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CC2/GE 2: Syllabus

Aliphatic Hydrocarbons

Functional group approach for the following reactions (preparations & reactions) to be studied in context to their structures.

Alkanes: (up to 5 Carbons). *Preparation:* catalytic hydrogenation, Wurtz reaction, Kolbe's synthesis.

Alkenes: (up to 5 Carbons). *Preparation:* elimination reactions: dehydration of alcohols and dehydrohalogenation of alkyl halides; *cis* alkenes (partial catalytic hydrogenation) and *trans* alkenes (Birch reduction). *Reactions:* addition of bromine, addition of HX [Markownikoff's (with mechanism) and anti-Markownikoff's addition], hydration, ozonolysis.

Alkynes: (up to 5 Carbons). *Preparation:* acetylene from CaC_2; by dehalogenation of tetra halides and dehydrohalogenation of vicinal dihalides.
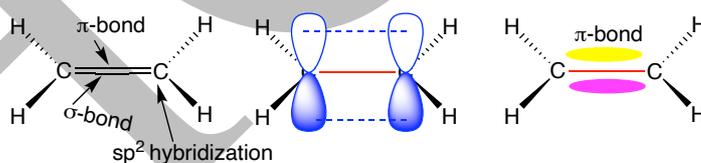*Reactions:* formation of metal acetylides, hydration reaction.

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Alkenes

Introduction:
Carbon-carbon double (-C=C-) bond containing hydrocarbons are known as Alkenes. They are also known as Olefins. General formula of Alkenes is C_nH_{2n}; where n = 1,2,3 etc. The sources of various alkenes are natural gas, petroleum and paraffin wax.
Structure of Alkene:

Figure-1: Structure of Alkene

It has three sp^2 hybrid orbitals that lie in a plane with angles of 120°. One of the carbon–carbon bonds in a double bond is the σ-bond, formed by the overlap of a sp^2 orbital of one carbon with a sp^2 orbital of the other carbon (*Figure-1*). The second carbon–carbon bond in the double bond is formed from side-to-side overlap of the remaining *p*-orbitals of the carbons. These two *p*-orbitals must be parallel to each other to achieve maximum orbital-orbital overlap. Therefore, all six atoms of the double-bond system are in the same plane (*Figure 1*). Since there is maximum side-to-side overlap, rotation about a double bond does not occur.
Alkenes are said to be **unsaturated hydrocarbon** because they are capable of adding hydrogen in the presence of a catalyst. But the alkane is called as **saturated hydrocarbon** because it cannot react with any more hydrogen.
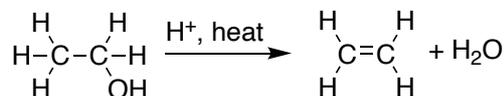……..

Synthesis of Alkenes:

Alkenes can be synthesized by elimination reactions. The various methods of preparation of alkenes are-
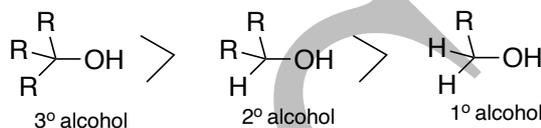
1. **Dehydration of Alcohols:**

Most alcohols undergo dehydration to form an alkene when heated with a strong acid. Concentrated sulfuric acid or concentrated phosphoric acid are often used as reagents.

Scheme-1: Dehydration of alcohols to alkenes

Alcohols that form stable carbocations can easily undergo dehydration. The relative ease with which alcohols undergo dehydration is as follows (*Figure-2*):

Figure-2: Structure of Alkene

Tertiary alcohol undergoes dehydration easily as it form relatively stable tertiary carbocation. For example, cyclopentanol, 2-methylcyclohexanol and cycloxanol give the corresponding alkenes on dehydration (*Scheme 2*).
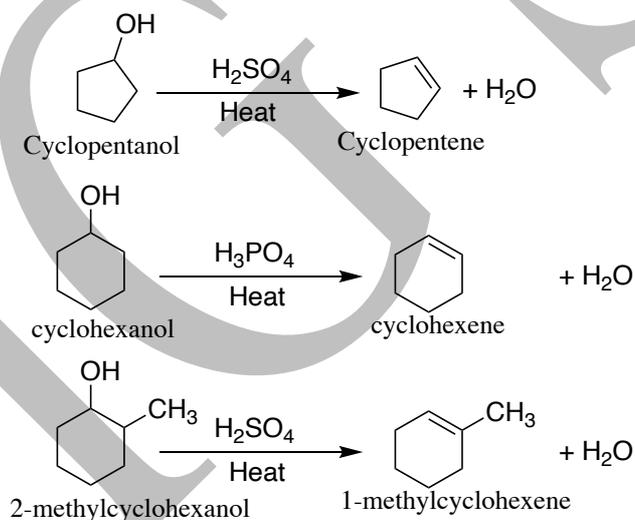
Scheme-2: Dehydration to alkene formation

