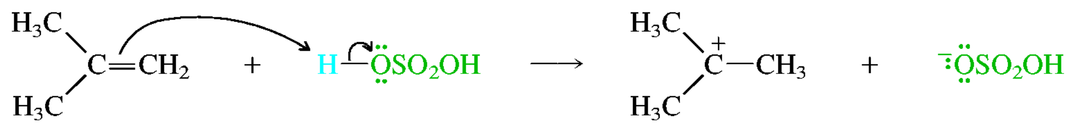
With molecular formulas corresponding to twice that of the starting alkene, the products of this reaction are referred to as dimers of alkene, which is, in turn, called the monomer. The suffix **-mer** is derived from the Greek meros, meaning "part." Three monomeric units produce a **trimer**, four a **tetramer**, and so on. A high-molecular weight material comprising a large number of monomer subunits is called a **polymer**.

CATIONIC POLYMERIZATION

The two dimers of $(CH_3)_2C{=}CH_2$ are formed by the mechanism shown:

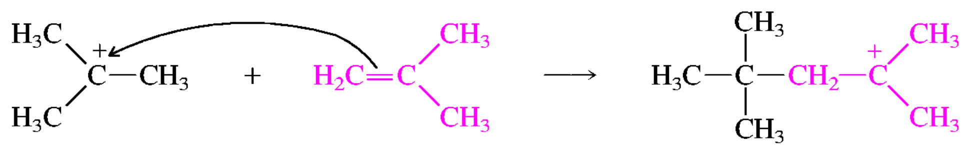
1. Protonation of the double bond generates a small amount of tertbutyl cation in equilibrium with the alkene.
2. The carbocation is an electrophile and attacks a second molecule of 2-methylpropene in step 2, forming a new carbon-carbon bond and generating a C_8 carbocation.
3. This new carbocation loses a proton in step 3 to form a mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene.

Step 1: Protonation of the carbon–carbon double bond to form *tert*-butyl cation:



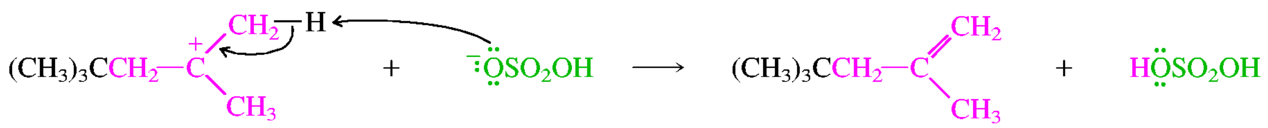
2-Methylpropene — Sulfuric acid — *tert*-Butyl cation — Hydrogen sulfate ion

Step 2: The carbocation acts as an electrophile toward the alkene. A carbon–carbon bond is formed, resulting in a new carbocation—one that has eight carbons:

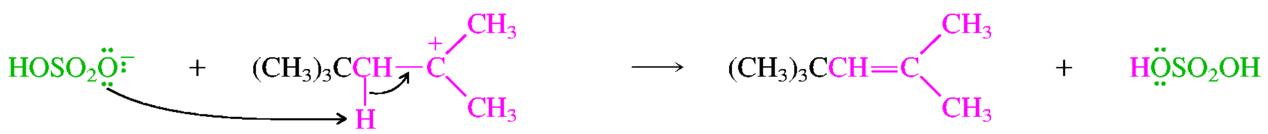


tert-Butyl cation — 2-Methylpropene — 1,1,3,3-Tetramethylbutyl cation

Step 3: Loss of a proton from this carbocation can produce either 2,4,4-trimethyl-1-pentene or 2,4,4-trimethyl-2-pentene:



1,1,3,3-Tetramethylbutyl cation — Hydrogen sulfate ion — 2,4,4-Trimethyl-1-pentene — Sulfuric acid



Hydrogen sulfate ion — 1,1,3,3-Tetramethylbutyl cation — 2,4,4-Trimethyl-2-pentene — Sulfuric acid

