Unit-III

Alkenes & Alkynes

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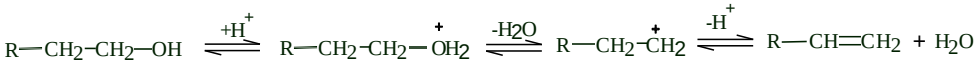
1). Dehydration of alcohol

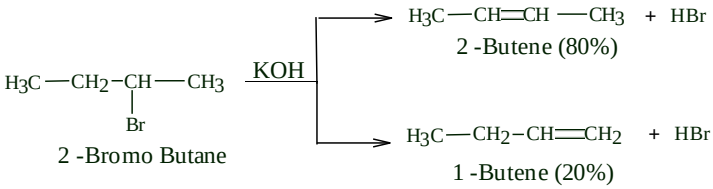
Dehydration of alcohols with Conc. H_2SO_4 at 100^0c or phosphoric acid at 200^0c to form alkenes.

Mechanism



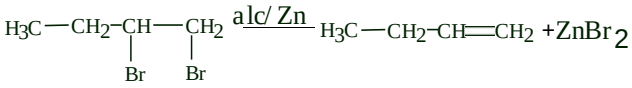
2). De hydro halogenation of alkyl halides

Dehydro halogenation of alkyl halides with alcoholic KOH/NaOH gives alkenes.



3). De Hydro halogenation of Vicinal di halides

De halogenation of Vicinal halide with Zn dust in alcohol gives alkenes.



1,2 Di -Bromo Butane

4). From acetylene When acetylene is treated with $Pd/BaSO_4$ catalyst to form Cis alkenes

Elimination reactions

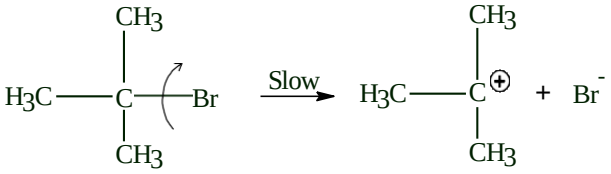
A elimination reaction is a type of organic reaction in which two substituents are removed from a molecule in either a one step or two step mechanism.

The one step mechanism is known as the E2 reaction(Bimolecular) and two step mechanism is known as (unimolecular)E1 reaction. Elimination reaction produce a new pi(π) bond in the modified substance.

E_1(Unimolecular elimination reaction)

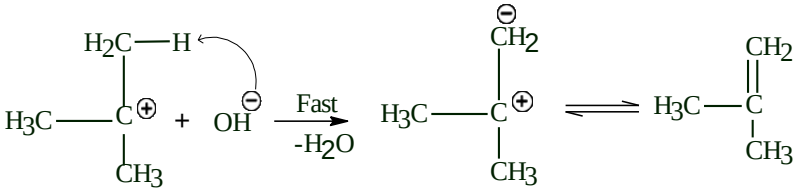
Step:1 It is a two step reaction. First, there is a heterolytic cleavage of alkyl halide, which is slow & rate determine step. Since the rate of the reaction is depends upon the only concentration of the reactants & it follows First ordered kinetics and the reaction is unimolecular.

Ex: Consider the tertiary butyal bromide Reaction with NaOH to form alkene



In this rate of the reaction is depends only on Concentration of the tertiary butyal bromide.

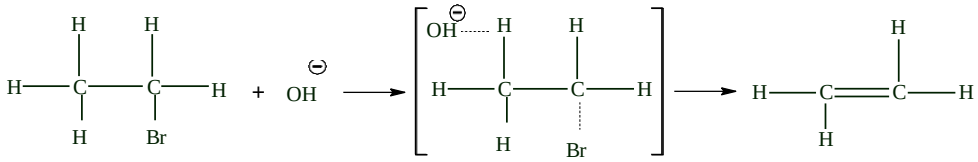
Step:2 In the second step base abstracts a proton (H+) from carbon adjacent to the +ve charged carbon atom(β-carbon). Increasing the concentration of the base has no effect on the rate of the reaction.



E2(Bimolecular Elimination reaction)

In which alkenes are formed by the abstracts of proton from the β-carbon atom by base and removal of halogen from α- carbon take place simultaneously through the formation of state. In the transition state newly formed π bond is become a stronger. sigma bond of halogen is much weaker. It is single step process.