2. **Dehydrohalogenation of Alkyl halides:**

Dehydrohalogenation of alkyl halides takes place by E1 or E2 elimination mechanisms. E2 elimination of dehydrohalogenation takes place in one step, in which base abstracts a proton from one carbon and leaving group leaves the adjacent carbon.
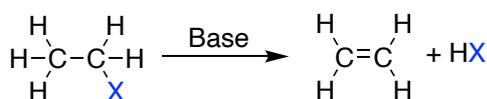
Scheme-3: Dehydrohalogenation to alkene formation

Zaitsev's Rule: A more substituted alkene is favored with small base. For example, (2-bromoethyl) cyclopentane in the presence of ethoxide (a small base) follows Zaitsev's rule to give more substitute alkene as major product (*Scheme -4*)

less substituted product
Minor

more substituted product
Major
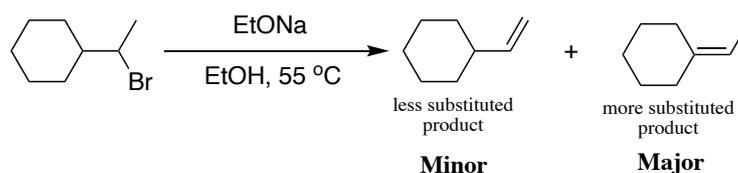
Scheme-4: Dehydrohalogenation follows Zaitsev's Rule

Hoffman Rule: A less substituted alkene is favored with bulky base. Dehydrohalogenation with a bulky base such as *tert*-butoxide (*t*-BuOK) in *tert*-butyl alcohol (*t*-BuOH) favours the formation of less substituted alkene. The large *tert*-butoxide ion seems to have difficulty in removing a *β*-Hydrogen atom because of greater crowding (*Scheme 5*).

less substituted product
**Major**

more substituted product
Minor
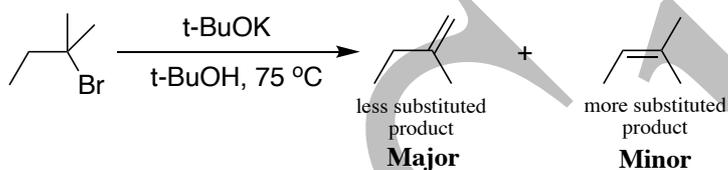
Scheme-5: Dehydrohalogenation follows Hoffman Rule

3. Partial Catalytic hydrogenation of alkyne

### (a) For cis alkene preparation:

Alkynes are hydrogenated with hydrogen in the presence of a catalyst. Several different catalysts can be used for this purpose such as- Pt, Pd, of Ni. Under typical hydrogenation conditions(H_2/Pd), the hydrogenation of an alkyne does not stop at the stage of an alkene but an alkane is formed by complete hydrogenation of the alkyne. To convert an alkyne to a cis-alkene, the catalytic hydrogenation reaction can be carried out with '**Lindlar catalyst**" which is a finely powdered palladium deposited on calcium carbonate and modified with lead salts and quinoline (*Scheme-6*). This is essentially a less reactive version of the normal transition metal catalyst used in hydrogenation of alkenes.

$$H_3C-C\equiv C-CH_3 \xrightarrow[\substack{Pd/CaCO_3 \\ Quinoline \\ Lindlar\ catalyst}]{H_2}$$
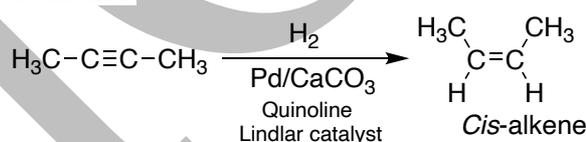
Cis-alkene