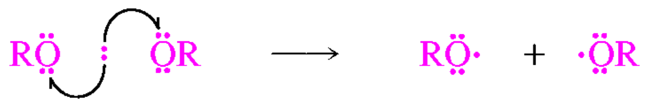
Dimerization in concentrated sulfuric acid occurs mainly with those alkenes that form tertiary carbocations. In some cases reaction conditions can be developed that favor the formation of higher molecular-weight polymers. Because these reactions proceed by way of carbocation intermediates, the process is referred to as **cationic polymerization.**

FREE-RADICAL POLYMERIZATION

Most of the ethylene is converted to polyethylene, a high-molecular-weight polymer of ethylene. Polyethylene cannot be prepared by cationic polymerization, but is the simplest example of a polymer that is produced on a large scale by free-radical polymerization.

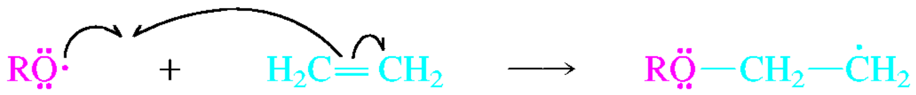
In the free-radical polymerization of ethylene, ethylene is heated at high pressure in the presence of oxygen or a peroxide.

Step 1: Homolytic dissociation of a peroxide produces alkoxy radicals that serve as free-radical initiators:



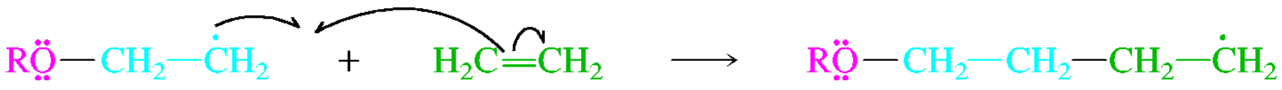
Peroxide — Two alkoxy radicals

Step 2: An alkoxy radical adds to the carbon–carbon double bond:



Alkoxy radical — Ethylene — 2-Alkoxyethyl radical

Step 3: The radical produced in step 2 adds to a second molecule of ethylene:



2-Alkoxyethyl radical — Ethylene — 4-Alkoxybutyl radical

The radical formed in step 3 then adds to a third molecule of ethylene, and the process continues, forming a long chain of methylene groups.

Dissociation of a peroxide initiates the process in step 1. The resulting peroxy radical adds to the carbon-carbon double bond in step 2, giving a new radical, which then adds to a second molecule of ethylene in step 3. The carbon-carbon bond-forming process in step 3 can be repeated thousands of times to give long carbon chains.

The properties that make polyethylene so useful come from its alkane-like structure. Except for the ends of the chain, which make up only a tiny portion of the molecule, polyethylene has no functional groups so is almost completely inert to most substances with which it comes in contact.

COPOLYMERIZATION

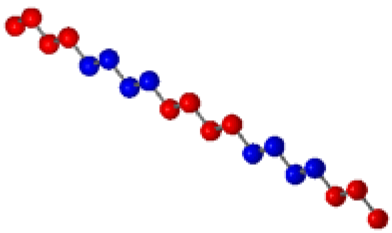
When two different types of monomers are joined in the same polymer chain, the polymer is called a **copolymer**. Let's imagine now two monomers, which we'll call A and B.
A and B can be made into a copolymer in many different ways.

A separate kind of chain structure arises when more that one type of monomer is involved in the synthesis reaction.

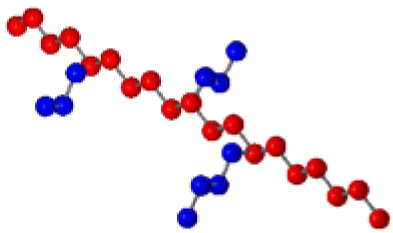
These polymers that incorporate more than one kind of monomer into their chain are called **copolymers**.

There are three important types of copolymers.

