DATE : / 20
PAGE No

01/05/19

Unit-

Types of Organic Rx^n

* **Substitution Rx^n:**

The Rx^n in which one or more atom or groups attached to a carbon atom are replaced by other atoms or groups are known as Substitution Rx^n. the saturation or unsaturation of original compound remains unchanged during the Rx^n. i.e the total no. of = bond and ≡ bonds in reactant and products remains the same.

for Ex

$$CH_3 - CH_3 + Cl_2 \xrightarrow[\text{Sunlight}]{\text{Diffused}} CH_3 - CH_2 - Cl + HCl$$

$$CH_3 - CH = CH_2 + Cl_2 \xrightarrow{500^\circ C} Cl - CH_2 - CH = CH_2 + HCl$$

3 chloro propene

(2) **Addition Rx^n:**

The Rx^n in which atom or molecules are added to carbon atoms or other atoms, resulting in the formation of more saturated product are known addition Rx^n.

Ex-

$$CH_2 = CH_2 + Br_2 \longrightarrow BrCH_2 - CH_2Br$$

(3) **Elimination Rx^n:** Rx^ns in which atoms or groups attached to two adjecent carbon atom are removed resulting in the formation of a more unsaturated product.

NH4CNO ⇌ NH2CONH2

DATE : / 20
PAGE No

are called elimination Rxn.

for Ex:

$$BrCH_2-CH_2Br + Zn \longrightarrow CH_2=CH_2 + 2ZnBr$$

7) Rearrangement Rxn:

Rxn in which some atoms or groups present in a molecule interchange their positions to form a new product are called Rearrangement Rxn.

for Ex:

$$CH_3-CH_2-CH_2-CH_3 \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-CH_3$$

n-Butane → iso Butane

$$NH_4CNO \xrightarrow{\Delta} NH_2CONH_2$$

(I) mechn of Substitution Rxn:

Alkyl halides give a number of Rxns in which halogen atoms is replaced by another atoms or groups

for Ex:

$$C_2H_5Br + KOH_{(aq)} \longrightarrow C_2H_5OH + KBr$$

It may also be written as ~~C_2H_5Br~~

$$C_2H_5Br + OH^{\ominus} \longrightarrow C_2H_5OH$$

(nucleophile).

Here nucleophile is attacking reagent therefore above Rxn is known as Nucleophilic Substitution Rxn (SN).

DATE : / 20
PAGE No

Following two mechanism have been proposed for about Rxn

(i) Unimolecular Nucleophilic Substitution Rxn (SN1)

2) Bimolecular " " " (SN2)

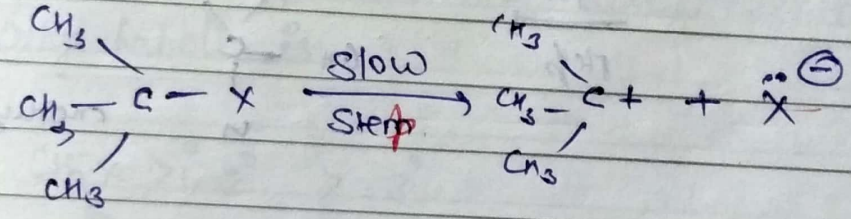
(1) Unimolecular Nucleophilic Substitution Rxn (SN1):

