

★ OXIDATION ★

Definitions :-

In Atomic Form ;

“Addition of oxygen in Atomic form is called oxidation.”

OR

“Removal of Hydrogen is called oxidation.”

OR

“Replacement of less Electro-Negative Atom with High Electro-Negative Atom is known to be oxidation.”

OR

“Increase of oxygen Bond is called oxidation.”

OR

“Decrease of Hydrogen Bond.”

In Term of Electron :-

“Loss of Electron increase the oxidation.”

Parts of Reaction

A Reaction includes Following parts.

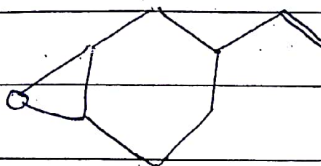
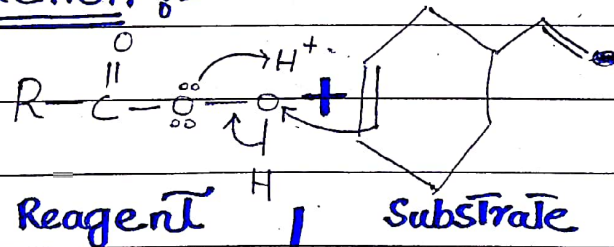
- 1) Substrate.
- 2) Reagent.
- 3) Catalyst.

④ Substrate :-

"The molecule or chemical structure upon which chemical changes or chemical process occur — is called a substrate."

In oxidation, substrate will always be an Electron Rich substance so that it can lose Electron.

Reaction :-



Reaction occur at more substituted Double Bond.

② Reagent :-

"The substance which give atom or group of atoms to substrate OR Take electron (electron) from a substrate is called a Reagent."

In Oxidation, Two kinds of Reagent act as oxidizing Agent.

* Oxidizing Agent :-

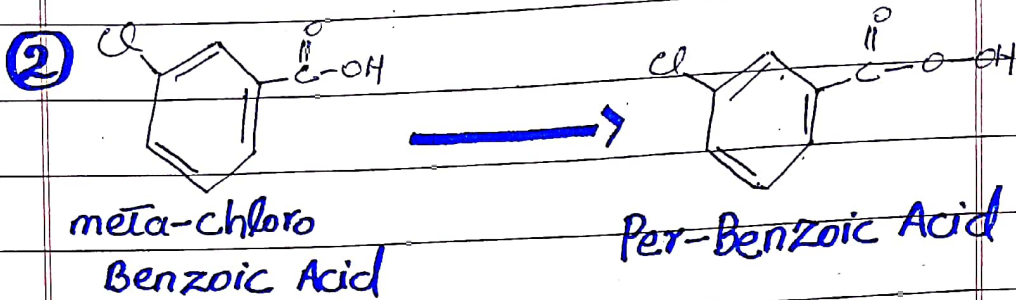
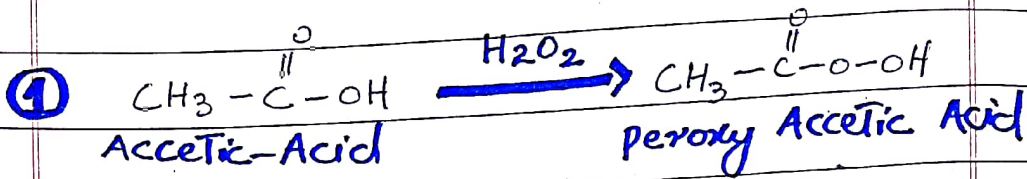
"A Reagent that oxidize other and reduce itself in a chemical reaction is known to be oxidizing Agent."

⇒ Case I (Per-oxy Acid)

"The specie in which there is a single bond between oxygen and oxygen act as oxidizing Agent and is known to be Peroxy-Acid."

Example :-

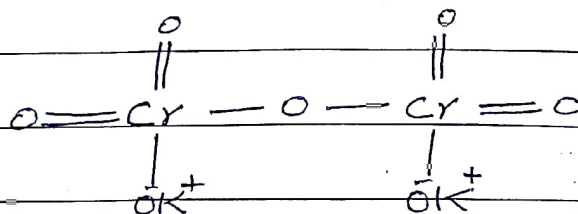
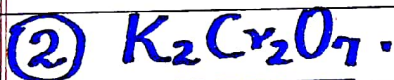
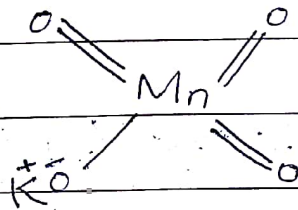
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➔ Case II (metal oxide)

"The Molecule in which There is Bond between metal and oxygen act as oxidizing Agent."

Example :-



③ CrO_3 (Chromic Acid)

④ V_2O_5 (Vanadium Pentoxide)

3) Catalyst :-

"A substance in a chemical reaction which affects the reaction and is regenerated at the end of reaction."

Example :-

"Ni" is used as catalyst in the hydrogenation of oil.

Question :- \longleftrightarrow

★ Why oxidation does not occur in Alkanes.?

\Rightarrow Ans :- In Alkanes ; Bonds are more stable ; No availability of electrons — Also sigma bond exists in Alkanes that is a strong bond and can not be broken —.

Hence ;

oxidation of Alkanes is not possible.

$\text{CH}_3-\text{CH}_2-\text{CH}_3$ \longrightarrow No oxidation
Alkanes

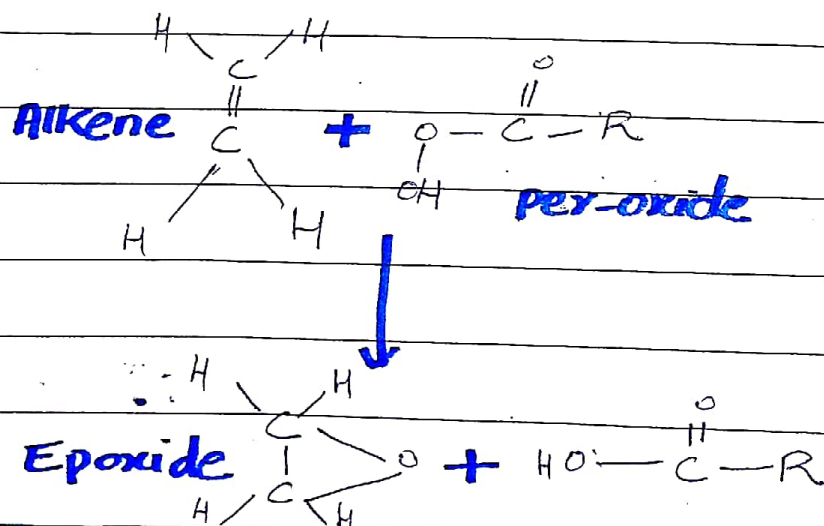
Oxidation Reactions

(ALKENES)

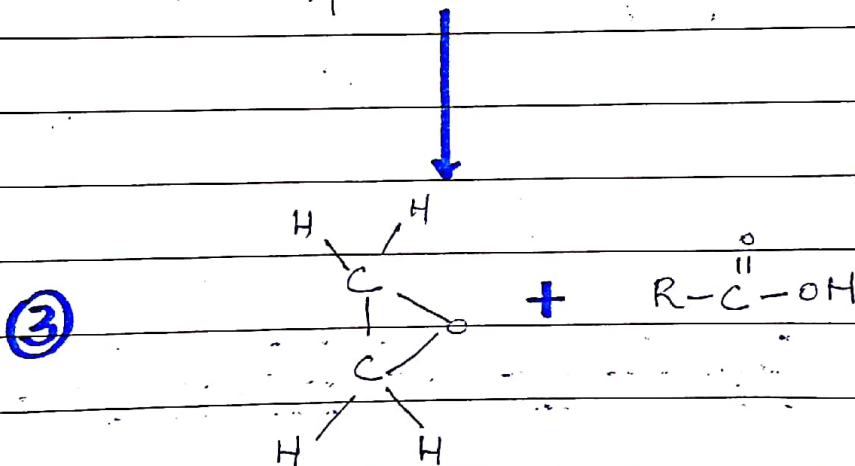
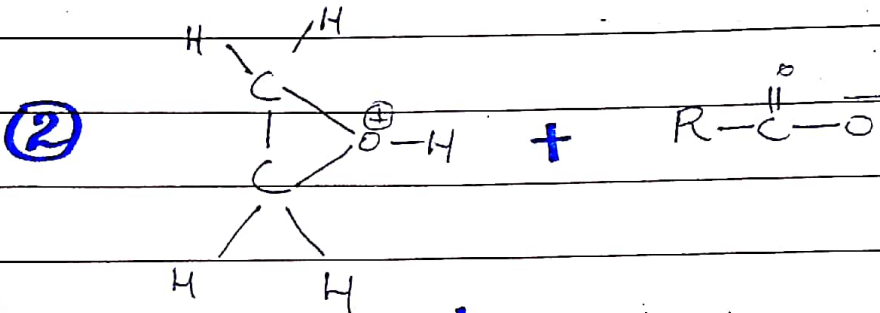
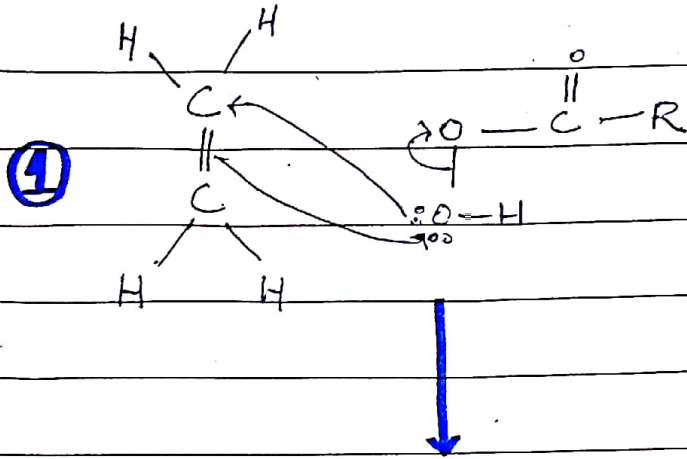
Alkenes are more oxidative and more reactive as compared to Alkanes because in **Alkenes** π -Bond which is a weaker bond less stable and there is more availability of electrons.

★ Epoxidation :-

"When Alkenes reacts with per-acids and per-oxides, it forms epoxide and the process is called Epoxidation."



Mechanism :-



★ Intermediate - State :-

"Epoxide act as intermediate state. It can (not) be studied as they are little bit 'stable'."

★ Transition-State :-

"Transition state is Imaginary state. It can't be studied because in Transition state Bond formation and Bond Breaking occur simultaneously."

★ Three Membered Ring :-

Epoxide is a 3-member Ring and unstable due to angle strain.

It further reacts with different compounds and give different products.

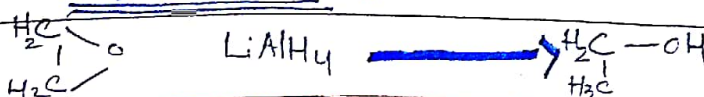
A) Products of Epoxide :-

i) With LiAlH_4 :-

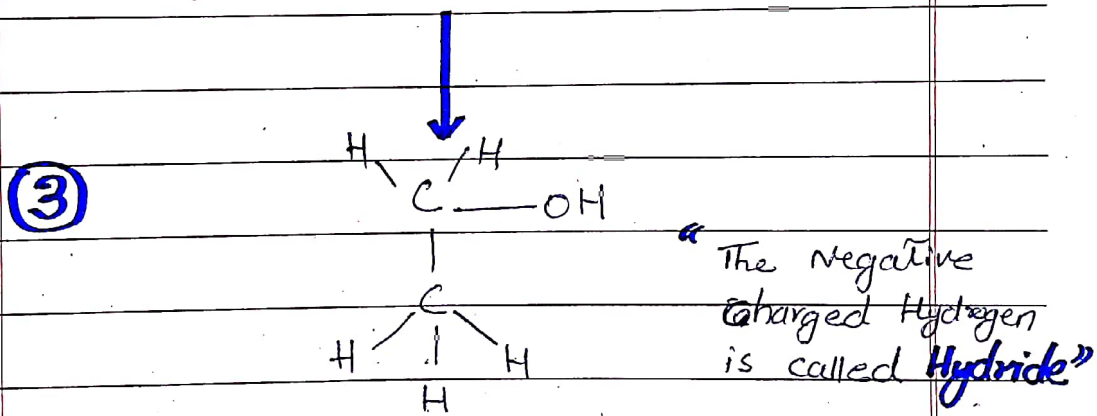
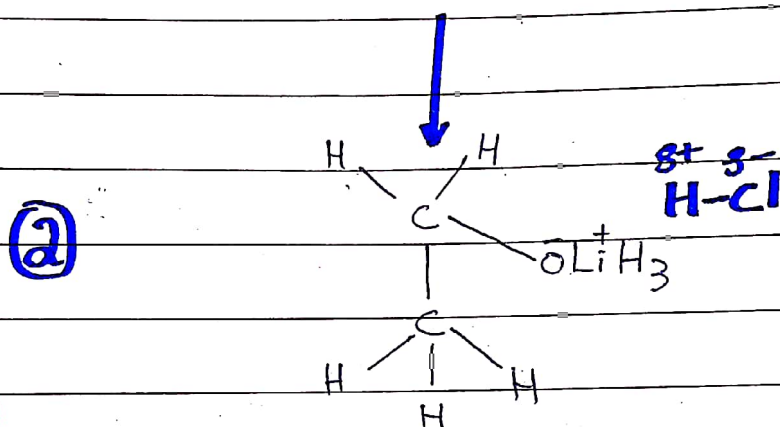
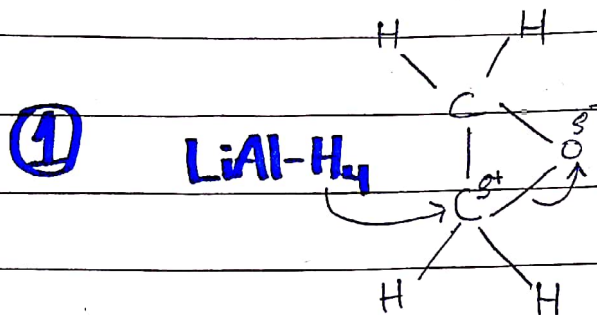
Hydride Donor Agents like

LiAlH_4 give Alcohols on Reduction of Epoxide.

Equation :-

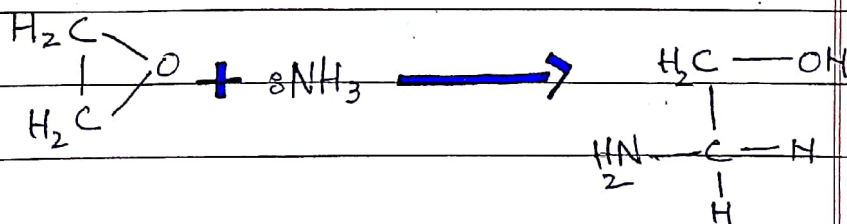


Mechanism :-



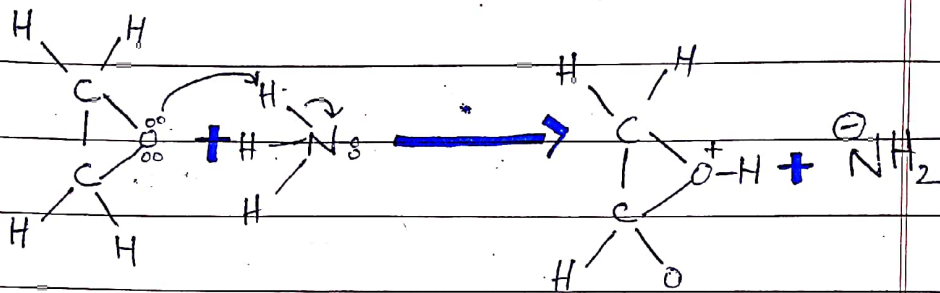
ii) With NH_3 :-

Equation :-

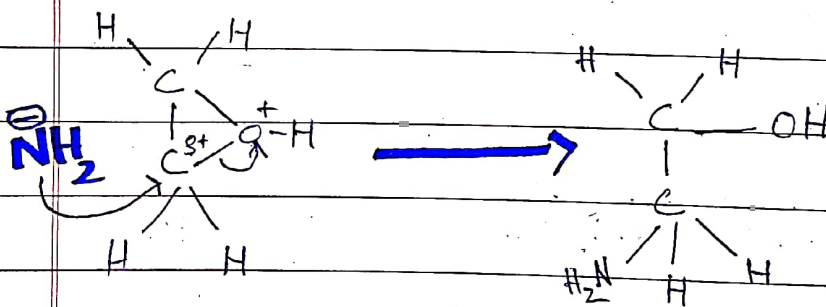


Mechanism :-

- ① In The first step, oxygen of Epoxide picks up Hydrogen of Ammonia by donating one of its Lone pair.

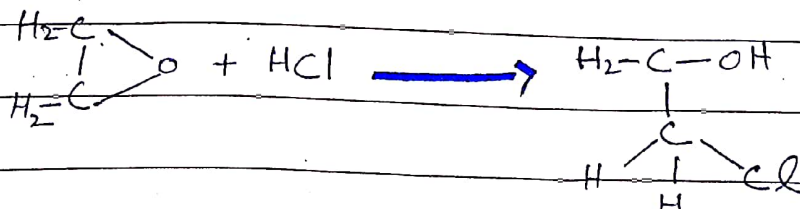


- ② In The second step, $\ominus \text{NH}_2$ attacks on partial positively charged carbon which transfers its bond with oxygen to oxygen as a whole.