Scheme-6: Partial hydrogenation of alkyne

(b) For trans alkene preparation-Birch Reduction

Alkynes are selectively converted into *trans* alkenes when they are reduced by a solution of sodium (or lithium) in liquid ammonia that contains stoichiometric amounts of an alcohol, such as ethanol (*Scheme-7*). This reaction is known as Birch Reduction.


$$R-C\equiv C-R \xrightarrow[EtOH]{Na/NH_3\ (liq.)}$$

trans-alkene
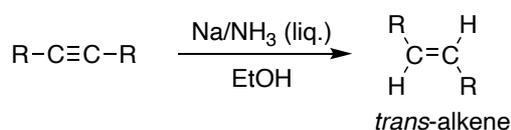
Scheme-7: Birch Reduction

Reactions of Alkenes:

Alkenes have double bond where the π-electrons are loosely held. The π-electrons can attract strong Electrophiles (E[+]). So, **"Electrophilic addition reaction"** is the most common reaction for alkenes. Many different reagents could add to the double bond of the alkene to form more stable products. In some cases catalyst has to be added to have convenient reaction rates.

The general reactivity pattern of alkenes are shown below (Figure-3)-

Step 1: Attack of the π-bond on the electrophile-
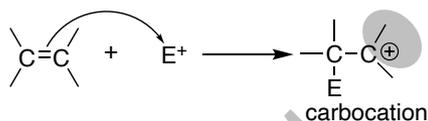
**Step 2:** Attack of the Nucleophile (Nu⁻) on the carbocation

Figure-3: General reactivity pattern of alkene

First, a strong electrophile(E[+]) attracts the loosely held electrons from the π-bond of an alkene and forms carbocation. The carbocation reacts with a nucleophile(Nu⁻) to form an addition product (*Figure 2*).
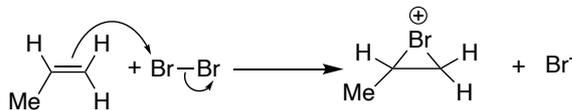
(1)   Addition of Bromine to Alkenes:

Bromine adds to alkenes to form vicinal dibromides. The nucleophilic alkene attacks the electrophilic nucleus of one bromine atom(Br+), and the other bromine atomserves as the leaving group, departing as bromide ion(Br⁻). For example, the reaction of propene with bromine follows (Scheme-8):
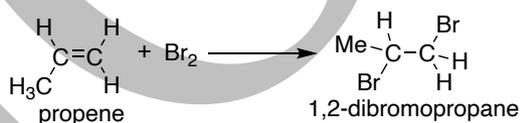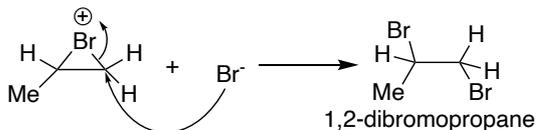

Scheme-8:Bromine Addition to Alkene

The mechanism of this reaction is shown below-

**Step 1:** *Electrophilic attack forms a bromonium ion.*

Step 2: *Bromide ion opens the bromonium ion.*

Scheme-9: Mechanism of Bromine Addition to Alkene

In first step, a bromonium ion(Br^+) results, containing a three-membered ring with a positive charge on the bromine atom. Unlike a normal carbocation, all the atoms in a bromonium ion have filled octets. The three-membered ring has considerable ring strain, which makes the bromonium ion strongly electrophilic. Attack by a nucleophile, a bromide ion(Br^-), opens the bromonium ion to give 1,2-dibromo derivative (Scheme 9).

The addition of bromine to alkene is a **stereospecific reaction.** For example, the addition of bromine with cyclopentane gives, *trans*-1,2-dibromocyclopentane, an *anti*-addition product (Scheme 10).

cyclopropene

trans-1,2-dibromocyclopentane
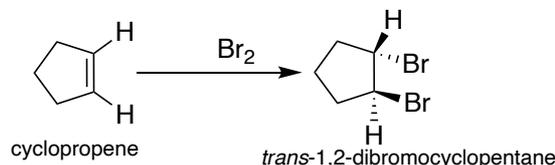
Scheme-10: Stereoselectivity of Bromine Addition Reaction

(2)   Addition of HX (X= Cl, Br) to Alkenes:

The proton in HX (X = Cl, Br) is electrophilic; thus, it reacts with the alkene to form a carbocation. Halide ion (X^-)reacts rapidly with the carbocation to give a stable product in which the elements of HX have added to the ends of the double bond. For example, 2-methyl-2-butene reacts with hydrogen bromide to give *2-bromo-2-methylbutane* (Scheme 11).

