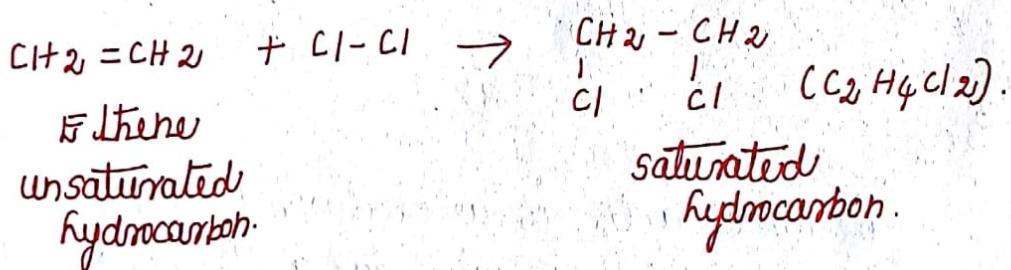


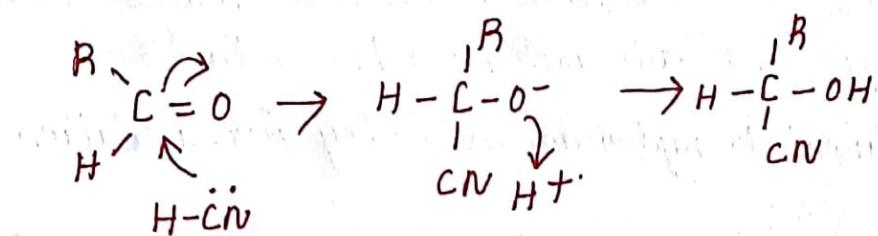
Addition reactions:

- An addition reaction is a reaction where two smaller molecules react to form a bigger molecule with no other products.
- Alkenes are unsaturated hydrocarbons. They give addition reactions.
- This is because all unsaturated hydrocarbons tend to become saturated hydrocarbons.
- When an addition reaction happens, carbon-carbon double bond or triple bond of an organic compound is broken. The electron shift to connect to hydrogen atoms.
- Any organic reaction in which one 'π' bond and one 'σ' bond is converted into '2σ' bond is called an addition reaction.
- If this change is brought about by an electrophile it is called as electrophilic addition reaction.
- If this change is brought about by an nucleophile it is called an nucleophilic addition reaction.



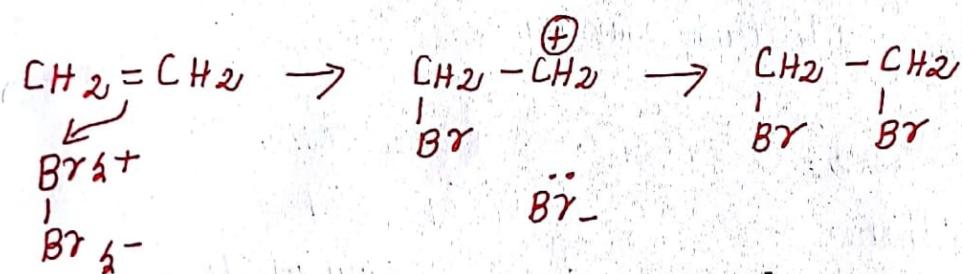
- It does not replace any hydrogen atoms.
- By changing the double bonds of ethene to single bond.
- Each carbon atoms has to satisfy the tetravalency so it has to form four covalent bonds. Unsaturated ethene converted into saturated by addition reactions.

Nucleophilic addition of hydrogen cyanide to aldehydes or ketones



The nucleophilic electron pair, donating cyanide ion attacks the positive carbon of the polarised C=O bond forming C-C bond. The π electron pair of the original C=O bonds moves on to the oxygen to give it a whole negative charge. The cyanide ion is the nucleophile - donating a electron pair to a partially positive carbon atom. The intermediate formed is a strong conjugate base and will abstract a proton to give the cyanohydrin.

Electrophilic addition of bromine to ethene



Bromine act as a electrophile because bromine is a very polarisable molecule. The electrons in the bond are very easily pushed to one end or the other. As the bromine molecule approaches the ethene, the electrons in the pi bond tend to repel the electrons in the bromine - bromine bond leaving the nearer bromine slightly positive & the further one slightly negative. The bromine molecule therefore acquires an induced dipole.

The electrons from the pi bond move down towards the slightly positive bromine atom. In this process, the electrons in the Br-Br bond are repelled down until they are entirely on the bottom bromine atom, producing a bromide ion. The ion with a positive charge on the carbon atom is called carbocation or carbonium ion.

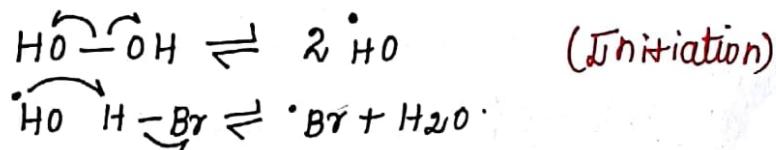
the lone pair of electrons on the bromide ion is strongly attracted to the positive carbon and moves towards it, until a bond is formed.

Free radical addition reactions

These reactions are brought about by free radicals.

