MAA OMWATI DEGREE COLLEGE, HASSANPUR (PALWAL)

NOTES

SUBJECT : Organic Chemistry

CLASS : B.SC 3rd Sem

SESSION : 2021-2022

B. Sc. IIIrd Semester

Paper XI (Theory) Organic Chemistry **Max. Marks: 29**

CH-303 **Time: 3 Hrs.**

Note: Examiner will set nine questions and the candidates will be required to attempt five questions in all. Question number one will be compulsory containing five short answer type questions covering the entire syllabus and will be of five marks. Further, examiner will set two questions from each section and the candidates will be required to attempt one question from each section which will be o f s ix marks each

Section-A

1.Alcohols

Monohydric alcohols □ nomenclature, methods of formation by reduction of aldehydes, ketones, carboxylic acids and esters. Hydrogen bonding. Acidic nature. Reactions of alcohols. Dihydric alcohols — nomenclature, methods of formation, chemical reactions of vicinal glycols, oxidative cleavage [$Pb(OAc)_4$ and HIO_4] and pinacol-pinacolone rearrangement.

2. Epoxides

Synthesis of epoxides. Acid and base-catalyzed ring opening of epoxides, orientation of epoxide ring opening, reactions of Grignard and organolithium reagents with epoxides

Section-B

.Phenols

Nomenclature, structure and bonding. Preparation of phenols, physical properties and acidic character. Comparative acidic strengths of alcohols and phenols, resonance stabilization of phenoxide ion. Reactions of phenols — electrophilic aromatic substitution, Mechanisms of Fries rearrangement, Claisen rearrangement, Reimer-Tiemann reaction, Kolbe's reaction and Schotten and Baumann reactions.

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Section-C

. Ultraviole t (UV) absorption spectroscopy

Absorption laws (Beer-Lambert law), molar absorptivity, presentation and analysis of UV spectra, types of electronic transitions, effect of conjugation. Concept of chromophore and auxochrome. Bathochromic, hypsochromic, hyperchromic and hypochromic shifts. UV spectra of conjugated enes and enones,Woodward- Fieser rules, calculation of $\square_{max}$ of simple conjugated dienes and □,□ -unsaturated ketones. Applications o f UV Spectroscopy in structure elucidation of simple organic compounds.

B.Sc – 2nd year.
3rd & 4th

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Organic Chemistry

Unit : 1.

#. Nomenclature of Monohydric Alcohols :-

Monohydric alcohols are named by three different System.

i) The common system :-

Acc. to the system, which is used only for the simpler alcohols, alcohols are named by adding the word alcohols to the ~~same~~ name of alkyl group present in the molecule.

for eg :-

CH_3OH

Methyl alcohol.

2. The carbonyl system :-

Acc. to the System, Methyl alchol is called carbinol and other alcohol are named as alkyl deriatives of carbinol

for eg:-

$CH_3 - CH_2OH$

methyl carbinol.

IUPAC system:-

In this system alcohols are named in accordance with the general IUPAC rule.

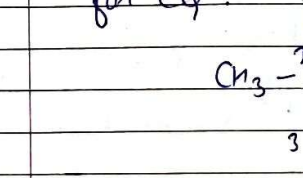
Main point of this system:-

a) The longest carbon chain containing the carbon atom carrying the hydroxial group is selected as corrosponding to the parent hydrocarbon The alcohol is named as derivative of this hydrocarbon by replacing the final 'e' of the name of hydrocarbon by the suffix -ol.

b). The parent chain of carbon atom is numbered from that end which gives the longest possible number to carbon carrying the hydroxyl group.

c). The name of alcohol is then written as one word by writing the name of the side chains or substituents along with their position. in alphabetical order followed by the name of parent alcohol.

for eg:-



2 methyl propan-2-ol.

Method of formation Reduction of Carbonyl Compound:-

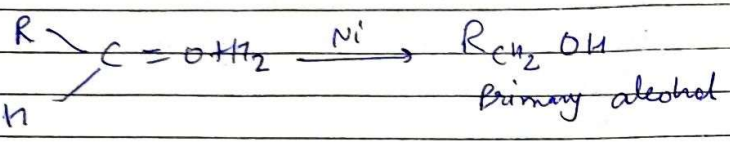
i) Reduction of aldehydes and ketones:-

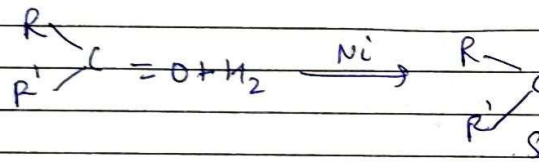
Aldehydes can be reduced to primary alcohols and ketones to secondary alcohol in a no of ways.

a) Catalytic hydrogenation:-

Aldehydes and ketones can easily be reduced to primary and secondary alcohols respectively by hydrogenation in the presence of catalyst such as Ni, Pd, or Pt.

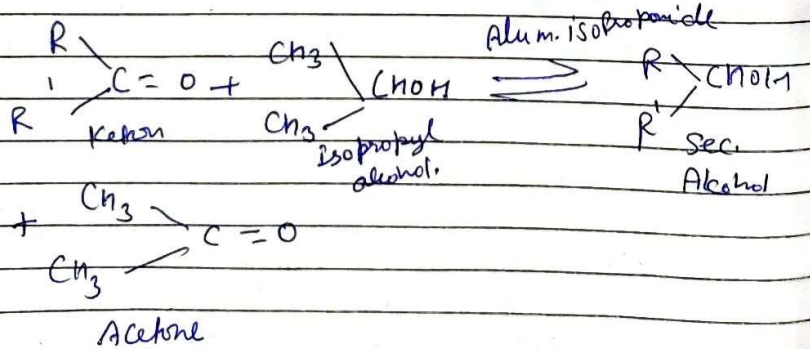
for eg :-



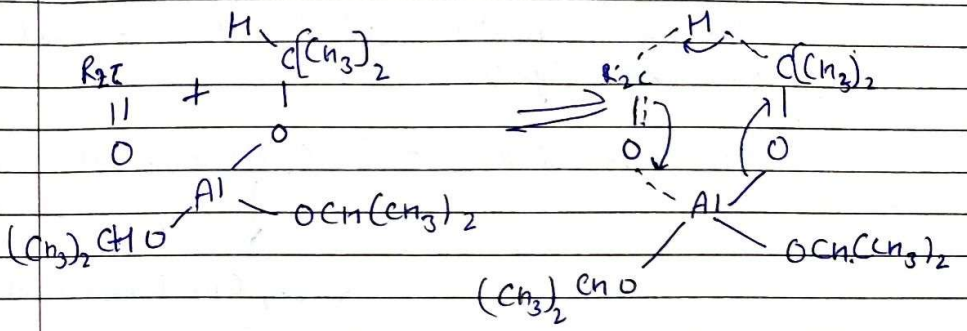


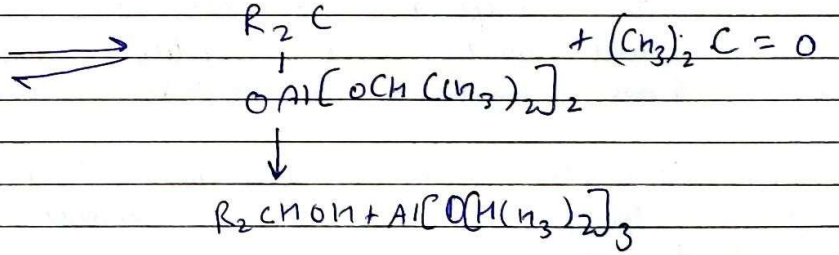
b). Meerwein-Pandorf-Verley reduction :-

It is commonly used rxn for the reduction of ketones to sec. Alcohol. This rxn is carried out by heating the carbonyl compound in isopropyl alcohol in the presence of aluminium isoproposide.