2-methyl-2-butene

2-bromo-2-methylbutane
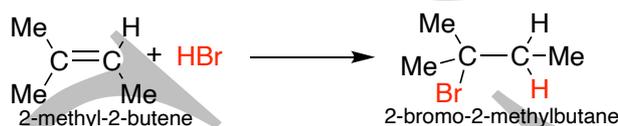
Scheme-11: Addition Reaction to Alkene

Markovnikov's Rule: when a hydrogen halide adds to an unsymmetrical alkene, the addition occurs in such a manner that the halogen attaches itself to the double-bonded carbon atom of the alkene bearing the lesser number of hydrogen atoms. When the proton adds to the secondary carbon, a tertiary carbocation results. When the proton adds to the tertiary carbon atom, a secondary carbocation results. The tertiary carbocation is more stable, so the corresponding product is favored (Figure 4).

tertiary carbocation
more stable

secondary carbocation
less stable

Figure-4: Stability of carbocation

(3) Hydration reaction of Alkenes:

When alkenes are treated with aqueous acids, most commonly H_2SO_4, corresponding alcohols are formed.
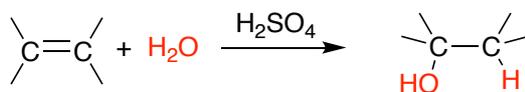

Scheme-12: Birch Reduction

Reaction proceeds via protonation to give the more stable carbocation intermediate(*Scheme-13*). Regioselectivity predicted by **Markovnikov's rule**.
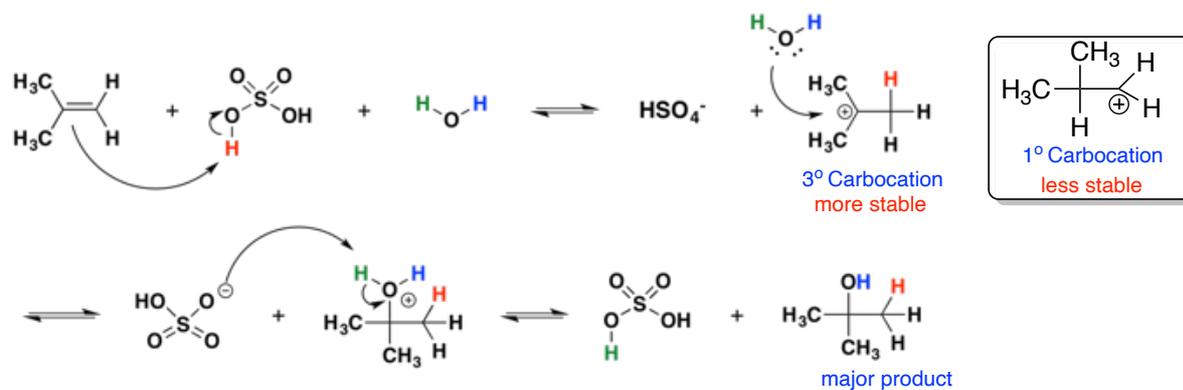
Scheme-13: Mechanism of Hydration Reaction

(4) Ozonolysis reaction of Alkenes:

Ozonolysis is an organic reaction where the unsaturated bonds of alkenes, are cleaved with ozone. Alkenes forms organic compounds in which the multiple carbon–carbon bond has been replaced by a carbonyl group to give ketones or aldehydes (Scheme 14).
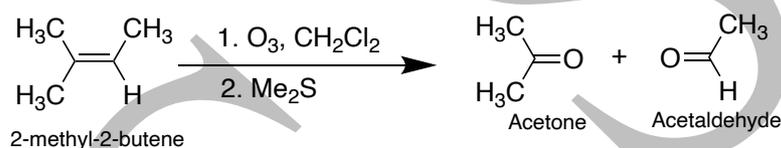
Scheme-14: Ozonolysis Reaction