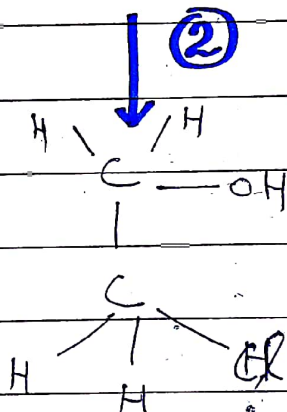
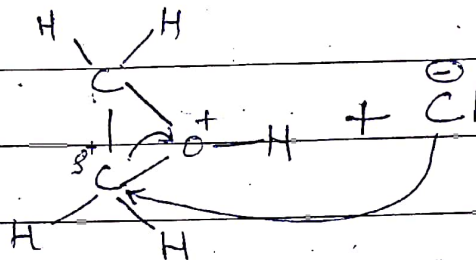
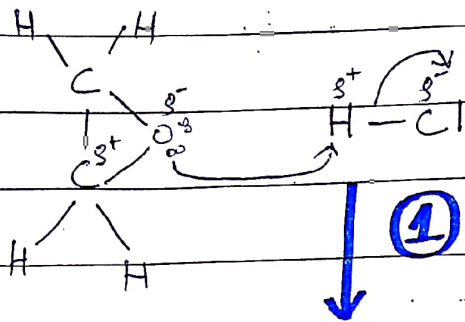


iii) With HCl :-

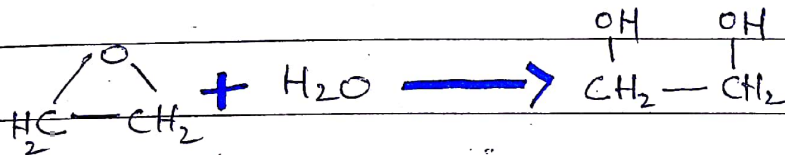
Equation :-



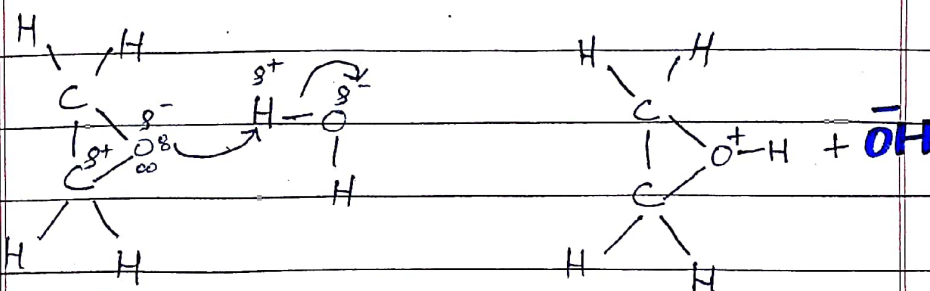
Mechanism 8-

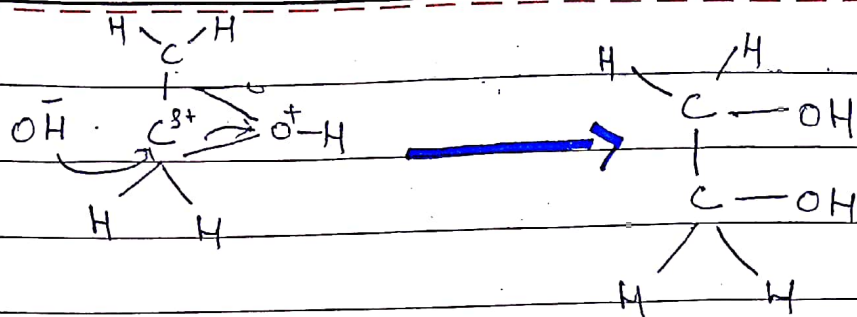


iv) Hydrolysis of Epoxide 8-

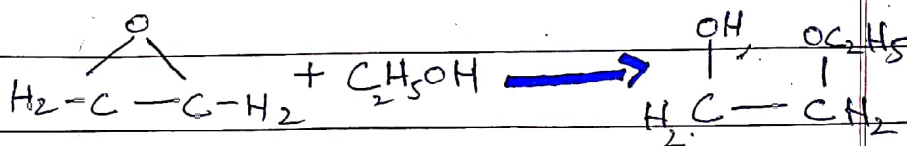


Mechanism 8-

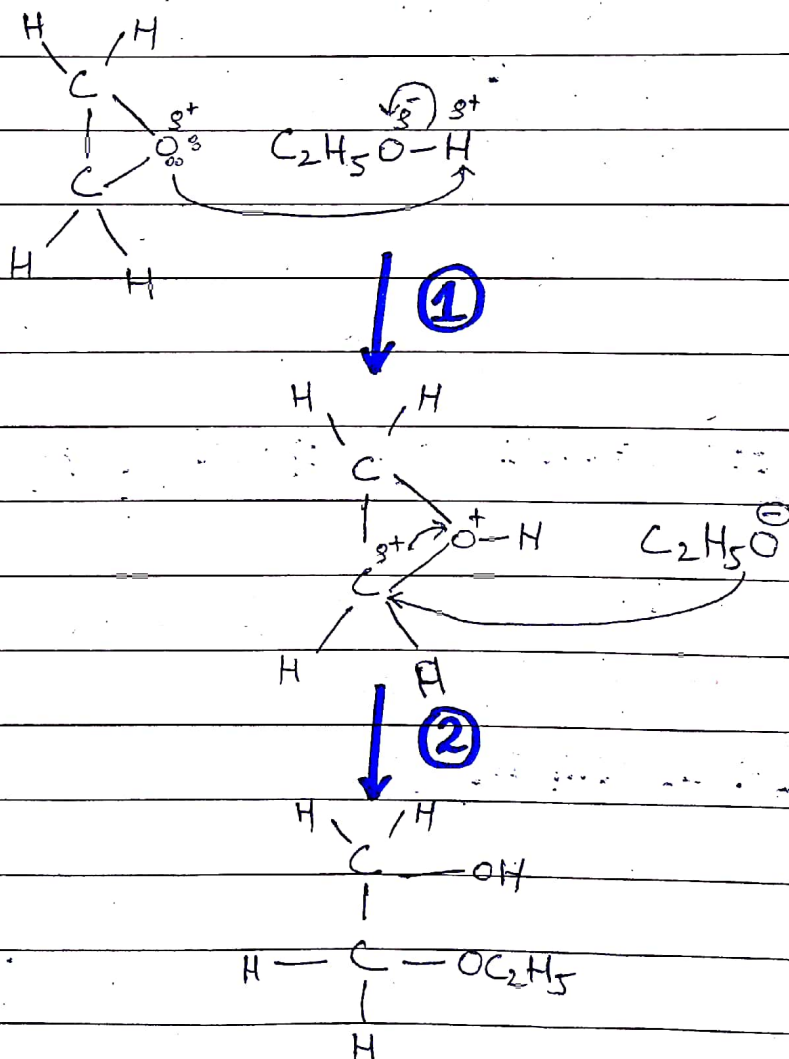




v) With Alcohol :-



Mechanism :-



* Electron Rich Atom

NUCLEOPHILE

BASE

Nucleophile :-

"An Electron Rich substance that attacks other than hydrogen atom in a chemical reaction is known to be a nucleophile."

Base :-

"An Electron Rich atom or substance that attacks an electron-deficient hydrogen atom in a chemical reaction is called a base."

* Electron Deficient Atom

ELEROPHILE

ACID

Electrophile :-

"An Electron-Deficient (Hydrogen) atom other than Hydrogen upon which a Nucleophile attacks in a chemical Reaction is called an Electrophile."

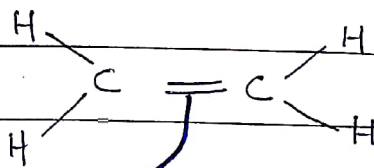
Acid :-

"An Electron-Deficient Hydrogen will act as an Acid in a chemical Reaction upon which a Base attacks."

2. Diol Formation :-

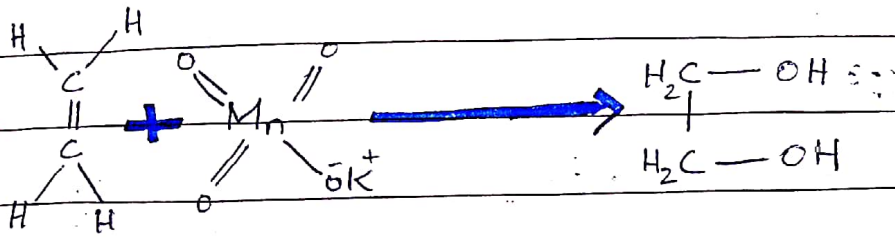
Alkenes are converted into following Diol compounds on treatment with some of the oxidizing agent.

i) With $KMnO_4$:- (Bayer's Reagent)



π -Bonds are weaker Bonds in Alkenes.

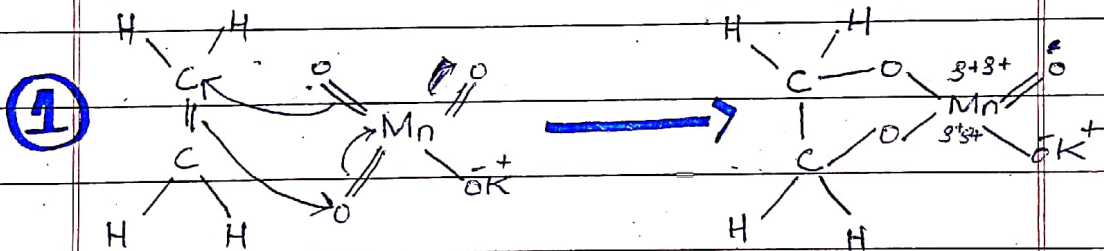
Equation :-



Mechanism :-

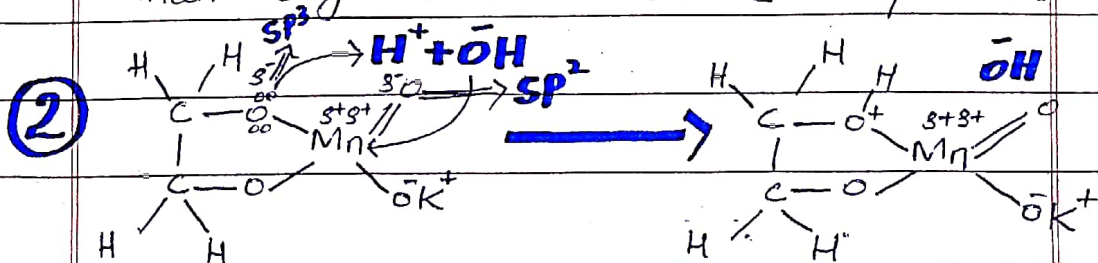
Step I

π -Bonds are weaker bonds in alkenes. So, they can be donated or moved. Hence they are broken easily.

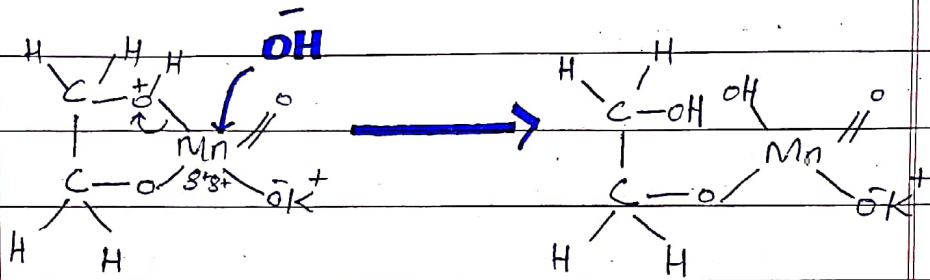


Step II :-

Incoming Electron Rich will now further react with "**Mn**" which has Low Electro-Negativity and Large Size. And **Hence "Mn"** is more partial positively charged than any atom in above compound.

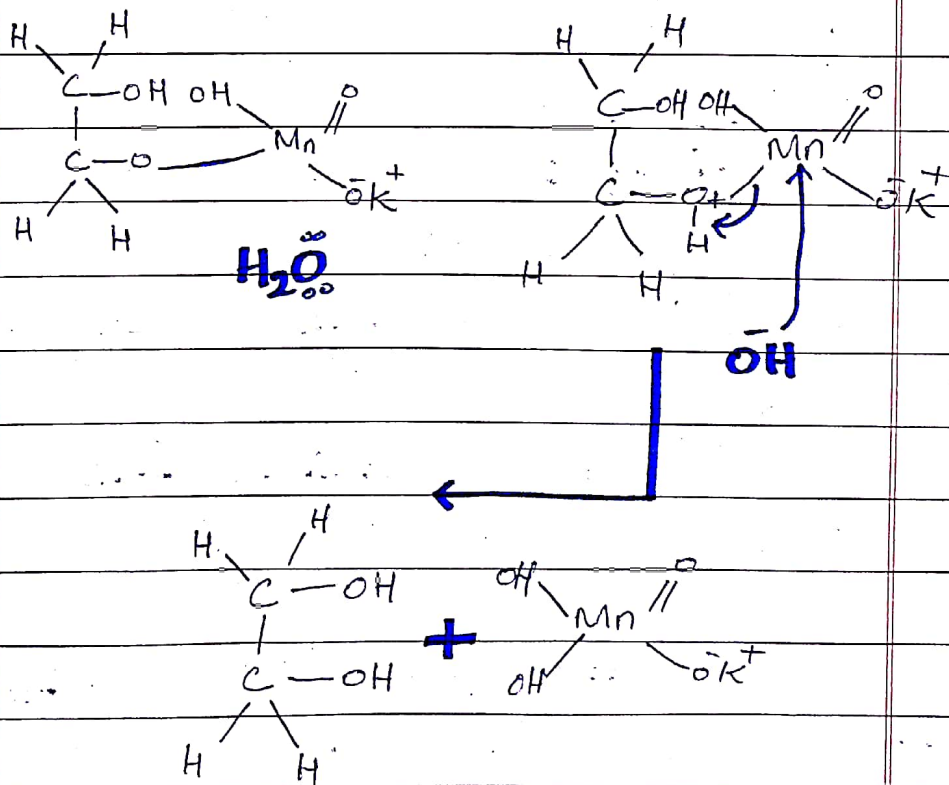


H^+ has reacted with "O" which is sp^3 hybridized. The Reason is sp^3 hybridized is more Electron Rich Than sp^2 and That's why Electron deficient H^+ goes to sp^3 -hybridized oxygen...



STEP III

By Another Attack of H_2O on above Product.

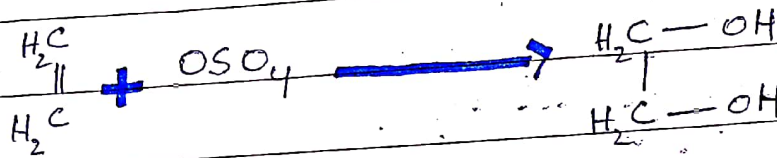


Cis-Diol

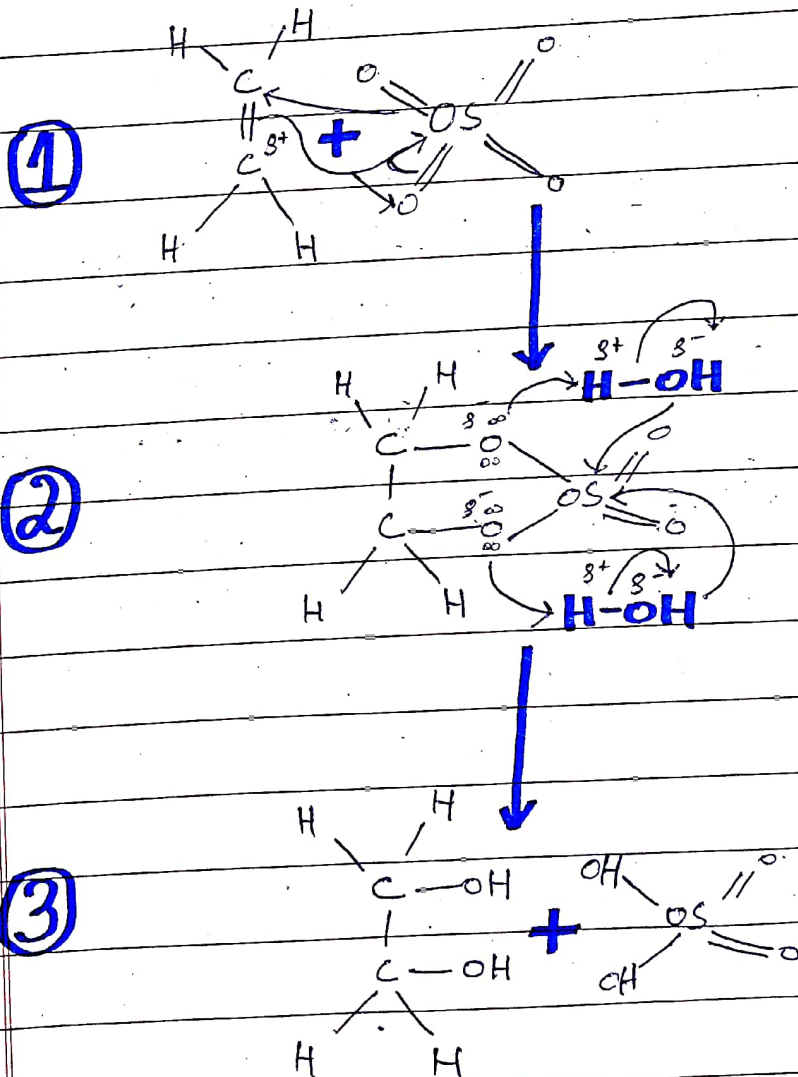
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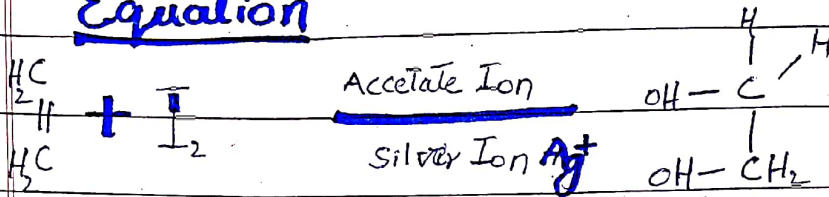
Alkene always Give **Cis-Diol** with reacting on any oxidizing Agent.

ii) With Osmium Tetroxide :-



Mechanism :-

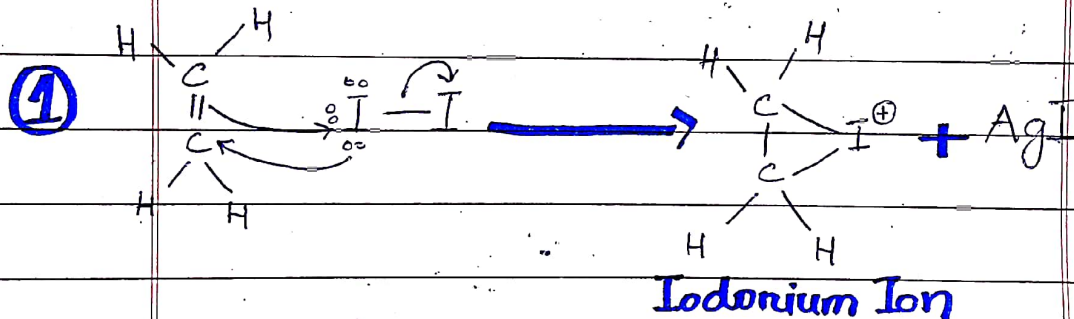


iv) With Iodo-Silver AcetateEquationa) Wet Method :-

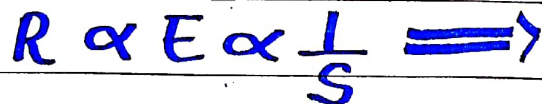
This method yields cis-Diol.