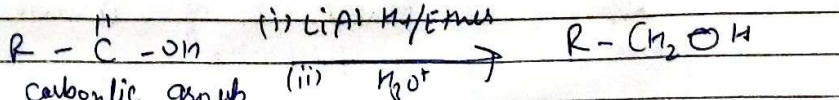
Mechanism :-





Reduction with Carboxylic Acid :-

Primary alcohols can be obtained by the reduction of carboxylic acid by lithium aluminium hydride. In this rxn the carboxylic part of carboxylic group is reduced to CH_2 group.



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Mechanism :-

The reduction take place through the formation of intermediate alkoxide which yield the alcohol on hydrolysis.

$$4RCOOH + 3LiAlH_4 \longrightarrow (RCH_2O)_4AlLi + 4H_2O \xrightarrow{H_3O^+} 2LiAlO_2$$

$$4RCH_2OH + LiOH + Al(OH)_3$$

This method is Generally employed for the preparation of alcohols from acid which are readily available from natural source.

Carboxlic acid can be reduced rapidly to primary alcohols by the action of diborane

$$3R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{B_2H_6} (RCH_2O)_3B \xrightarrow{H_3O^+}$$

$$3RCH_2OH.$$

Reduction with easter :-

Reduction of easter Constituents convenient method of preparation of Alcohols

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The reduction is generally carried out by the following method.

a) Bouveault-Blanc reduction :-

This method involves the reduction of easter to Alcohol by treatment with Sodium in alcohol. The rxn leads to the formation of a mixture of two alcohols one is formed by alkoxy group ($R'OH$) and the second is acyl group (RCH_2OH).

$$R-\overset{O}{\overset{\|}{C}}-OR' \xrightarrow{Na/C_2H_5OH} RCH_2OH + R'OH$$

for eg :-

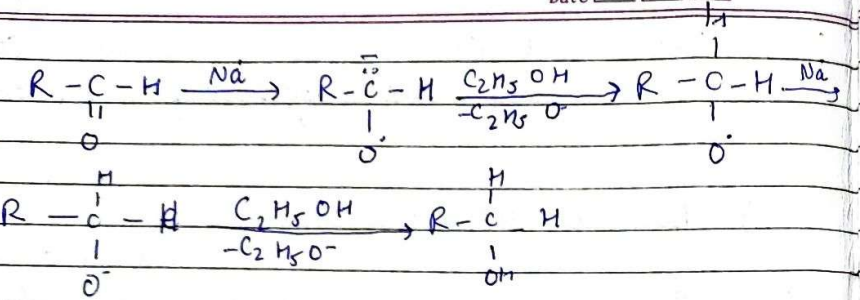
$$CH_3CH_2COOC_2H_5 \xrightarrow{Na/C_2H_5OH} CH_3CH_2CH_2OH + C_2H_5OH.$$

Mechanism :-

The rxn leads to the formation of a mixture of two Alcohols.

$$R-\overset{O}{\overset{\|}{C}}-OR \xrightarrow{Na} R-\overset{\ddot{O}^-}{\overset{|}{C}}-OR \xrightarrow[-C_2H_5O^-]{C_2H_5OH} RCH(O^-)-$$

$$OR \xrightarrow{Na} RCH(O^-)-OR \xrightarrow[-RO^-]{Na}$$



Catalytic hydrogenation :-

On an industrial scale, alcohols are obtained from esters by catalytic hydrogenation in the presence of copper chromite catalyst. For eg :-

$$CH_3\cdot CH_2\cdot COOC_2H_5 + 2H_2 \xrightarrow{\text{Copper chromite}} CH_3CH_2CH_2OH + C_2H_5OH$$

ethyl propionate → n-Propanol + Ethanol

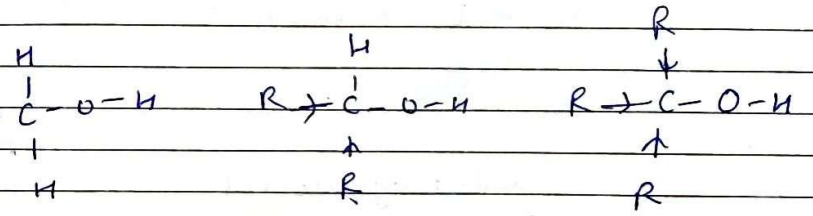
Hydrogen Bonding & Acidic nature Rxn of alcohols :-

The general order of reactivity of alcohols in this type of rxn is

Primary > Secondary > Tertiary alcohol.

Explanation :-

In the cleavage of O-H bond, Oxygen take away both the e⁻ of the shared e⁻ pair. Therefor the relative reactivity of alcohol in these rxn can be explained in terms of e⁻ releasing (+I) Inductive effect of alkyl group.



Primary Alcohol | Secondary Alcohol | Tertiary Alcohol.

1. Rxn with metals : Acidic Nature :-

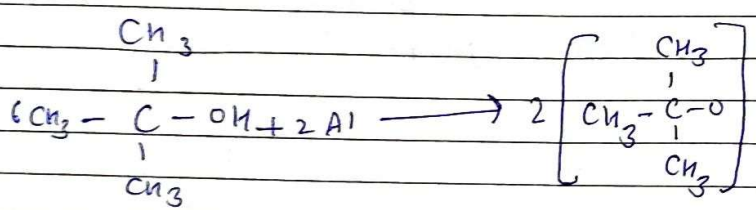
Alcohol react with active metals like sodium, potassium magnesium, and Aluminium to liberate hydrogen and form metal alcoholates or alkoxides

for eg :-

$$2ROH + 2M \longrightarrow 2RO^-M^+ + H_2$$

$2CH_3.CH_2OH + 2Na \longrightarrow 2CH_3CH_2ONa + H_2$

Ethyl Alcohol — Sodium ethoxide



$Al + 3H_2$

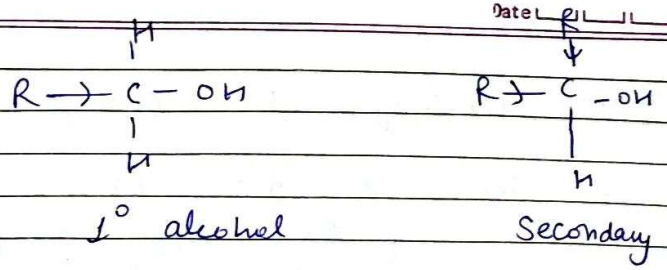
tert Butyl Alcohol

This rxn suggests that alcohol are acidic in nature. This is quite understandable since the -OH group contains highly electronegative oxygen attached to hydrogen.

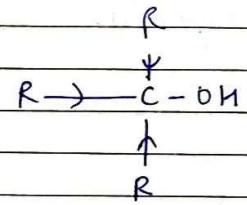
Comparison of acid strength of 1°, 2° & 3° Alcohols :-

Since the +I effect would be maximum in tertiary alcohols and least in primary alcohols the order of acidic of alcohol is

1° > 2° > 3°



1° alcohol — Secondary Alcohol

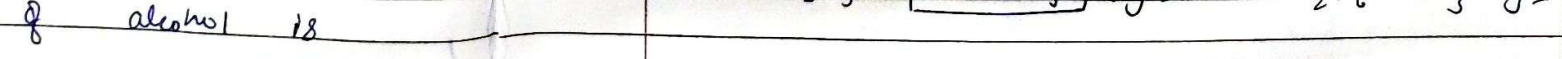


3° Alcohol.

