Abdelhafid BOUSSOUF University Center - Mila
Process engineering department
2nd year L.M.D – Organic Chemistry
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Chapter 5: The major reactions in organic chemistry

V.1. Reagents and reaction intermediates;
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Chapter 2: Classification of organic functions

II.1. Saturated aliphatic hydrocarbons (linear, branched),
II.2. Alkenes (preparation, reactivity),
II.3. Alkynes (preparation, reactivity),
II.4. Aromatic compounds (preparation, reactivity),
II.5. Alcohols, thiols, aldehydes (preparation, reactivity),
II.6. Ketones, carboxylic acids (preparation, reactivity).

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II.1/ Saturated aliphatic hydrocarbons (linear, branched)

- Alkanes are saturated non-cyclic hydrocarbons, having the chemical formula C_nH_{2n+2}, ending **–ane**, with a symbol **RH**: Methane; Ethane

II.1.1. Physical properties of alkanes and cycloalkanes

- From methane to butane, alkanes occur in the gaseous state.
- Natural gas is essentially made up of methane. Oils contain a mixture of hydrocarbons (including alkanes ranging from CH_4 to $C_{40}H_{82}$).
- From C_5, we encounter liquids and from C_{17}, solids.
- Liquid or solid alkanes have a fairly low density (around 0.7). They are insoluble in water; on the other hand, they are miscible with most organic liquids and are themselves solvents for many compounds organic.
- Boiling temperature increases with molecular weight. For branched alkanes, the boiling and melting temperatures are lower than that of normal alkane even number of carbon atoms.

e.g.

	Compound	boiling temperature (°C)
C_5H_{12}	Pentane	36
	Methyl butane	25
	Dimethyl propane	9

- Cyclic alkanes generally have boiling and melting temperatures above those of linear alkanes with the same number of carbon atoms.

II.1.2. Reactivity of alkanes and cycloalkanes

- Generally speaking, alkanes are relatively unreactive, in other words stable. This is explained by the fact that the C-C and C-H bonds are quite strong: C-C = 82.6 kcal/mol, C-H = 100 kcal/mol
- Alkanes can react in several reactions:

II.1.2.1. Combustion reactions (complete and partial)

- The combustion of alkanes is an exothermic reaction, it occurs by breaking the C-C bond (the skeleton of the molecule). These types of reactions are used as a source of energy calorific (fuels, heating, etc.)
- There are two types (Example with methane):
  ⇨ The complete which produces carbon dioxide and water:

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$$

$$C_nH_{2n+2} + (3n+1)/2\ O_2 \longrightarrow n\,CO_2 + (n+1)\,H_2O$$

⇨ When there is not enough oxygen or there is too much methane, combustion is called incomplete. It may form carbon monoxide, carbon or both.

$$CH_4 + O_2 \longrightarrow C + 2\,H_2O$$

$$2\,CH_4 + 3\,O_2 \longrightarrow 2\,CO + 4\,H_2O$$

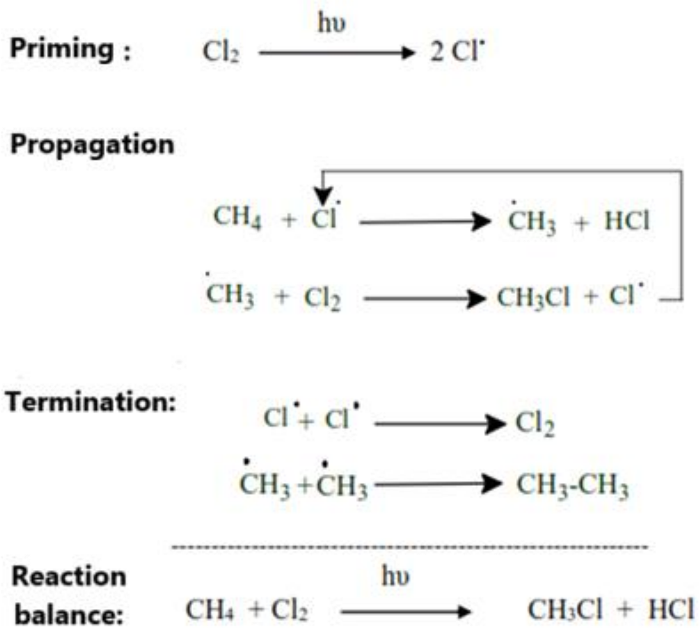
II.1.2.2. Halogenation reactions

- When the alkane is used in excess compared to the halogen, only monohalogenation is observed.

Example: Chlorination of methane

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

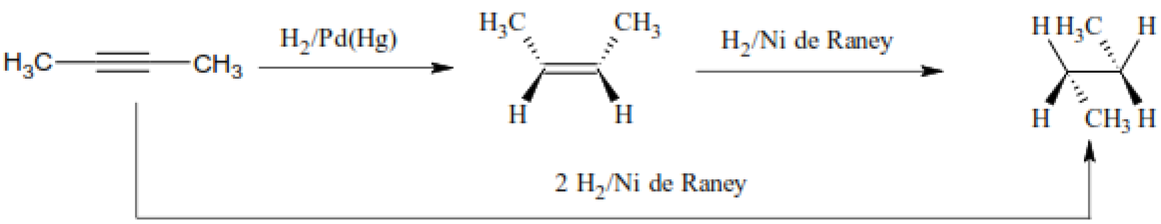
- Under heat and between 350 and 600°C, or in the presence of light ($\lambda < 490$ nm), we obtain a mixture of CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4.
- The proportions of the various products depend on the initial Cl_2/CH_4 ratio.
- The mechanism of methane monochlorination as for all radical processes, includes three stages: initiation, propagation and termination.



II.1.3. Preparation of alkanes and cycloalkanes

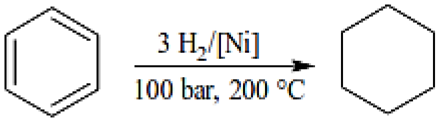
II.1.3.1. Catalytic hydrogenation of alkenes and alkynes

- It is the addition of hydrogen to an unsaturation (C=C, or C≡C).
- These reactions take place at low temperatures and in the presence of a catalyst (Pd, Pt, Raney Ni). The more the connection is congested, the slower the reaction.



II.1.3.2. Catalytic hydrogenation of aromatic compounds

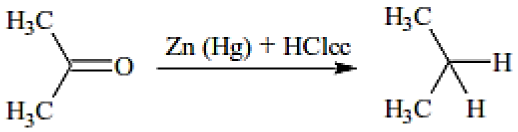
- The hydrogenation of benzene and its derivatives takes place in bulk and leads to cyclohexane. These reactions are generally slower and require high temperatures and pressures significant in hydrogen.