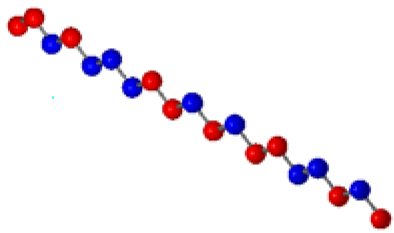
A **random copolymer** contains a random arrangement of the multiple monomers.
A **block copolymer** contains blocks of monomers of the same type.
Finally, a **graft copolymer** contains a main chain polymer consisting of one type of monomer with branches made up of other monomers. The following diagram displays the different types of copolymers.



Block Copolymer

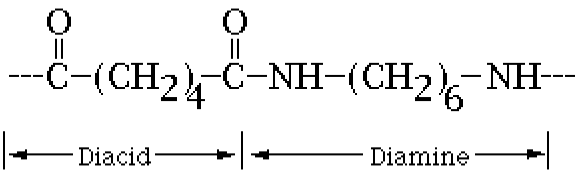


Graft Copolymer



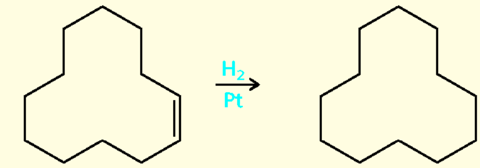
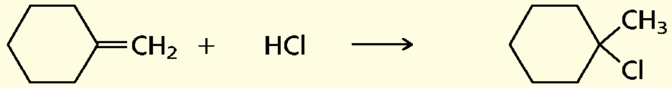
Random Copolymer

An example of a common copolymer is Nylon. Nylon is an alternating copolymer with 2 monomers, a 6 carbon diacid and a 6 carbon diamine. The following picture shows one monomer of the diacid combined with one monomer of the diamine:



Mostly all biomolecules are copolymers.

3. REACTIONS OF THE ALKENES (TABLE)

Reaction (section) and comments	General equation and specific example
Catalytic hydrogenation (Sections 6.1–6.3) Alkenes react with hydrogen in the presence of a platinum, palladium, rhodium, or nickel catalyst to form the corresponding alkane.	$R_2C{=}CR_2 + H_2 \xrightarrow{\text{Pt, Pd, Rh, or Ni}} R_2CHCHR_2$ Alkene Hydrogen Alkane  *cis*-Cyclododecene Cyclododecane (100%)
Addition of hydrogen halides (Sections 6.4–6.7) A proton and a halogen add to the double bond of an alkene to yield an alkyl halide. Addition proceeds in accordance with Markovnikov's rule; hydrogen adds to the carbon that has the greater number of hydrogens, halide to the carbon that has the fewer hydrogens.	$RCH{=}CR'_2 + HX \longrightarrow RCH_2{-}CR'_2(X)$ Alkene Hydrogen halide Alkyl halide  Methylenecyclohexane Hydrogen chloride 1-Chloro-1-methylcyclohexane (75–80%)
Addition of sulfuric acid (Section 6.9) Alkenes react with sulfuric acid to form alkyl hydrogen sulfates. A proton and a hydrogen sulfate ion add to the double bond in accordance with Markovnikov's rule. Alkenes that yield tertiary carbocations on protonation tend to polymerize in concentrated sulfuric acid (Section 6.21).	$RCH{=}CR'_2 + HOSO_2OH \longrightarrow RCH_2{-}CR'_2(OSO_2OH)$ Alkene Sulfuric acid Alkyl hydrogen sulfate $H_2C{=}CHCH_2CH_3 + HOSO_2OH \longrightarrow CH_3{-}CH(OSO_2OH)CH_2CH_3$ 1-Butene Sulfuric acid *sec*-Butyl hydrogen sulfate
Acid-catalyzed hydration (Section 6.10) Addition of water to the double bond of an alkene takes place in aqueous acid. Addition occurs according to Markovnikov's rule. A carbocation is an intermediate and is captured by a molecule of water acting as a nucleophile.	$RCH{=}CR'_2 + H_2O \xrightarrow{H^+} RCH_2CR'_2(OH)$ Alkene Water Alcohol $H_2C{=}C(CH_3)_2 \xrightarrow{50\%\ H_2SO_4/H_2O} (CH_3)_3COH$ 2-Methylpropene *tert*-Butyl alcohol (55–58%)