Acc. to this mechanism about Substitution Rxn takes place in two steps as

Rate Determining step and Reacting molecules

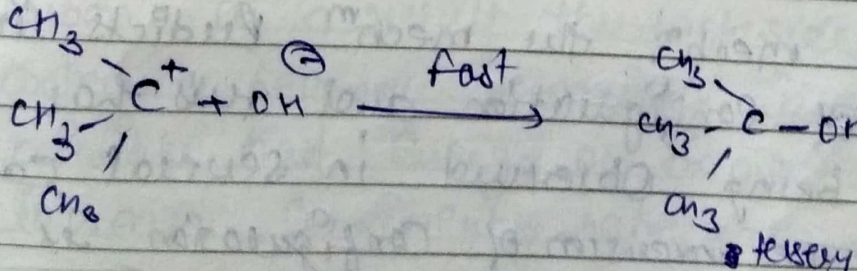
Step:1

alkyl halide Breaks slowly to form carboninum ions as



Step:2

The carboninum Combines with on⊖ Nucleophile rapidely to give final product

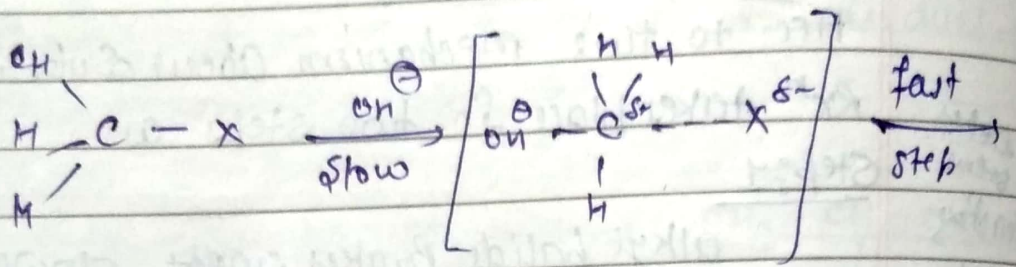


Here step-1, (slow step) is rate determining step. In that steps, only one reacting molecule is taking part therefore, it is known as

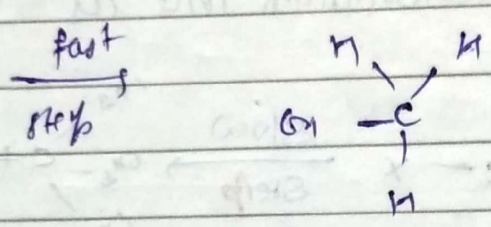
unimolecular Nucleophilic substitution mech^{n}.

(2) Bimolecular Nucleophilic Sub. (S_N2):

Acc. to this mech^{n} the substitution of alkyl halide takes place in one step only



Transition state



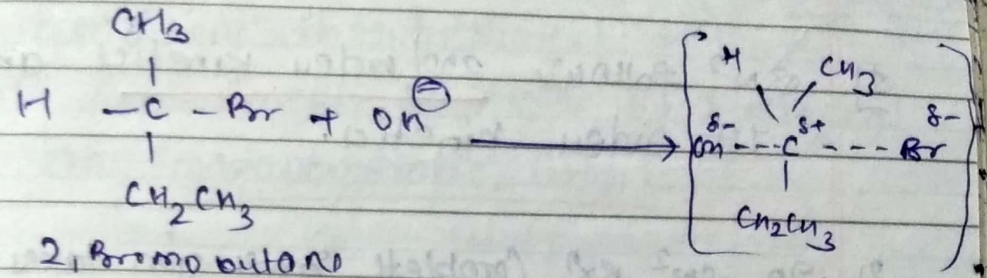
methyl alcohol

* S_N2 Rx^{n} proceed with complete stereochemical inversion:

The stereochemistry of the proposed S_N2 mech^{m} serve as evidence for this mech^{m}. the mech^{m} predicts inversion of configuration and this has actually being observed in several cases. The inversion of configuration is known as walden Inversion

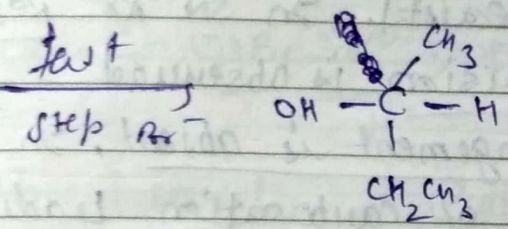
DATE : / 20
PAGE No

for ex, let us Consider the attack of chiral carbon by the Nucleophile $OH^{\ominus}$



2, Bromobutane

Transition state



Butanol.

There is thus complete stereochemical inversion

ii) for SN^2 Rxn the order of reactivity of alkyl halide is

$$CH_3X > 1^\circ > 2^\circ > 3^\circ$$

This order in SN^2 Rxn are chiefly due to steric factors. As H atom are Replaced by the longer methyl group, there is increased Crowding (or steric hinderence) about the carbon. As a result the backside of the molecule becomes Increasingly ~~in~~ inaccessible and Energy of transition state increases Consiquently rate falls off.