II.1.3.3. Reduction of carbonyls

A) Clemmensen reduction (acidic medium)

Clemmensen reduction is a reduction reaction of the carbonyl function (ketone and aldehyde) aliphatic or aromatic in saturated hydrocarbons in the presence of Zinc amalgamated with Mercury in concentrated HCl.

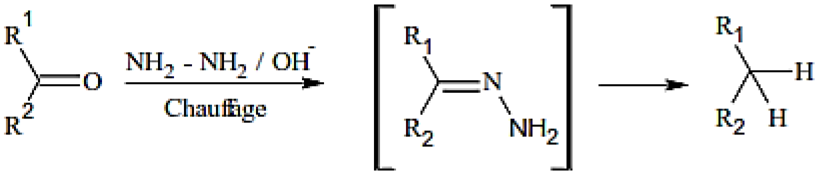


e.g. the reduction of benzaldehyde (C_6H_5CHO) would yield toluene ($C_6H_5CH_3$):

$$C_6H_5CHO \xrightarrow{Zn/Hg,HCl} C_6H_5CH_3$$

B) Wolff-Kishner reduction (basic medium)

The Wolff-Kishner reduction is a reaction for the reduction of the carbonyl function to a saturated hydrocarbon. It is done in two stages: the condensation of the carbonyl with hydrazine, which gives hydrazone, which transforms into saturated hydrocarbon under the action a strong base (NaOH, KOH, etc.).



e.g. the reduction of acetone (CH_3COCH_3) would yield propane ($CH_3CH_2CH_3$):

$$\mathrm{CH_3COCH_3} \xrightarrow{N_2H_4,KOH} \mathrm{CH_3CH_2CH_3}$$

II.1.3.4. Dehalogenation (metallic coupling with Zn)

- The reaction between a halogenated derivative and zinc leads to an organo-zincic compound. This last one is then treated with a proton donor such as hydrochloric acid.

$$CH_3Cl + Zn + HCl \longrightarrow CH_4 + ZnCl_2$$

II.1.3.5. Wurtz reaction (metallic coupling with sodium)

The reaction allows the formation of an organo-sodium and the carbanion formed causes a nucleophilic substitution on the halogenated derivative:

$$R{-}X \;+ 2\,Na \longrightarrow R^{-},Na^{+} + NaX$$

II.1.3.6. Reaction of a Grignard reagent with water

The reaction goes through the stage of formation of an organo-magnesium (Grignard reagent) in anhydrous ether, then the latter transforms into alkane in the presence of water.

RX + Mg/ether ---------> RMgX (Organomagnesien)

RMgX + H_2O ---------> RH + MgXOH

II.2. Alkenes (Preparation and reactivity)

- Alkenes are non-cyclic unsaturated hydrocarbons with the formula C_nH_{2n}.
- We call also ethylenic compounds any chemical species containing at least one C=C double bond.
- The main chain is the one with the greatest number of links.

II.2.1. Physical properties of alkenes

The physical properties of alkenes are similar to those of alkanes:

- Boiling points are slightly lower than those of alkanes.

- They are insoluble in water, soluble in non-polar solvents such as: benzene, ether, chloroform.

- They are essentially nonpolar molecules interacting weakly with each other.

- Alkenes containing fewer than four carbon atoms are gaseous.

- Boiling temperatures increase with molecular weight; branching decreases the boiling temperature.

e.g.

Compound	Boiling T (°C)	Compound	Boiling T (°C)
Butane	-0.5	But-1-ene	-6,5
Isobutane	-11,7	Isobutane	-7

But-2ene	4	But-2-ene	1

II.2.2. Reactivity of alkenes

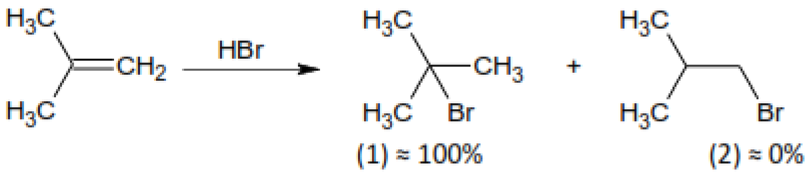
Alkenes are characterized by: addition and redox reactions following the presence of the π bond of the C=C double bond (weaker than a single C-C σ bond), and the reactions which involve the nucleophilic properties of alkenes resulting from the richness in polarizable electrons at the C=C double bond.

II.2.2.1. Addition of hydrogen halides (H-X):

a) Markovnikov type HX addition

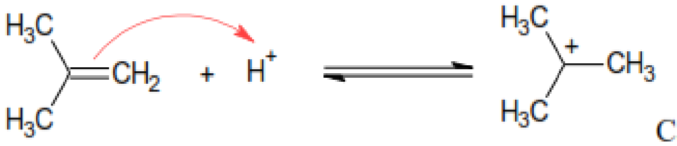
This is an electrophilic addition reaction. The addition of HX to an alkene shows that the halogen atom (X = Cl, Br, I)) is generally found on the most substituted carbon atom and the hydrogen atom attaches to the carbon atom giving rise to the formation of the most stable carbocation: tertiary > secondary > primary (Markownikov rule).

e.g. The reaction between HBr dissolved in ethanoic acid and 2-methylpropene at 20 °C gives mainly 2-bromo-2-methypropane (1) and only traces of 1-bromo-2methylpropane (2). It is regioselective.



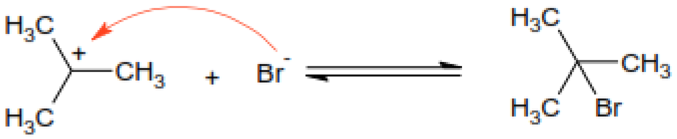
Mechanism:

First step: The alkene reacts with the proton to form the most stable carbocation.



Carbocation tertiaire plus stable

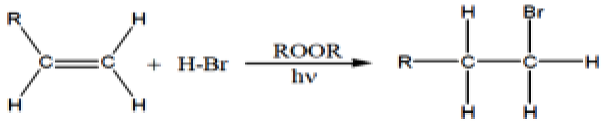
Second step: The nucleophilic halide anion attacks the carbocation formed during the first stage.