Mechanism :-Step I:-

Iodine has bigger size, so it has capability of picking up electron.

Step II :-

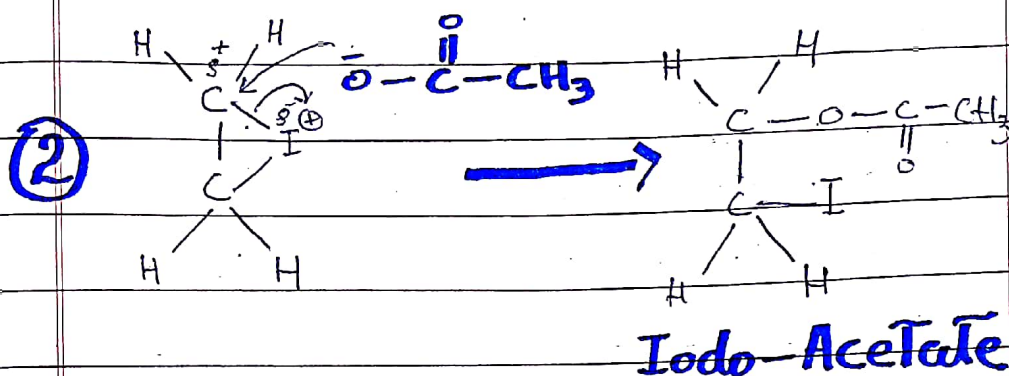
Iodonium Ion is unstable due to Three-Member Ring, Angle Strain and sp^3 -Hybridization. Hence it is more reactive.



Iodine has partial (δ^-) -ve charge

due To high E.N and large size.

Acetate Ion ($\text{CH}_3-\overset{\ominus}{\text{O}}-\overset{\parallel}{\text{C}}-\text{O}$) is a weak Nucleophile, so it attacks on an Electrophile.

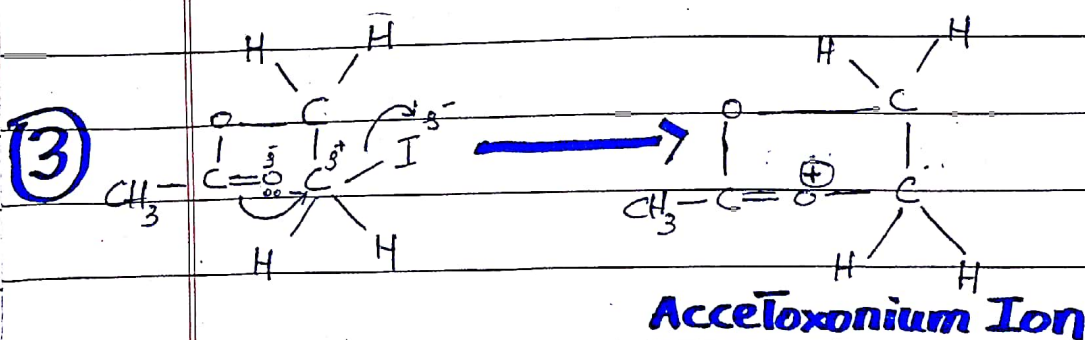


STEP III :-

Iodide Ion is a weak Base. Weak Base is always a good Leaving Group. Here Achimoric Assistance phenomenon applies.

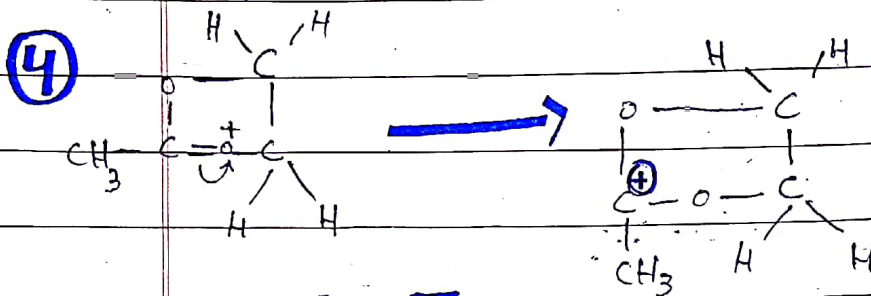
Achimoric Assistance :-

"When an internal Nucleophile attacks on Internal Electrophilic site, This is called Achimoric Assistance."

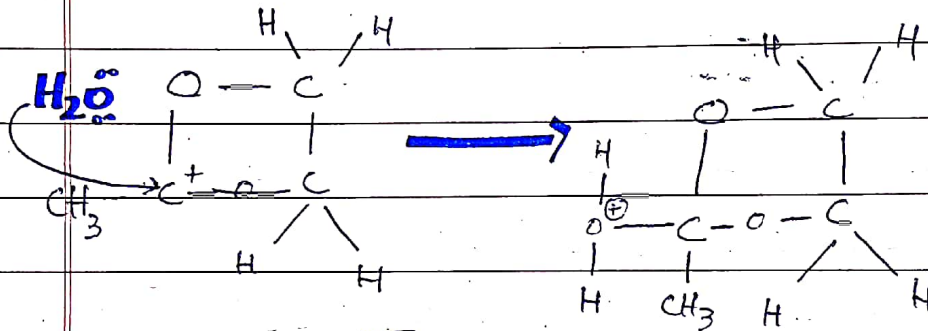


Step IV :-

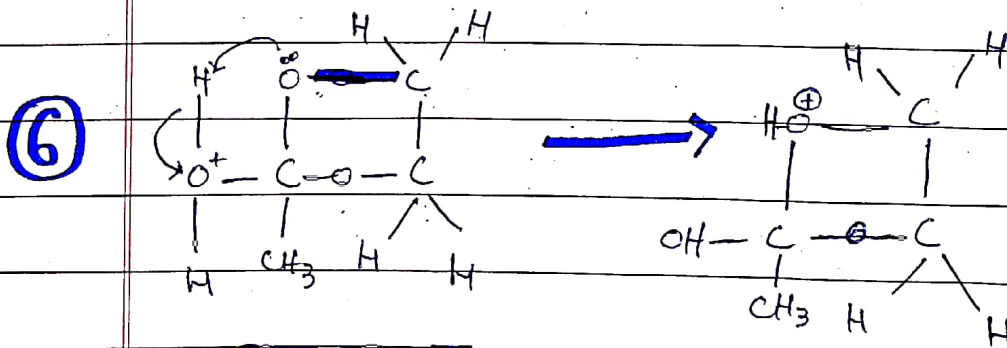
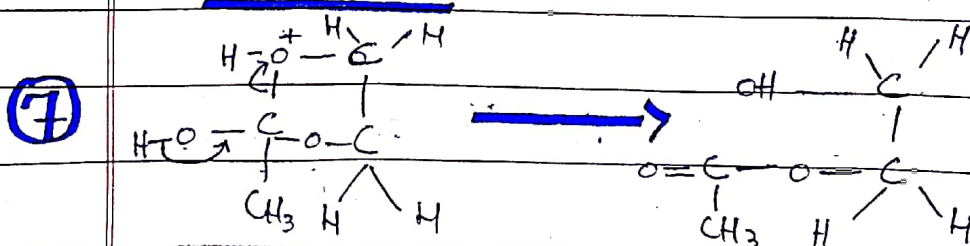
(Water reacts with acetoxonium Ion)

Step V :-

⑤ Now The above Product reacts with water. This is wet-Method step.

Step VI :- Hydroxy-Acetate

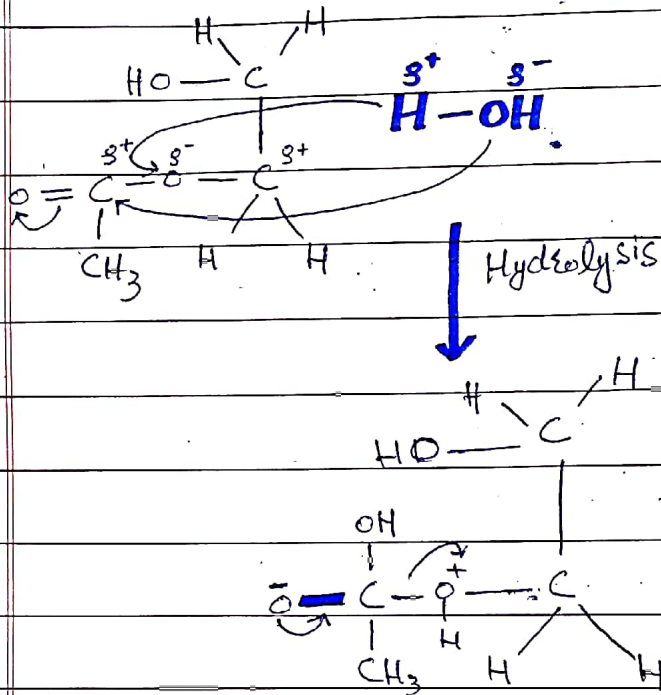
Now oxygen picks up one Hydrogen from water.

Step VII :-

STEP VIII :-

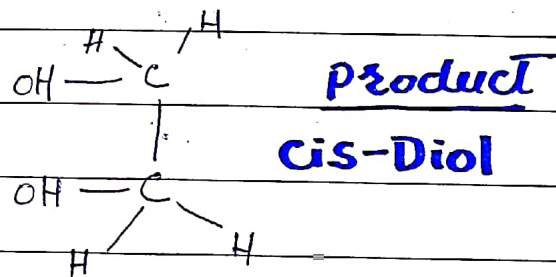
(This step is wet-Method step)
Hydrolysis of product is done.

8



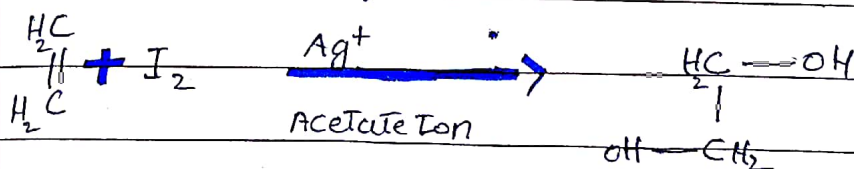
STEP-IX

9

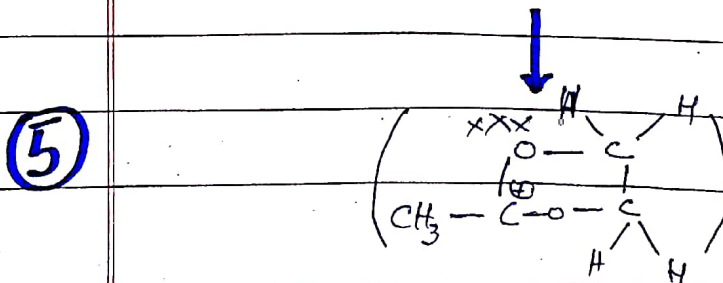
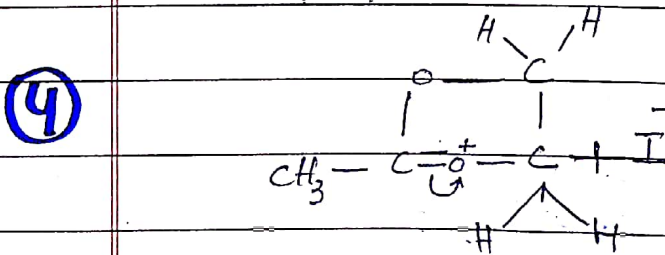
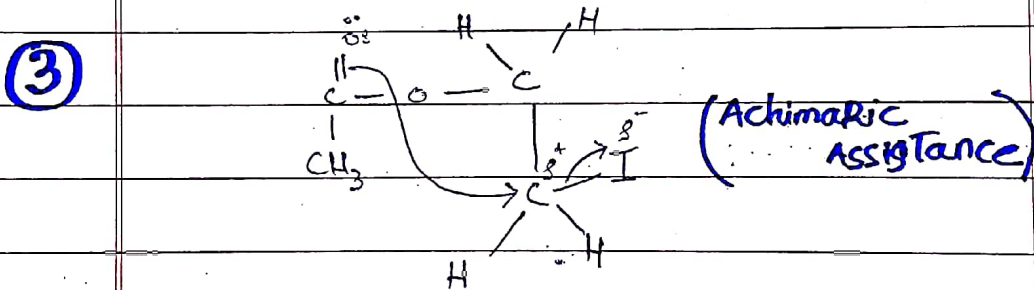
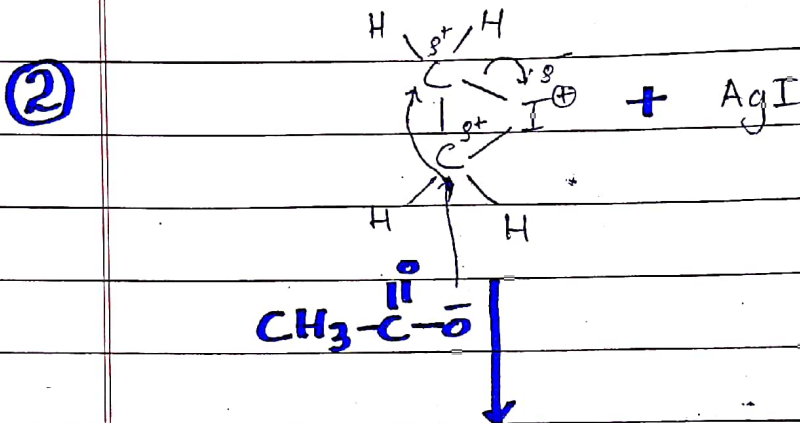
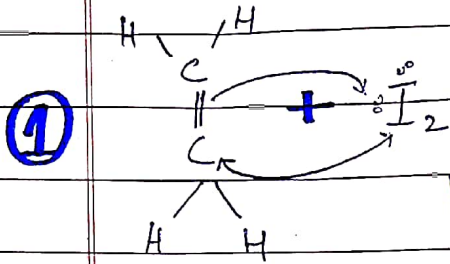


b) Dry Method :-

Equation :-

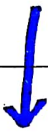
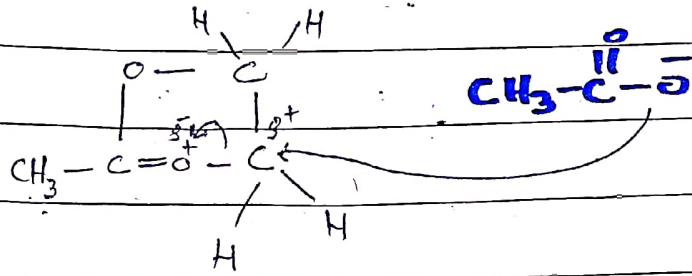


Mechanism :-

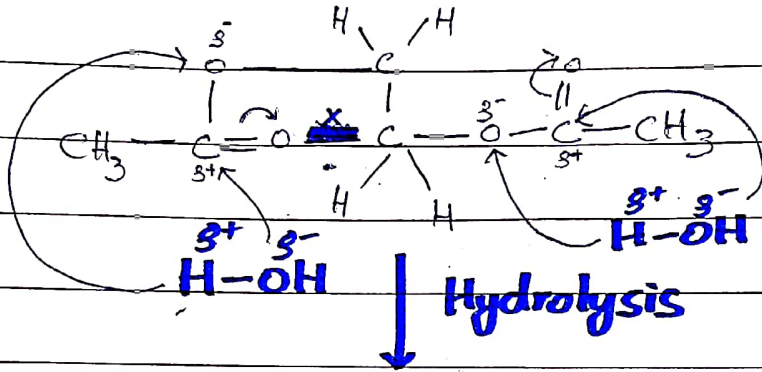


Step V :- (Dry method step)