DATE: / 20
PAGE No

* Important points of Nucleophilic substitution Rxn: (Diff b/w SN^1 and SN^2 Rxn):

1] SN^2 follows 2nd order kinetics and SN^1 follows 1st order kinetics.

2] In SN^2 Rxn complete inversion takes place (when chiral carbon exist). In SN^1 Rxn Resimisation as well as inversion is observed

3. In SN^2 rearrangement is absent, In SN^1 Rxn rearrangement of carbocation leading to more stable carbocation is observed.

4. High Conc^n of the Nucleophile favours SN^2 Rxn while Low Conc^n favour SN^1 Rxn

5. The higher the polarity of the solvent the greater the tendency for SN^1 Rxn.

* Electrophilic substitution Rxn:

As the Rxn involves substitution and an electrophile attacks first, the mech^n is known as Electrophilic substitution mech^n.

It is also of two type substitution

i) SE^1 (unimolecular electrophilic Rx^n)

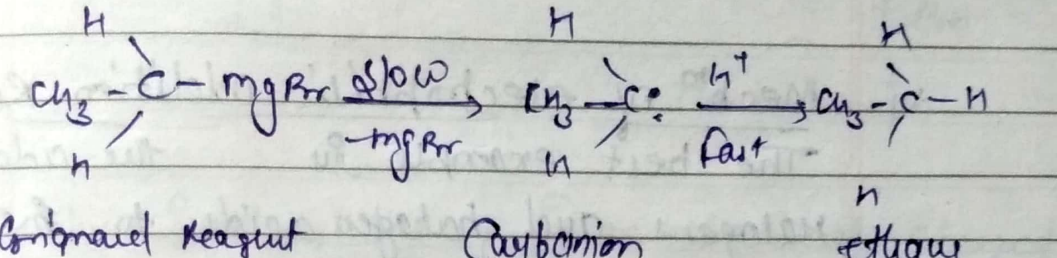
(ii) SE^2 (Bimolecular " ")

i.

Resou dehydrating reagent organometic metal combine w/th compound.

DATE: / 20
PAGE No

(1) S_E1 (Unimolecular Electrophilic substitution Rx^n):
The mechanism is not very common. It however, involves the formation of a carbanion as a transitory intermediate.
for Ex: Replacement of metal by hydrogen in an organometalic Comp.



Grignard Reagent Carbanion ethane

(2) S_E2 (Bimolecular Electrophile substitution Rx^n):

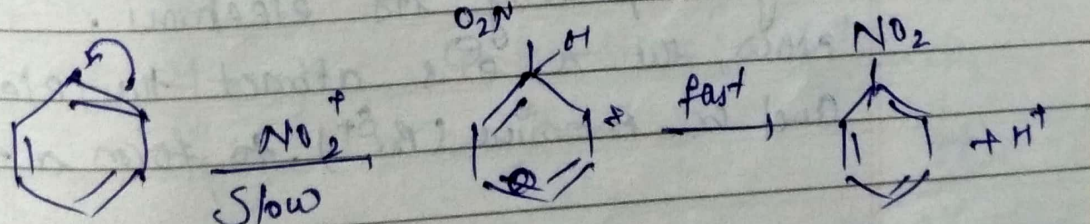
Aromatic substitution Rx^{n}s such as Halogenation, Nitration, Sulfonation proceed by this mechanism.

Keplace H by NO_2

for Ex:-

$$C_6H_6 + HNO_3 \xrightarrow{Conc.\ H_2SO_4} C_6H_5NO_2 + H_2O$$

$$HNO_3 + H_2SO_4 \longrightarrow HSO_4^- + H_3O^+ + NO_2^+$$



$$\ominus HSO_4^{\oplus} + H_3O^+ + H^+ \longrightarrow 2H_2SO_4 + H_2O$$

* Addition Rxn & Mechanism :

It is of two types

i) electrophilic addition Rxn

ii) Nucleophilic addition Rxn

i) Mechm of electrophilic addition Rxn;

The best example for the addition of Halogens and halogen acids to Molecules Let us discuss the addition of Bromine to ethylene as a standard. which may be represented by the following Rxn