The reaction is therefore a strongly regioselective addition

b) Addition of anti-Markovnikov type HBr

The reaction of HBr with an alkene in the presence of peroxide, we obtain an addition of which the orientation is anti-Markownikow: it is a radical addition reaction on alkenes:



$$RCH{=}CH_2 + HBr \xrightarrow[h\upsilon]{ROOR} RCH_2\text{-}CH_2Br$$

Mécanisme

Initiation $R\text{-}O\text{-}O\text{-}R \xrightarrow{h\upsilon} 2\ R\text{-}O^{\bullet}$

$R\text{-}O^{\bullet} + HBr \longrightarrow R\text{-}O\text{-}H + Br^{\bullet}$

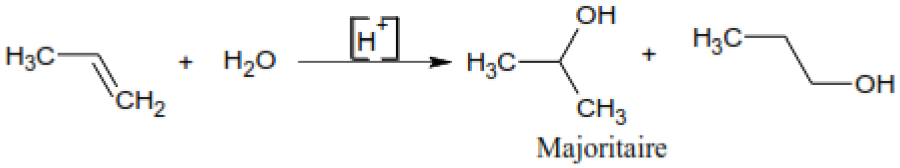
Propagation $R\text{-}CH{=}CH_2 + Br^{\bullet} \longrightarrow R\text{-}CH^{\bullet}\text{-}CH_2\text{-}Br$

Formation du radical le plus stable

$R\text{-}CH^{\bullet}\text{-}CH_2\text{-}Br + HBr \longrightarrow R\text{-}CH_2\text{-}CH_2\text{-}Br + Br^{\bullet}$

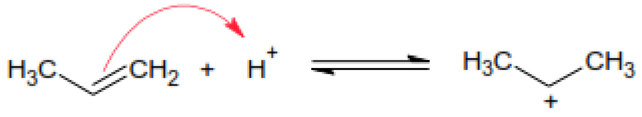
II.2.2.2. Hydration in an acidic environment:

The addition of water to alkenes gives access to alcohols according to the Markovnikov rule.

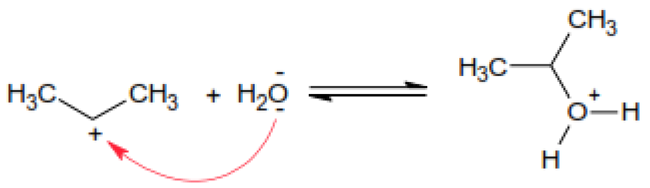


⇨ ***Mechanism:***

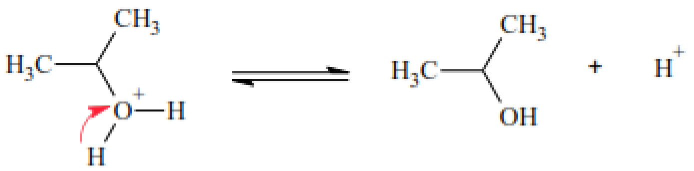
First step: The alkene reacts with the catalyst proton added to the medium (addition of acid sulfuric for example) to form a carbocation.



Second step: Water which is a nucleophile, attacks the carbocation formed during the first step.

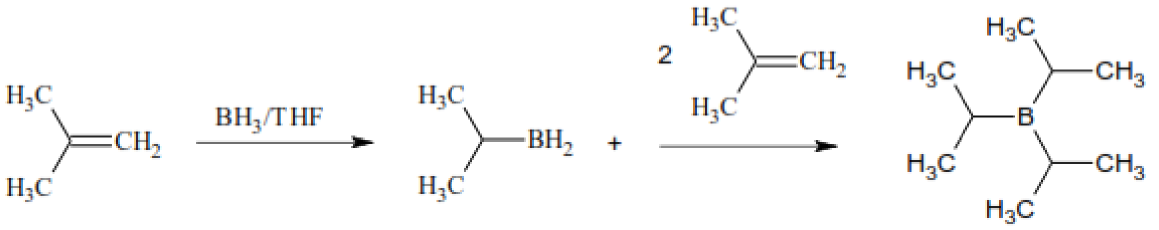


Third step: deprotonation and regeneration of the catalyst proton.



II.2.2.3. Hydration by hydroboration

The reaction leads to the replacement of the three hydrogen atoms of BH_3 and we obtain a trialkylborane.

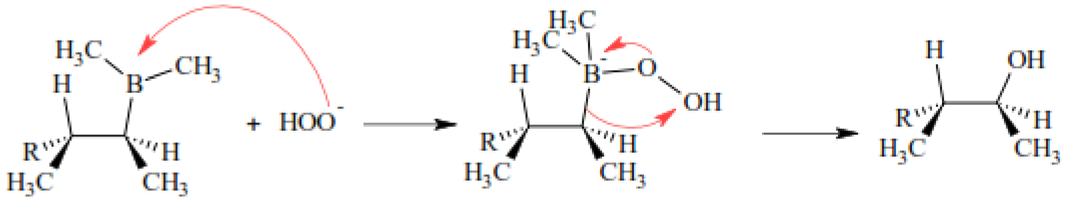


Trialkylborane

- Boron adds to the least hindered carbon (electronic and steric effects)
- Addition syn: H and B add on the same face of the alkene

Oxidative hydrolysis by hydrogen peroxide in a basic medium.

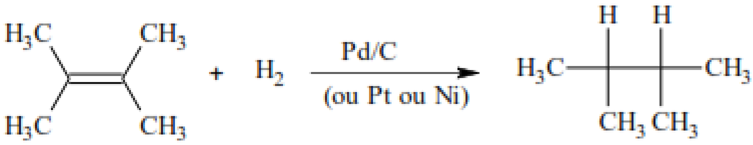
$$H_2O_2 + HO^- \longrightarrow H\text{-}O\text{-}O^- + H_2O$$



Hydroboration followed by the action of hydrogen peroxide in a basic medium leads to an addition of H_2O to an anti-Markownikow type alkene.

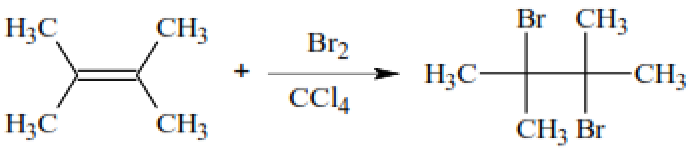
II.2.2.4. Catalytic hydrogenation (or addition of hydrogen, H_2)

The hydrogenation of an alkene requires the use of a catalyst, most often metallic, among which we can cite Raney nickel (prepared by the action of sodium hydroxide on the alloy of Raney Ni-Al), platinum or its oxide (Adams catalyst), palladium and zinc oxide.



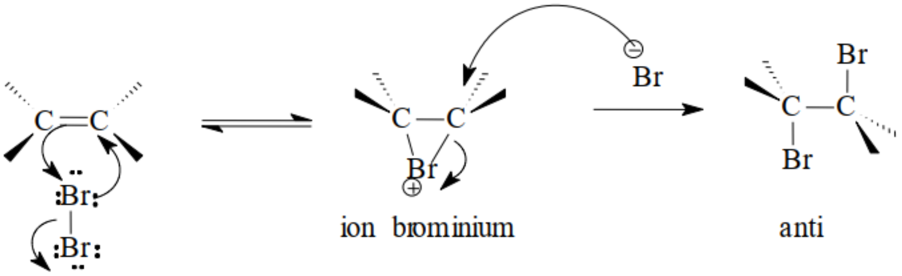
II.2.2.5. Halogenation (or addition of halogens, X2)

Alkenes react quickly with Br_2 or Cl_2 in nonpolar solvents (such as CCl_4). The addition of the dihalogen is carried out in anti, that is to say that the two atoms of halogen enter on either side of the plane of the double bond (trans-addition).