Rxn with Grignard reagents :-

Alcohols react with Grignard reagents to produce hydrocarbons as shown below

for eg :-



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Rxn involving the cleavage of C-OH bond:-

In this rxn, the bond b/w carbon of the Alkyl group and oxygen of the hydroxyl group gets ruptured.

1° > 2° > 3°

Explanation :-

~~In these rxn, the bond b/w~~

The above order of reactivity can also be explained in terms of +I effect of alkyl group. As we move from 1° to 2° to 3° alcohols the no of Alkyl groups attached to carbon carrying the -OH group inc.

Rxn with hydrogen halides:-

Alcohols react with hydrogen halides to form alkyl halides and water

$$ROH + HX \longrightarrow RX + H_2O$$

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for eg:-

$$C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$$

Mechanism :-

The mechanism of the rxn is believed to be as follow except in case of methanol and most of the primary alcohols.

i) $R-\ddot{O}H + HX \rightleftharpoons R-\overset{+}{O}H_2 + X^-$

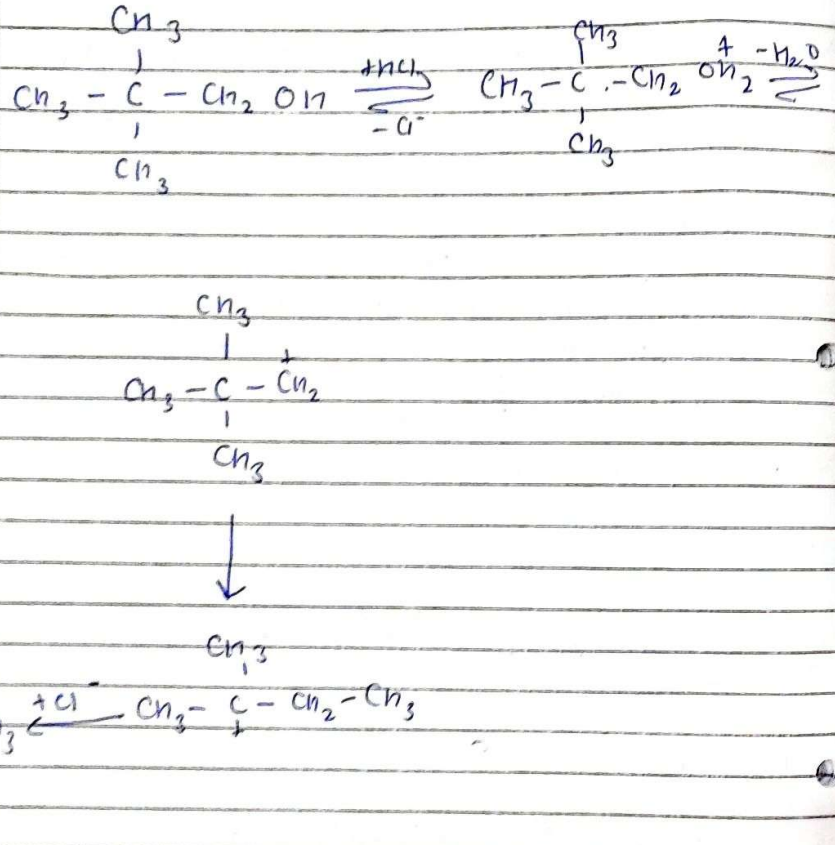
ii) $R-\overset{+}{O}H_2 \xrightleftharpoons{slow} R^+ + H_2O$

iii) $R^+ + X^- \longrightarrow RX$

This is obviously an S_N1 mechanism involving a protonated alcohol as the substrate and the halide ion as the nucleophile.

The formation of rearranged product in many cases further supports the intermediate formation of carbocation

for eg:-



Rxn with thionyl Chloride :-

Alcohol react with thionyl chloride, preferably in the presence of a base such as a 3° amine to form alkyl chloride.

$$ROH + SOCl_2 \longrightarrow RCl + SO_2 + HCl$$

Alcohol — Thionyl Chloride — Alkyl Chloride

for eg :-

$$C_2H_5OH + SOCl_2 \longrightarrow C_2H_5Cl + SO_2 + HCl$$

Ethyl Chloride.

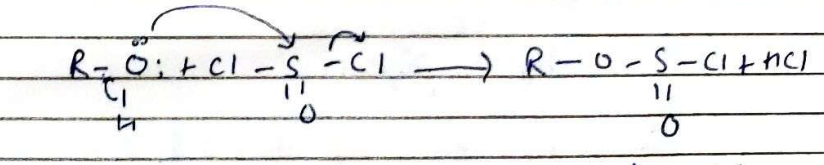
The base promotes the rxn by reacting with HCl.

$$R_3N: + HCl \longrightarrow R_3NH + Cl^-$$

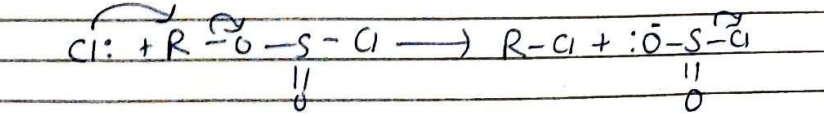
3° Amine.

Mechanism :-

The rxn is belived to take place as follow.



Alkyl chlorosulphite



Nomenclature of Dihydric Alcohols:-

1. Common names:-

The two hydroxy groups in a glycol are usually attached either to adjacent carbon ~~chain~~ atoms or carbon atoms. Situated at the extreme ends of the carbon chain. In this common system vicinal glycols are named after the common name of the corresponding alkene while polymethylene glycol are named acc. to the no. of methylene groups.

$CH_2 \cdot OH$
|
CH_2OH

Ethylene glycol.

Some time the positions 1,2; 1,3 and 1,4 etc are indicated α(1,2-), β(1,3-) and γ(1,4-).

for eg:-

$CH_3 - CHOH - CH_2OH$

α Propylene glycol.

Method of preparation:-

1. Hydroxylation of alkenes:-

Glycol can be prepared conveniently by the hydroxylation alkenes by treatment with potassium permanganate Soln. or osmium tetroxide.

$$>C=C< \xrightarrow[\text{or } OsO_4]{KMnO_4/H_2O} -\underset{|}{\overset{OH}{C}}-\underset{|}{\overset{OH}{C}}-$$

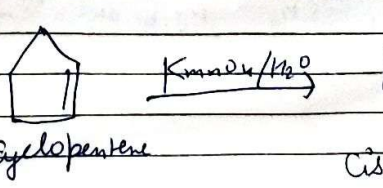
for eg:-

$$CH_2=CH_2 \xrightarrow{KMnO_4/H_2O} \underset{OH}{CH_2}-\underset{OH}{CH_2}$$

Ethylene

Ethylene glycol.

The rxn is known as cis-hydroxylation as it proceeds in a stereospecific manner leading to the formation of cis-diols. for eg.



