

BOOKS

- 1) Organic Chemistry Structure and Function, K. Peter C. Vollhardt, Neil Schore, 6th Edition
- 2) Organic Chemistry, T. W. Graham Solomons, Craig B. Fryhle
- 3) Organic Chemistry: A Short Course, H. Hart, L. E. Craine, D. J. Hart, C. M. Hadad,
- 4) Organic Chemistry: A Brief Course, R. C. Atkins, F.A. Carey

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3. ALKENES

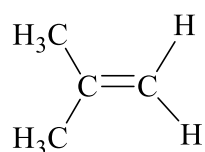
3.1 Nomenclature of Alkenes

Alkenes are named using the same general naming rules for alkanes, except that the suffix is now -ene.

C_3H_6 , $CH_3-CH=CH_2$ propene (common name is, propylene)

C_4H_8 , $CH_3-CH_2-CH=CH_2$ 1-Butene (common name is, butylene)

C_4H_8 $CH_3-CH=CH-CH_3$ 2-Butene (common name is, butylene)

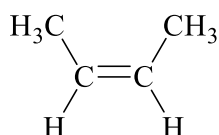


2-Methylpropene

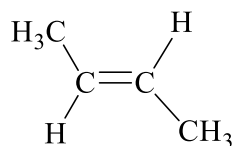
- If more than one double bond is present, the prefixes di-, tri-, tetra-, etc. are used before the -ene.

C_6H_{10} , $CH_3-CH=CH-CH_2-CH=CH_2$ 1,4-Hexadiene

- Cis/trans used for 1,2-disubstituted ethene. For example, there are two 2-butenes, which are geometric isomers:

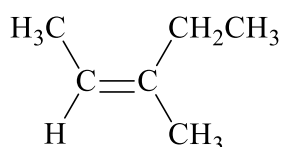


cis-2-butene

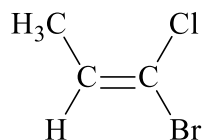


trans-2-butene

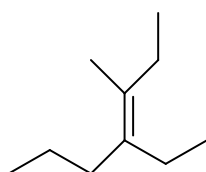
- For tri- and tetrasubstituted alkenes, it is necessary to use E, Z (or cis/trans) nomenclature to indicate which isomer it is. E/Z system is recommended by IUPAC for the designation of geometric isomerism.



(Z)-3-methyl-2-pentene
(3-methyl-*cis*-2-pentene)



(E)-1-bromo-1-chloropropene



(E)-4-ethyl-3-methylhept-3-ene

3.2 Isomers of Alkenes

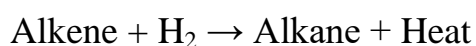
The presence of a carbon-carbon double can create two possible structures; *cis* isomer - two similar groups on same side of the double bond and *trans* isomer similar groups on opposite sides.

(E)-(Z) System :

The Cahn-Ingold-Prelog convention issued to assign the groups of highest priority on each carbon. Priority of groups is based on the atomic mass of attached atoms. If the group of highest priority on one carbon is on the same side as the group of highest priority on the other carbon the double bond is *Z* (zusammen). If the highest priority groups are on opposite sides the alkene is *E* (entgegen).

3.3 Relative Stabilities of Alkenes

The relative stabilities of alkenes can be measured using the exothermic heats of hydrogenation. Heat of hydrogenation:

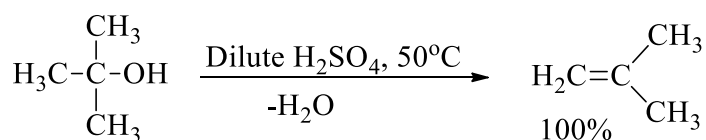
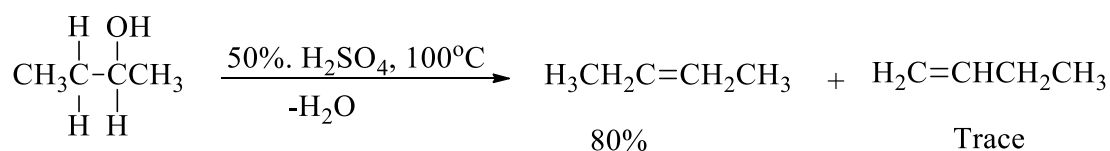
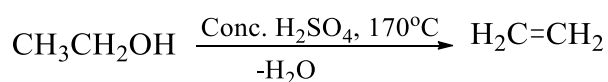
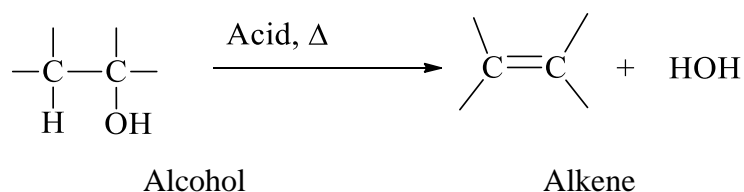