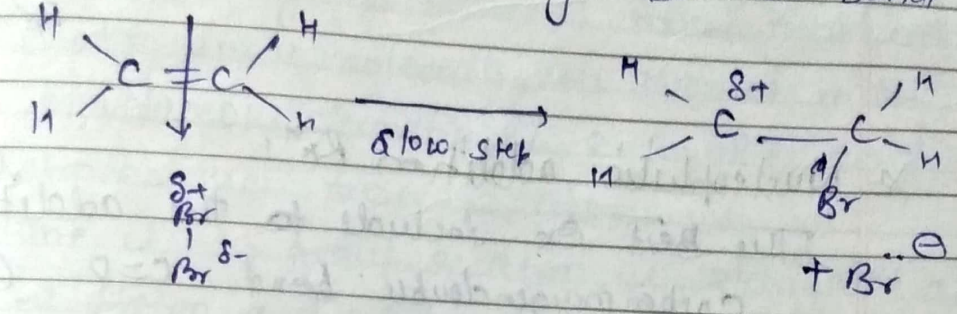
$$H_2C = CH_2 + Br_2 \longrightarrow BrCH_2 - CH_2Br$$

Mechm: The addition of Bromine to ethylene is a two step process in which the two Bromine atoms enter the ~~two~~ ~~carbon~~ Polymer one by one from opposite side i.e trans addition.

Step-1 In the first step, the π electrons of ethylene polarised the Br molecule by repelling its electrons.

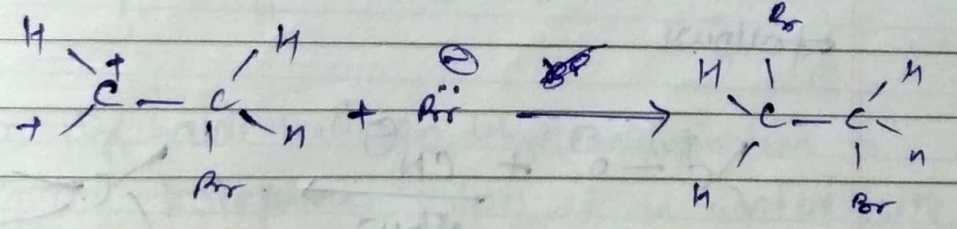
Now, the π $e^{\ominus}$s attract the electrophilic end or Bromine ($Br^{\delta+}$). to form a π complex

which immidately forms an intermediate Carbonium ion through polarisation of ethylene π electrons. and breaking Br – Br bond

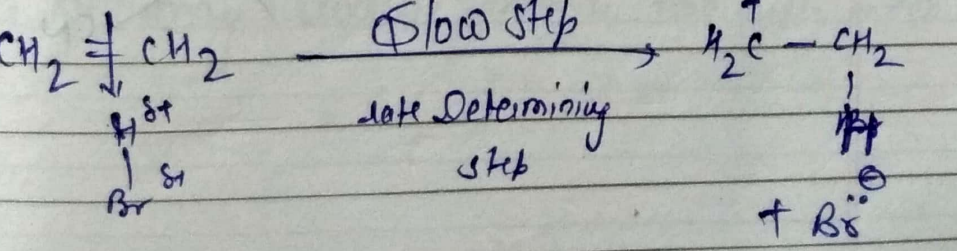


Carbonium ion

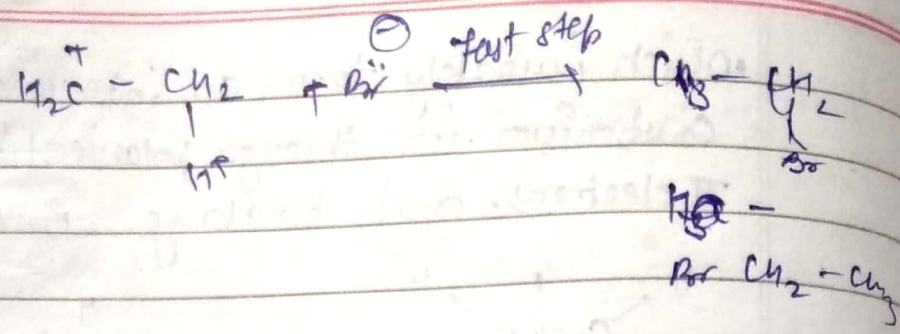
Step-2 Now immediately the $Br^{\ominus}$ ion on the +vely charged Carbon of Carbonium ion from the side opposite to where 1st Bromine atom is attached (it is due to steric effect and electrostatic repulsion caused by already attached Bromine atom.