Cyclopentene

Cis cyclopentane 1,2-diol

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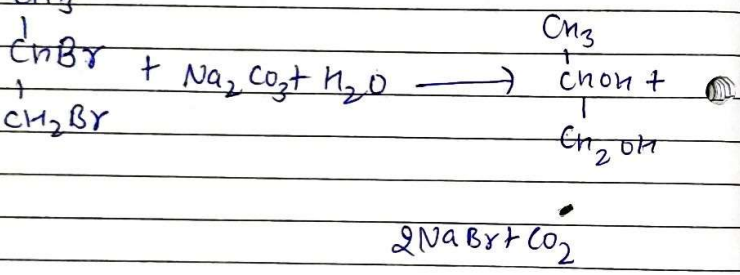
Hydrolysis of dihaloalkanes:-

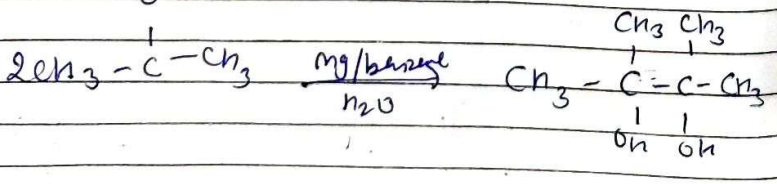
Diols can be easily prepared by the hydrolysis of dihaloalkanes for eg:-



Bimolecular reduction of carboxyl compound:-

When treated with magnesium in an inert solvent such as benzene and ether under alkaline conditions, aldehydes and ketones undergo bimolecular reduction to form vicinal glycol.

for eg:-



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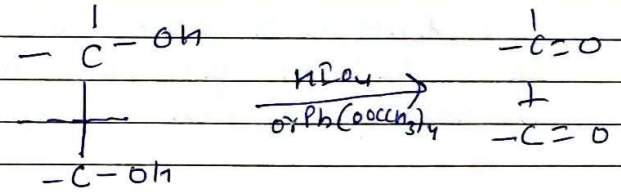
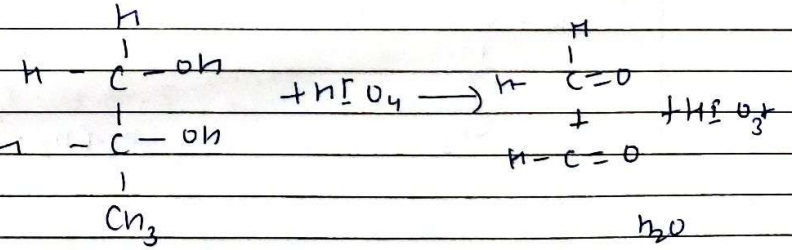
Oxidation Cleavage of 1,2-glycols:-

When treated with periodic acid (HIO_4) or lead tetra acetate [$Pb(OOCCH_3)_4$], compound containig two or more -OH groups attached only to adjecent carbon atoms undergo oxidative cleavage.



for eg:-

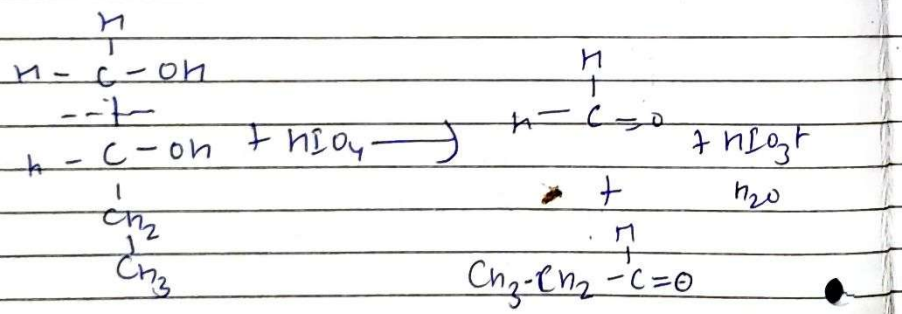


The oxidation of 1,2 glycol with periodic acid also known as malaprade rxn.

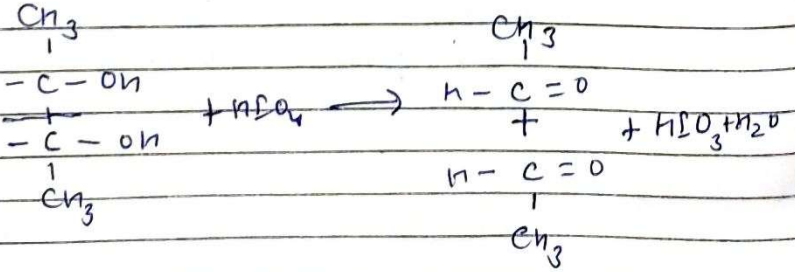
a) Structure determination:-

Let us Consider the oxidative cleavage of three isomeric butanediols (1,2 butanediol) 2,3 butandiol and 1,3 butanediol with periodic acid.

1). 1,2 butanediol react with one mole of HIO_4 to give a mixture of formaldehyde and propionaldehyde.



2) 2,3 butanediol also react with one mole of HIO_4 to give only acetaldehyde.

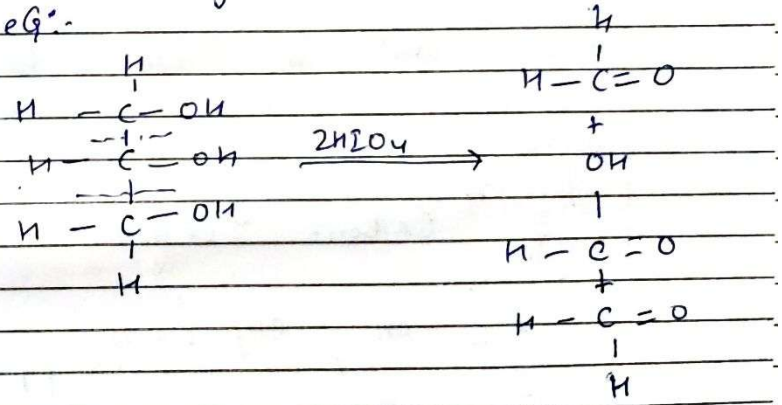


3). 1,3 Butandiol does not react with HIO_4 because it does not have the -OH groups attached to adjacent carbon atoms.

b). Determination of no -OH groups on adjacent carbons:-

In case of polyhydric alcohols, the no of moles of oxidising agent used in the rxn also indicates the no of -OH groups present on adjacent carbon.