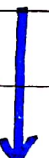
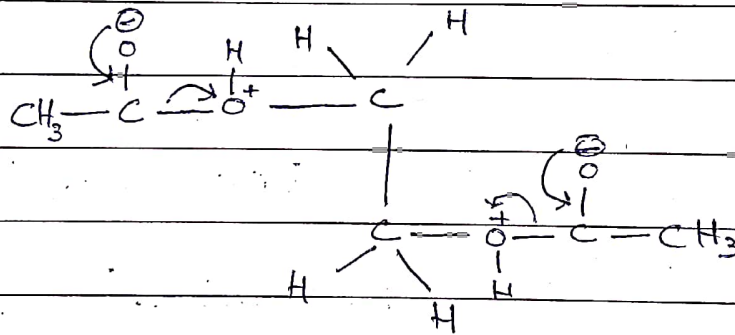
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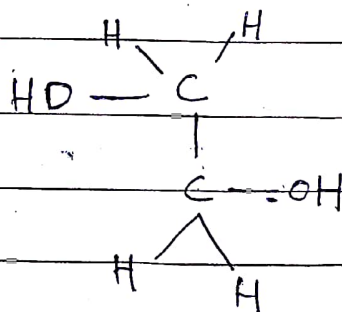
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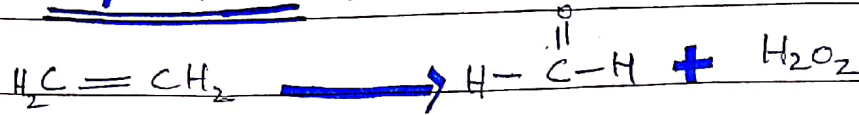
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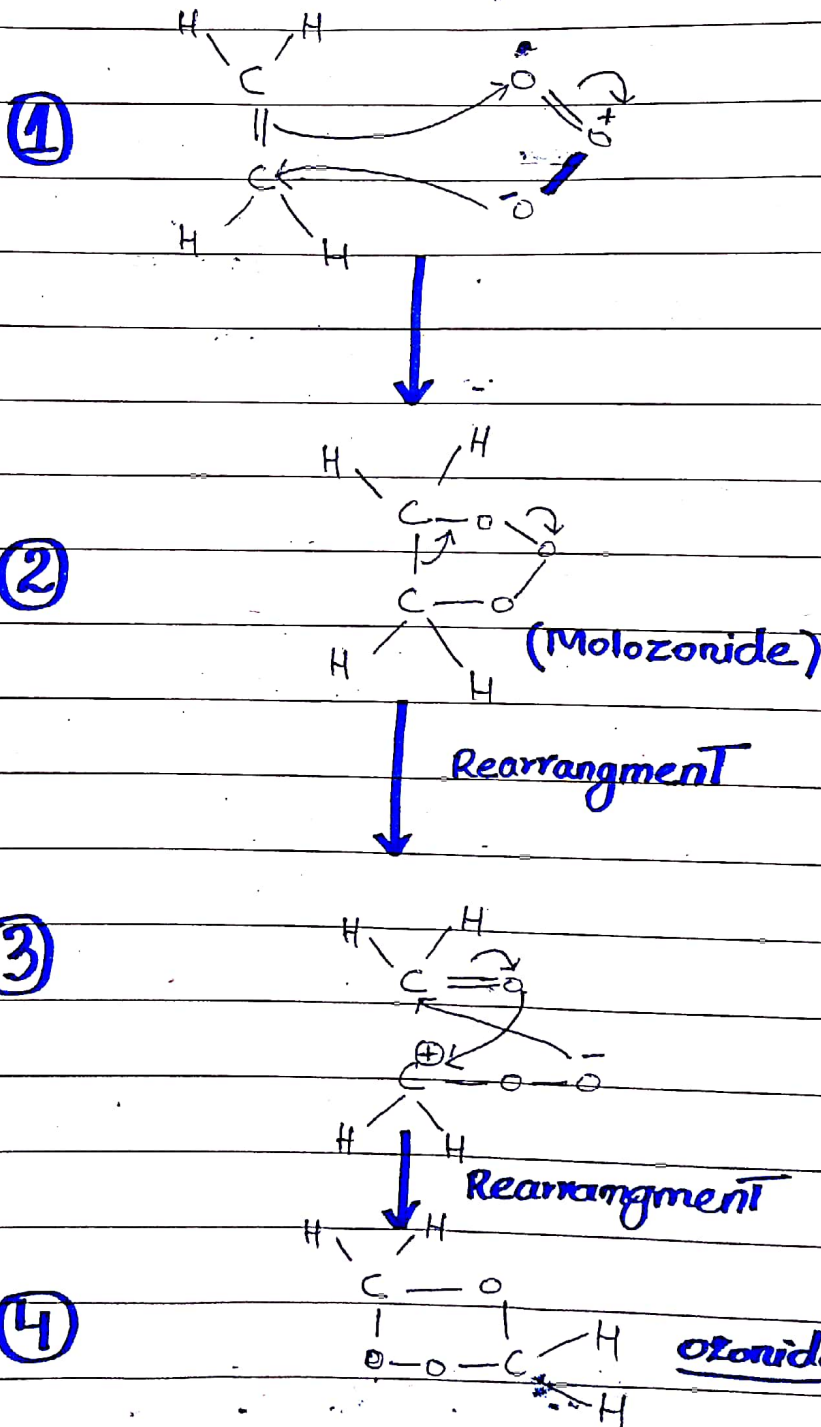
~~Diol~~ **Trans-Diol**

3. Ozonolysis :-

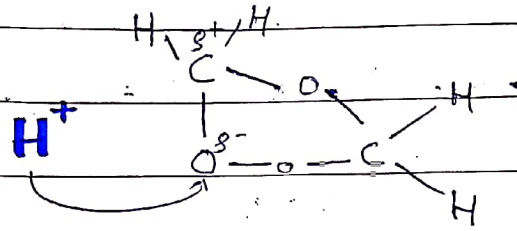
Equation :-



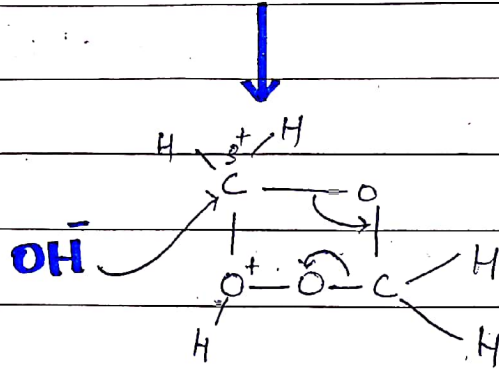
Mechanism :-



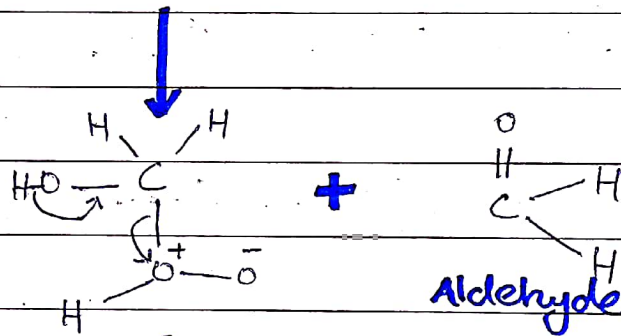
STEP IV Hydrolysis 8-



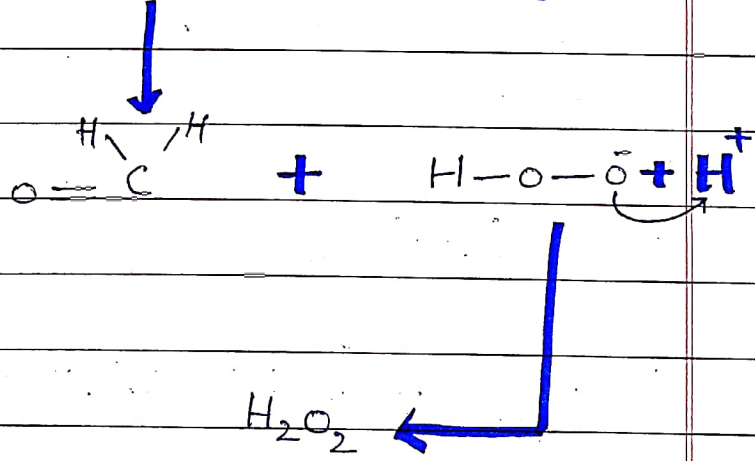
④



⑤



⑥



(ALCOHOLS)

Functional Group :-

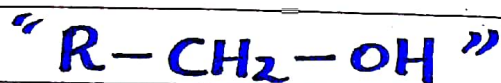
"A molecule containing $-OH$ as functional group is an Alcohol."



Types of Alcohols :-

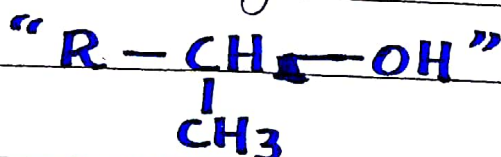
1) Primary Alcohols :-

"The Alcohols in which functional group carbon is further attached with one carbon is called Primary Alcohols."



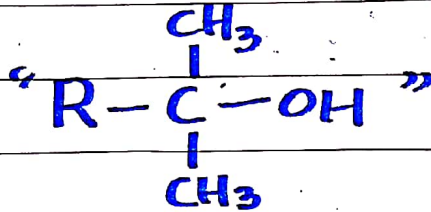
2) Secondary Alcohols :-

"The Alcohol where functional group carbon is further attached with two carbons directly is called Secondary Alcohols."

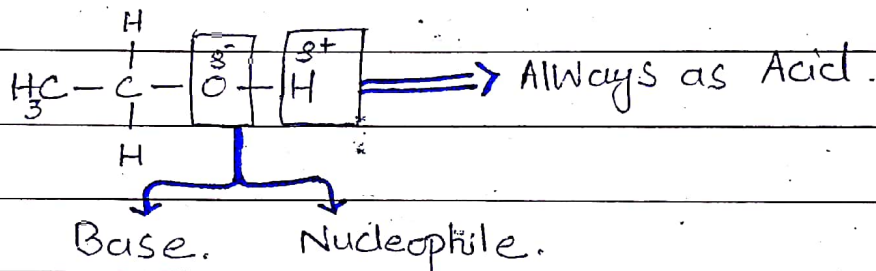


3) Tertiary Alcohols :-

"The Alcohol where Functional group carbon is directly Attached with Further Three Carbon Atoms."



(Imp:- Alcohols can act as Base, Acid and as Nucleophile)

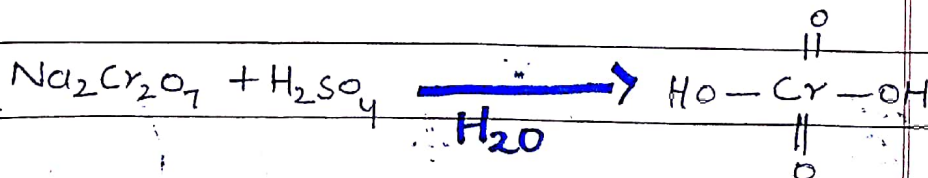


1) Primary Alcohols With Jone's Reagent

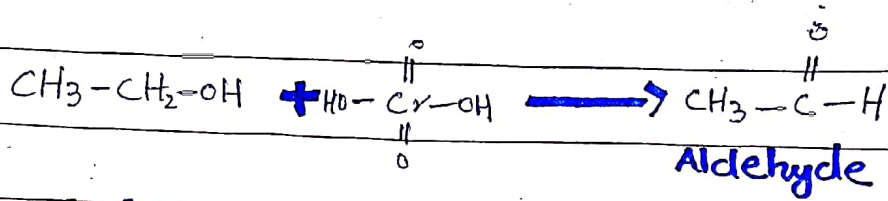
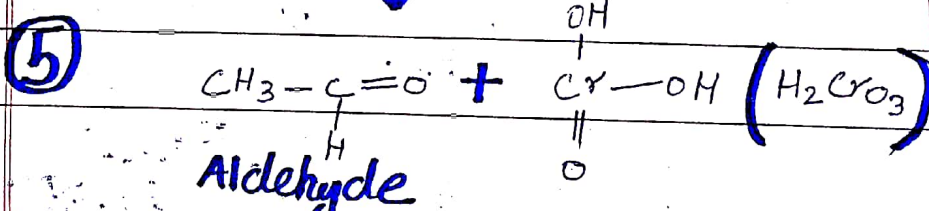
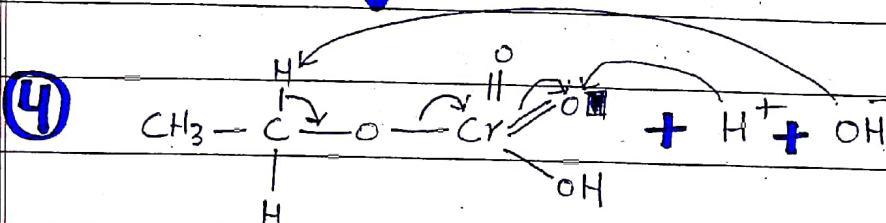
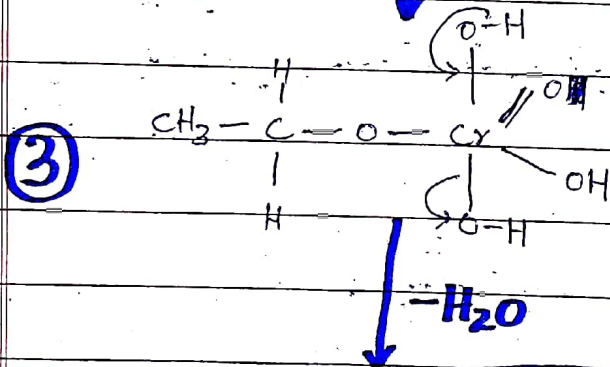
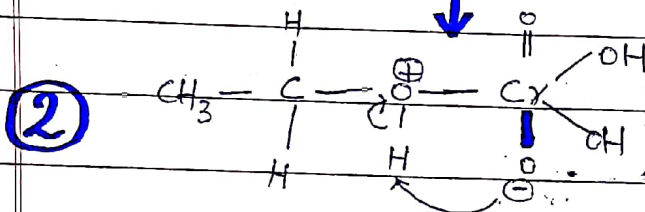
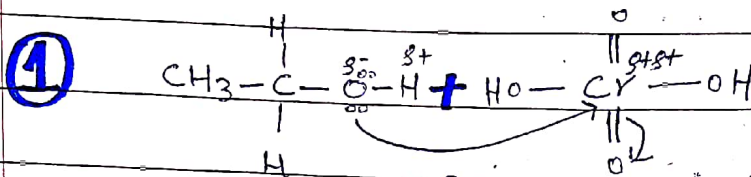
Jone's Reagent :-

"Chromic Acid is called Jone's Reagent."

It is attained by Following Reactions.



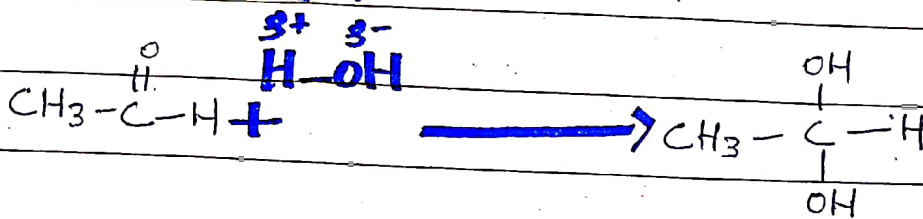
Jone's
Reagent

Equation 8-Mechanism :-

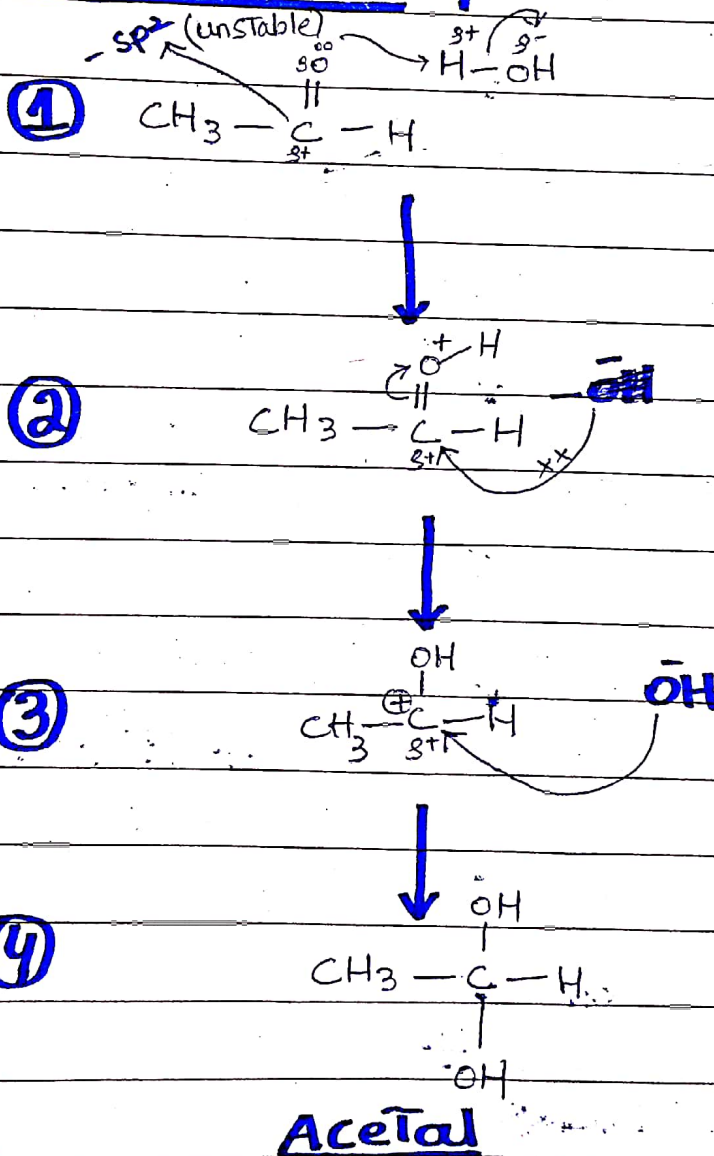
* Hydration of Aldehydes :-

"Addition of water is known to be Hydration"

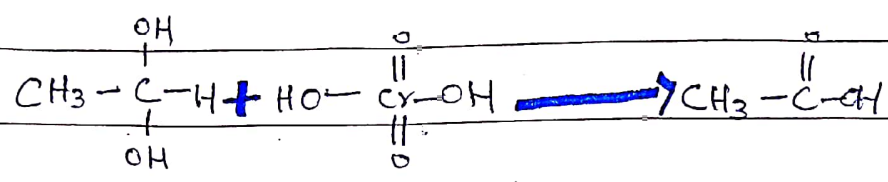
Equation :-



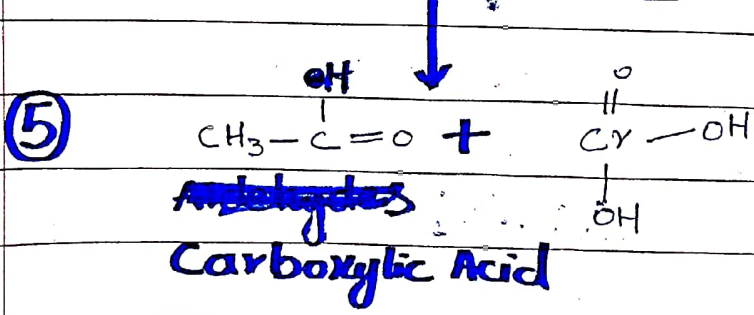
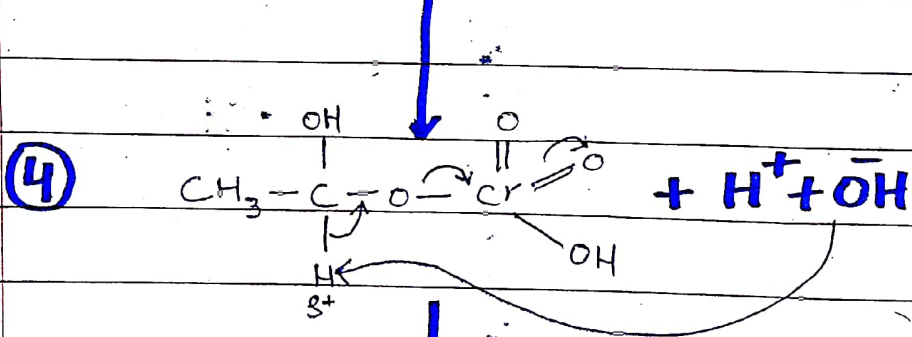
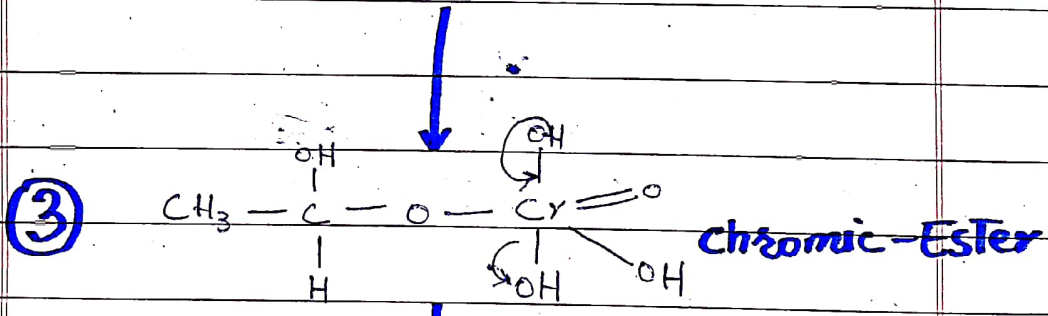
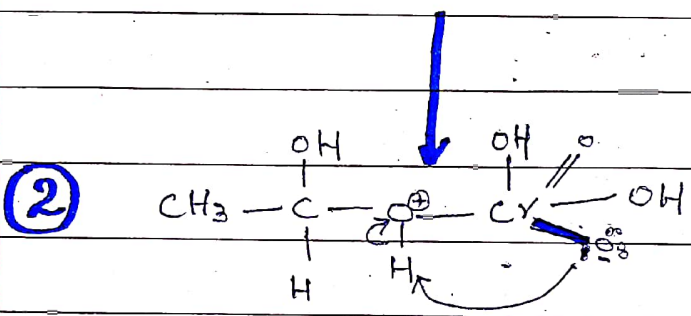
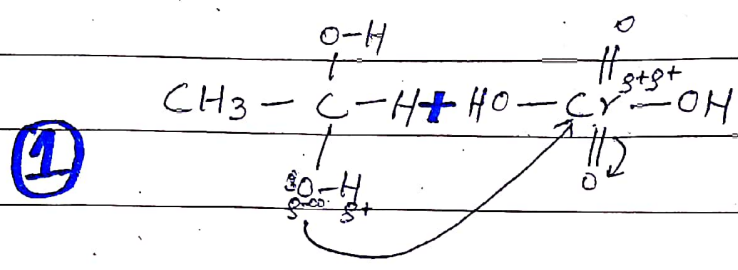
Mechanism :-