Heats of hydrogenation of three butene isomers are -30.3, -28.6 and -27.6 kcalmol⁻¹ for 1-butene, cis-2-butene and trans 2-butene, respectively. Less stable isomer is higher in energy and gives off more heat. Hence, generally cis alkenes are less stable than trans alkenes because of steric hindrance. Internal alkenes are more stable than terminal alkenes.

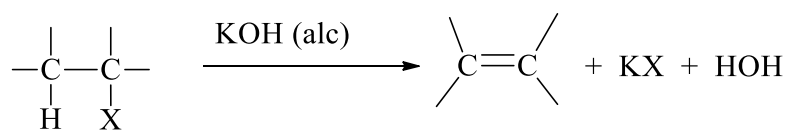
3.4 Synthesis of alkenes:

3.4.1 Dehydration of Alcohols

When alcohols heated with acids are converted into alkenes removing water. The reaction is acid catalyzed dehydration of alcohols and elimination is favored over substitution at higher temperatures. Typical acids used in dehydration are sulfuric acid (H₂SO₄) and phosphoric acid (H₃PO₄).

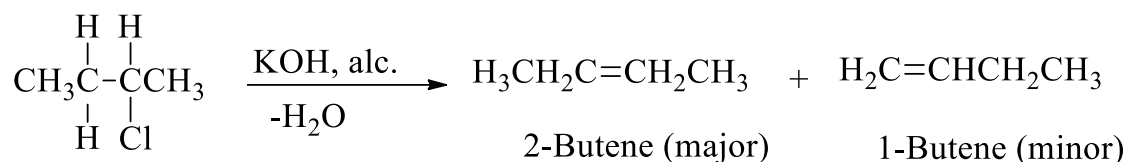


3.4.2 Dehydrohalogenation of alkyl halides

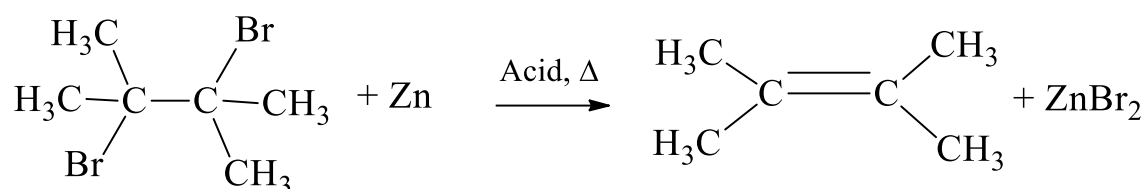


Alkoxide bases such as sodium ethoxide or potassium *tert*-butoxide are used as base in these reactions. Some hydrogen halides can eliminate to give two different alkene products.

Zaitzev's Rule: when two different alkene products are possible in an elimination, the most highly substituted (most stable) alkene will be the major product.



3.4.3 From Dihaloalkanes- dehalogenation

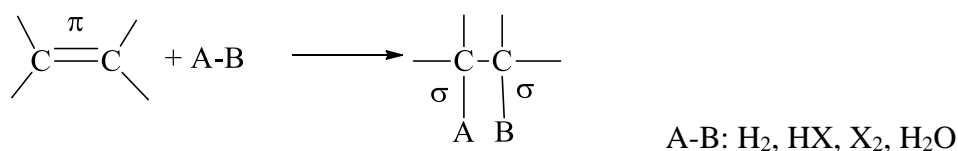


3.4.4 Hydrogenation of Alkynes - Reduction

Reaction of hydrogen using metal catalysts such as Pt, Pd, or Ni results in formation of the alkane. However, alkynes can be partially reduced to *cis*-alkenes with H₂ in the presence of poisoned catalysts and *trans*-alkenes with Na or Li metal. The Lindlar's catalyst (Pd/CaCO₃/quinoline) results in syn- addition of one equivalent of hydrogen to a triple bond and produces *cis*-alkenes from alkynes. A metal reaction which uses lithium or sodium metal in low temperature ammonia or amine solvent produces *trans*-alkenes. Anti-addition occurs by formal addition of hydrogen to the opposite faces of the double bond.