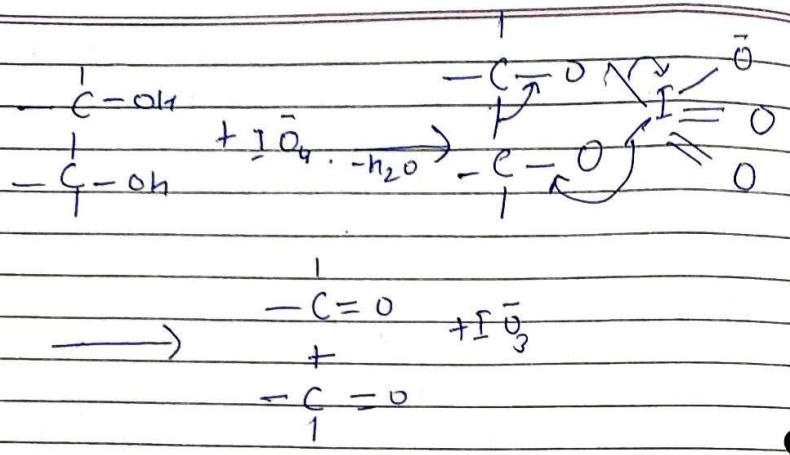
for eg:-



mechanism:-

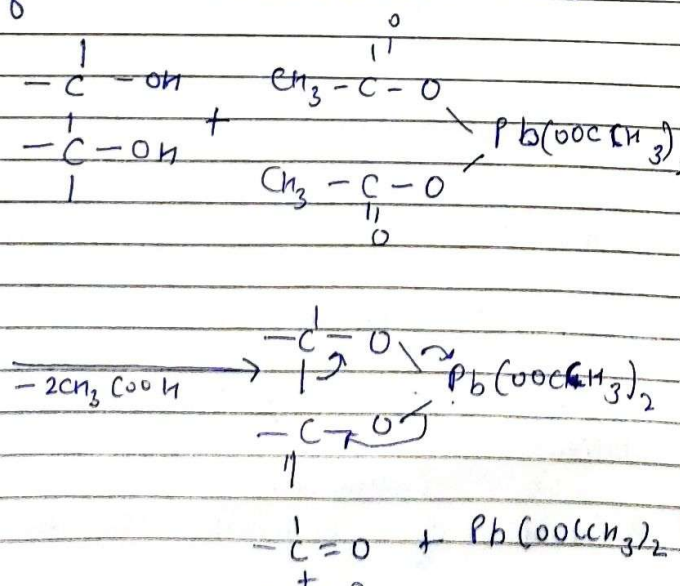
a) Oxidation with periodic acid:-

Oxidative Cleavage with periodic acid is believed to take place through a cyclic intermediate formed by the attack of periodate ion on glycol.



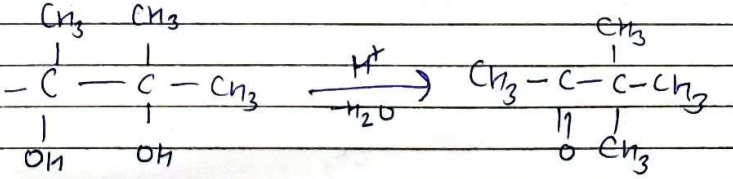
b) Oxidation with lead tetraacetate:-

This rxn is also belived to occurs through a cyclic intermediate which undergoes an oxidation-reduction process leading to the cleavage of Carbon-carbon bond.



Pinacol-Pinacolone Rearrangement :-

It is a typical rxn of higher glycols involving formation of rearranged products. It was first observed in case of pinacol i.e 2,3-dimethyl-2,3-butanediol and hence the name pinacol rearrangement. It was found that on treatment with Sulphuric acid pinacol undergoes dehydration with molecular rearrangment to form methyl tert. butyl ketone, also known as pinacolone.



Many other vicinyl glycols are now known to undergo similar acid-catalysed rxn. All these rxn are therefore, collectively known as pinacol-pinacol-one rearrangment.

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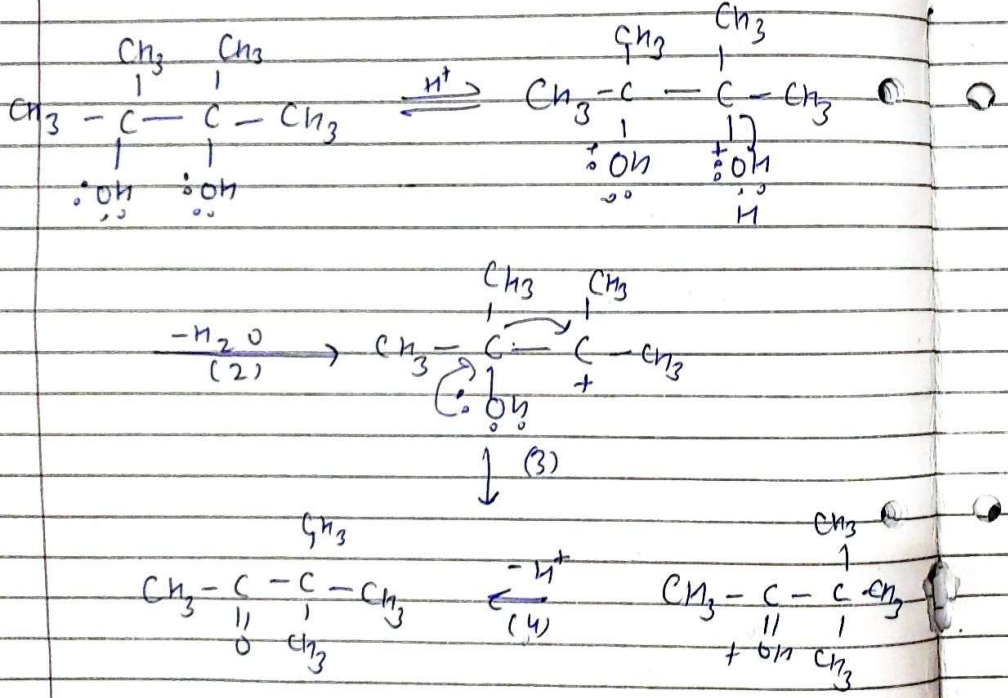
Mechanism :-

The pinacol rearrangement take place through stepwise mechanism as depicted below



Step(I) involves protonation of pin acol
Step (II) the protonated species loses a molecule of water to form carbo cation.

Step(III) the carbocation undergoes rearrangment involving a 1,2-Shift to the e⁻ deficient carbon to generate a new more stable ion.

Step(IV) to yield the final product.

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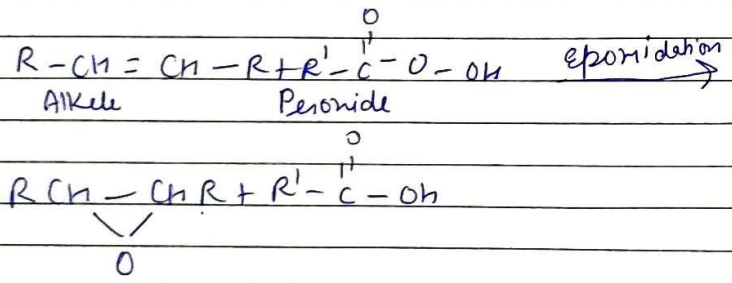
Unit-1

Ch-2.

#. Synthesis of epoxides:-

1) Epoxidation of alkenes:-

Epoxides are usually prepared by sxn b/w an alkene and an organic peroxyacid. This sxn is known as epoxidation



peroxyacid are commonly used in this sxn are peroxyformic acid, peroxyacetic acid, peroxybenzoic acid and m-Chloroperoxybenzoic acid.

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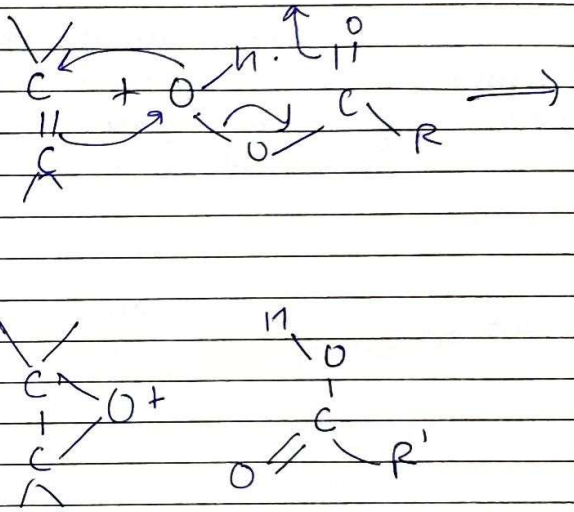
mechanism:-

The mechanism of epoxidation involves the transfer of an electrophilic oxygen atom from peroxyacid to alkene as depicated below

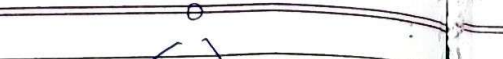


2) From halohydrins:-

When halohydrins, prepared by sxn of aqueous sdn of Chlorine or bromine with alkenes, are treated with a base, HX is eliminated to yield an epoxide.