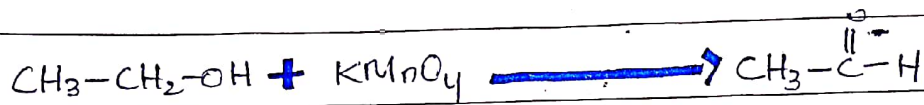
* Acetal With Chromic Acid :-



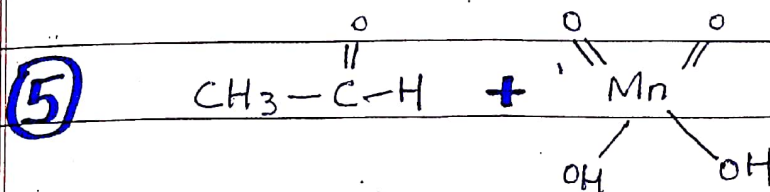
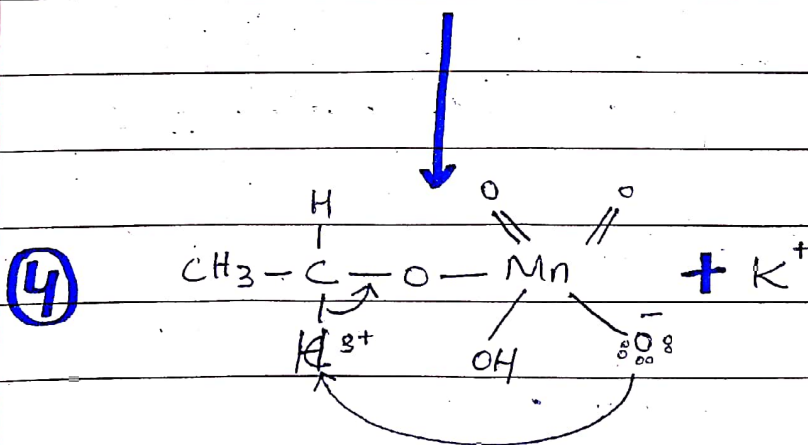
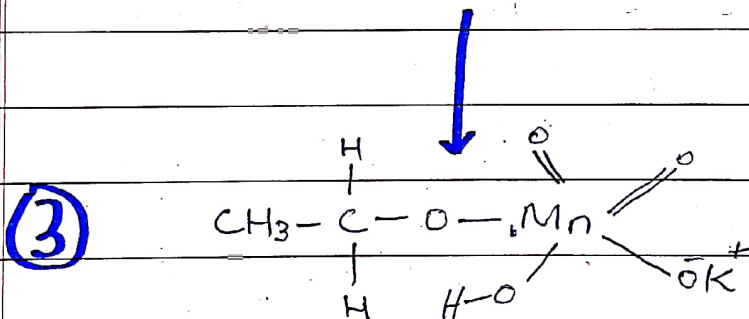
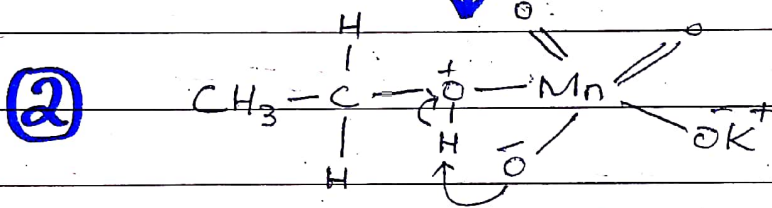
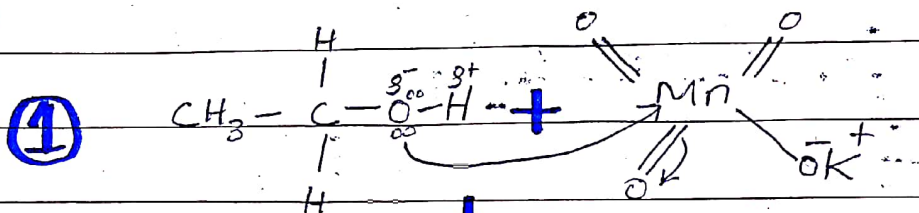
Mechanism :-



2. Primary Alcohol With KMnO_4 .

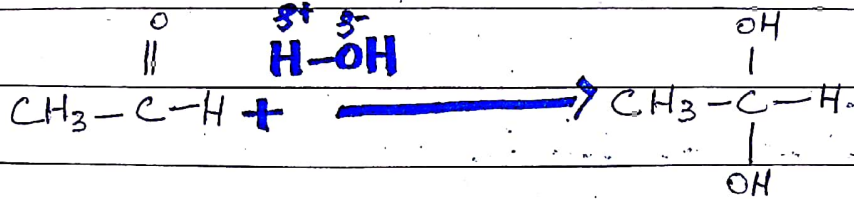


Mechanism :-



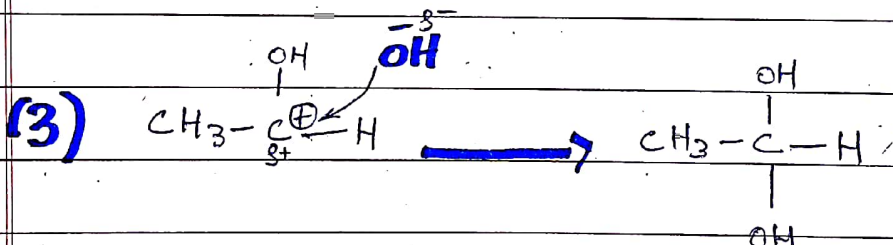
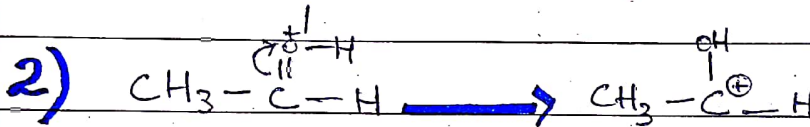
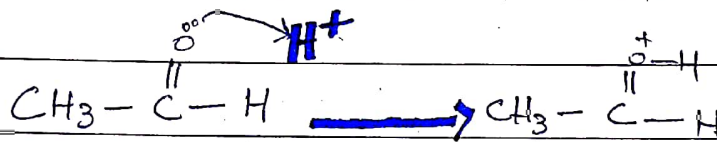
* Hydration of Aldehydes

Equation :-

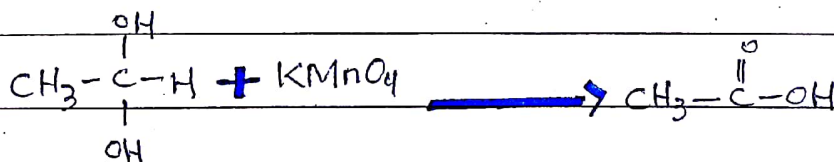


Mechanism :-

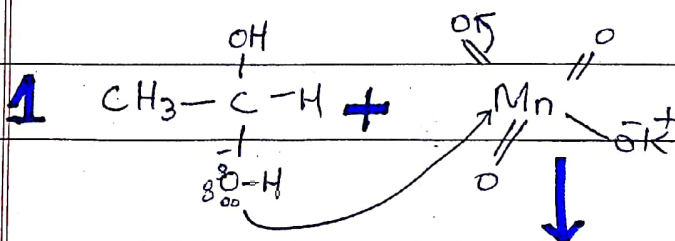
- 1) Make attack of H^+ first, so that carbon becomes a carbocation -



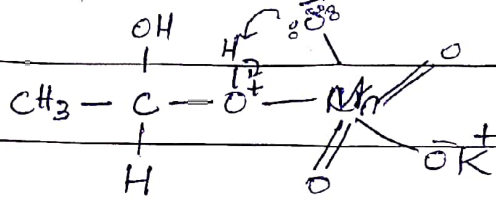
* Acetal With KMnO_4 :-



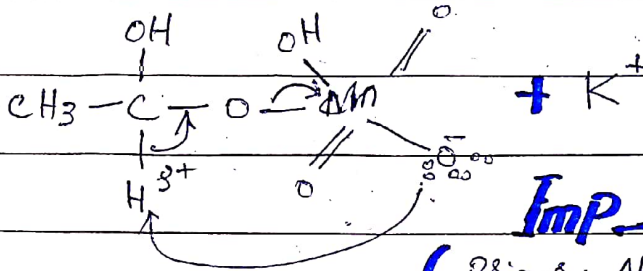
Mechanism :-



②

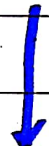


③

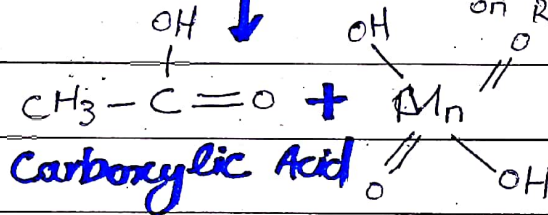


Imp:-

(Primary Alcohol is always converted into carboxylic on reacting with Jones's Reagent)



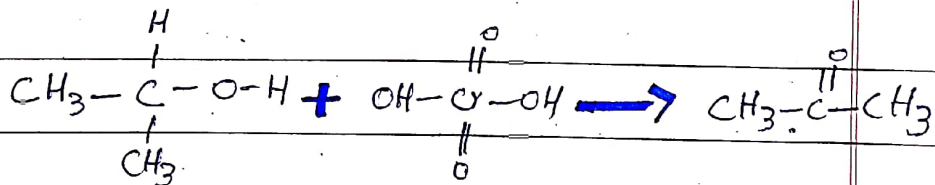
④



3. Secondary Alcohol

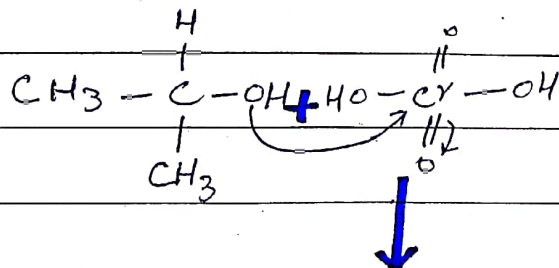
With Jones's

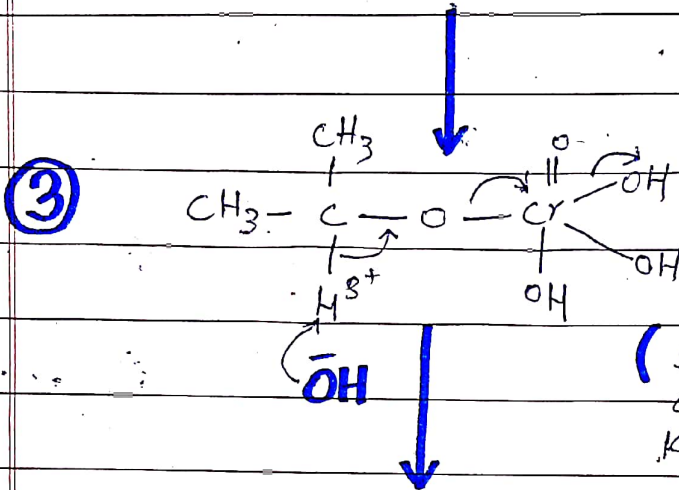
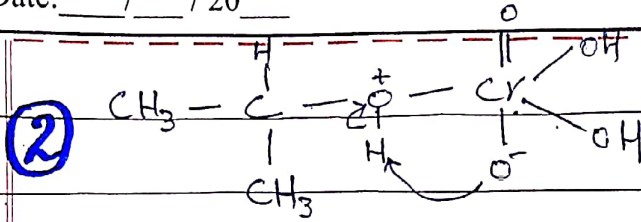
Equation :-



Mechanism :-

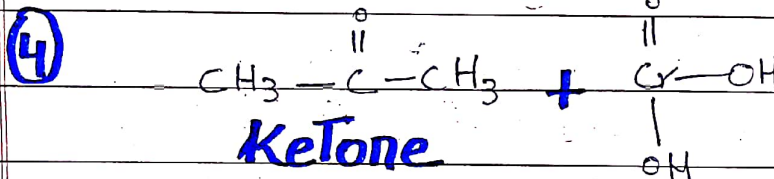
①





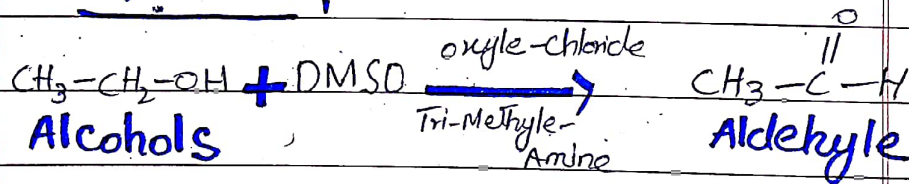
Imp-:

(Secondary Alcohol is always converted into Ketone on Treatment with any oxidizing Agent.)

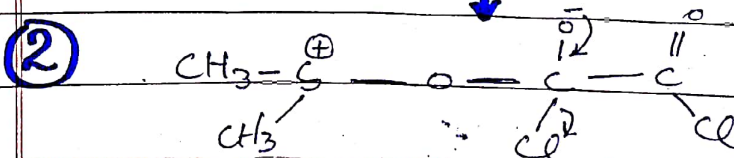
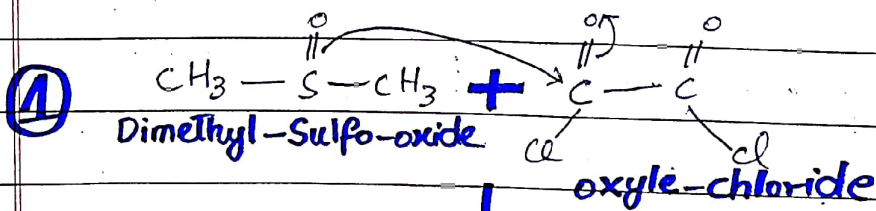


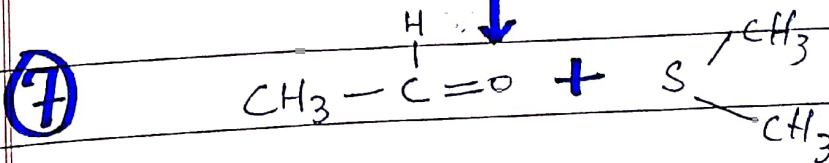
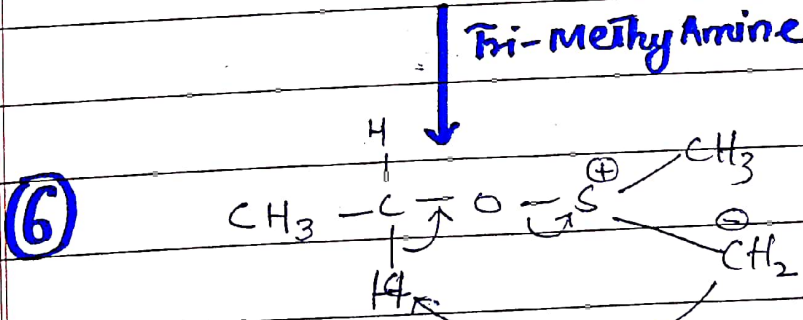
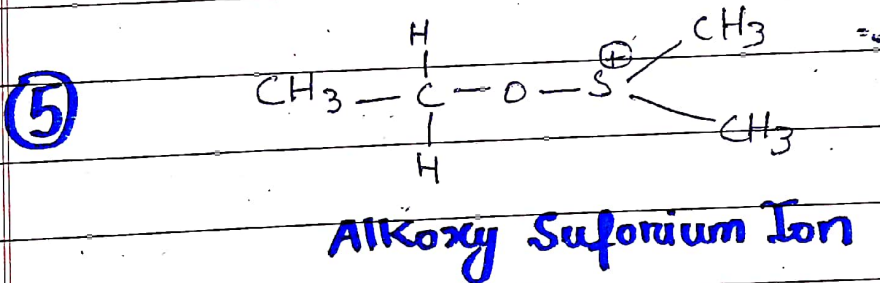
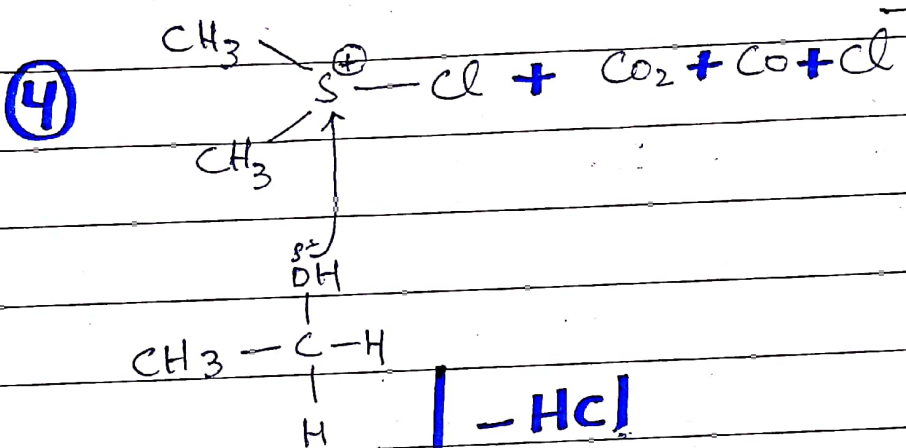
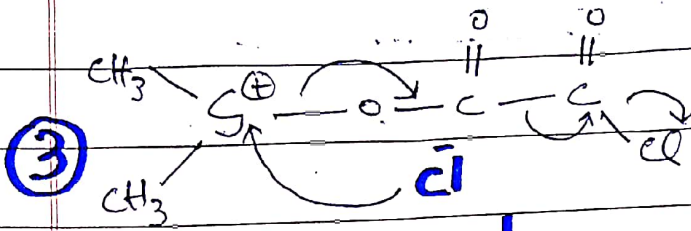
4). Swern Oxidation :-