Similarly, the mechanism of addition of halogen acids (for Ex – HBr) to an polythene, ethylene may be shown as

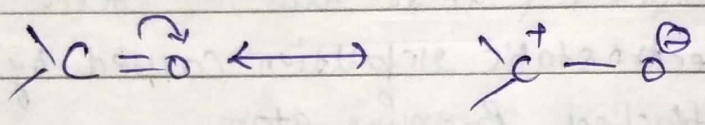


DATE : / 20
PAGE No

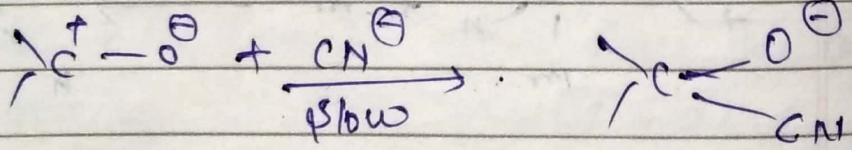


* Nucleophilic addition Rx^{n}:

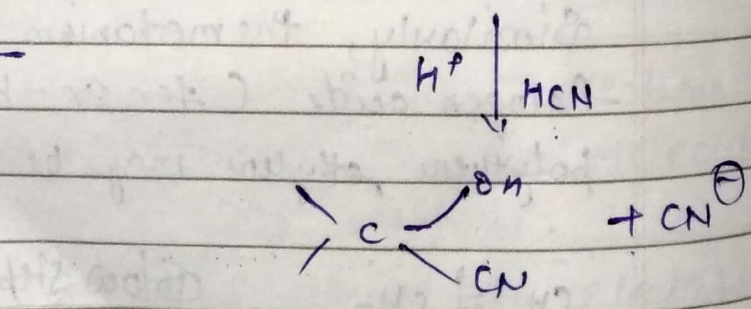
The Best ex. include to the addition carbon oxygen double bond C=O Carbonyl group. The oxygen atom takes a greate share of $\pi e^{\ominus}$s of the double Bond present b/w carbon and oxygen and is therefore Best represented by the following two resonating forms



The addition takes place in two steps as follows



$HCN \rightarrow H^{+} + CN^{\ominus}$



alc. KOH Soln of KOH in alc.

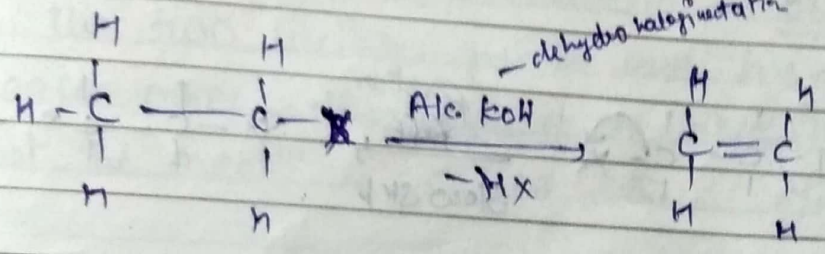
DATE : / 20
PAGE No

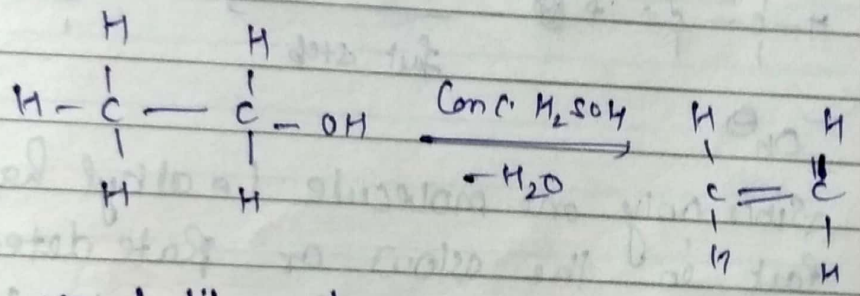
* Elimination Rxn

Eliminations Rxn are those in which two atoms or groups attached two to adjacent C atom in a molecule are removed with simultaneous formation of a multiple bond between the two C atoms

One of the group of atom is eliminated as a proton and the other as an anion.