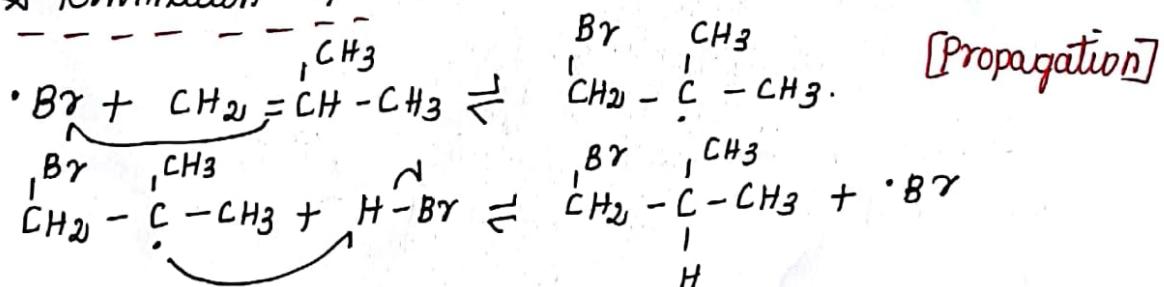
Addition of HBr to propene in presence of peroxide.

Initiation steps



Hydrogen peroxide is an unstable molecule. If we heat it, or shine it with sunlight, two free radicals of OH will be formed. These OH radicals will go on and attack HBr , which will take the hydrogen and create a bromine radical. Hydrogen radicals do not form as they tend to be extremely unstable with only one electron, thus bromine radical which is more stable will be readily formed.

Propagation & Termination steps:



The bromine radical will go on and attack the less substituted carbon of the alkene. This is because after the bromine radical attacked the alkene a carbon radical will be formed. A carbon radical is more stable when it is at a more substituted carbon due to induction & hyperconjugation. Thus, the radical will be formed at the more substituted carbon, while the bromine is bonded to the less substituted carbon. After a carbon radical

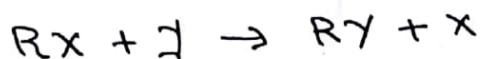
is formed, it will go on and attack the hydrogen of a HBr, which a bromine radical will be formed again.



In a termination step two bromine radicals combined to give bromine.

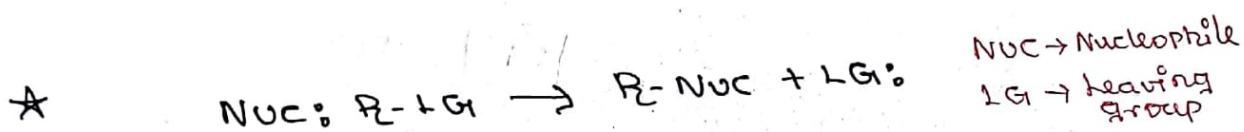
SUBSTITUTION REACTION

Substitution reactions involve the replacement of one atom (or) group by another:

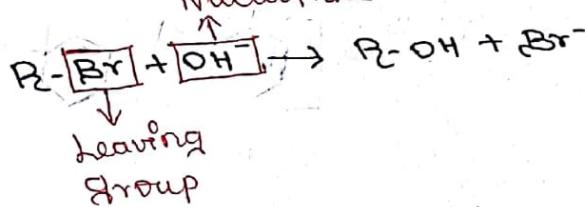


NUCLEOPHILIC SUBSTITUTION

- * NF is a fundamental class of reactions in which an electron rich nucleophile selectively bonds with the positive charge of an atom or a group of atoms to replace the leaving group.
- * The positive atom is referred to as an electrophile.



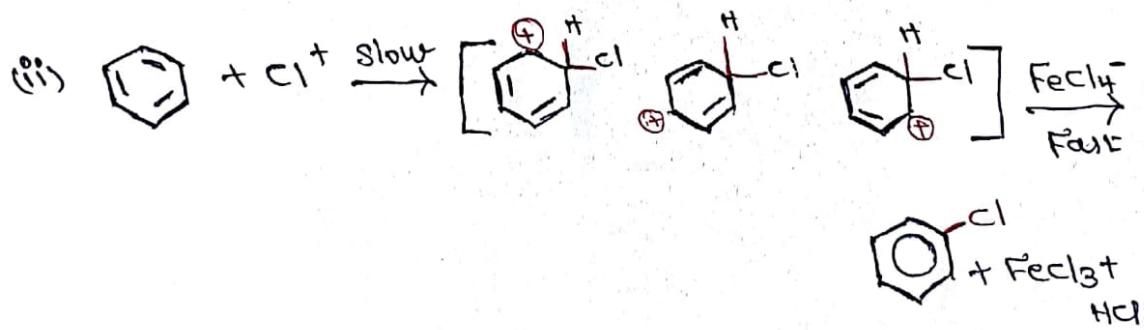
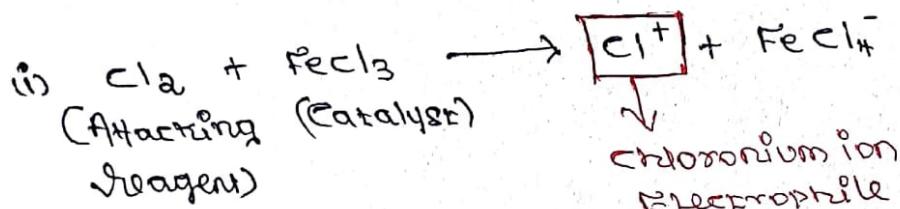
- * Example: Hydrolysis of an alkyl bromide



- (i) R_2-Br under basic conditions
- (ii) attacking Nucleophile is OH^-
- (iii) leaving group is Br^-