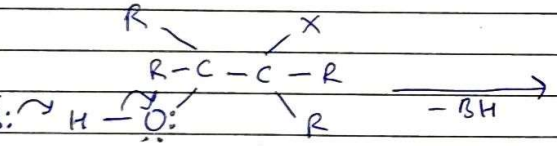
for eg:-

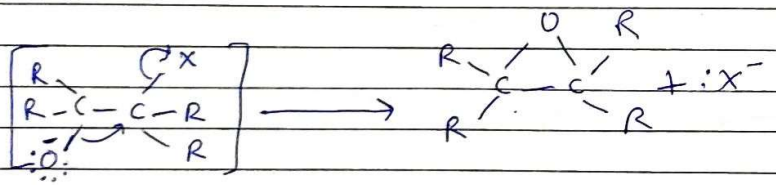
$$CH_2=CH_2 + Cl_2 + H_2O \longrightarrow HOCH_2-CH_2Cl + HCl$$



Mechanism:-

The base attacks the ~~hydro~~ halohydrin to abstract the hydrogen from OH group of halohydrin to form an alkoxide ion.

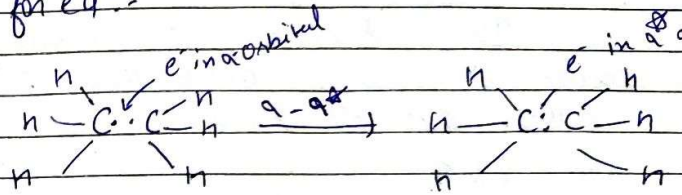




It may be seen that the rxn involves intramolecular nucleophillic substitution and is, therefore, treated as intramolecular Williamson synthesis.

It should also be noted that as in S_N2 rxn, the attack of nucleophile takes place from the backside of C-X bond.

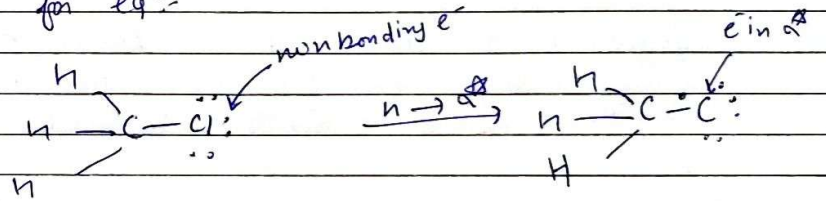
for eg:-



2. $n-\sigma^*$:-

These are the electronic excitations from a non bonding atomic orbital to an antibonding σ^* orbital.

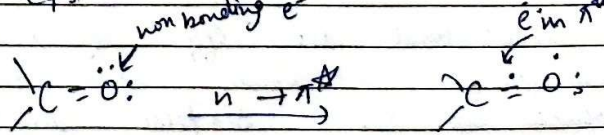
for eg:-



3. $n-\pi^*$:-

These are the transition in which an e^- in a non bonding atomic orbital is promoted to an antibonding π^* orbital.

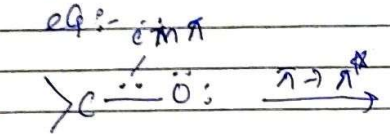
for eg:-



4. $\pi \rightarrow \pi^*$:-

The transition in which a πe^- is excited to an antibonding π^* orbital. are called $\pi \rightarrow \pi^*$ transition.

for eg :- e^- in π



Effect of Conjugation :-

Conjugation of double bond lowers the energy required for the electronic transition. As a result molecules Containg conjugated system such as $>C=C-C=C<$ and $>C=\overset{|}{C}-\overset{|}{C}=O$ absorb the radiations of longer wavelength then in case of non conjugated systems and absorptions bands appear in the ordinary UV Range. For instant butadine shows λ_{max} 217 nm in contrast to ethylene which shows λ_{max} 175nm.

To understand the effect of conjugation on λ_{max} 217 nm let us start with ethylene which is the simplest unconjugated alkene.

Chromophore :-

It is defined as any group which exhibits absorption of electromagnetic radiations in the visible or ultraviolet region.

Chromophore are two types :-

i) chromophore such as $>C=C<$ and $-C\equiv C-$ which contain πe^- and undergo $\rightarrow \pi^*$ transition.

ii) Chromophores such as $>C=O$, $-N=N-$ and NO_2 which contain both π and n e^- they can undergo $\pi \rightarrow \pi^*$ as well as $n \rightarrow \pi^*$ transition.

Auxochrome :-

An auxochrome is a group which itself does not act as a Chromophore but when attached to a chromophore it shifts the absorption maximum towards longer wave length along with an inc. in intensity of absorption

$$CH_2=CH-\ddot{N}R_2 \longleftrightarrow \ddot{C}H_2-CH=\overset{+}{N}R_2$$

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Bathochromic effect or red shift :-

It involves the shift of absorption maximum toward longer wave length.
It can be brought about by three diff. methods.

a) By attachment of an auxochrome to the chromophore :-

When an auxochrome such as -OH or $-NH_2$ is attached to a chromophore. It leads to conjugation or help in extending conjugation. As a result absorption shifts to longer wavelength.

b) By conjugation of two or more chromphoric groups :-

Bathochromic shift is also produced if two or more chromphores are present in conjugation in a molecule.

c) By using Solvent of lower polarity :-

It is also posible to achieve bathochromic shift by using solvent of lower polarity.

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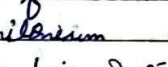
Hypsochromic shift :-

It involves the shift of absorption maximum toward shorter wavelength
It can be brought by two parts.

a) By removal of conjugation in a system. :-
for eg :-
protonation of aniline causes a blue shift from 280 nm to 203nm. This is because anilinium ion thus formed  has no lone pair of e^- on nitrogen which can conjugate with benzene ring.

b) By using Solvent of higher polarity :-
Use of Solvent of higher polarity can also bring about hypsochromic shift.

Hyperchromic effect :-

This effect involves an inc. in the intensity of absorption.
It is usually brought about by introducing of an auxochrome.

Hypochromic effect :-

It involves a dec. in the intensity of absorption. It it brought about by groups which distort the geometry of the molecule.

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Ultraviolet Spectra of conjugated Enes and Enos

The UV Spectra of all enes, whether Conjugated or non Conjugated, involves the $\pi \rightarrow \pi^*$ transition still the spectra of Conjugated enes are markedly diff. from non-conjugated enes. This is basicelly due to the fact that in Conjugated enes, the energies of π and π^* orbitals are much closer together than in simple enes. As a result, the conjugated system requires lesser excitation energy as compared non conjugated system and therfore, the absorption shift to longer wavelength.

$CH_2 = CH_2$

$CH_2 = CH - CH = CH_2$

1, 3 - butadiene

U.V Spectra of Conjugated enones :-

Conjugated enones exhibit strong absorption in the region 215-250 nm due to $\pi \rightarrow \pi^*$ transition and weak absorption in the 310-330nm range due to $n \rightarrow \pi^*$ transition. As compared to unconjugated ketones there is a red shift in both the type of absorption due to conjugation.

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$CH_3 - \overset{O}{\overset{\|}{C}} - CH_3$ $\lambda_{max} = 190nm$

Woodward - Fieser rule for calculating Absorption Maxima :-

Woodward In 1941 deduced certain rule for correlating λmax with molecular structure. The calculated values are generally within 2 or 3nm of experimental values.

We will now consider these rules briefly for different classes of compounds.