REACTIONS OF THE ALKENES (continue)

Hydroboration–oxidation (Sections 6.11–6.13) This two-step sequence achieves hydration of alkenes in a stereospecific syn manner, with a regioselectivity opposite to Markovnikov's rule. An organoborane is formed by electrophilic addition of diborane to an alkene. Oxidation of the organoborane intermediate with hydrogen peroxide completes the process. Rearrangements do not occur.

$$RCH{=}CR'_2 \xrightarrow[\text{2. } H_2O_2,\ HO^-]{\text{1. } B_2H_6,\ \text{diglyme}} RCH(OH)CHR'_2$$

Alkene — Alcohol

$$(CH_3)_2CHCH_2CH{=}CH_2 \xrightarrow[\text{2. } H_2O_2,\ HO^-]{\text{1. } H_3B\cdot THF} (CH_3)_2CHCH_2CH_2CH_2OH$$

4-Methyl-1-pentene — 4-Methyl-1-pentanol (80%)

Addition of halogens (Sections 6.14–6.16) Bromine and chlorine add to alkenes to form vicinal dihalides. A cyclic halonium ion is an intermediate. Stereospecific anti addition is observed.

$$R_2C{=}CR_2 + X_2 \longrightarrow X{-}CR_2{-}CR_2{-}X$$

Alkene — Halogen — Vicinal dihalide

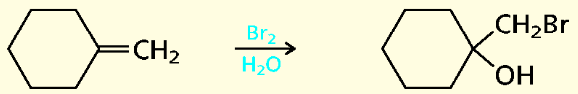
$$H_2C{=}CHCH_2CH_2CH_2CH_3 + Br_2 \longrightarrow BrCH_2{-}CH(Br)CH_2CH_2CH_2CH_3$$

1-Hexene — Bromine — 1,2-Dibromohexane (100%)

Halohydrin formation (Section 6.17) When treated with bromine or chlorine in aqueous solution, alkenes are converted to vicinal halohydrins. A halonium ion is an intermediate. The halogen adds to the carbon that has the greater number of hydrogens. Addition is anti.

$$RCH{=}CR'_2 + X_2 + H_2O \longrightarrow X{-}CH(R){-}C(R')_2{-}OH + HX$$

Alkene — Halogen — Water — Vicinal halohydrin — Hydrogen halide

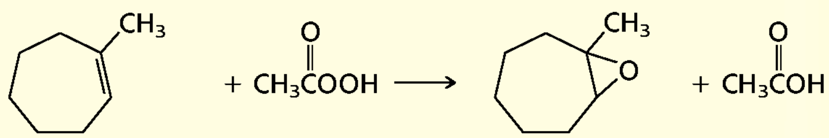


Methylenecyclohexane — (1-Bromomethyl)cyclohexanol (89%)

Epoxidation (Section 6.18) Peroxy acids transfer oxygen to the double bond of alkenes to yield epoxides. The reaction is a stereospecific syn addition.

$$R_2C{=}CR_2 + R'COOH \text{ (}R'C(=O)OOH\text{)} \longrightarrow R_2C\overset{O}{-}CR_2 + R'COH \text{ (}R'C(=O)OH\text{)}$$

Alkene — Peroxy acid — Epoxide — Carboxylic acid



1-Methylcycloheptene — Peroxyacetic acid — 1-Methyl-1,2-epoxycycloheptane (65%) — Acetic acid