Regarding the mechanism, ozone reacts with an alkene to form a cyclic compound called a molozonide which has peroxy (-O-O-) linkages, so it is quite unstable. It rearranges rapidly to form an ozonides that could be reduced by reducing agents such as dimethyl sulfide (Scheme 15).
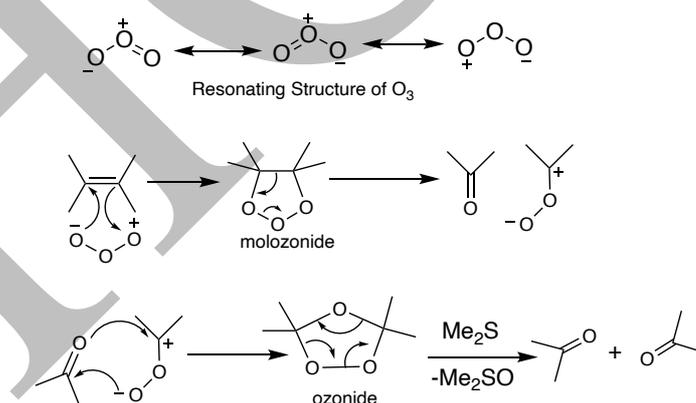
Scheme-15: Mechanism of Ozonolysis Reaction

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Alkynes:

Introduction

Alkynes are hydrocarbons that contain carbon-carbon triple bonds(. Many of the reactions of alkynes are similar to the corresponding reactions of alkenes because both involve π-bonds between two carbon atoms. Like the π-bond of an alkene, the π-bonds of an alkyne are also electron rich, and readily undergo addition reactions.

Alkynes are relatively nonpolar and quite soluble in most organic solvents. Acetylene, propyne, and the butynes are gases at room temperature. Alkynes have one σ-bond and two π-bonds. Hybridization of the *s* orbital with one *p*-orbital gives two linear *sp* hybrid orbitals that are used to form the σ-bond with each carbon atoms and with the hydrogen s orbitals. Two π-bonds result from overlap of the two remaining unhybridized *p*-orbitals on each carbon atom (Figure 1).
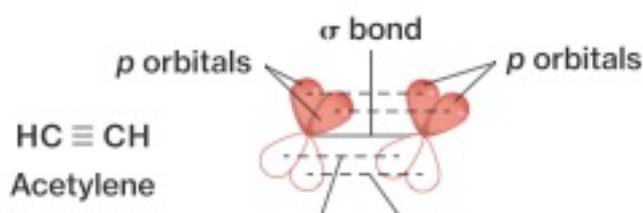

Figure-5: Structure of Alkyne

Preparation of Alkynes:

(1) **Preparation from CaC₂:**

The reaction of calcium carbide with water, producing acetylene and calcium hydroxide, was discovered by Friedrich Wöhler in 1862.

$$CaC_2 \ + \ 2H_2O \longrightarrow C_2H_2 \ + \ Ca(OH)_2$$
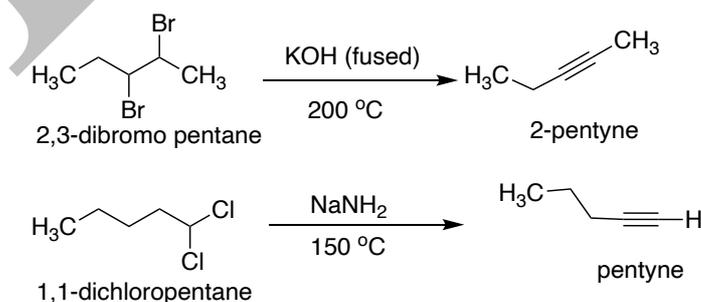$$\text{Acetylene}$$

Scheme-16: Acetylene Preparation

This reaction was the basis of the industrial manufacture of acetylene, and is the major industrial use of calcium carbide.

(2) Preparation by dehalogenation and dehydrohalogenation:

Carbon-carbon triple bond can be generated by eliminating two molecules of HX from a dihalide under strong basic conditions. In the first step vinyl halide is formed by dehydrohalogenation of a geminal or vicinal dihalide. Second dehydrohalogenation occurs only under strong basic conditions since it involves dehydrohalogenation of a vinyl halide. Dihalide is usually heated to 200 °C with strong base such as fused KOH or alcoholic KOH. Sodium amide can also be used for the double dehydrohalogenation that can take place at a lower temperature (Scheme 4)

Scheme-17: Alkyne Preparation

Reactions of alkynes:

Terminal alkynes are much more acidic than other hydrocarbons. Abstraction of an acetylenic proton gives a carbanion that has the lone pair of electrons in the *sp* hybrid orbital. Hydroxide ion and alkoxide ions are not strong enough bases to deprotonate alkynes but very strong bases such as sodium amide, deprotonate terminal acetylenes to form acetylide ions (Scheme 1).

$$CH_3CH_2-C\equiv C-H \quad + \quad NaNH_2 \quad \longrightarrow \quad CH_3CH_2-C\equiv C^-: Na^+ \quad + \quad NH_3$$

1-butyne sodium amide sodium butynide

cyclohexylacetylene + NaNH₂ ⟶ sodium cyclohexylacetylide + NH₃
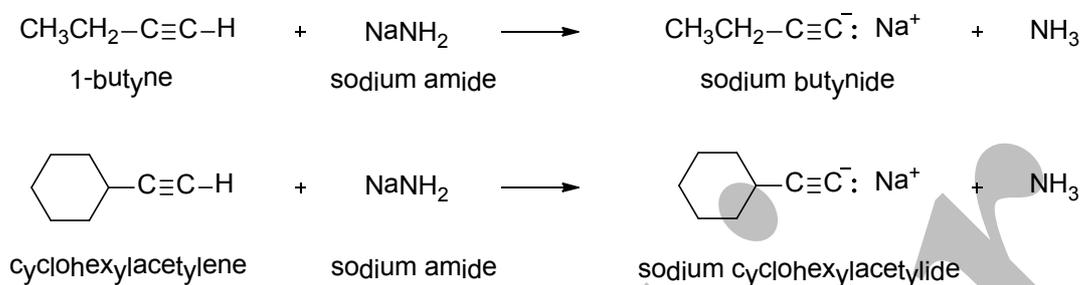
Scheme-18: Formation of metal acetylide

An acetylide ion is a good nucleophile that can displace a halide ion from an alkyl halide to give substituted acetylene (Scheme 19).
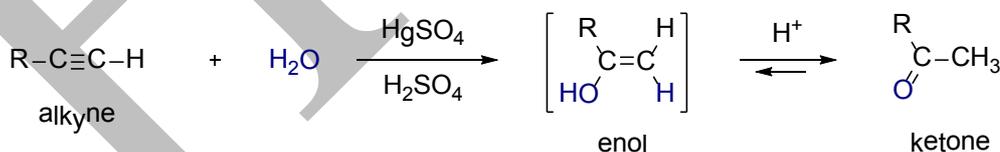
cyclohexylacetylene + H_3C—Br $\xrightarrow{NaNH_2}$ 1-cyclohexyl-1-butyne (—C≡C–CH₂CH₃)