ELECTROPHILIC SUBSTITUTION

- * Electrophilic substitution reactions are chemical reactions in which an electrophile displaces a functional group in a compound.
 - * Electrophilic aromatic substitution reactions are characteristic of aromatic compounds
- ↓
- Reaction in which the hydrogen atom of an aromatic ring is replaced as a result of an electrophilic attack on the aromatic ring
- * Example 1: Halogenation of arenes



Mechanism of Nucleophilic Substitution Reaction

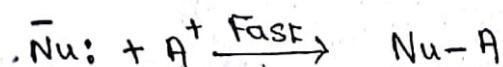
of nucleophilic substitution reaction may proceed through either of two mechanisms:

2

Two-step substitution mechanism (S_N1):

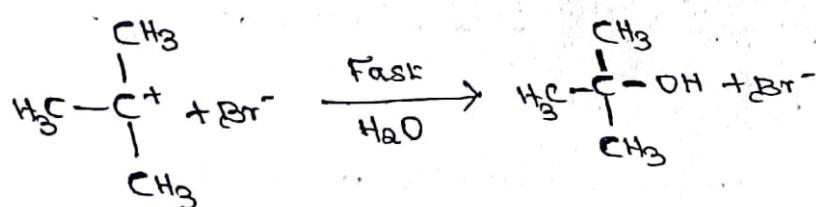
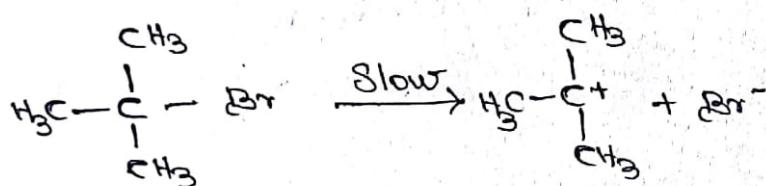
* STEP-1: SLOW STEP - OLD BONDS BREAK

* STEP-2: FAST STEP - NEW BONDS FORMATION



Example:

The nucleophilic substitution of tert-butyl bromide

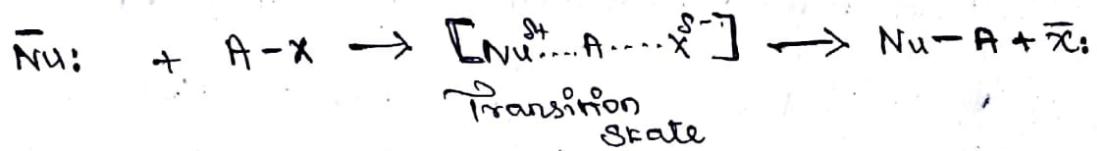


- * first step is the rate-determining step
- * first step does not involve attacking nucleophile
- * The rate of the reaction depends only on the molar concentration of one reactant
- * The overall reaction follows first order kinetics

II

ONE STEP SUBSTITUTION MECHANISM (S_N2)

- * This type } involves simultaneous bond breaking + making
of reaction }



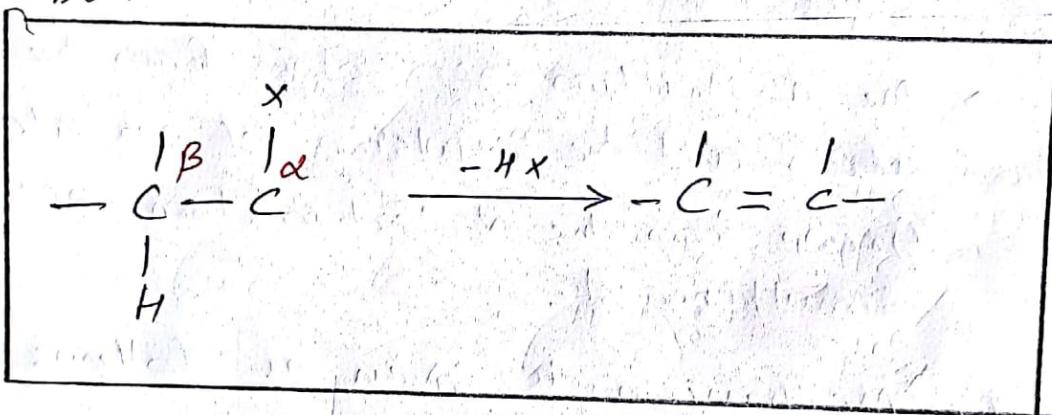
In this attacking nucleophile Nu:
↓
at carbon in
substrate A-X
↓
Forming a high
energy transition
state

- (a) The bond Nu-Carbon is in the process of forming
- (b) Bond X-Carbon is in the process of breaking with simultaneous elimination of the leaving group, X.