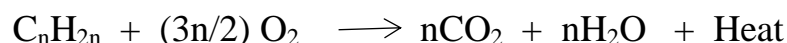
3.5 Reactions of Alkenes

Alkenes contain the unsaturated C=C functional group which characteristically undergo addition reactions. Electrophilic addition reactions of alkenes:



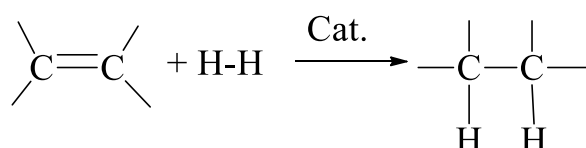
3.5.1 Combustion Reactions

Alkenes burn in presence of oxygen to produce carbon dioxide and heat.



3.5.2 Hydrogenation of Alkenes

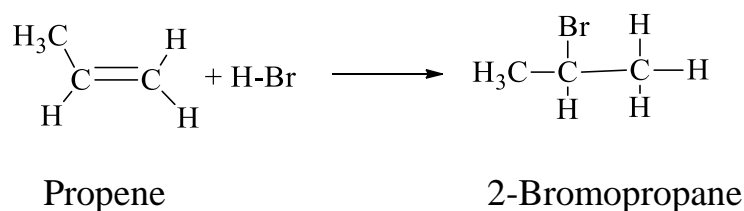
Hydrogen adds to alkenes in the presence of metal catalysts. This process is called a reduction or hydrogenation. An unsaturated compound becomes a saturated (with hydrogen) compound.



3.5.3 Addition of Hydrogen Halides

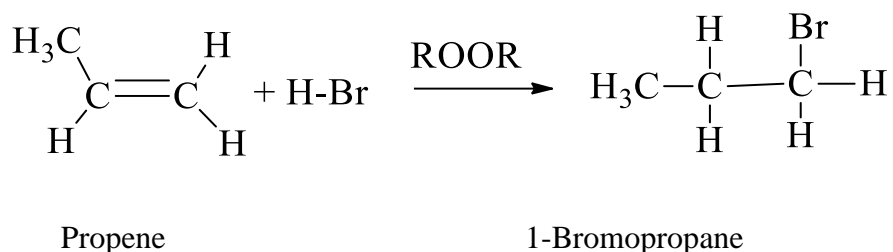
Addition of hydrogen halides to the alkenes is electrophilic addition and reaction products are halo alkanes. Hydrogen halide reactivity order is HI > HBr > HCl > HF. The protonation occurs at the least highly substituted end of alkenes so that the cation produced is at the most highly substituted end.

Markovnikov's Rule: The addition of a proton acid to the double bond of an alkene results in a product with the acid hydrogen bound to the carbon atom that has the greater number of hydrogens attached.



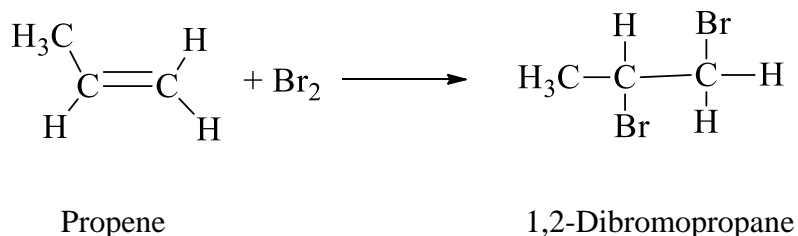
3.5.4 Free Radical addition to Alkenes

It is possible to obtain anti-Markovnikov products when HBr is added to alkenes in the presence of free radical initiators such as peroxide. Only HBr has the most suitable bond energy for this reaction HCl and HI do not give this reaction.

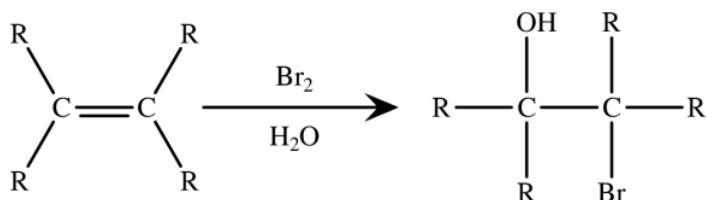


3.5.5 Addition of Halogens

X-X (Cl, Br) is non-polar molecule, but gets polarized during approach to alkene. Addition products are vicinal dihalides. This reaction is used as a test for alkenes because the red color of the bromine reagent disappears when an alkene (or alkyne) is present.