Mechanism of halogen addition:

Results in the formation of an intermediate halonium ion.



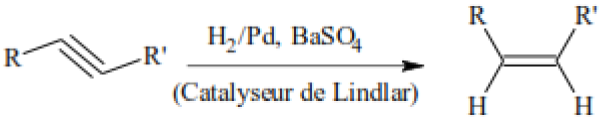
Note: alkenes participate in several other reactions mentioned: Oxymercuration -demercuration, Mild oxidation with diluted potassium permanganate, Strong oxidation with $KMnO_4$ or concentrated $K_2Cr_2O_7$, Ozonolysis, epoxidation, Cycloadditions, Diels-Alder reaction etc.

II.2.3. Preparation of alkenes

II.2.3.1. Catalytic partial hydrogenation of alkynes

a) Controlled reduction of alkynes (formation of cis alkenes)

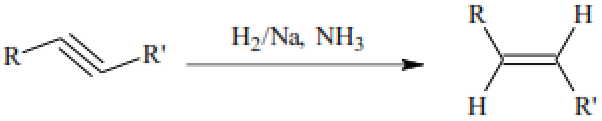
The hydrogenation of alkynes to alkenes uses the Lindlar catalyst (palladium deposited on calcium carbonate or barium sulfate). The addition leads to the cis alkene.



$BaSO_4$ or $CaCO_3$ is used to disactivate the catalyst; in the absence of $BaSO_4$ and $CaCO_3$, the reduction will be total and leads to an alkane.

b) Controlled reduction of alkynes (formation of trans alkenes)

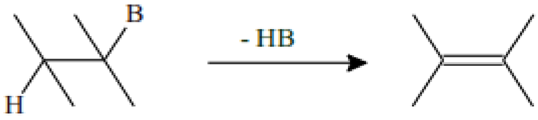
In the presence of Na/NH_3 or Li/NH_3, the trans alkene is obtained.



II.2.3.2. Order 2 or Order 1 elimination reactions

Elimination reactions correspond to the intramolecular removal of two groups or atoms A and B carried by one or two elements. A is most often a hydrogen atom and B an electro-attractor group (–I). When the two groups (or atoms) are adjacent, it is then a β-elimination (or 1,2 elimination); it leads to the formation of a double or triple bond.

- ✓ If B is a halogen (Cl, Br or I) it is a dehalogenation reaction, it takes place in presence of a strong base (KOH or $NaNH_2$).
- ✓ If B is an (OH) it is a dehydration reaction in an acidic medium (H_2SO_4 conc).
- ✓ If B is a (NH_2) it is a deamination reaction (Hofmann elimination).

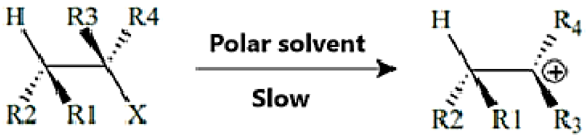


Mechanisms of elimination reactions: There are two types of mechanisms for elimination reactions (named E1 and E2) which have a lot of resemblance to the mechanisms of SN1 and SN2 substitution reactions respectively.

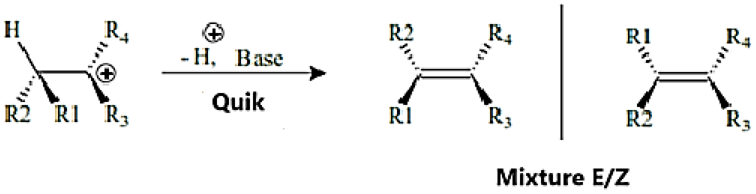
E1 elimination mechanism:

E1 type elimination reactions have a mechanism close to that of SN1. He takes place in two stages:

The first step is slow, and gives the speed of the total reaction. She permits the ionization of the C-X bond (X is an electron-attractor group) under the action of a polar solvent, with formation of a carbocation and the anion X^-. This step is identical to the first step of SN1.

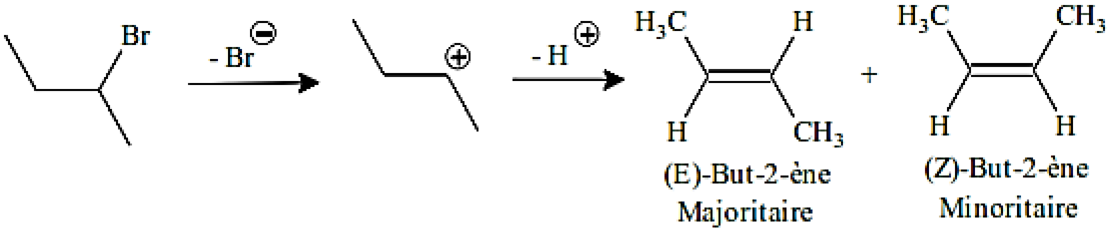


The second step, very rapid, corresponds to the removal of a proton under the action of a basis to form a double bond. The elimination speed E1 is of order 1.



Elimination E1 gives a mixture of two alkenes (Z + E) in which the form (E) is in the majority because of its greater stability, therefore it is non-stereospecific.

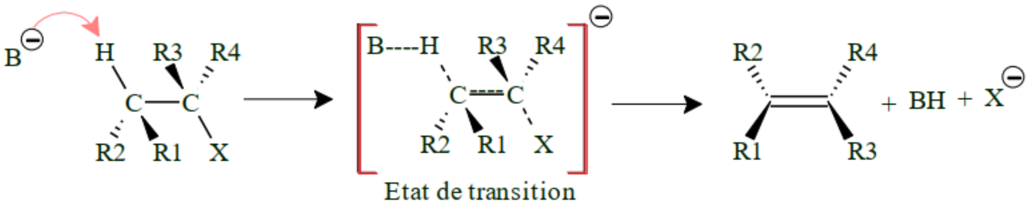
Example: Elimination of HBr from 2-bromobutane.



Note: Due to the formation of a carbocation in the first step (SN1 or E1), the base can tear of a proton (E1) but in certain cases it can enter the reaction as a nucleophile (SN1). Therefore, there is a competition between the SN1 mechanism and E1. The increase in temperature favors E1 elimination compared to SN1, and E2 compared to SN2.