bromoethane
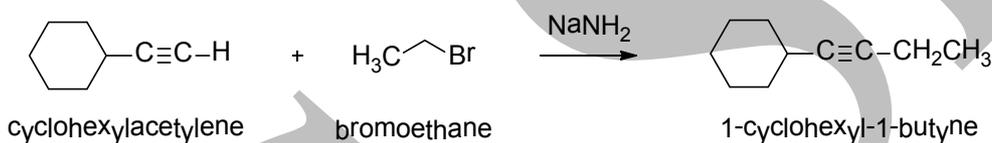
Scheme-19: Reaction of metal acetylide with alky halide
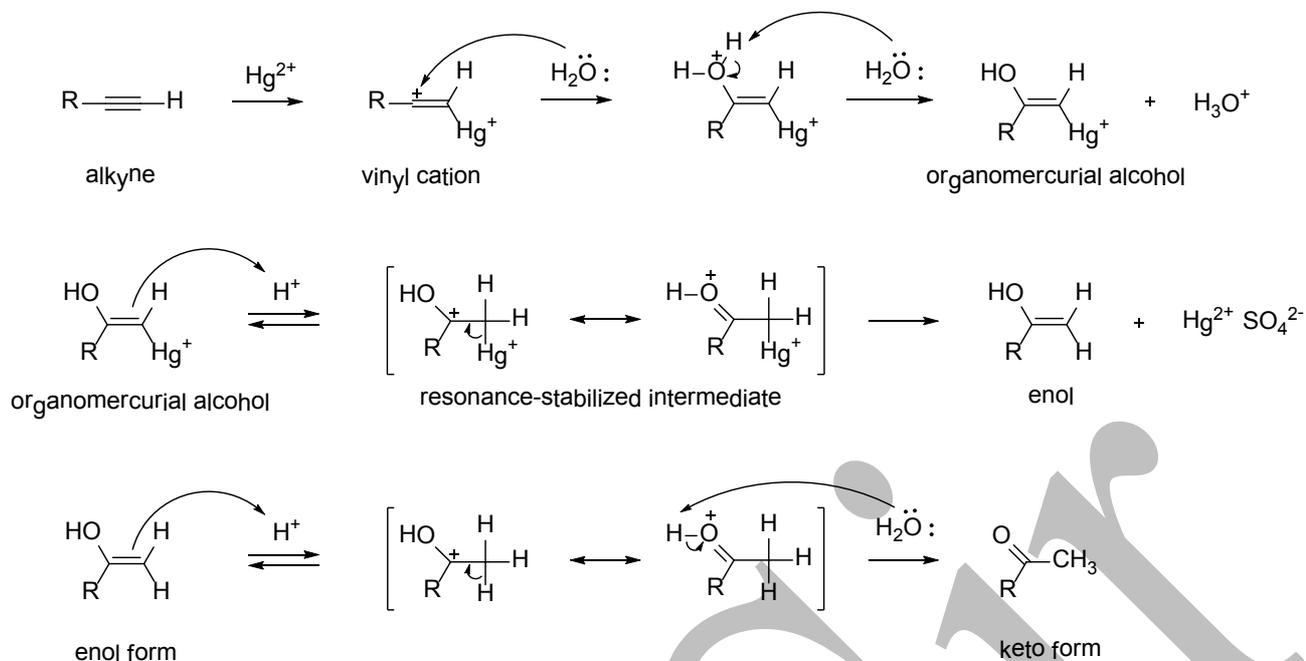
Hydration Reation of Alkyne:

Many addition reactions of alkynes are similar to the corresponding reactions of alkenes since both involve π-bonds. Reagents add across the triple bonds of alkynes just as they add across the double bonds of alkenes and the reaction is usually exothermic.

Alkynes undergo acid-catalyzed addition of water across the triple bond in the presence of a mixture of mercuric sulfate in aqueous sulfuric acid. The hydration of alkynes also goes with Markovnikov's orientation (Scheme 20).

$$R-C\equiv C-H \quad + \quad H_2O \quad \xrightarrow[H_2SO_4]{HgSO_4} \quad \left[\begin{array}{c} R \quad\quad H \\ C=C \\ HO \quad\quad H \end{array}\right] \quad \underset{}{\overset{H^+}{\rightleftharpoons}} \quad \begin{array}{c} R \\ C-CH_3 \\ O \end{array}$$

alkyne enol ketone
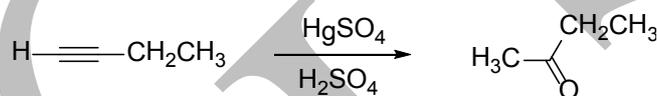
Scheme-20: Hydration of Alkyne

Electrophilic addition of mercuric ion gives a vinyl cation, which reacts with water and loses a proton to give an organomercurial alcohol. Under acidic conditions, mercury is replaced by hydrogen to give an enol which is unstable and isomerizes to the ketone (Scheme 21).

R—≡—H $\xrightarrow{Hg^{2+}}$ vinyl cation $\xrightarrow{H_2\ddot{O}:}$ $\xrightarrow{H_2\ddot{O}:}$ organomercurial alcohol + H_3O^+

alkyne   vinyl cation   organomercurial alcohol

organomercurial alcohol $\xrightarrow{H^+}$ [resonance-stabilized intermediate] → enol + $Hg^{2+}\ SO_4^{2-}$

enol form $\xrightarrow{H^+}$ [resonance-stabilized intermediate] $\xrightarrow{H_2\ddot{O}:}$ keto form

Scheme-21: Mechanism of hydration of alkyne

The hydroxyl proton in the enol is lost, and a proton is regained at the methyl position, while the π-bond shifts from the C = C position to the C = O position. This type of equilibrium is called as tautomerism (Scheme-22).

Example:

$H—≡—CH_2CH_3 \xrightarrow[H_2SO_4]{HgSO_4}$ $H_3C—\overset{\displaystyle CH_2CH_3}{\underset{\displaystyle O}{C}}$

Scheme-22: Tautomerism