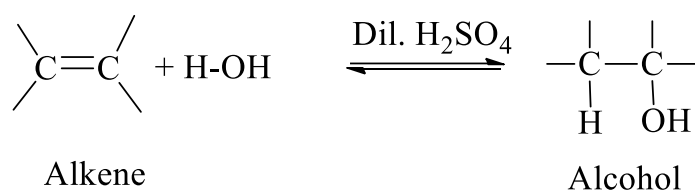
Halogens in aqueous solution: When chlorine and bromine reacts with alkenes in aqueous media, the product is a halohydrine containing hydroxyl and halogen on adjacent carbons.



3.5.6 Addition of Water

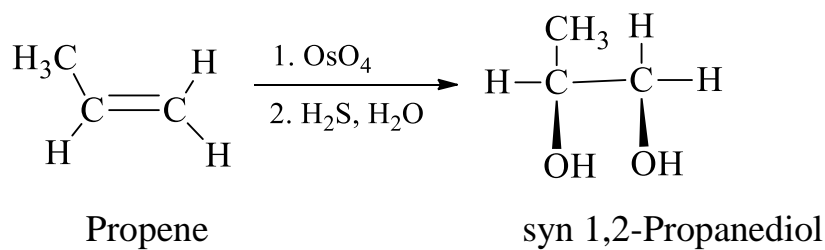
Alkenes can be converted to alcohols in the presence of an acid such as diluted H₂SO₄. It is the reverse reaction of the dehydration of alcohols to give alkenes.

The hydration of alkenes is regiospecific and reaction follows Markovnikov's rule.



3.5.7. Oxidation of Alkenes

The two most common reagents are osmium tetroxide with hydrogen peroxide, or potassium permanganate and hydroxide ion. Syn hydroxylation of alkenes gives syn 1,2-diols.

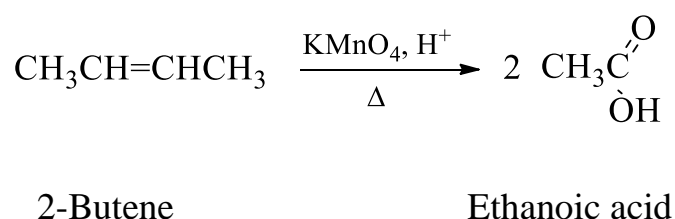


3.5.7 Oxidative Cleavage of Alkenes

Mild oxidizing conditions will not break the alkene's double bond. Strong oxidizing conditions will break the alkene's double bond.

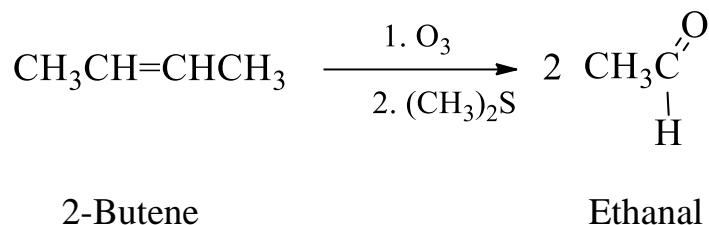
3.5.7.1 Reaction of an alkene with hot KMnO_4

If either acid or heat is used with permanganate, cleavage and further oxidation can occur producing ketones and/or aldehydes. The aldehydes further oxidize to carboxylic acids. This can be used as a chemical test for alkenes in which the purple color of the KMnO_4 disappears and forms brown MnO_2 residue if alkene (or alkyne) is present.



3.1.1.1 Ozonolysis of Alkenes

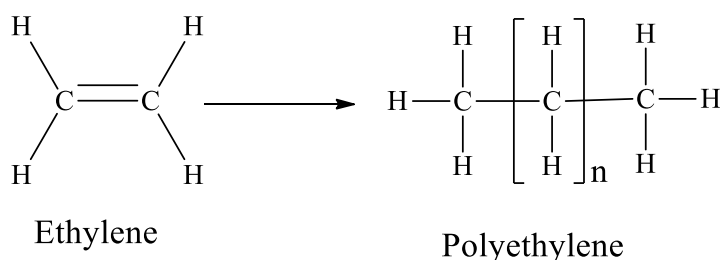
Cleavage of alkenes with ozone and workup with zinc in acetic acid leads to less highly oxidized carbons than products from cleavage with hot KMnO_4 .