Equation :-



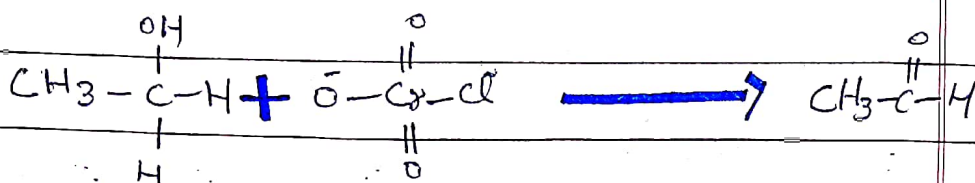
Mechanism :-



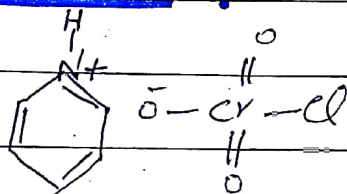


5. With Pyridinium Chloro-Chromate (PCC)

Equation

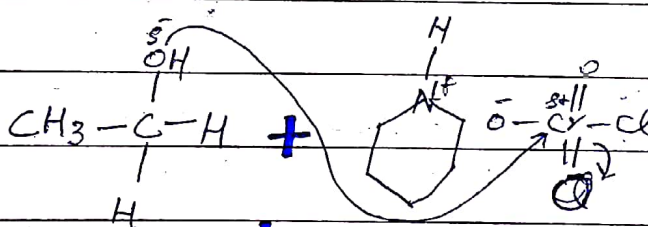


Mechanism :-

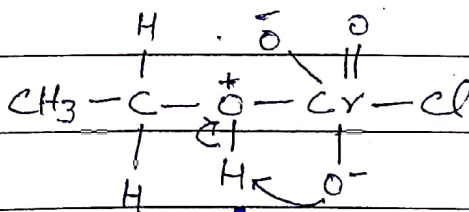


Pyridinium Chloro-Chromate

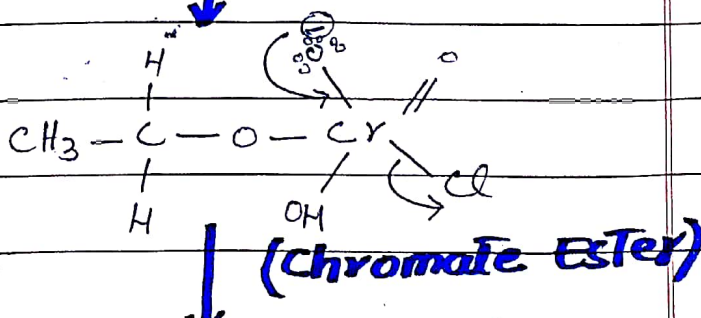
①

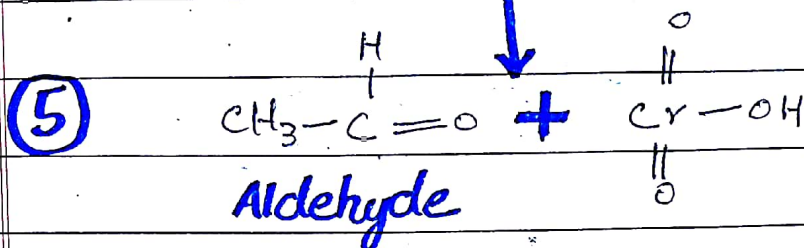
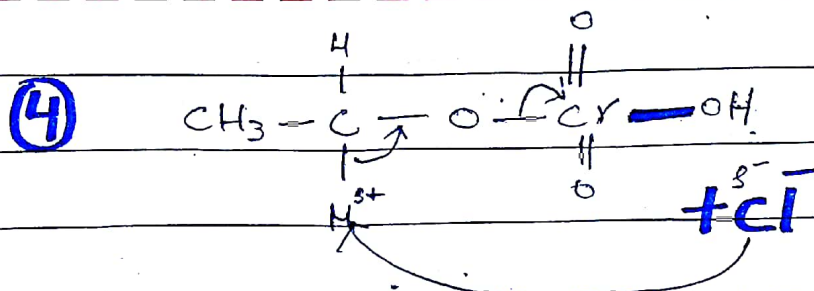


②



③

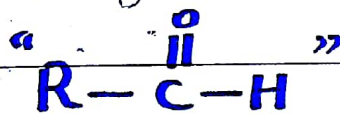




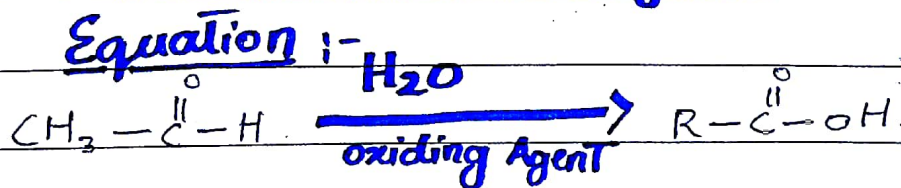
ALDEHYDE

Functional Group :-

"The Compounds containing " $\overset{\text{O}}{\parallel} \text{C} - \text{H}$ " as Functional Group are known to be Aldehydes."



1. With Jones Reagent :-

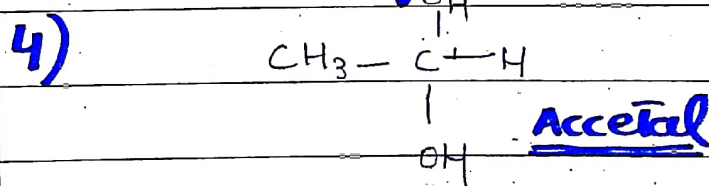
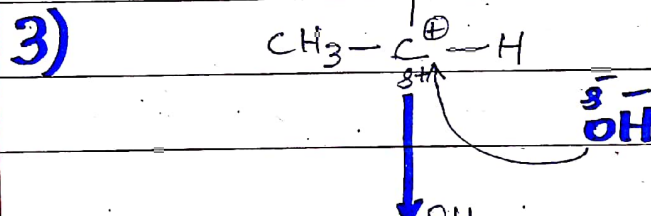
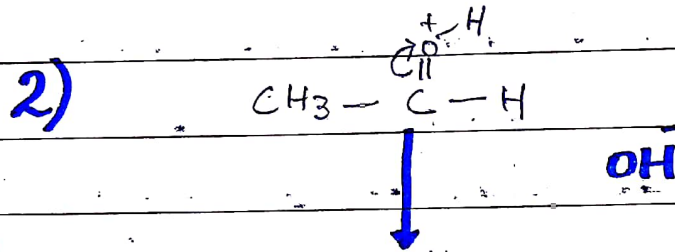
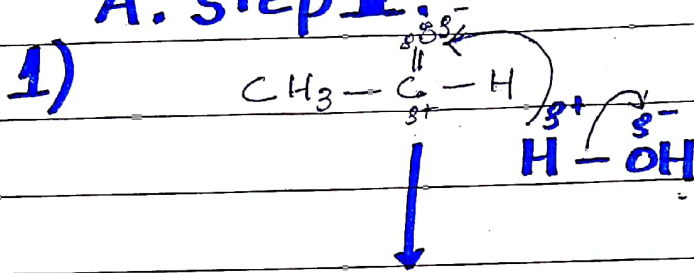


Mechanism :-

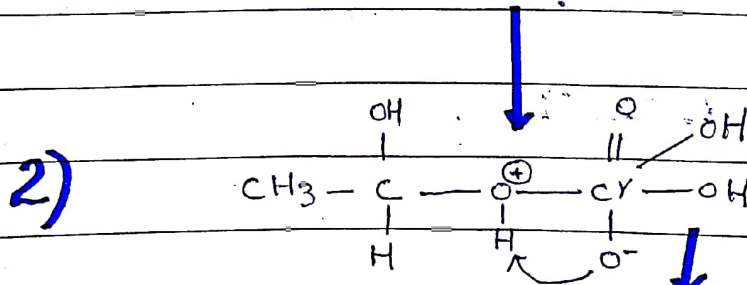
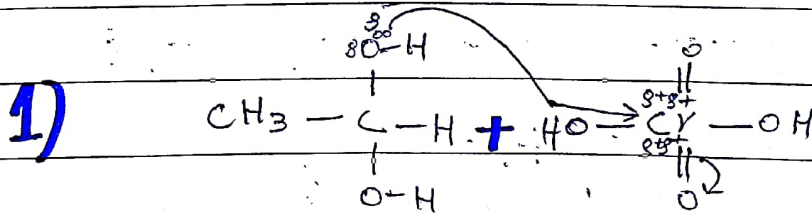
This Reaction Takes place in

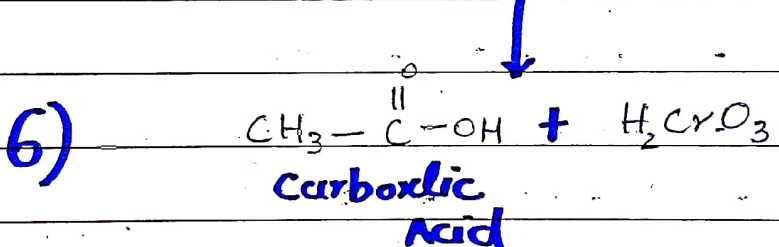
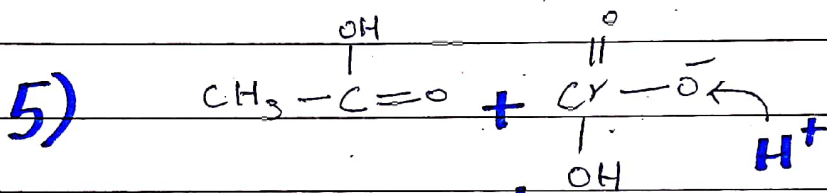
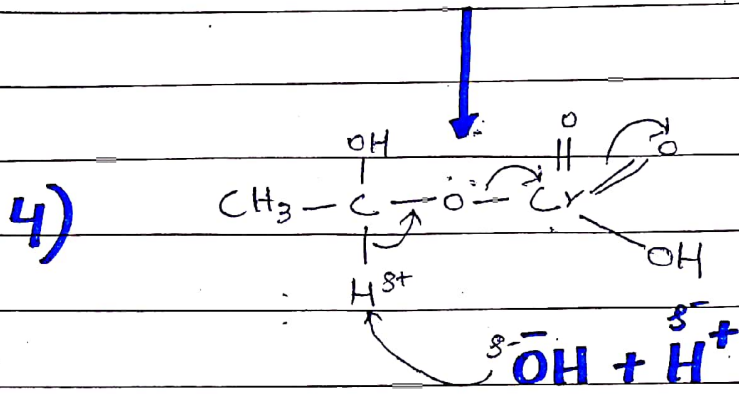
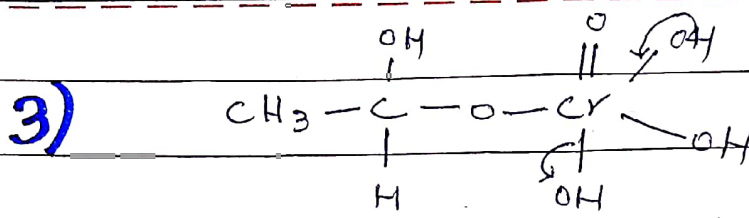
Two Phases. First it is reacted with 'H₂O' and then the product obtained from this reaction is reacted with Jones Reagent.

A. Step I.



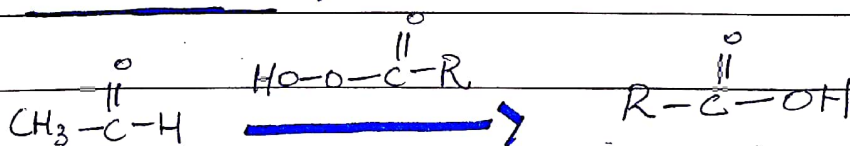
B. Step II.



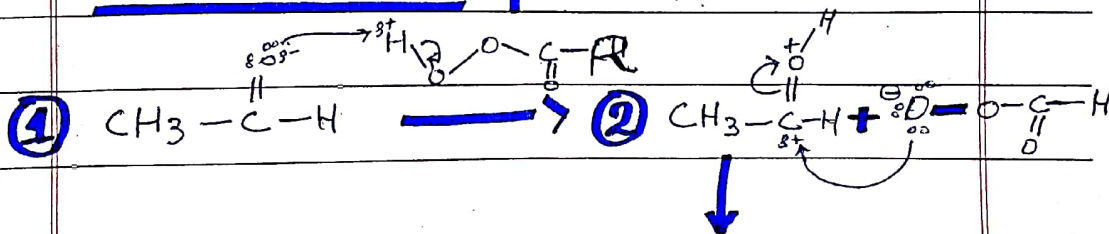


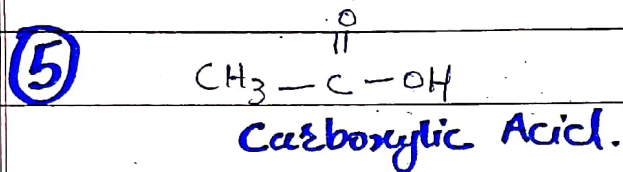
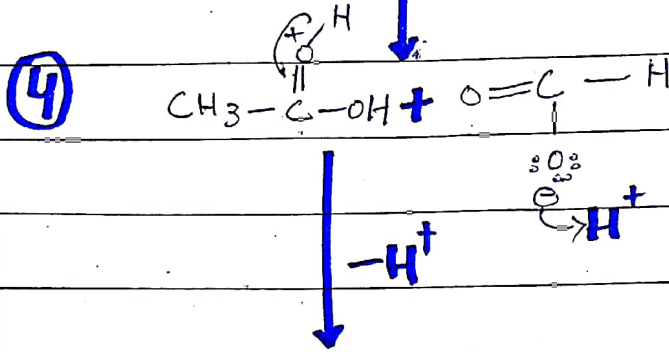
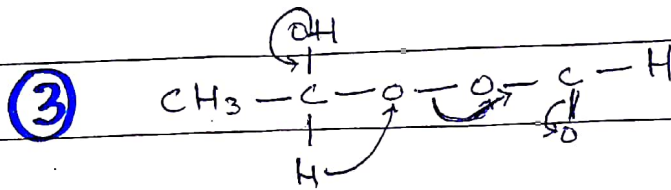
2. Baeyer Villiger Oxidation :-

Equation :-



Mechanism :-





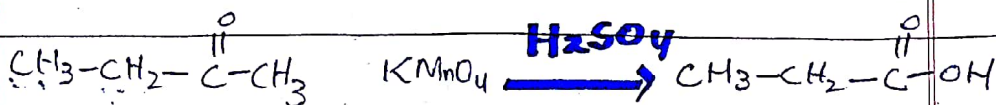
(KETONES)

Functional Group :-

"The molecules containing functional group $\text{R} - \overset{\text{O}}{\parallel} \text{C} - \text{R}$ are called as ketones."

1. Oxidation With KMnO_4 :-

Equation :

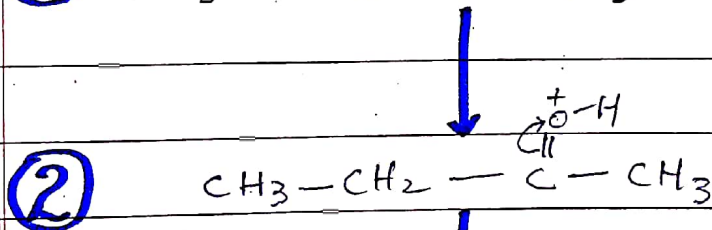
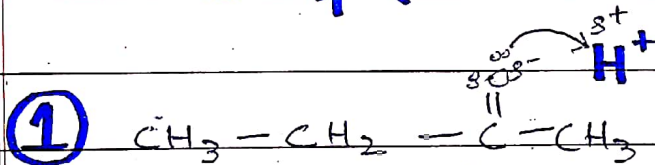
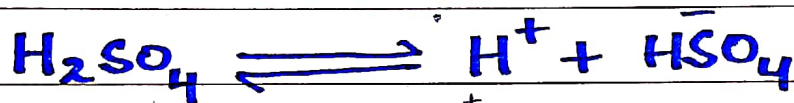


Mechanism :-

This Reaction Takes place in Two Step. First with ' H_2SO_4 ' and Then with $KMnO_4$.

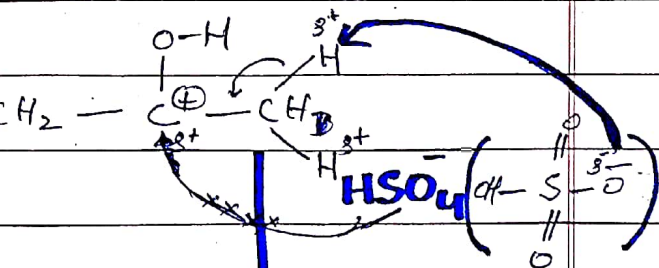
A. STEP I

⇒ Always make Attack of Acid (H^+) first which activates The Electrophilic site, makes ketone unstable and more Reactive.