E2 elimination mechanism:

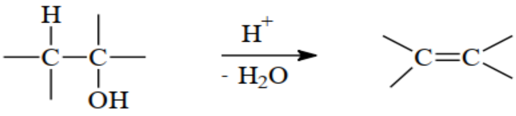
In the E2 mechanism, the action of a base leads to the elimination of a hydrogen acidic character (results from the -I electro attractant effect of X), and will continue with the removal of X with the formation of an alkene. The reaction goes through a transition state which represents the highest level of activation energy. All connections are formed and break simultaneously. E2 is said to be a concerted trans elimination.



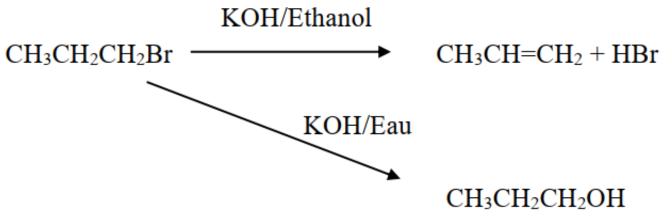
⇨ In the transition state, the hydrogen atom (undergoing elimination) and the halogen are in the trans position, the E2 elimination reaction is stereospecific.

Examples of elimination reactions:

1- Dehydration of alcohols in an acidic medium: In the presence of acids, such as H_2SO_4 (sulfuric acid) or H_3PO_4 (Phosphoric acid), alcohols are dehydrated to form alkenes.



2- Dehydrohalogenation: dehydrogenation of alkyl halides is a very classic reaction for the preparation of alkenes. In the presence of a base like alcoholic potash (KOH), potassium tertiary butoxide, $NaNH_2$. On the other hand, KOH in aqueous solution appears as Nu, and leads to a nucleophilic substitution.

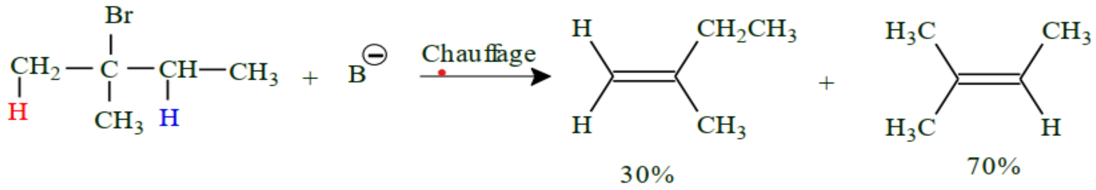


$$CH_3CH_2CH_2Br \xrightarrow{KOH/Ethanol} CH_3CH{=}CH_2 + HBr$$

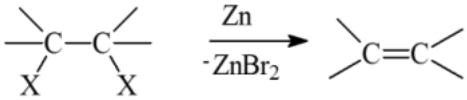
$$CH_3CH_2CH_2Br \xrightarrow{KOH/Eau} CH_3CH_2CH_2OH$$

Zaitsev's rule:

> When several possibilities present for forming alkenes by elimination, the majority alkene formed will be the most substituted. This is the rule given by ***Zaitsev***.



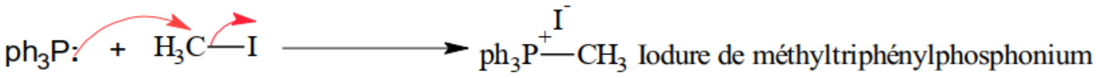
II.2.3.3. Dehalogenation (metallic coupling with Zn)



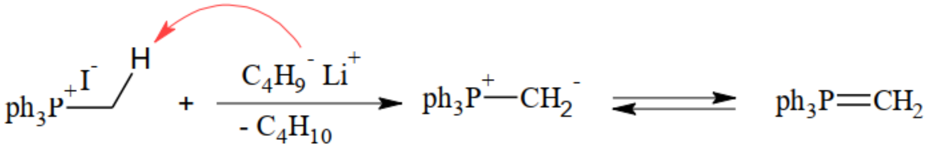
II.2.3.4. WITTIG’s reaction

This reaction allows the transition from a carbonyl compound (ketone or aldehyde) to an alkene. Phosphorus and sulfur ylides prepared from phosphonium or sulfonium are rapidly condense with carbonyl compounds to produce alkenes. The reaction takes place in three stages:

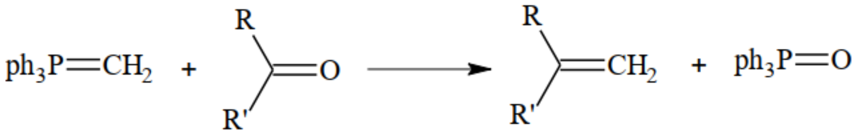
1) Formation of phosphonium salts:



2) Action of a strong base on methyl-triphenyl-phosphonium iodide to give the ylure:



3) Action of ylure on a carbonyl:



II.3. Alkynes (Preparation and reactivity)

Alkynes are linear hydrocarbons with the formula C_nH_{2n-2}. A monoalkyne is named by replacing the suffix “**ane**” with “**yne**”

e.g. CH3 — CH2 — C≡CH: but-1-yne.

II.3.1. Physical properties of alkynes

- Van der Waals interactions are more important than in alkenes and alkanes = corresponding which shows that the boiling temperatures are higher than those homologous alkanes and alkenes:

$T_{éb}\ C_2H_6$ = -88,6°C ; $T_{éb}\ C_2H_4$ = –102°C ; $T_{éb}\ C_2H_2$ = –83°C.

- The enthalpy of combustion of C2H2 is very high, the oxyacetylene flame can reach a temperature of 3000°C.

II.3.2. Reactivity of alkynes

II.3.2.1. Double addition: HX; X_2 and H_2

a) HX Addition

Two equivalents of HX can be added on alkyne. An equivalent is added to such so that the X is on the most substituted carbon atom (Markownikov rule). In the second addition the orientation depends on the mesomeric effects of the first halogen.

$$R\text{-}C\equiv C\text{-}H \xrightarrow{\quad HBr \quad} R\text{-}CBr{=}CH_2 \xrightarrow{\quad HBr \quad} R\text{-}CBr_2\text{-}CH_3$$

b) X_2 Addition

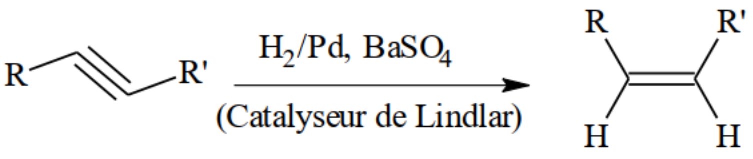
The rules of orientation and stereochemistry applied to alkenes also apply to alkynes:

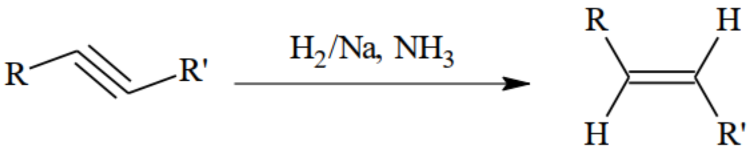
$$R\text{-}C\equiv C\text{-}R' \xrightarrow[CCl_4]{Br_2} R\text{-}CBr{=}CBr\text{-}R'\ (E) \xrightarrow[CCl_4]{Br_2\ (\text{excès})} R\text{-}CBr_2\text{-}CBr_2\text{-}R'$$

c) Addition of H_2 (Catalytic Hydrogenation)

The addition of H_2 to give alkenes is easily carried out in the presence of a catalyst metallic to give E or Z isomers. In the presence of Nickel Raney, Pt or Pd both unsaturation's are hydrogenated to give an alkane.