Ex Consider the Bromo Ethane Reaction with NaOH to form alkene



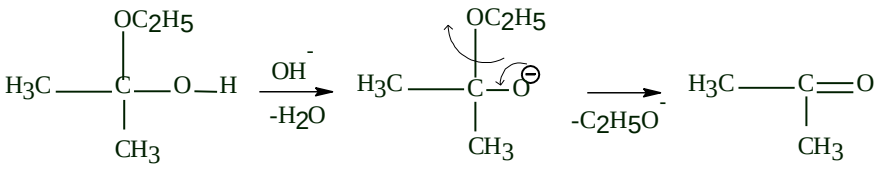
In this rate of reaction depends on the concentration of reactant's & base. so, it is bi molecular Elimination reaction.

iii). E1(CB) (Elimination uni molecular conjugated base) reaction

This reaction occurs basic conditions., where the hydrogen to be removed is relatively acidic. It is two step process. First, base abstracts the relatively acidic proton to generate a stabilised anion. The first step of which may or may not be reversable.,

while the leaving group is relatively poor one. usually, a moderate to strong base is present. The lone pair of electrons on the anion then moves to the adjacent atom, thus expelling the leaving group and forming a double bond.

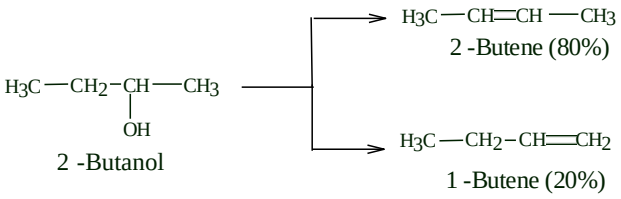
Ex:



Saytzeff's Rule

The Unsymmetrical 2^0 & 3^0 alcohols that can undergo elimination in two different ways resulting in two different products.

According to saytzeff's rule Alkenes with less number of hydrogens on the double-bonded carbon atoms are the preferred product. i.e. Hydrogen is eliminated from the carbon atoms with less number of hydrogens. This process is known as Saytzeff's rule.

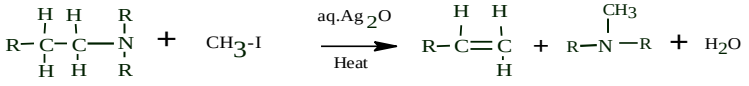


In this above 2-Butanol follow the saytzeff's rule to form 2- Butene is major product.

It is also states that ' greater the number of alkyl groups attached to the double bonded carbon atoms the more stable is the alkene

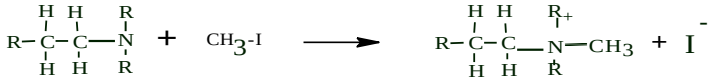
$R_2C=CR_2 > R_2C=CHR > R_2C=CH_2 > RCH=CHR > RCH=CH_2 > CH_2=CH_2$

Hoffmann's Elimination reaction When amines contains at least one β-Hydrogen atom is treated with methyl Iodide ,aq. Silver oxide followed by Heat is converted into alkenes. It is one of the most favoured alkenes produced method by using least substituted. This rule in known as Hoffmann Rule.

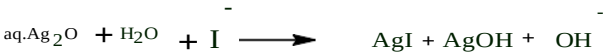


Mechanism

1).



2).



3).

Chemical properties of Alkenes.

Markovnikov's rule

When reagent is added to un-symmetrical alkene, then the negative part of the reagent is added to double bonded carbon atom, which has minimum number of hydrogen.

Mechanism

1). HBr ⟶ $H^+ + Br^-$

In second step Two carbonium ions are formed.

2). $H_3C-CH=CH_2 + H^+$ (Propane) → $H_3C-\overset{+}{C}H-CH_3$ (2 Carbonium ion) / $H_3C-CH_2-\overset{+}{C}H_2$ (1 Carbonium ion)

In which Secondary carbonium ion is more stable than primary carbonium ion.

3). $H_3C-\overset{+}{C}H-CH_3 + Br^-$ → $H_3C-CH(Br)-CH_3$

2 Bromo Propane

Anti Markovnikov's rule

When reagent is added to un-symmetrical alkene, then the negative part of the reagent is added to double bonded carbon atom, which has Maximum number of hydrogen.