(i)





An alkyl halide undergo dehydrohalogenation to form ~~polyene~~ olefin when it is heated with alk. KOH

$$R-CH_2-CH_2-X + KOH \xrightarrow[\Delta]{alk.} RCH=CH_2 + KX + H_2O$$

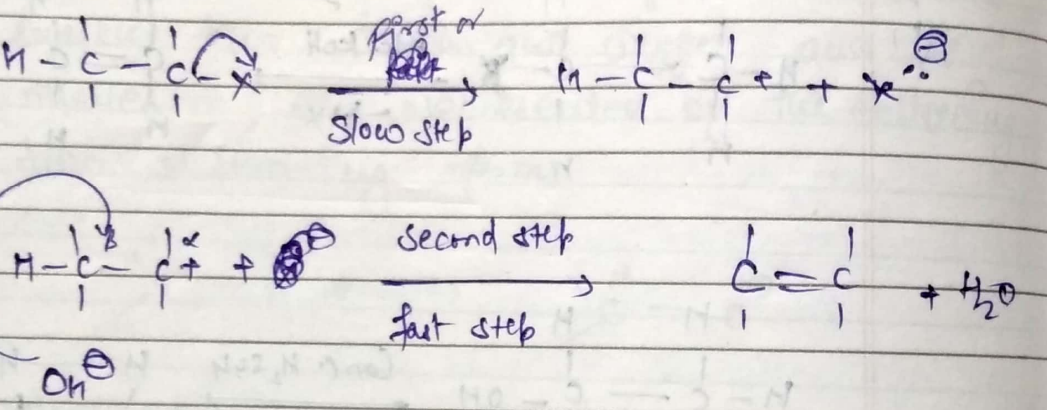
The Rxn may proceed through two diff. mechm.

DATE : / 20
PAGE No

(I) Two step elimination Rxn mechm : (E_1)

The first or slow step involves the Heterolytic fission of carbon-halogen bond to form a Carbonium ion and halogen ion.

The second or fast step involves the elimination of a proton from β carbon with the help of $OH^{\ominus}$, to produce an olifin



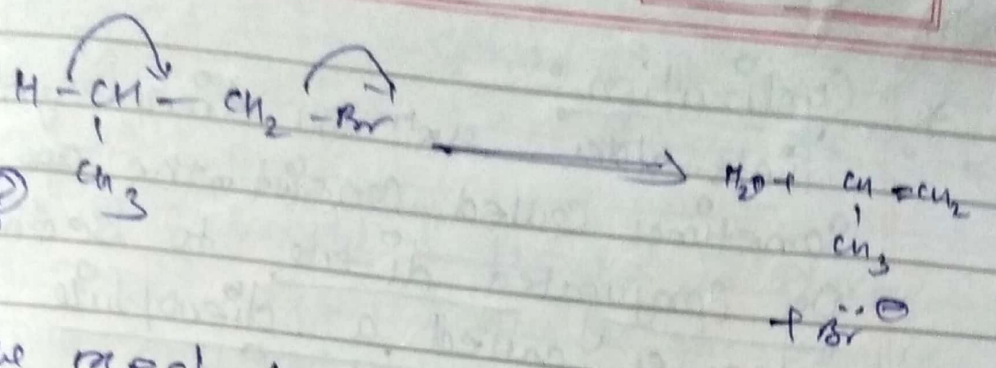
Since only one molecule i.e alkyl halide take part in the slow or Rate determining step, it is called E_1 mechanism

(II) One step elimination Rxn Mechm : (E_2) :

This type of mechm involves the abstraction of a proton from β c-atom by a Base with the Similtaneous Loss of a halide ion from the alpha carbon of the alkyl halide molecule.