- * The molar concentrations of two reactants are changed.
- * The reaction follows 2nd order kinetics
- * Hence it is called S_N2 reaction

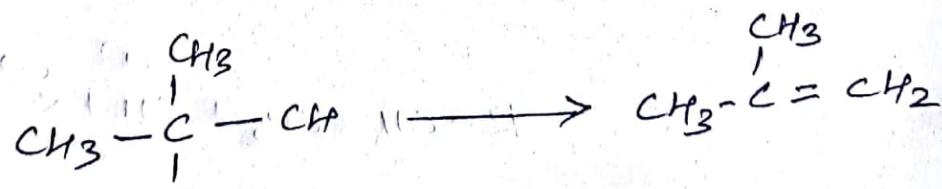
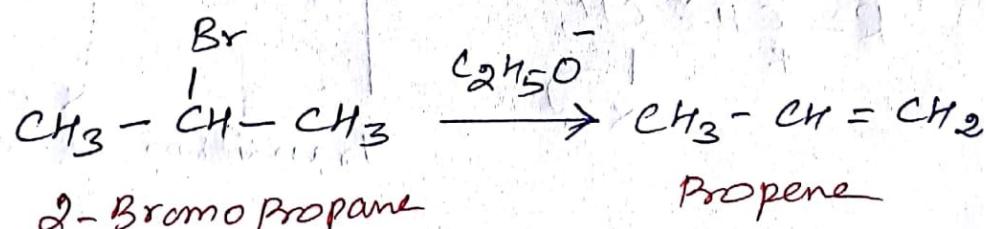
Elimination Reactions.

- Elimination Reactions are reverse of addition reactions.
- In these reactions two atoms or Group attached to adjacent carbon atoms of the substrate is eliminated to form a multiple bond



This method is used to prepare alkenes and alkynes.

e.g.



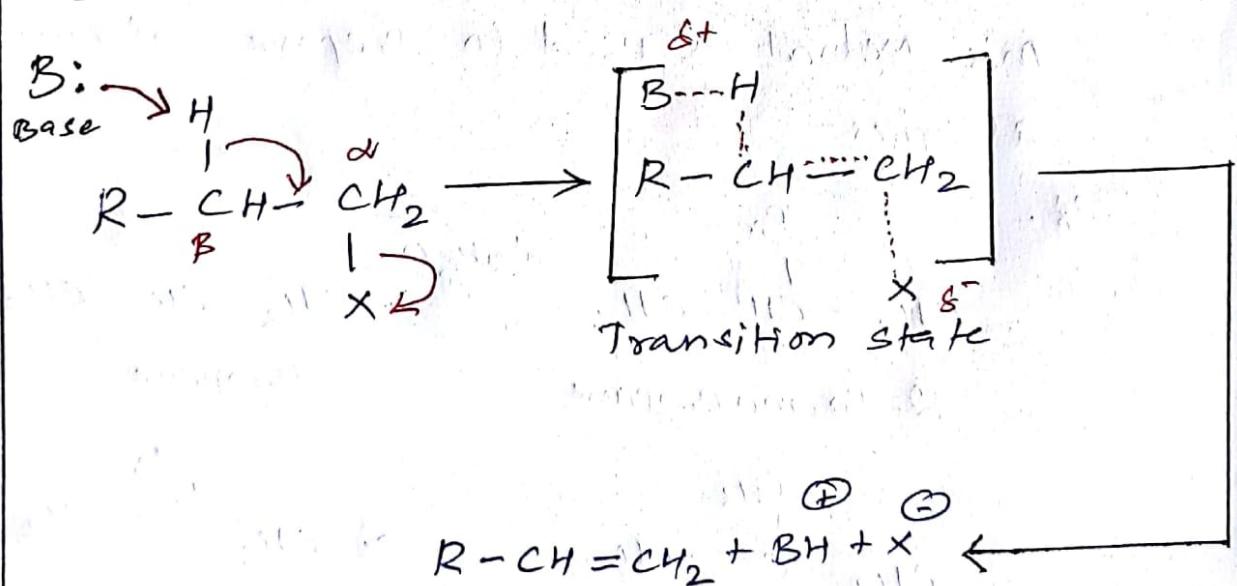
t-Butyl alcohol

2-methyl Propene

Bimolecular-Elimination Reactions (E_2)

- The rate of elimination depends on the substrate and nucleophile.
- The rate of the reaction is second order.
- It is represented as E_2 .
- Like SN^2 , the E_2 reaction is also one step process.
- The abstraction of Protons from the β -carbon atom and the expulsion of an atom or group from the α -carbon atom occur simultaneously.

The mechanism is given as follows:

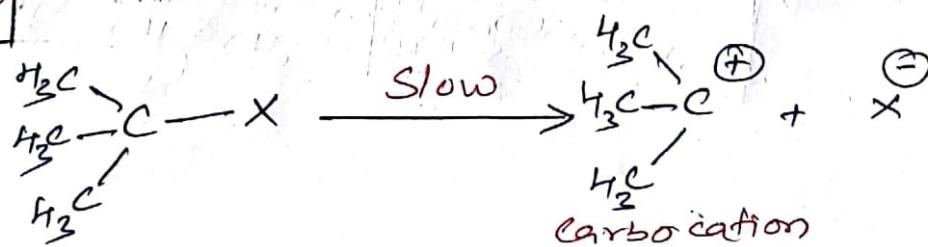


This is also called 1,2-elimination or β -elimination. Two groups to be eliminated are trans in each other. Hence it is called trans elimination.