4. REACTIONS OF THE ALKYNES (TABLE)

1. Preparation of Alkynes

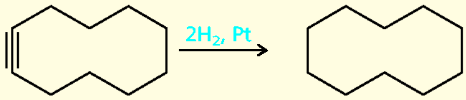
Reaction (section) and comments	General equation and specific example
Alkylation of acetylene and terminal alkynes (Section 9.6) The acidity of acetylene and terminal alkynes permits them to be converted to their conjugate bases on treatment with sodium amide. These anions are good nucleophiles and react with methyl and primary alkyl halides to form carbon–carbon bonds. Secondary and tertiary alkyl halides cannot be used, because they yield only elimination products under these conditions.	$\underset{\text{Alkyne}}{RC\equiv CH} + \underset{\text{Sodium amide}}{NaNH_2} \longrightarrow \underset{\text{Sodium alkynide}}{RC\equiv CNa} + \underset{\text{Ammonia}}{NH_3}$ $\underset{\text{Sodium alkynide}}{RC\equiv CNa} + \underset{\text{Primary alkyl halide}}{R'CH_2X} \longrightarrow \underset{\text{Alkyne}}{RC\equiv CCH_2R'} + \underset{\text{Sodium halide}}{NaX}$ $\underset{\text{3,3-Dimethyl-1-butyne}}{(CH_3)_3CC\equiv CH} \xrightarrow[\text{2. } CH_3I]{\text{1. } NaNH_2,\ NH_3} \underset{\text{4,4-Dimethyl-2-pentyne (96\%)}}{(CH_3)_3CC\equiv CCH_3}$
Double dehydrohalogenation of geminal dihalides (Section 9.7) An E2 elimination reaction of a geminal dihalide yields an alkenyl halide. If a strong enough base is used, sodium amide, for example, a second elimination step follows the first and the alkenyl halide is converted to an alkyne.	$\underset{\text{Geminal dihalide}}{R\underset{H}{\overset{H}{C}}-\underset{X}{\overset{X}{C}}R'} + \underset{\text{Sodium amide}}{2NaNH_2} \longrightarrow \underset{\text{Alkyne}}{RC\equiv CR'} + \underset{\text{Sodium halide}}{2NaX}$ $\underset{\text{1,1-Dichloro-3,3-dimethylbutane}}{(CH_3)_3CCH_2CHCl_2} \xrightarrow[\text{2. } H_2O]{\text{1. } 3NaNH_2,\ NH_3} \underset{\text{3,3-Dimethyl-1-butyne (56–60\%)}}{(CH_3)_3CC\equiv CH}$
Double dehydrohalogenation of vicinal dihalides (Section 9.7) Dihalides in which the halogens are on adjacent carbons undergo two elimination processes analogous to those of geminal dihalides.	$\underset{\text{Vicinal dihalide}}{R\underset{X}{\overset{H}{C}}-\underset{X}{\overset{H}{C}}R'} + \underset{\text{Sodium amide}}{2NaNH_2} \longrightarrow \underset{\text{Alkyne}}{RC\equiv CR'} + \underset{\text{Sodium halide}}{2NaX}$ $\underset{\text{1,2-Dibromobutane}}{CH_3CH_2\underset{Br}{C}HCH_2Br} \xrightarrow[\text{2. } H_2O]{\text{1. } 3NaNH_2,\ NH_3} \underset{\text{1-Butyne (78–85\%)}}{CH_3CH_2C\equiv CH}$

2. Conversation of Alkynes, Alkanes, Alkenes

Reaction (section) and comments | **General equation and specific example**

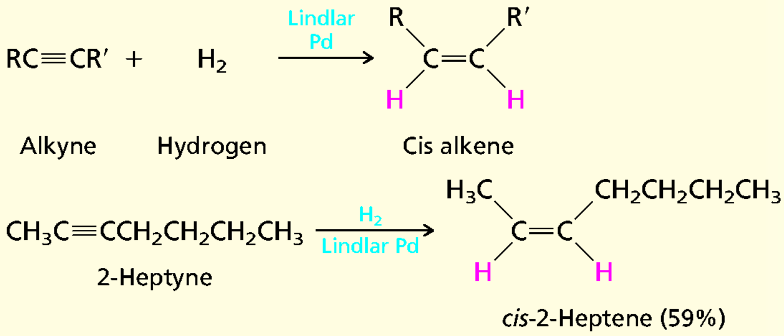
Hydrogenation of alkynes to alkanes (Section 9.9) Alkynes are completely hydrogenated, yielding alkanes, in the presence of the customary metal hydrogenation catalysts.