DATE : / 20
PAGE No

For Ex:



The mechanism thus takes place in one step but it is kinetically it is second order. i.e 1st order Rn Substrate (Halide). The E_2 mechanism is stereospecific If the two leaving groups are trans to each other, they depart in opposite dir. and the mech^m is called n_s elimination

DATE: / / 20
PAGE No

3/4/19

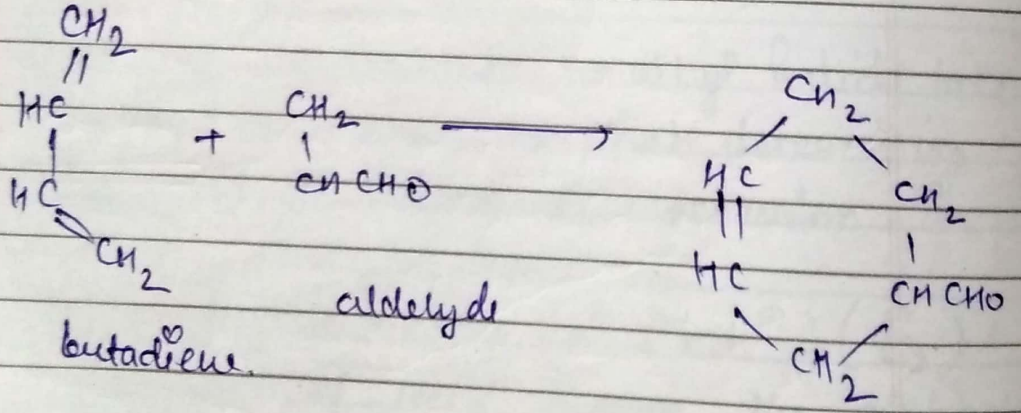
* **Cyclization :**

diels-alder rxn or diene-synthesis, as sometimes called consist in the 1-4 addition of conjugated di-ene to second unsaturated molecule called a dienophile to form a six membered ring.

A simple example of diels-elder Rx^{4} is the addition to a conjugated di-ene of an ethylenic compound in which the double bond is adjesent to a carbonyl group,

for ex:

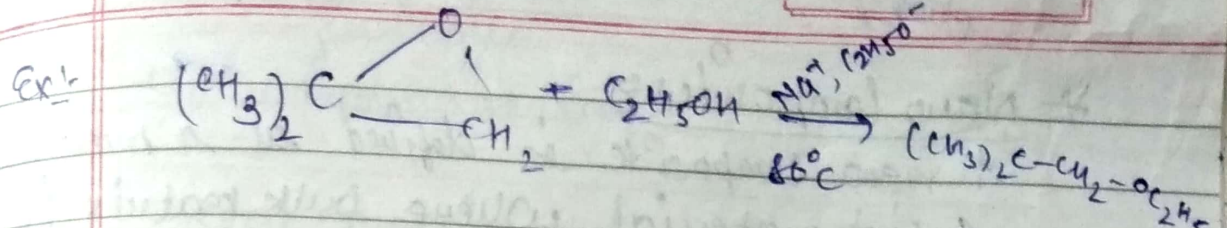
Butadiene combines with an aldehyde at 100° to form tetra hydro benzylaldehyde.



* **Ring opening Rx^{4} :**

epoxide readily undergo Rx^{4} in which the epoxide ring is opened by nucleophile

DATE : / 20
PAGE No

Ex:- 

A Rx^{n} of this type is S_N2 Rx^{n} in which the epoxid oxygen serves as the leaving group does not depart as the seperate entity, but rather remains with in the same ~~Compo~~ product molecules

*

matrix phase
+ nano particles

DATE : / 20
PAGE No

Unit-5

* Nano Composites

A nano composite is defined as a multiphase solid material where bulk matrix phase is reinforced with nano dimensional additive.

The nano reinforcement phase has one of 1, 2, or 3 Dim. of less than 100 nm.
The nano composite material has structures having nanoscale repeat distances b/w the different phases that make up the material

Types of nano composite:
nano composite material can be classified into following three type depending upon the matrix phase

(i) Ceramic ceramic matrix nano composite:
They have ceramic as matrix phase and a metal as the reinforcement is added to them. Then two components (ceramic and metal) are finally dispersed in each other to obtained a nano composite material.

ceramic matrix nano composite material exhibit improved optical, electrical, magnetic, corrosion resistance and

DATE: / 20
PAGE NO

Properties
other ~~Productive~~ properties

(2) Metal-matrix nano composite:
They have metal as matrix phase and nano scale re-inforcement is added to them.

(3) Polymer matrix :M.C:
They have Polymer as matrix phase and nano particlates are added to enhance their performance.