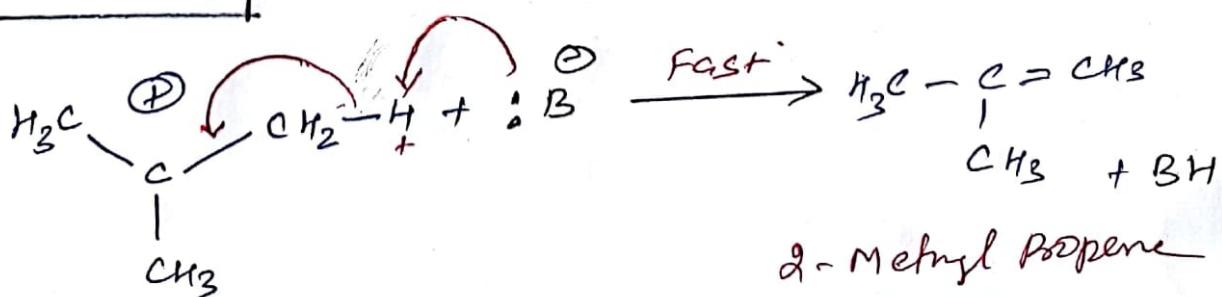
Unimolecular Elimination Reaction (E_1)

- In this reaction, Rate of elimination depends only the concentration of the Substrate.
- The reaction is of the First order Reaction
- like S_N^1 reaction, the E_1 reaction is also a two step process.
 - The First Step is the slow ionization of alkyl halide to give the carbocation.
 - The Second Step involves the abstraction of a proton from the adjacent, β -carbon atom giving rise ^{to} the formation of an alkane

First Step:



Second Step:



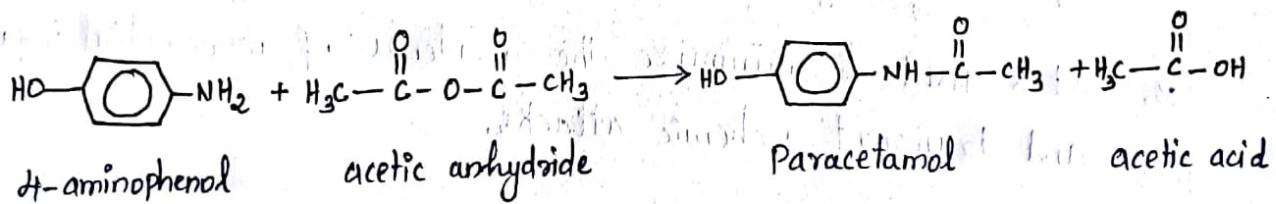
SYNTHESIS OF COMMONLY USED DRUG MOLECULE

Drugs Introduction

Drugs are chemicals of low molecular masses (~100-500). These interact with Macromolecular targets and produce a biological response. When the biological response is therapeutic and useful, these chemicals are called medicines and are used in diagnosis, prevention and treatment of diseases. If the doses are taken in higher amount than the recommended amount, most of the drugs used as medicines are potential poisons. Use of chemicals for therapeutic effect is called chemotherapy.

Synthesis of paracetamol

Paracetamol is made by reacting 4-aminophenol with ethanoic anhydride (more commonly called acetic anhydride). This reaction forms an amide bond and ethanoic acid as a byproduct. When the reaction is complete the paracetamol is then isolated. The crude product can be purified by recrystallization from water/Ethanol mixture (1:1) or from other appropriate solvents.

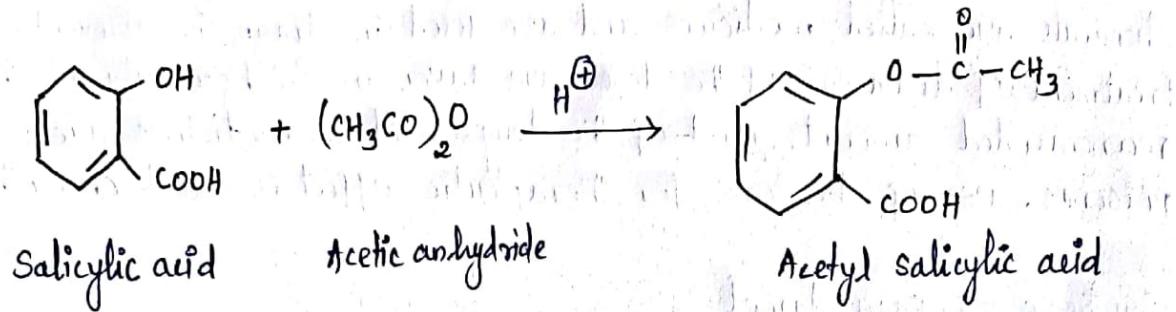


Uses.

1. It is used as an antipyretic and analgesic drug.
2. It can be effectively used for arthritic and rheumatic conditions linked with musculoskeletal pain, headache, neuralgias, myalgias and dysmenorrhea.
3. It is particularly useful in aspirin sensitive patients.

Synthesis of Aspirin and its uses.

The reaction of Salicylic acid with acetic anhydride yields Aspirin. The crude product thus obtained may be recrystallized from benzene, mixture of acetic acid and water (1:1) and various other non-aqueous solvents.

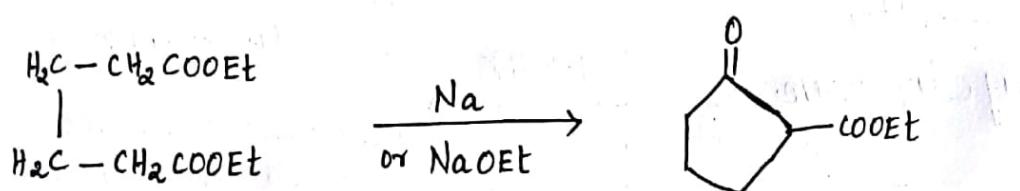


USES

1. It is used as an antipyretic, anti-inflammatory and analgesic drug for treating headache, discomfort and fever associated with common cold, muscular pain and aches.
2. It is regarded as the drug of choice for reducing fever because of its high degree of effectiveness and safety.
3. It is used to minimize the incidents of myocardial infarction and transient ischemic attacks.