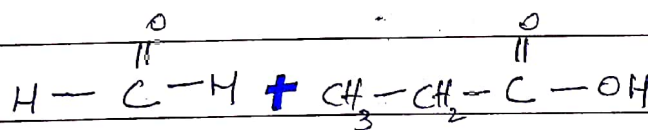
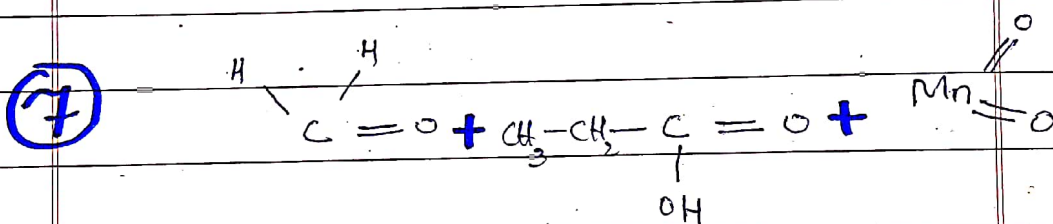
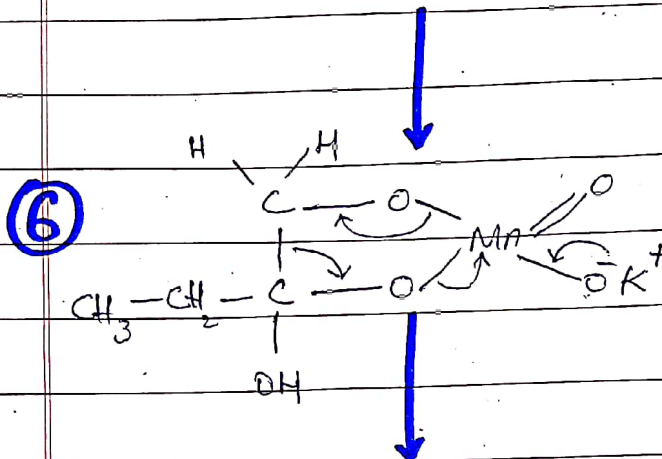
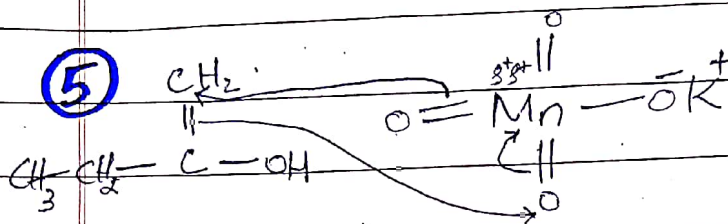
③ Imp :-

(H_2SO_4 is being use as catalyst in This Reaction)

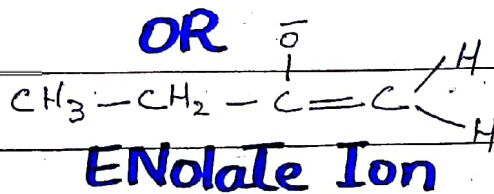
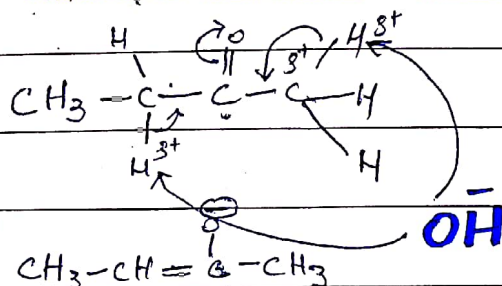


④ $CH_3-CH_2-\overset{\overset{OH}{|}}{C}=\overset{\overset{H}{|}}{C}$
This is The Tautomer of Initial Molecule.

B. Step II :-

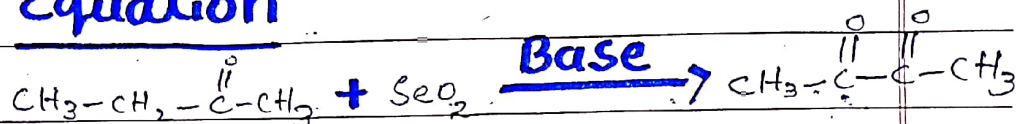


2. * Formation of ENolate Ion :-



2. With Selenium Dioxide :-

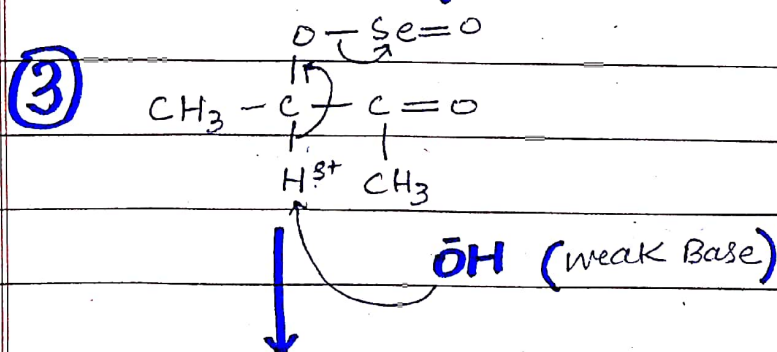
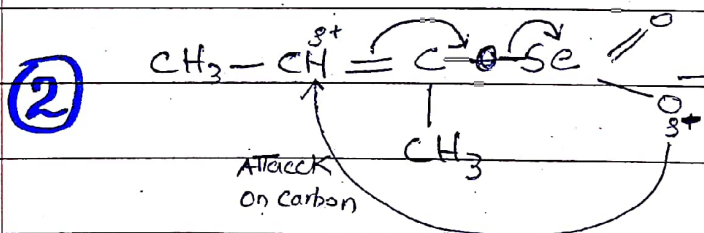
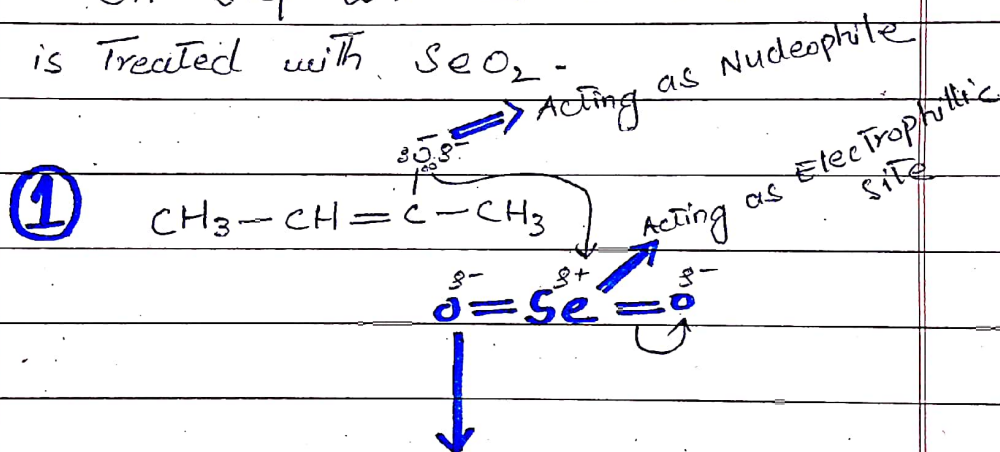
Equation

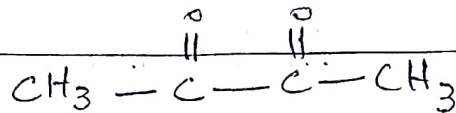


Mechanism :-

The Reaction involves two steps. First ketone is reacted with a base to attain "Enolate Ion" as we have attained.

In step 2, This Enolate Ion is treated with SeO_2 .

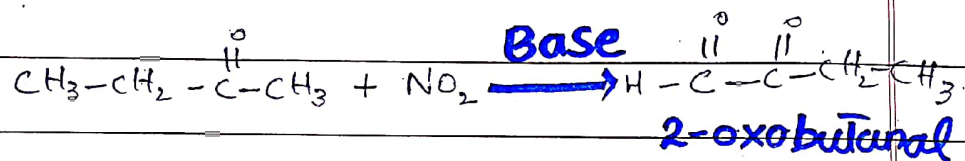




di-ketone

3. With Nitrites :-

Equation :-

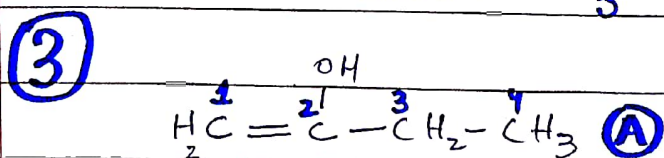
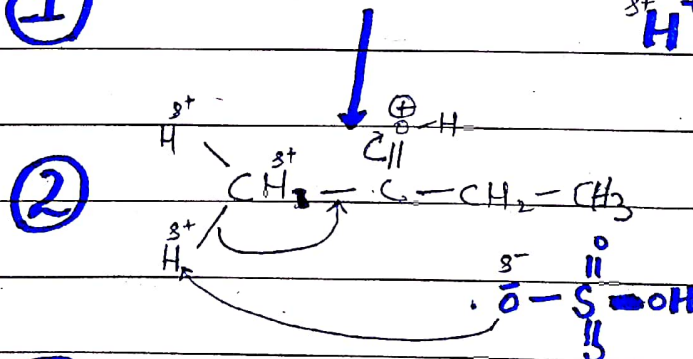
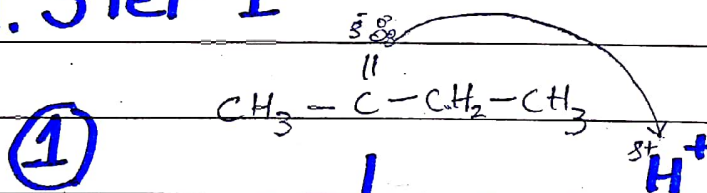


Mechanism :-

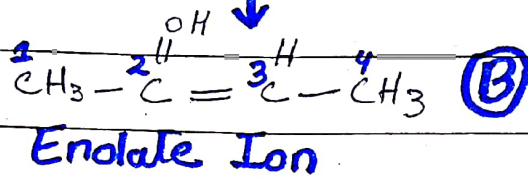
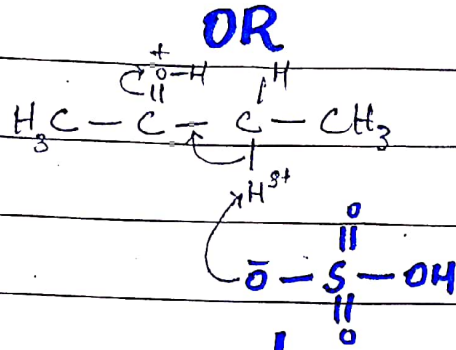
This mechanism involves two steps -

- i) with Base (H_2SO_4)
- ii) with Nitrites (NO_2)

A. STEP I



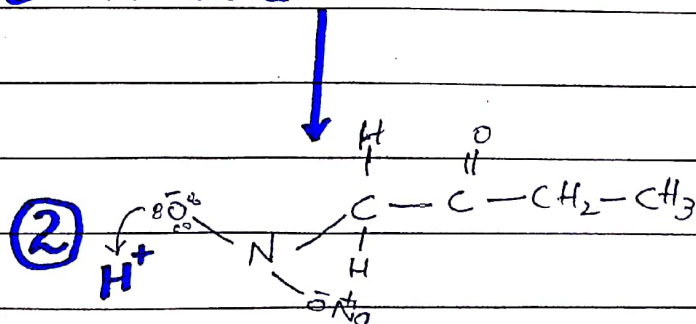
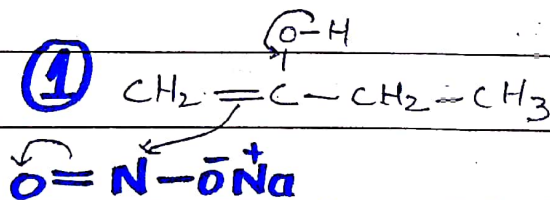
Enolate Ion

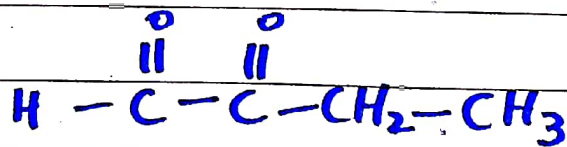
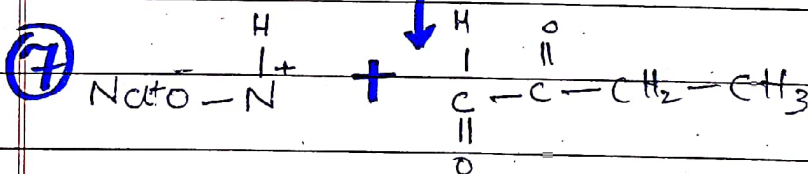
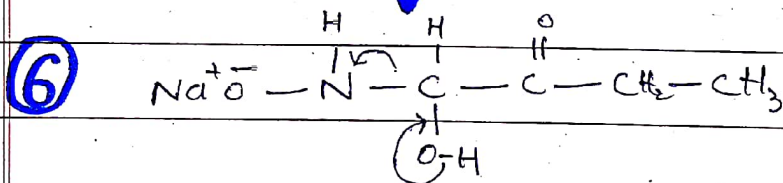
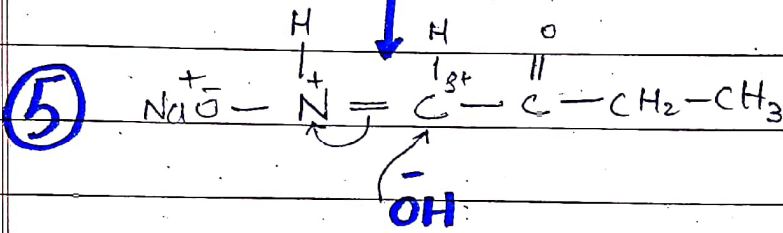
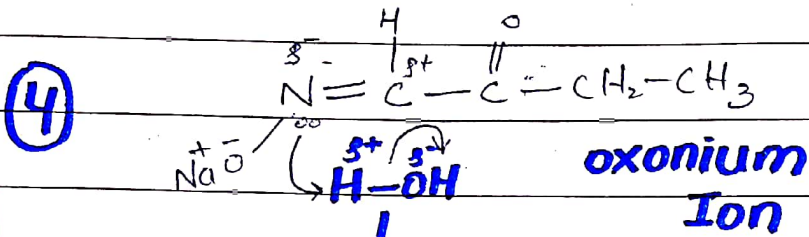
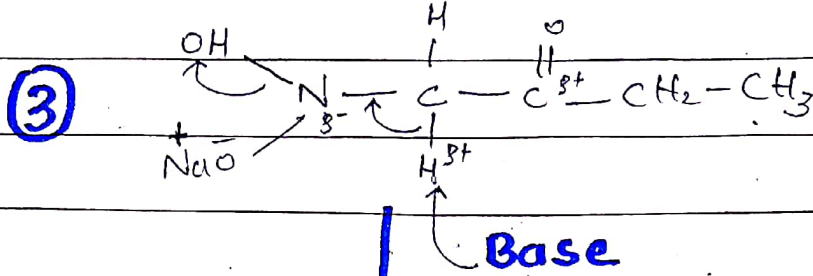


Between $\textcircled{\text{A}}$ and $\textcircled{\text{B}}$ Enolate Ion

$\textcircled{\text{A}}$ will act as nucleophile in further reaction because it has no steric hindrance at carbon No. 1 **while** there is lot of steric hindrance at carbon in $\textcircled{\text{B}}$ so α -hydrogen is not removed easily.

B. Step II.



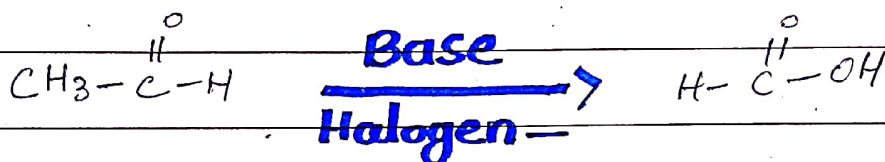


2-oxobutanal

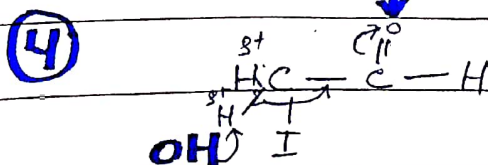
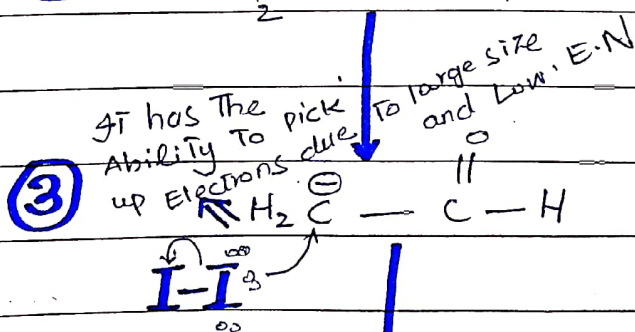
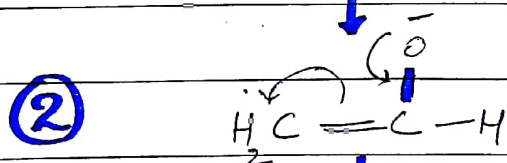
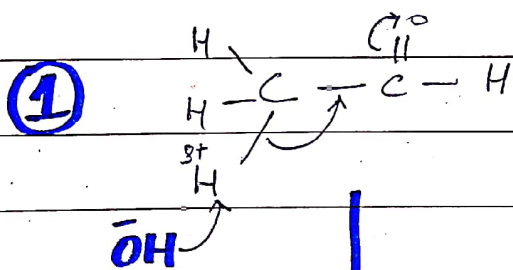
* Haloform Test

"The Test in which identification of presence of methyl is done in ketone — and Aldehyde is called a Haloform Test."