$$\underset{\text{Alkyne}}{RC\equiv CR'} + \underset{\text{Hydrogen}}{2H_2} \xrightarrow{\text{metal catalyst}} \underset{\text{Alkane}}{RCH_2CH_2R'}$$

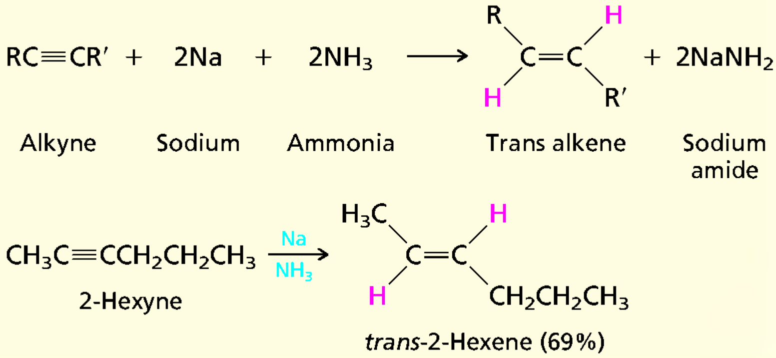


Cyclodecyne → Cyclodecane (71%)

Hydrogenation of alkynes to alkenes (Section 9.9) Hydrogenation of alkynes may be halted at the alkene stage by using special catalysts. Lindlar palladium is the metal catalyst employed most often. Hydrogenation occurs with syn stereochemistry and yields a cis alkene.



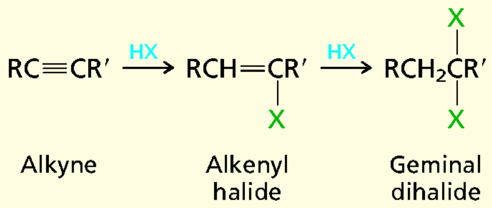
Metal–ammonia reduction (Section 9.10) Group I metals—sodium is the one usually employed—in liquid ammonia as the solvent convert alkynes to trans alkenes. The reaction proceeds by a four-step sequence in which electron-transfer and proton-transfer steps alternate.

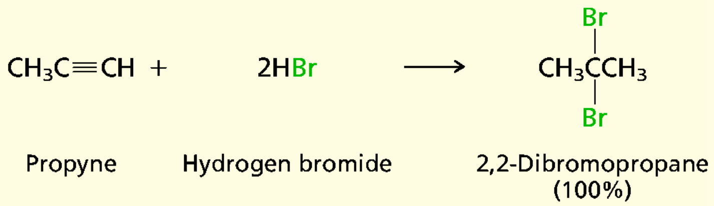


2. Electrophilic Addition to Alkynes

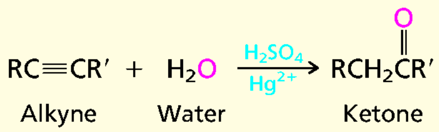
Reaction (section) and comments	General equation and specific example

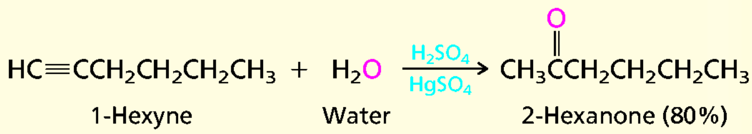
Addition of hydrogen halides (Section 9.11) Hydrogen halides add to alkynes in accordance with Markovnikov's rule to give alkenyl halides. In the presence of 2 moles of hydrogen halide, a second addition occurs to give a geminal dihalide.





Acid-catalyzed hydration (Section 9.12) Water adds to the triple bond of alkynes to yield ketones by way of an unstable enol intermediate. The enol arises by Markovnikov hydration of the alkyne. Enol formation is followed by rapid isomerization of the enol to a ketone.





Halogenation (Section 9.13) Addition of 1 mole of chlorine or bromine to an alkyne yields a trans dihaloalkene. A tetrahalide is formed on addition of a second equivalent of the halogen.