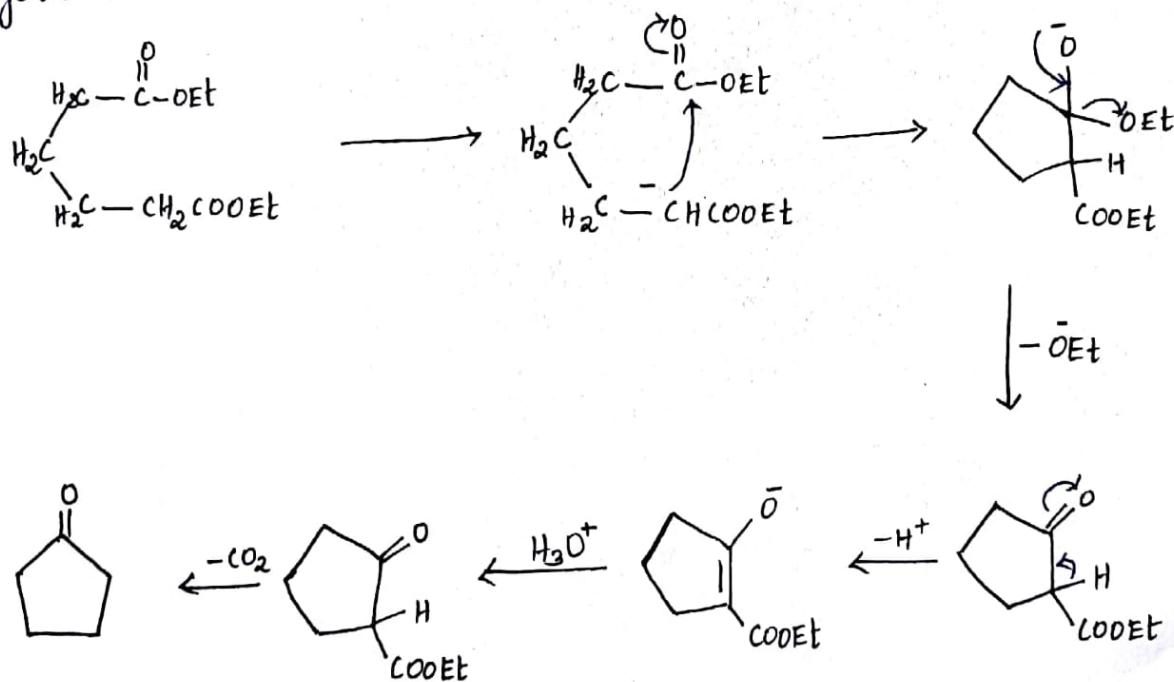
DIECKMANN CONDENSATION

It is an intramolecular claisen condensation and is useful for the preparation of cyclic ketones. Diesters of C₆ and C₇ dibasic acids give good yields of cyclic β -keto-esters. Thus, ethyl esters of adipic and pimelic acids (1 and 3) give 2-carboxycyclopentanone.



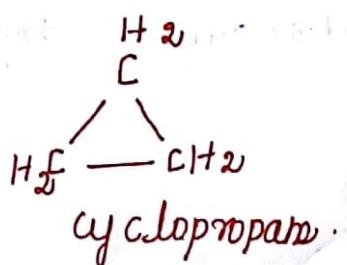
Mechanism

The mechanism involves the intermolecular attack of initially formed enolate anion to the carbonyl group of other ester group. The expulsion of ethoxide anion (EtO^-) leads to the formation of β -ketoester which on hydrolysis, followed by decarboxylation is converted into cyclic ketone.



Ring opening reactions

Addition of reagents such as Cl_2 , Br_2 , $\text{H}\bar{\text{T}}$, H_2SO_4 , H_2 to cyclopropane leads to ring opening and the corresponding reactions are given below.



Cl_2/Dark	$\text{ClCCl}_2\text{CH}_2\text{Cl}$	1,3-dichloropropane
Br_2	$\text{BrCCl}_2\text{CH}_2\text{Br}$	1,3-dibromopropane
$+ \text{HBr}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$	1-bromopropane
$\text{COH} \cdot \text{H}_2\text{SO}_4$ H_2O	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	Propanol
$+ \text{HI}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$	1-iodopropane

Oxidising Reagents \rightarrow It is defined as the oxidation of an organic cpds is the addition or gain of oxygen or removal of hydrogen.