To stop at alkenes, you must use a deactivated catalyst. For this we use Pd/$BaSO_4$ to produce Z isomers and sodium in liquid NH_3 as a reduction, for E isomers.

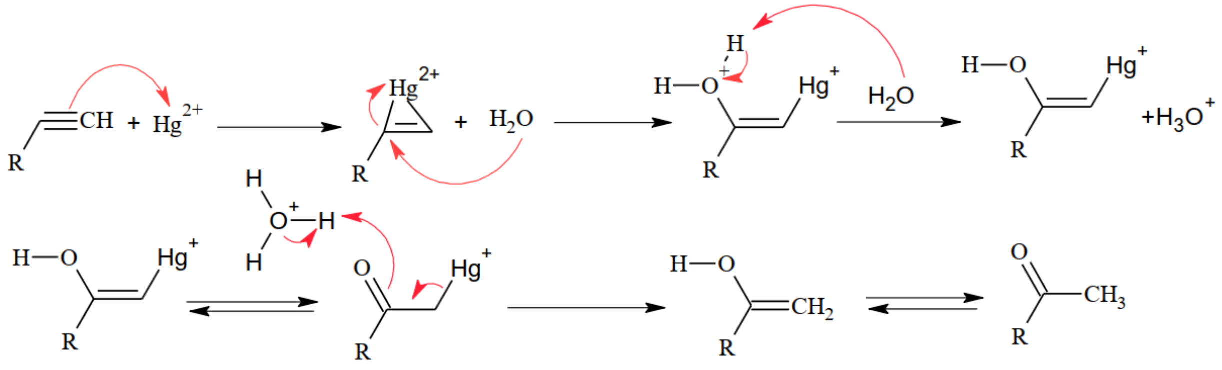




II.3.2.2. Hydration in an acidic environment in the presence of a mercury catalyst

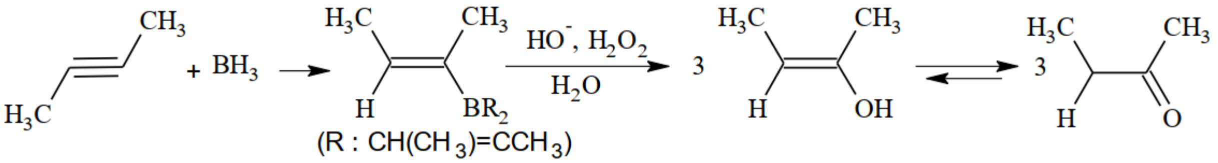
The hydration of alkynes in an acidic medium catalyzed by Hg^{2+} ions leads to compounds carbonyls: ethanal for the hydration of acetylene, on the other hand mono- and disubstituted alkynes provide ketones.

$$R\text{-}C\equiv C\text{-}H + H_2O + Hg^{2+} \longrightarrow R\text{-}CO\text{-}CH_3$$



II.3.2.3. Hydration by hydroboration

The addition of B_2H_6 follows the same rules of orientation and stereochemistry as for alkenes (anti-markovnikov water addition).



Note: alkynes participate in several other reactions like: Oxidation and ozonolysis; Acidity and specific reactions of true alkynes (R-C≡C-H)

II.3. Preparation of alkynes

II.3.1. Double dehydrohalogenation (double elimination)

A triple bond can be obtained by eliminating two HX molecules on one geminal dihalide or vicinal dihalide in the presence of a strong base (potash alcoholic, $NaNH_2$ etc.) hot.

Note: A geminal dihalide is a class of organic compounds containing two halogen atoms bonded to the same carbon atom within a molecule. In this case, the halogen atoms are situated on the same carbon, making them "geminal". This configuration is different from vicinal dihalides, where the halogen atoms are attached to neighboring carbons in the carbon chain.

The presence of these functional groups can influence the physical and chemical properties of organic molecules, and they are often used in organic synthesis to create specific compounds.

II.3.2. Inorganic synthesis: industrial process from coke and lime

The inorganic synthesis of an organic compound with a triple bond, such as ethyne (or acetylene), from coke (coal) and lime (calcium oxide), is achieved through a process called the carbide process (proceed de carboration). This process involves several steps and is typically carried out in an electric arc furnace under high temperature and pressure. Here are the main steps of this process:

$$CaCO_3 + 3\,C \xrightarrow{\qquad\qquad} CO + CaC_2 \text{ (carbure de calcium).}$$

Calcium carbide hydrolyzes very easily to acetylene:

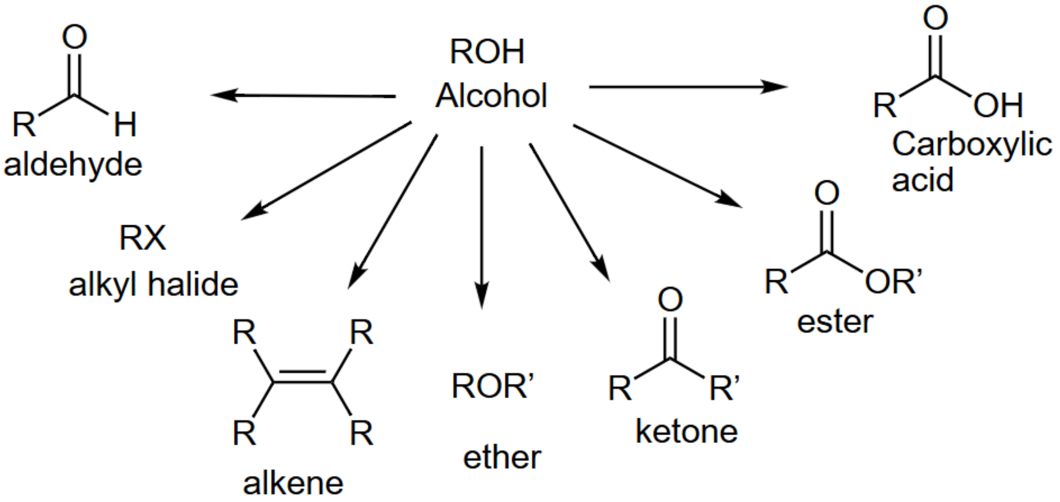
$$CaC_2 + 2H_2O \xrightarrow{\qquad\qquad} Ca(OH)_2 + H\text{-}C \equiv C\text{-}H$$

This carbide process is widely used in the industry to produce ethyne (acetylene) on a large scale from abundant resources such as coke (coal) and lime (calcium oxide).