3.5.8 Polymerization of Alkenes

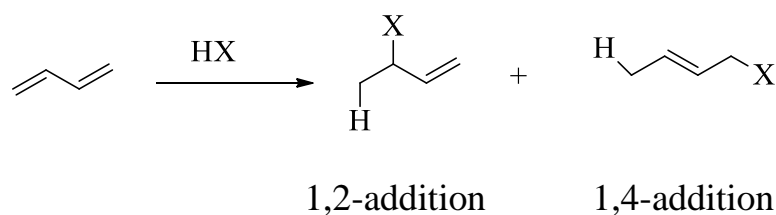
Polymerization is a process by which an organic compound reacts with itself to form a high-molecular-weight compound composed of repeating units of the original compound. Polymerization reactions proceed via either cationic, anionic or free-radical mechanisms.

The polymerization of ethene :



3.5.9 Addition to Conjugated alkenes

Dienes undergo electrophilic addition reactions in a similar manner to simple alkenes, but two addition products are possible. These differ based on the relative positions of **H** and **X** in the products. The distribution of the products depends on the reaction conditions.

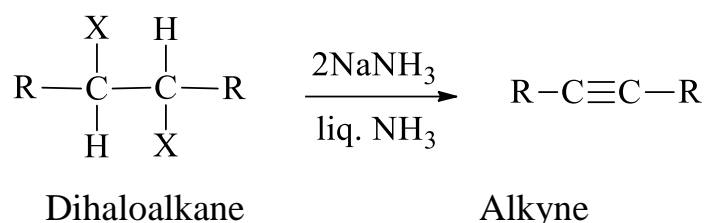


3.6 ALKYNES

Alkynes are organic molecules made of the functional group carbon-carbon triple bonds and molecular formula is C_nH_{2n-2} . Alkynes are unsaturated hydrocarbons. There are two types of alkynes: terminal and internal.

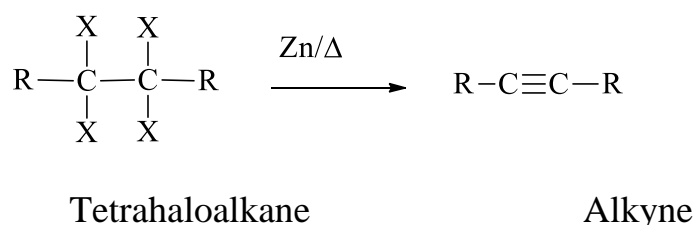
3.6.1 Synthesis of Alkynes

One simple method for alkyne synthesis is by double elimination from a dihaloalkane. The majority of these reactions take place using sodium amide, $NaNH_2$ with high temperatures.



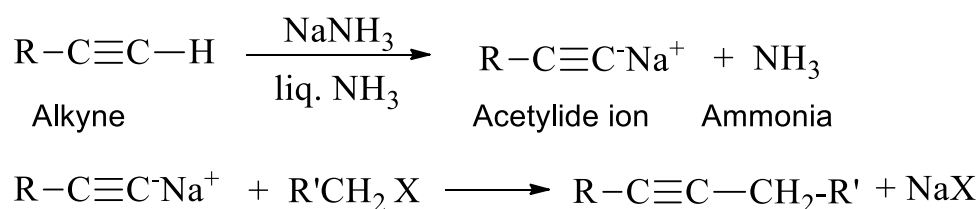
3.6.1.2 Elimination of Tetrahaloalkanes

A mechanism similar to above dehalogenation takes place with zinc metal.



3.6.2. Alkynes by Alkylation of Acetylene and Terminal Alkynes

Acetylide ions are strong nucleophiles and undergo nucleophilic substitution reactions with primary 1° alkyl halides to extend the chain.

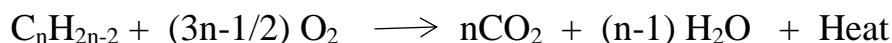


3.6.2 Reactions of Alkynes

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

3.6.2.1 Combustion Reactions

Alkynes burn in presence of oxygen to produce carbon dioxide and heat.