(i) Manganese (VII) oxidants

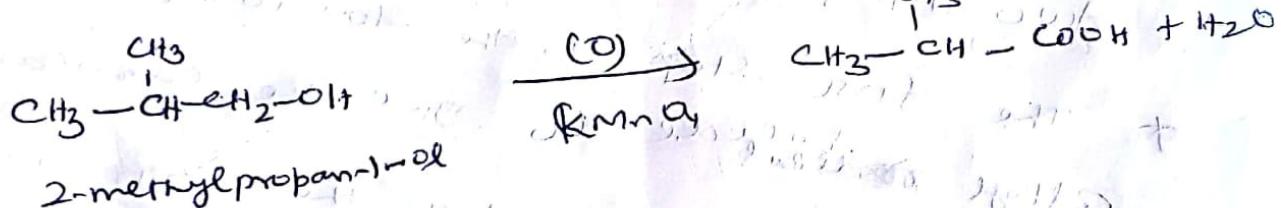
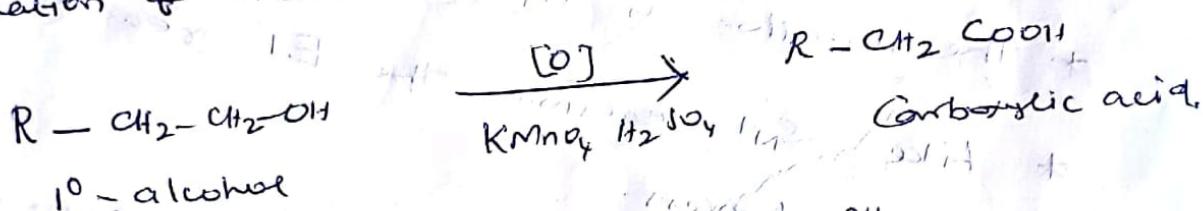
Potassium permanganate:

* derivative of heptavalent manganese is a powerful oxidising agent.

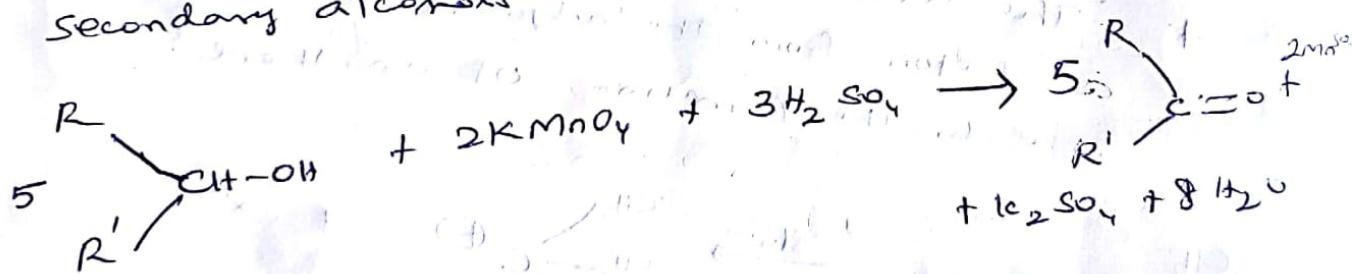
* In acid solution $Mn(VII)$ is reduced to divalent manganese (II) with a net transfer of 5 e⁻s.

* In neutral or basic medium manganese dioxide ($Mn(VII)$) $\rightarrow Mn(IV)$ is formed.

Oxidation of alcohols:

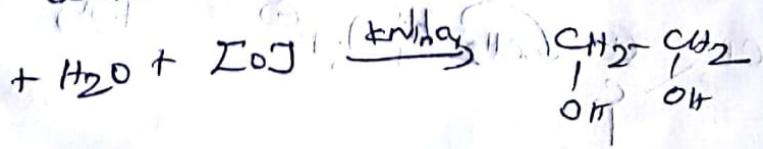


Secondary alcohols are oxidised to ketone



Oxidation of alkenes

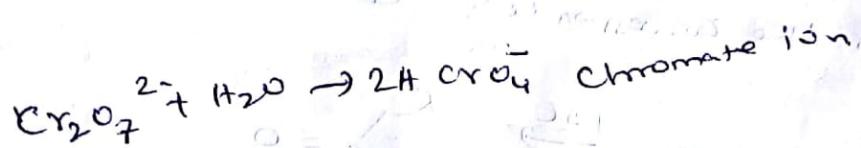
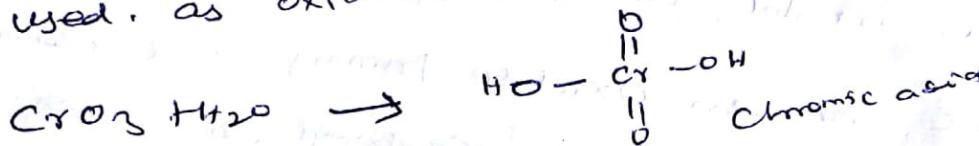
Alkenes reacts with dil. $KMnO_4$ solution in the presence of alkali to give 1,2-diol.



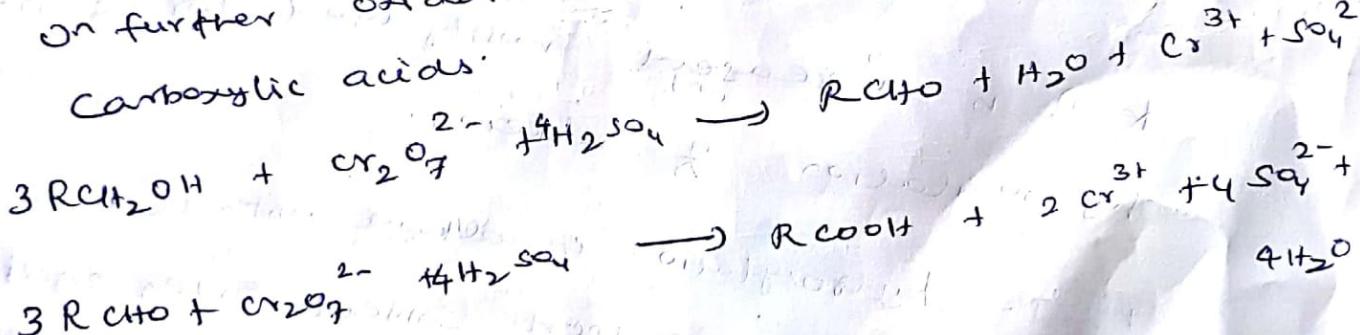
(ii) Chromium (VI) Oxidants

- * One of the most versatile oxidising agents is chromic acid, a derivative of hexavalent chromium.
- * During oxidation, the hexavalent chromium(VI) is reduced to chromium(III).