II.4. Alcohol (Preparation and reactivity)

Alcohols (ROH) are considered on of the more important functional groups in organic chemistry. They can be prepared from compounds containing a wide assortment of functional groups. Also, the can be used to create compounds with a wide variety of functional groups such as: alkenes, ketones, carboxylic acids, and others. Many functional group conversions can be accomplished through the preparation of an alcohol giving them an important central position in organic synthesis.

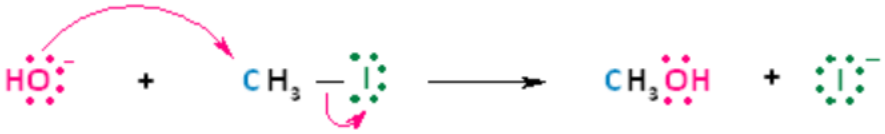
E.g. Alkene → Alcohol → Ketone.



II.4.1. Preparation of alcohols

II.4.1.1. Alcohols from Substitution Reactions

Methyl and primary alkyl halides can be converted to alcohols by using an S_N2 reaction with OH^- as a nucleophile. Also, secondary and tertiary alkyl halides can be converted to alcohols by an S_N1 reaction using water as the nucleophile (and it can even be the solvent). Recall that S_N1 reactions are promoted in polar, protic solvents.

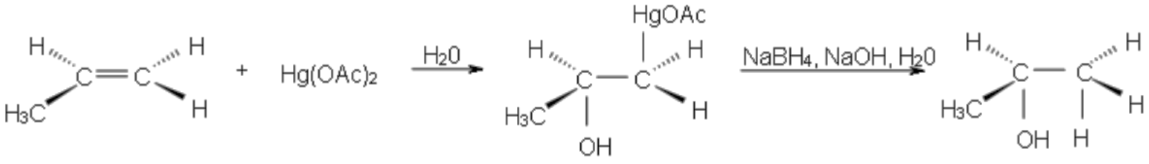


II.4.1.2. Alcohols from Alkenes

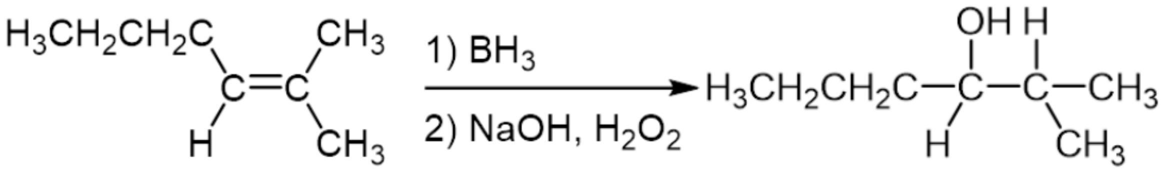
Throw a reaction of Oxymercuration. This reaction involves mercury undergoing electrophilic addition to the alkene double bond forming a *Mercurinium Ion Bridge*. A water molecule then attacks the most substituted carbon to open the mercurium ion bridge, followed by proton transfer to form a hydroxyl group (-OH).

The organomercury intermediate is then reduced by sodium borohydride. Notice that overall, the oxymercuration - demercuration mechanism follows Markovnikov's Regioselectivity with the OH group attached to the most substituted carbon and the H is attached to the least substituted carbon. Also, the H and OH species will be anti to each other in the product.

e.g.



e.g.

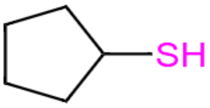


II.5. Thiols (Preparation and reactivity)

Thiols are often called “mercaptans,” a reference to the Latin term mercurium captans (capturing mercury), since the -SH group forms strong bonds with mercury and its ions. Thiols are analogous to alcohols. Thiols are weakly acidic (pK_a ~ 10) and are much stronger acids than alcohols (pKa ~ 16). However, thiols usually do not form hydrogen bonds due to the sulfur atom not have sufficient electronegativity. Thiols named using the same rules as alcohols except the parent chain is named as alkane with the suffix -thiol added. As a substituent the -SH group is called a **mercapto** group.

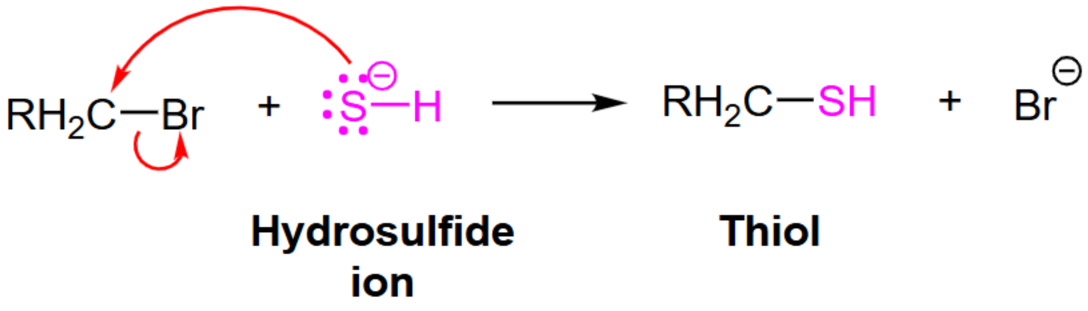
$CH_3CH_2CH_2SH$

Propanethiol



Cyclopentanethiol

Thiols are usually prepared by using the hydrosulfide anion (-SH) as a nucleophile in an S_N2 reaction with alkyl halides.

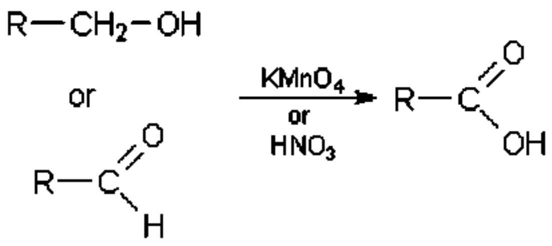


II.6. Carboxylic acid (Preparation and reactivity)

They are compound that contain **carbonyl and hydroxyl** groups attached to each other. There are various methods that can be used for the preparation of Carboxylic acids.