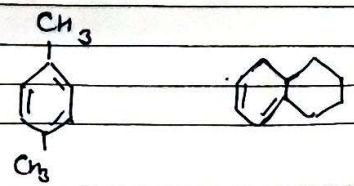
i For calculating λmax in Conjugated Dienes, Trienes and polyenes :-

Be we consider the rules for dienes, trienes, etc it will be useful to explain some terms involved in discussing the rules.

ii) Homoannular diene :-

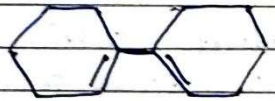
It is a cyclic diene which contains conjugated double bonds in the same ring.

for eg :-



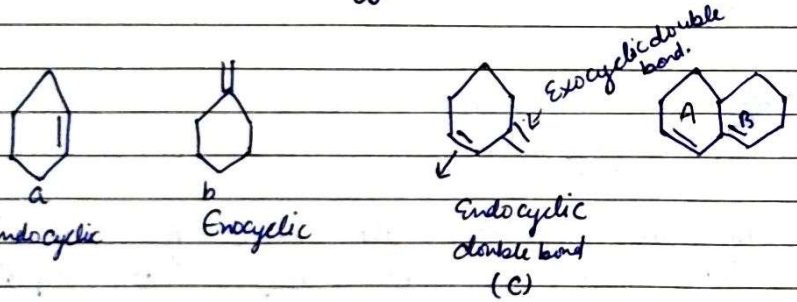
b) Heteroannular diene :-

It is a cyclic diene in which double bond in conjugation are present in different ring. for eg :-



c) Endocyclic double bond :-

It is a double present in a ring as shown in fig.



d) Exocyclic double bond :-

It is a double bond in which one of the doubly bonded atoms is a part of a ring system as shown above in (b).

ii) for conjugated Dienes, Trienes, polyenes, etc.

Acc. to these rules, each type of diene or triene system has a certain fixed value at which absorption takes place. This constitutes the basic value.

The contributions made by various alkyl substituent or ring residues, double bonds extending conjugation and polar groups such as -Cl, -Br and -OR are added to the basic value to get λ_{max} for a particular compound.

iii) Wood ward fishes rule for α, β-unsaturated carbonyl compounds :-

Wood - ward fishes rule for calculating λ_{max} for α, β-unsaturated carbonyl compound modified by scott may be summed up.

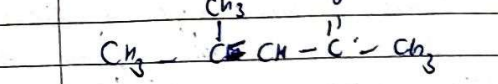
Application of UV spectroscopy :-

i) Detection of conjugation :-

U.V. spectrum helps two show whether a given compound contains certain group in conjugation with each other or not. The conjugation may be

i) b/w C-C double or triple bond.
ii) b/w C-C & C-O double bond
iii) b/w double bond and an aromatic ring.

for eg:-



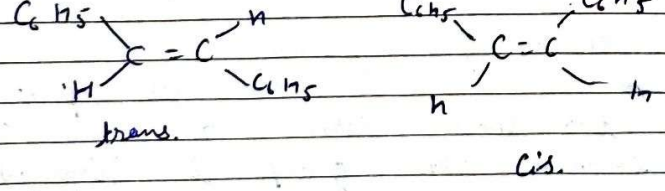
2. Extent of conjugation:-

UV Spectroscopy is also employed to estimate the extent of conjugation in polyenes $R-(CH=CH)_n-R$. With the inc. in the no of double bonds the absorption shifts to longer wavelength.

3. Determination of configuration of geometrical isomers:-

In case of geometrically isomeric compounds the trans isomers exhibit λ_{max} at slightly longer wavelength and have larger molar absorptivities than the cis form.

for eg:-



trans.

cis.

4. Detection of functional group:-

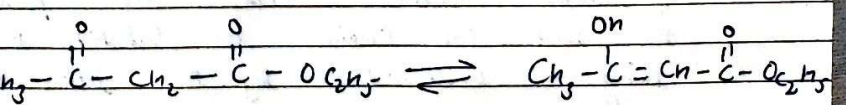
UV spectrum can be used for the detection of certain functional groups and other structural features if the absorption takes place above 200nm.

Even the absence of any absorption above 200nm is of some utility as it shows the absence of conjugation, carbonyl group and benzene ring in the compound.

5. Determination of strength of hydrogen bonding:-

If a compound forms hydrogen bonds with protic solvents such as water and alcohol, it is possible to find strength of hydrogen bonding by comparing the λ_{max} in the protic solvent with λ_{max} in non-polar solvent.

for eg:-



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Unit:- 4

Nomenclature of Carboxylic acid:-

1. Common System:-

The aliphatic monocarboxylic acid are commonly called fatty acid as many of them.

Branched chain acid having only one branch of a methyl group farthest away from the carboxyl group are named by adding the prefix iso to the name of corresponding straight chain.

$$CH_3-CH(CH_3)-CH_2COOH$$

iso Valeric acid.

other branched chain acid and substituted acid are named as appropriate derivatives of straight chain acids. The position of the acid side chain or substituent groups being indicated by the letters α, β, γ, or.

for eg:-

$$CH_3-CH_2-CH(CH_3)-COOH$$

α-methylbutyric acid

$$CH_2Cl-CH_2-COOH$$ β-Chloropionic acid

$$CH_3-CH_2-CH(CH_3)-CH(CH_3)-COOH$$ α,β-Dimethyl valeric acid.

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2. IUPAC System:-

The IUPAC name of carboxylic acid are obtained in accordance with the general IUPAC rule. The suffix used for the carboxyl group being oic acid.

For naming open chain carboxylic acids, the name of the parent chain the molecule is written. The final 'e' is replaced by oic acid. for eg.

$$\overset{4}{C}H_3-\overset{3}{C}H(CH_3)-\overset{2}{C}H_2-\overset{1}{C}OOH$$

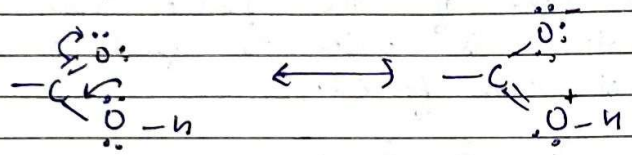
3 methyl butanoic acid.

Carboxylic acid having a carboxylic group attached to an alicyclic ring are named by adding the suffix Carboxylic acid to the name of ring.

Cyclohexane Carboxylic acid.

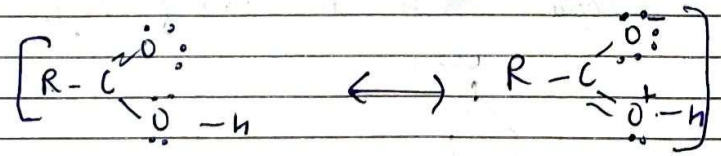
Structure and bonding of carboxylic acid :-

Even though the carboxyl group is generally represented by the structure $-C(=O)-OH$ actually it is a resonance hybrid of the following contributing structures.



① ②

It is evident that in the resonance hybrid, oxygen of the hydroxyl group carries some positive charge. As a result, the e⁻ pair of the O-H bond is largely displaced toward oxygen.



$\rightleftharpoons H^+ + RCOO^-$

Physical properties :-

Boiling point :-

Carboxylic ~~group~~ ~~is~~ acids form inter-molecular hydrogen bonding and therefore exist in the form of associated molecules. As such carboxylic acid have high boiling point.

Melting point :-

The melting point of acids containg even no of carbon atoms are higher than those of the immediately lower as well as immediately higher homologues containing odd no of carbon atoms. This is called oscillation or alternation effect.