$H_3C-CH=CH_2 + HBr \longrightarrow H_3C-CH_2-CH_2Br$

Propane — 1 Bromo propane

Mechanism

1). $HBr \longrightarrow H^\bullet + Br^\bullet$

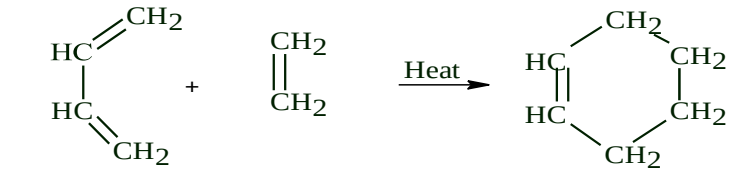
2). $H_3C-CH=CH_2 + H^\bullet$ (Propane) → $H_3C-\overset{\bullet}{C}H-CH_3$ (2 Free radical) / $H_3C-CH_2-\overset{\bullet}{C}H_2$ (1 Free radical)

3). $H_3C-CH_2-\overset{\bullet}{C}H_2 + Br^\bullet \longrightarrow H_3C-CH_2-CH_2Br$

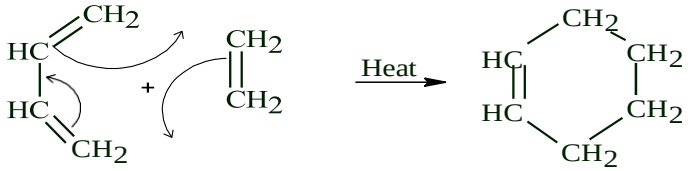
1 Bromo propane

Diel's-Alder reaction

When a conjugated diene like 1,3-Butadiene reacts with ethylene . which is a dienophile gives adduct of Diel's alder



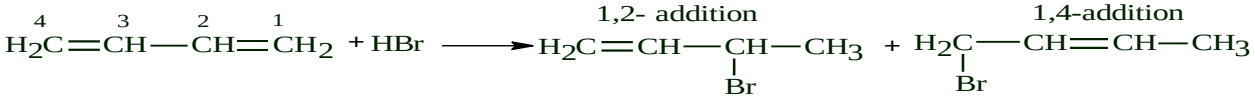
Mechanism



1,2 and 1,4 addition reaction

Dienes undergoes addition reaction. Conjugated dienes undergoes 1,2-addition & 1,4 addition at low temperature 1,2-addition product is major product. At high temperature 1,4- addition is major product.

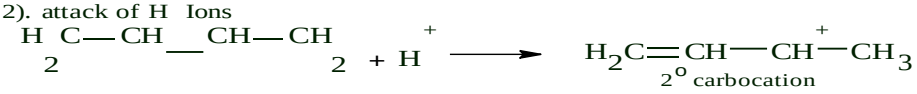
Ex:1,3 Butadiene react with HBr to form two products. i.e. 3-Bromo 1- butene, and 1-bromo 2- Butene.



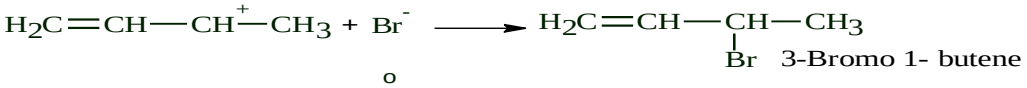
Mechanism

1). Ionisation of HBr

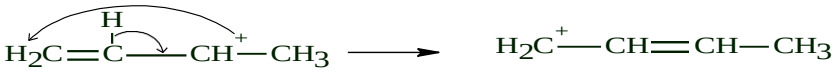
2). attack of H^+ Ions



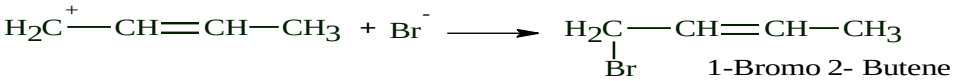
3) formation of 1,2- addition product



4). Resonance structures of 2° carbo cation



5) formation of 1,4-addition product



Alkynes

Aliphatic Unsaturated hydrocarbons that contain Carbon-Carbon triple bond are called Alkynes. They are also Called Acetylenes. General molecular formula of alkynes is C_nH_{2n-2}, they contain four hydrogen atoms less than the corresponding alkanes

Reactions of alkynes

Acidity of alkynes

Generally, S-orbital close to the nucleus is more electronegative as compared to the P-orbital. the carbon atom carrying a triple bond is SP hybridised. SP hybridised orbitals contains 50% s-character in an alkene, carbon carrying double bond in SP^2 Hybridised. SP^2 hybrid orbital contains 33% s-character. Due to Greater carbon atom should be more electronegative compared to double bond carbon atom.