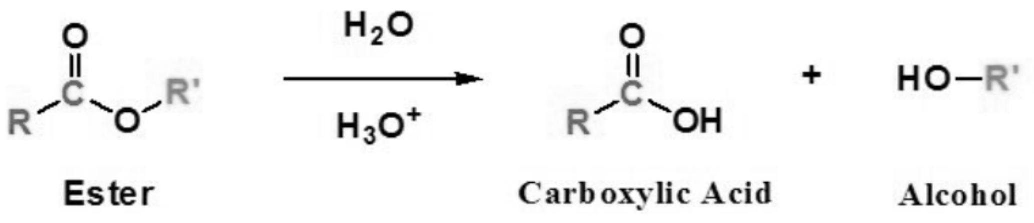
II.6.1 form alcohols and aldehydes

The primary alcohol gets oxidised to carboxylic acid when oxidising agents are added, such as potassium permanganate ($KMnO_4$), in an acidic, alkaline or neutral medium. By using a mild oxidising agent.



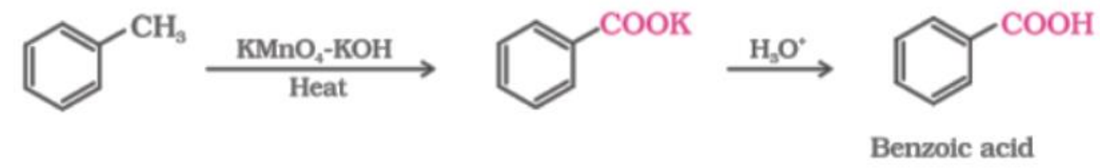
II.6.2 from esters

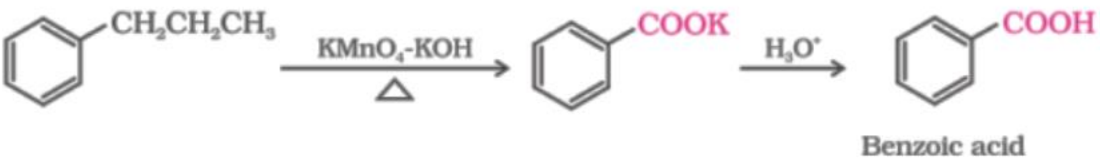
A carboxylic acid is produced after the acidic hydrolysis of esters and carboxylates are produced after the basic hydrolysis of an ester.



II.6.3 From Alkylbenzenes

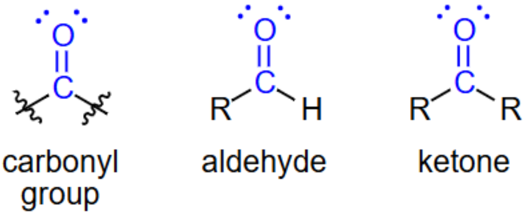
We can get aromatic carboxylic acids after vigorous oxidation of alkylbenzenes with chromic acid. Irrespective of the length of the chain, the whole side chain is oxidised to a carbonyl group. The oxidation of **primary and secondary** alkyl groups can be done in this manner while **the tertiary group is unaffected.**



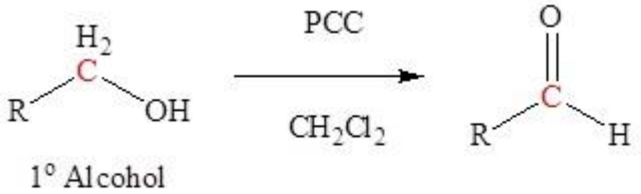


II.7. Aldehyde and Ketones (Preparation and reactivity)

Aldehydes and ketones are organic compounds which incorporate a **carbonyl functional group**, C=O. The carbon atom of this group has two remaining bonds that may be occupied by hydrogen, alkyl or aryl substituents. If at least one of these substituents is hydrogen, the compound is an **aldehyde**. If neither is hydrogen, the compound is a **ketone**.

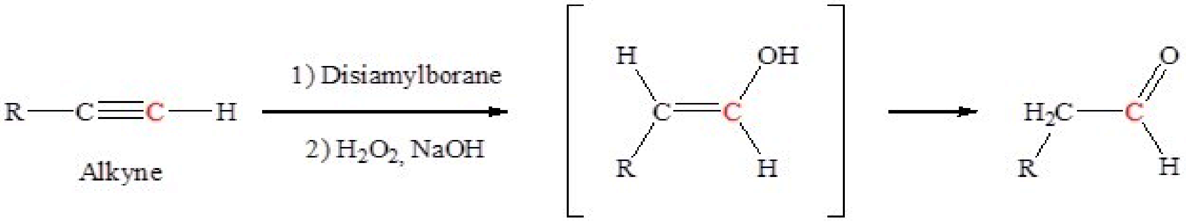


II.7.1 Oxidation of 1° alcohols with PCC to form aldehydes



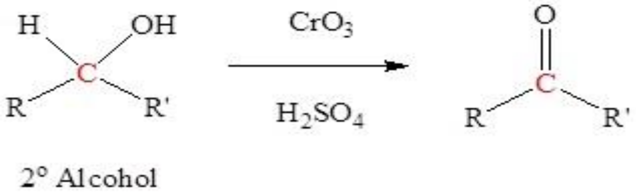
II.7.2 Hydration of an alkyne to form aldehydes

Anti-Markovnikov addition of a hydroxyl group to an alkyne forms an aldehyde. The addition of a hydroxyl group to an alkyne causes tautomerization which subsequently forms a carbonyl.



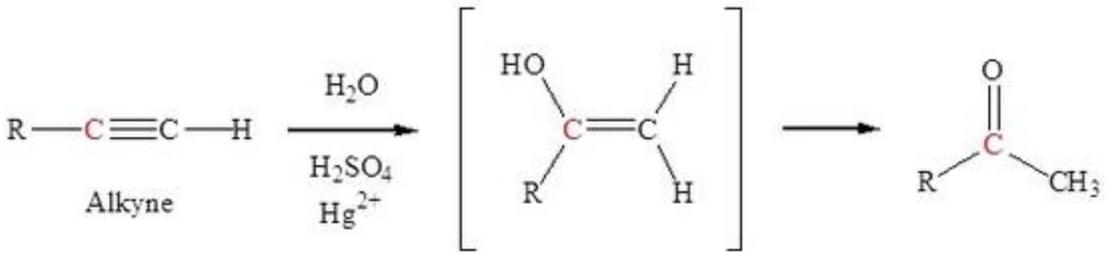
II.7.3 Oxidation of 2° alcohols to form ketones

Typically uses Jones reagent (CrO_3 in H_2SO_4) but many other reagents can be used



II.7.4 Hydration of an alkyne to form ketones

The addition of a hydroxyl group to an alkyne causes tautomerization which subsequently forms a carbonyl. Markovnikov addition of a hydroxyl group to an alkyne forms a ketone.



Note: **there are many other reactions, many other catalysts, many other reactions mechanisms for the synthesis of each chemical compounds, here we treat only the most important.**