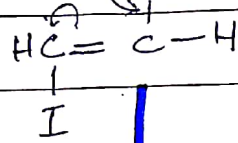
Equation :-



Mechanism :-

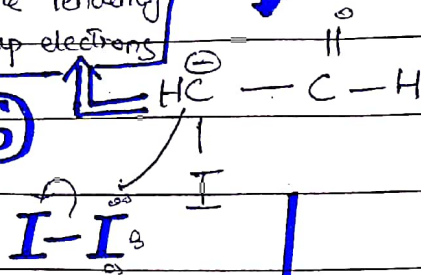


⑤

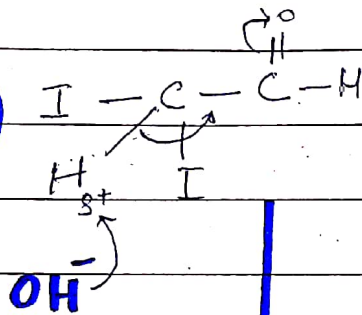


IT has the tendency to pick up electrons

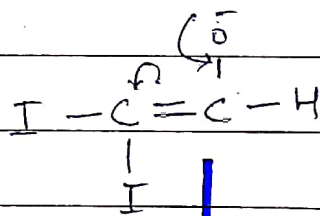
⑥



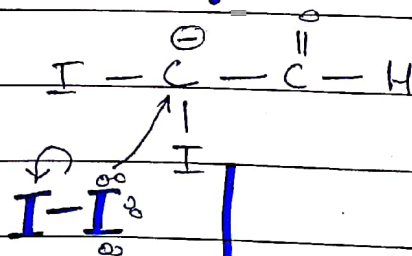
⑦



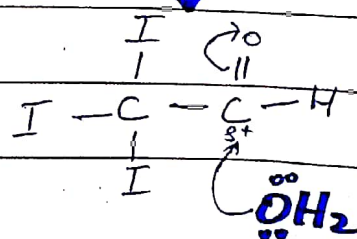
⑧



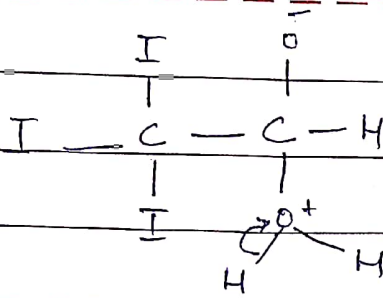
⑨



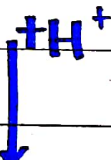
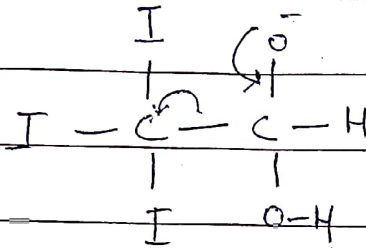
⑩



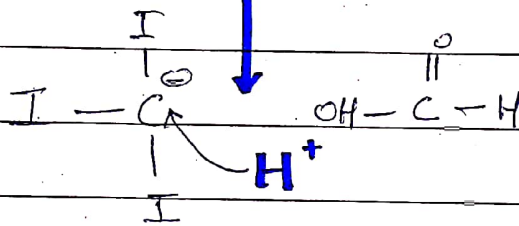
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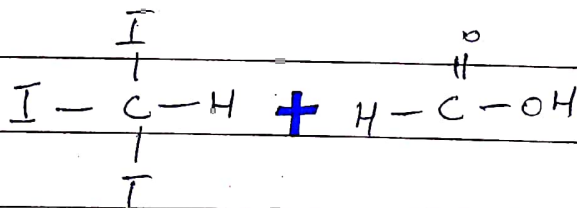
(12)



(13)



Products

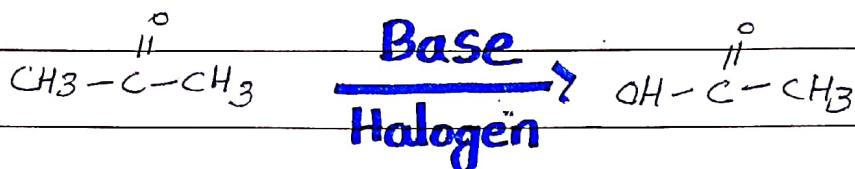


IodoForm
Test

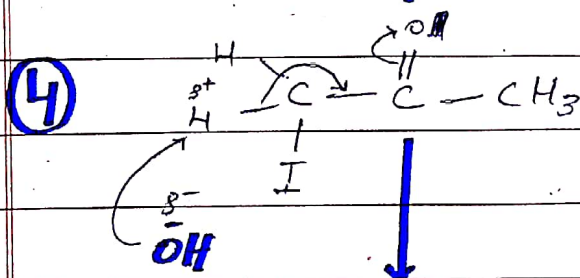
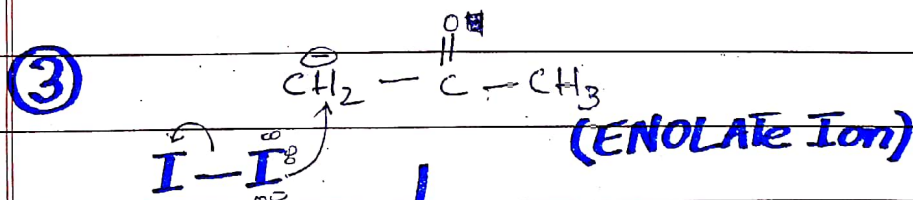
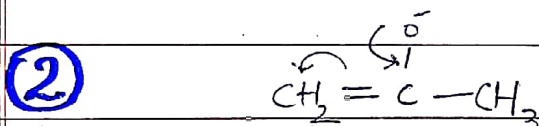
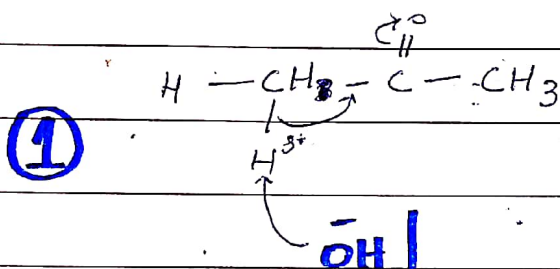
(Yellow
Precipitate)

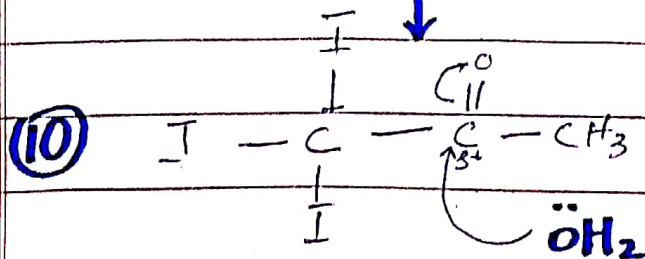
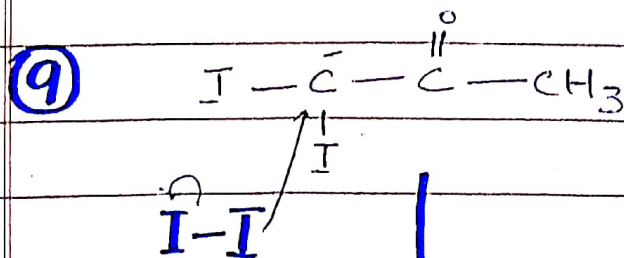
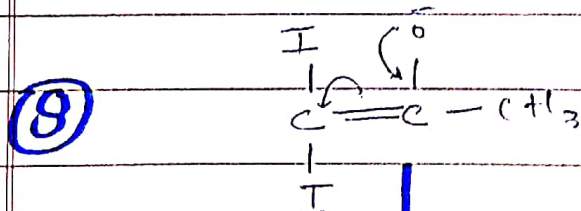
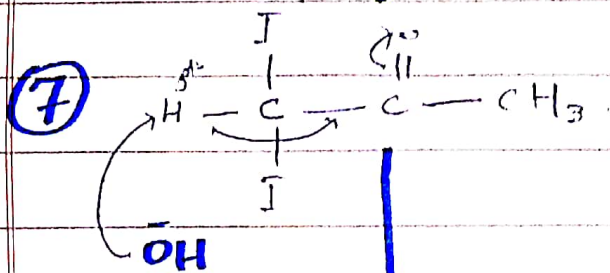
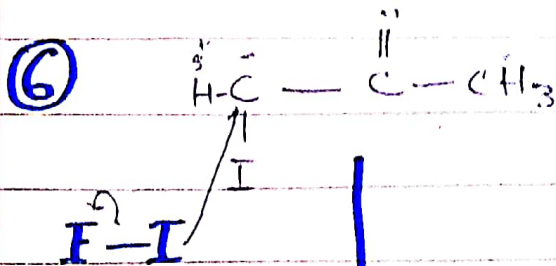
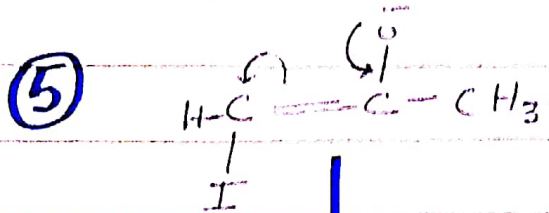
* Haloform For Ketones

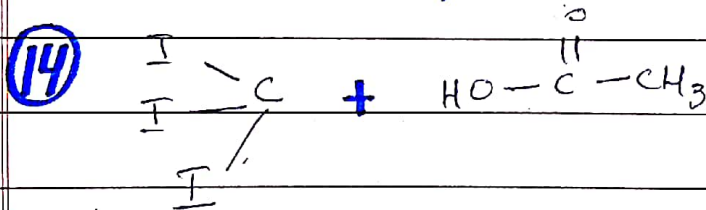
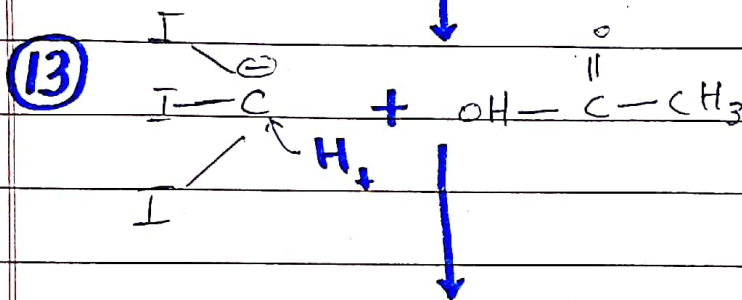
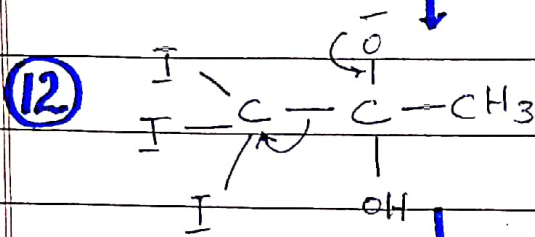
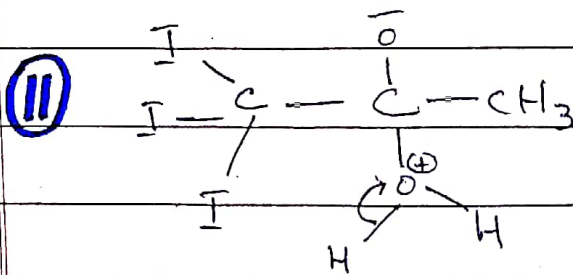
Equation :-



Mechanism :-







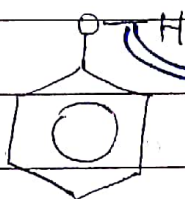
(Iodoform)

(Yellow Precipitates)

PHENOL

Functional Group :-

The molecules containing "**OH**" on Benzene Ring are known to be Phenols.



This bond is more reactive due to more polarity in this bond of **OH**.

* Oxidation of Phenol :-

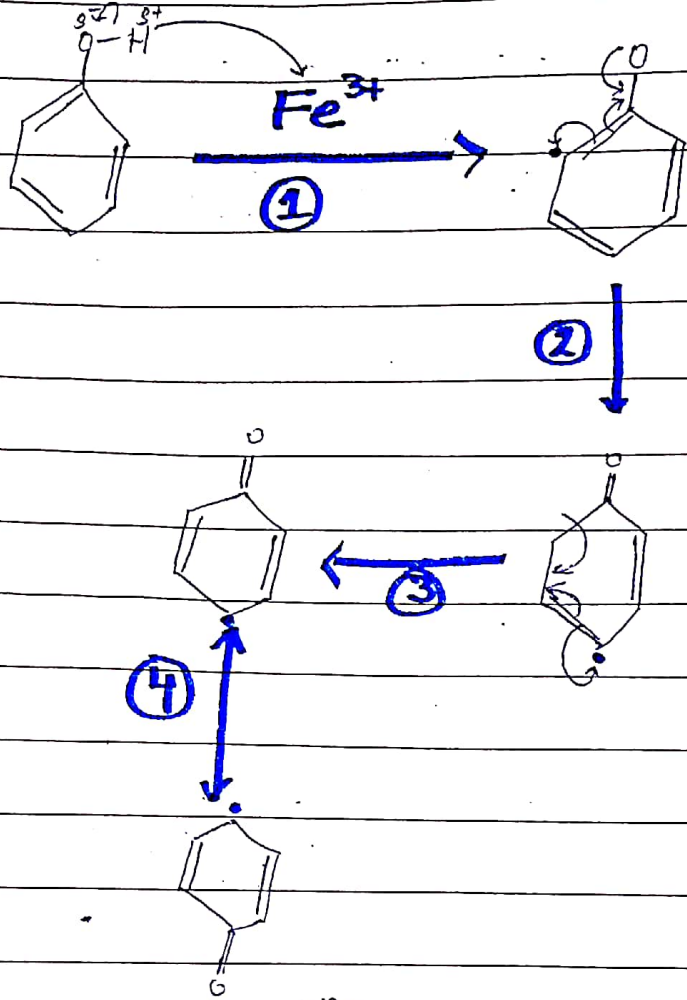
When Phenol is oxidized ; It shows Homolytic cleavage.

* Homolytic Cleavage :-

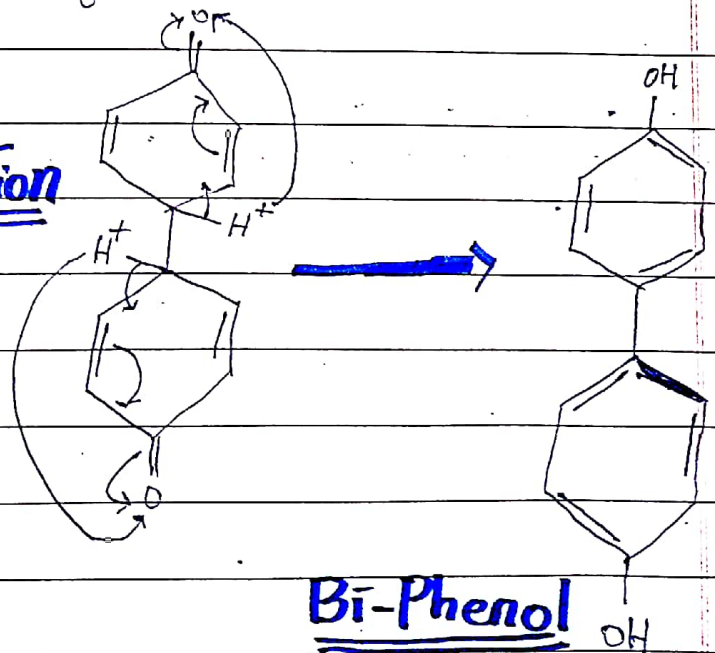
"The Breaking of a covalent bond in such a way that each fragment gets one of the shared electrons."

⇒ The phenol is oxidized by reacting it with a metal which show Homolytic cleavage and

as a result free Radical is obtained.

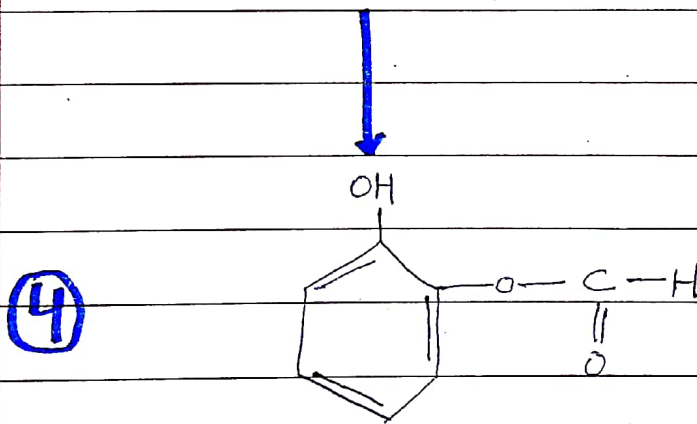
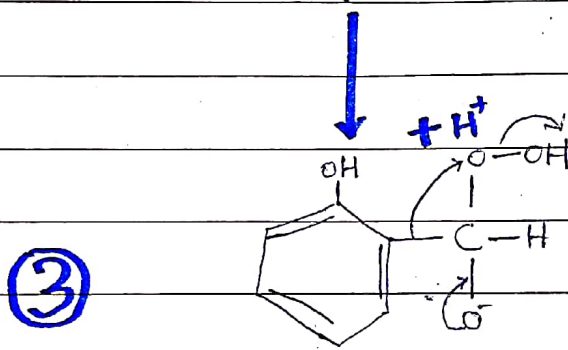
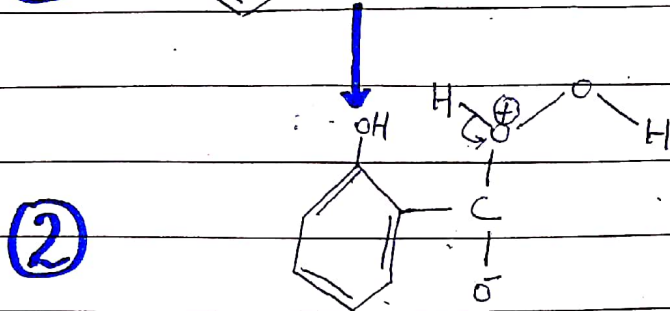
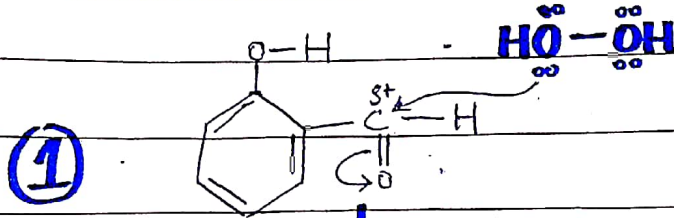


Reaction



Bi-Phenol

* With H₂O₂ :-



Hydrolysis :-