* Chromium(VI) oxide / $K_2Cr_2O_7$ / $Na_2Cr_2O_7$ can be used as oxidising agents.

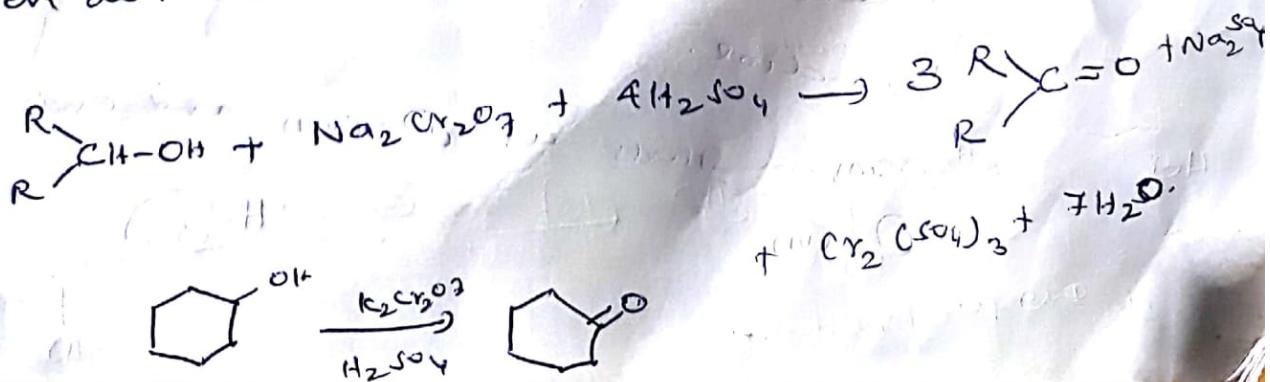


Primary alcohols on oxidation with $K_2Cr_2O_7$ / $Na_2Cr_2O_7$ in dil. H_2SO_4 , gives the corresponding aldehyde which on further oxidation with same reagent to give carboxylic acids.



Secondary alcohols on oxidation give ketones.

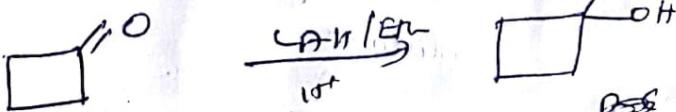
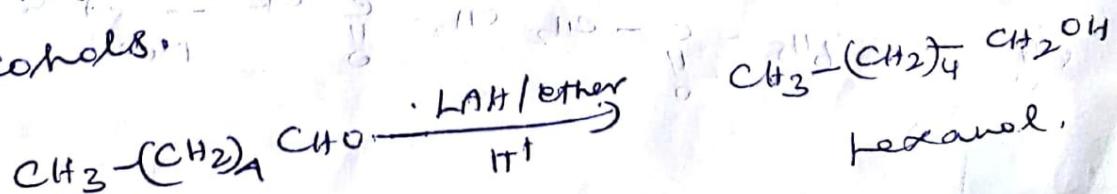
which do not undergo further oxidation.



Reducing agents: - Reducing agents are those which add hydrogen to an unsaturated group like a $C=C$ or $C=O$ or $C=N$ or $C\equiv N$ or $C\equiv O$ or $C\equiv C$ to an unsaturated nucleus.

e.g. LiAlH_4 , NaBH_4 , Raney Ni , Li/Na in Et_2O , $\text{Zn/C}_2\text{H}_5\text{OH}$.

LiAlH_4 : - It is the most important reagent for the reduction of ketones, carboxylic acids, esters, aldehydes, acid anhydrides, and epoxides to corresponding alcohols.

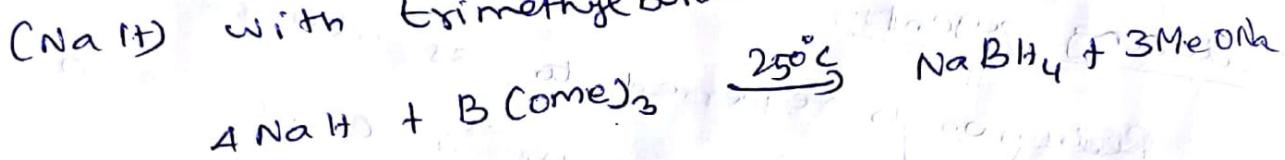


LAH - do not reduce the alkenes and alkynes.



② NaBH_4 Sodium borohydride.

It is prepared by the Rxn of sodium hydride (NaH) with trimethyl borate.



- It is insoluble in ether and soluble in water.

- The reagent is normally used as reducing agent in aqueous or alcoholic solution at

agent in aqueous or alcoholic solution at

R.T.

- It is a more selective reagent.

- It reduces aldehydes and ketones to alcohol.

- It reduces esters while the halogen, cyano, nitro, amido and ester

groups remain unaffected.

- It also does not reduce $\text{C}=\text{O}$ & $\text{C}\equiv\text{C}$.