The carbon atom acetylene being more electronegative attracts the bond pair between carbon and hydrogen more towards itself and Hydrogens goes out as a proton in the presence of very strong base like $NaNH_2$. That The increasing of order of acid strength of hydro carbons.

$HC\equiv CH > H_2C=CH_2 > H_3C-CH_3$

A hydrogen atom attached to triple bond C atom is said to be acidic. The acidic strength of alkynes decreases with alkylation.

$HC\equiv CH > R-C\equiv CH > R-C\equiv C-R$

The acidic nature of hydrogen in acetylene can also be shown by its reaction with sodium metal to form sodium acetylide.

$HC\equiv CH + Na \longrightarrow HC\equiv CNa + 1/2\ H_2$

It may be noted that Acetylene is a very weak acid. Its proton can only be removed by using a very strong base like sodamide, but $NaNH_2$, but can not removed by weak base like OH^-.

$HC\equiv CH + NaNH_2 \longrightarrow HC\equiv CNa + NH_3$

$HC\equiv CH + NaOH \longrightarrow$ No reaction

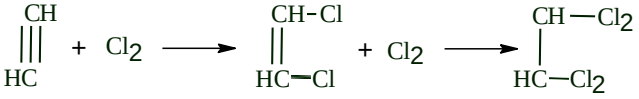
According to Bronsted-Loury theory proton releasing compound is an acid . that is why acetylene behaves as weak acid.

Electrophilic Addition reaction

C-C Triple bond is less reactive than C-C double bond towards electrophilic addition reactions. This is because in alkynes carbon atom is SP- Hybridization and thus more S-Character than that of SP2 Hybridized carbo atom, more strongly. Will be the attraction for Ⴖ- Electrons and hence lesse will be their availability for reaction.

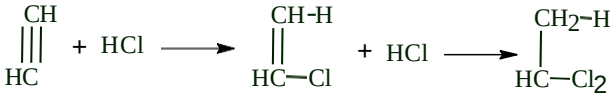
a). Addition of Halogens

Alkynes add one or two molecules of halogens to form di and tetra halides respectively. The order of reactivity of halogens is $Cl_2 > Br_2 > I_2$.



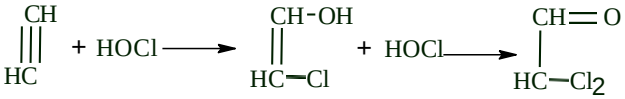
b). Addition of Halogen acids

Reactivity of halogen acids is HI > HBr > HCl



c). Addition of Hypohalous acids

Hypohalous acids add on acetylenes to form halo aldehydes or haloketones as the product

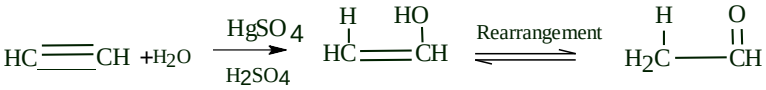


Nucleophilic addition reactions

Nucleophilic addition on alkynes form vinylic carbanion . when attacked by a nucleophile Vinyl carbanion is located on Sp2 carbon, while in alkyl carbanion is located on SP3 Carbon. more S- character of an orbital, greater is the electronegatively and hence more tightly will be its electron pair bound. Vinylic carbanion formed by alkynes will be more stable than alkyl carbanion formed by alkenes.

1). Addition of Water:

Alkynes add water molecule is presence of Sulphuric acid and mercuric sulphate to form aldehyde (or) Ketone.

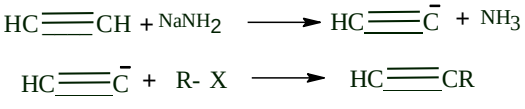


2). Alkylation of Terminal Alkynes

Terminal alkyne is an alkyne having a hydrogen substituent.

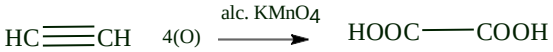
The Hydrogen of a terminal alkyne is acidic and can be removed with strong an alkynide.

Alkynide is treated with an alkyl halide to produce more complex alkynes. This reaction is known as alkylation.



3. Oxidation by alc. KMno4

Oxidation with alc. KMno4, generally cleaves the alkyne at the triple bond to form carboxylic acid having lesser no of carbon atom.



Oxidation with acidic KMno4 (or) $K_2Cr_2O_7$ alkynes causes hydroxylation at the triple bond to form diol, and it is converted to carboxylic acids having same no of carbon atoms.