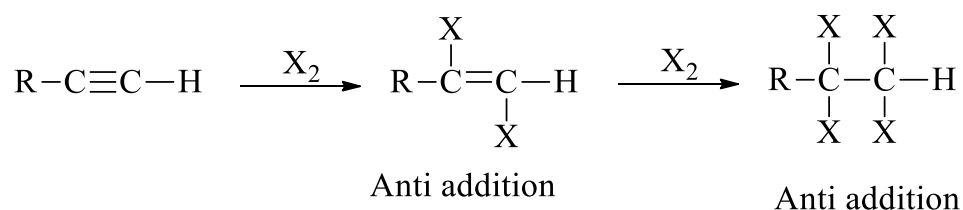
3.6.2.2 Hydrogenation

Alkynes undergo catalytic hydrogenation with the same catalysts used in alkene hydrogenation: platinum, palladium, or nickel. See the Section 3.4.4 (Hydrogenation of alkynes – reduction) for details.

3.6.2.3 Halogenation

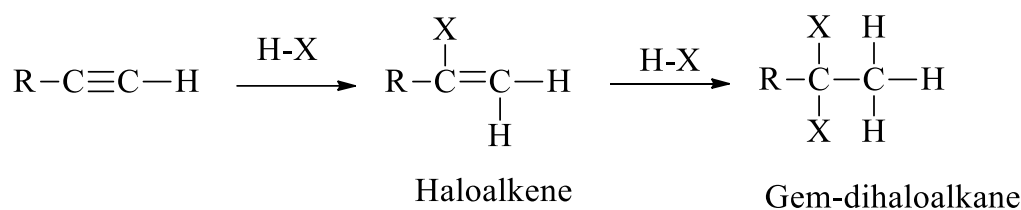
The addition of halogens to an alkyne proceeds in the same manner as halogen addition to alkenes. The halogen atoms add to an alkyne molecule, leading to the formation of the corresponding alkene, which undergoes further reaction to a tetrahaloalkane.

X :Cl, Br



3.6.2.4 Hydrohalogenation.

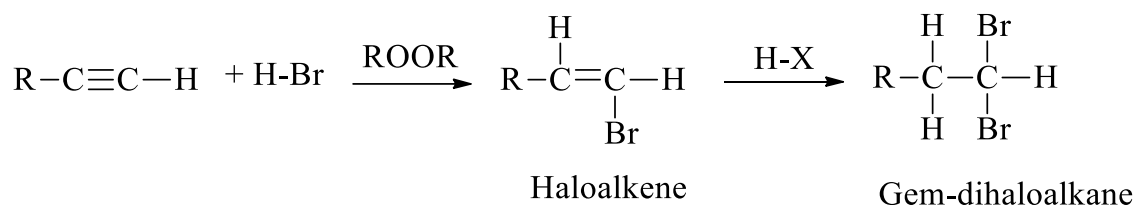
Hydrogen halides react with alkynes in the same manner as they do with alkenes. Both steps in the below addition follow the Markovnikov's rule.



HX: HCl, HBr or HI

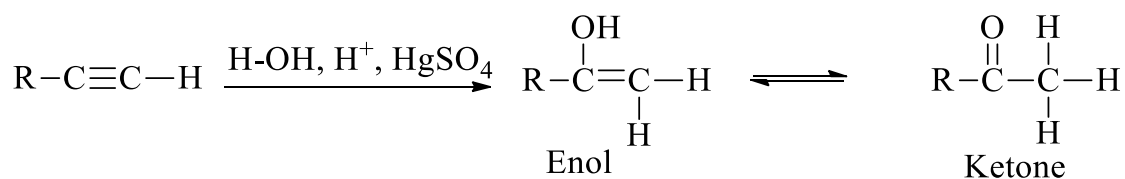
3.6.2.5 Anti Markovnikov Addition of HBr

The presence of the peroxides (radical mechanism) leads to the anti-Markovnikov addition. Br of the hydrogen bromide attaches to the less substituted 1-carbon of the terminal alkyne shown below and product form according to the anti-Markovnikov's rule.



3.6.2.6 Hydration

Hg (II) catalyzed hydration of alkynes is similar to alkenes. With the addition of water, alkynes can be hydrated to form enols that spontaneously tautomerize to ketones. Reaction is catalyzed by mercury ions and follows Markovnikov's rule.



Tautomerization is equilibrium between two tautomer, which differ by the migration of a proton and a π -bond. Keto-enol tautomerization normally favors the keto form (C=O).