Acidity of carboxylic acid :-

All carboxylic acid ionise in aqueous sol^n and exist in equilibrium with carboxylate anion and the hydronium ion. Thus they exhibit considerable acidic character

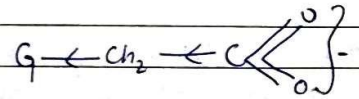
$$RCOOH + H_2O \rightleftharpoons R COO^- + H_3O^+$$

Effect of Substitution:-

An e⁻ withdrawing substituent :-

~~Carboxylic acid and water to furnish carboxylate anion~~

On the Carboxylate anion attract e⁻ towards itself and thus disppear the negative charge of the anion.



An e⁻ releasing substituent :-

On the Carboxylate anion intensifies the -ve Charge of the anion as these by destabilises the anion.

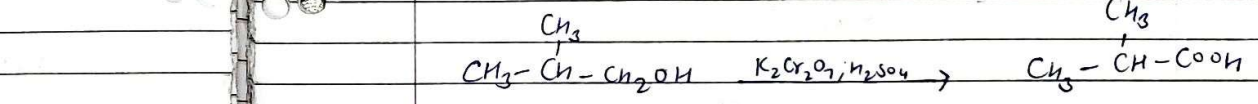
Preprabion of Carboxylic acid:-

i) Oxidation of primary alcohols or aldehydes:-

Carboxylic can be readily obtained by the oxidation of primary alcohols or aldehydes. The usual oxidising agents employed are acidified pott. dichromate, pott. permangate or nitric acid.

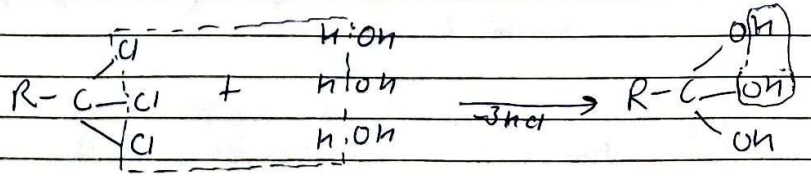
Primary alcohol or Aldehyde — Carboxylic acid.

for eG:-

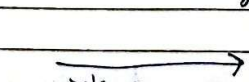


#2. Hydrolysis of trihalogen derivatives:-

Trihalogen derivatives having all the three halogen atoms attached to the same carbon atom give carboxylic acid on hydrolysis with an alkali.



Trihalogen derivatives.



Carboxylic acid

HVZ Rxn :-

In the presence of small amounts of red phosphorus, the α-hydrogen atoms of alkyl group of aliphatic acid can be replaced by chlorine or bromine to form a haloacid. this is known as HVZ Rxn.

for eg :-

$$CH_3 \cdot CH_2 COOH \xrightarrow[-HBr]{Br_2/P} CH_3 CHBr COOH$$

$$\xrightarrow[-HBr]{Br/2\ P} CH_3 CBr_2 COOH.$$

Reduction of Carbonylic acid :-

Carbonylic acid are resistent to catalytic hydrogenation. However they can reduced by lithium aluminium hydride to form primary alcohols. The carbonyl part of Carboxyl group getting reduced to CH_2

$$RCOOH \xrightarrow{LiAlH_4} RCH_2OH$$

Carboxylic acid — Primary alcohol.

The reduction proceeds via the formation of an alkoxide which yields the alcohol on hydrolysis for eg :-

$$C_{11}H_{23}COOH + 3LiAlH_4 \longrightarrow (C_{11}H_{23}CH_2O)_4 AlLi + 2Li_2AlO_2 + 4H_2$$

$$\downarrow +H_2O$$

$$C_{11}H_{23}CH_2OH + LiOH + Al(OH)_3$$

This method is employed for the preparation of alcohols form acid which are readily available from natural sources.

Mechanism of decarboxylation :-

The rxn takes place through the loss of a molecule of CO_2 form carboxylate anion to form a Carbanion. once formed, Carbonanion gets protonated to form the hydrocarbon.

$$R-CH_2-\overset{O}{\overset{\|}{C}}-ONa \rightleftharpoons R-CH_2-\overset{O}{\overset{\|}{C}}-O^{\ominus} + Na^+$$

$$R-CH_2-\overset{O}{\overset{\|}{C}}-\ddot{O}: \xrightarrow{-CO_2} R-\ddot{C}H_2 \xrightarrow{H_3O^+}$$

$$R-CH_3 + H_2O$$

Nomanclature of chlorides:-

The names of acid chlorides are obtained by changing the suffix -ic acid of the common or IUPAC name of corresponding acid to -yl chloride.

for eg.

HCOCl	HCOOH	Formyl chloride
Acid Chloride	Corrosponding acid	Common Name

Methanoyl Chloride
IUPAC name.

Preparation of Acid chlorides:-

1. From Carbonylic acids:-

Acid chlorides are generally prepared by the syn of corrosponding acids with thionyl chloride, phosphorous penta chloride or phosphorus trichloride.
for eg:-

$$CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2 + HCl.$$

From carbonylic acid salt:-

They can also be prepared by the action of phosp. trichloride, sulphuryl chloride or phosp. oxytrichloride on sodium or Calcium salts of acid for eg:-

$$3CH_3COONa + PCl_3 \longrightarrow 3CH_3COCl + Na_3PO_3$$

Sod. acetate — Acetyl chloride

$$(CH_3CH_2COO)_2Ca + SO_2Cl_2 \longrightarrow 2CH_3CH_2COCl + CaSO_4$$

Cal. Propionate — Sulphuryl Chloride — propionyl Chloride.

Nomanclature of Acid Anhydride:-

Acid anhydrides are named by changing the word acid of the common or IUPAC name of parent acid to the word anhydride.

for eg:-

$(CH_3CO)_2O$	CH_3COOH	Acetic anhydride
acid anhydride	Parent acid	Common name

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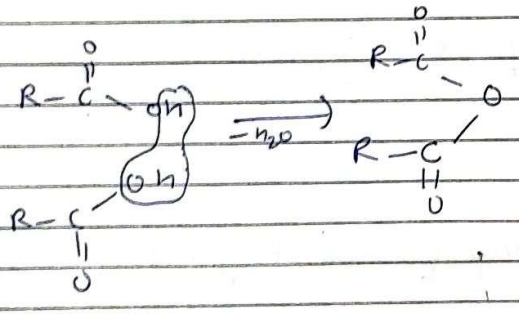
Ethanoic Anhydride
IUPAC name.

Preparation :-

Acid anhydride which is by far the most important obtain on a large scale by rxn b/w acetic acid and ketene

$CH_2 = C = O + CH_3 \cdot COOH \longrightarrow CH_3CO\text{-}O\text{-}OCCH_3$
Ketene — Acetic acid — Acetic anhydride

Structure :-



Nomanclature of Acid Amide :-

Primary amide are named by changing the suffix -ic acid of common or -oic acid of IUPAC name of corresponding acid by the suffix amide. for eg :-

Cyclopentane carboxamide

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Secondary or tertiary amide are named as nitrogen substituted primary amide. The letter N is written befor the name of the substituent group to indicate that the substituent is attached to nitrogen atom.
for eg :-

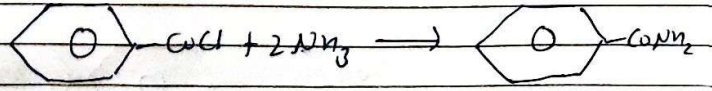
N-methylbenzamide.

Preparation :-

Acid amide can be obtained by the ammonolysis of acid chlorides, acid anhydrides or esters. In actual practice, the method generally employed is the ammonolysis of acid chloride.

$R COCl + 2NH_3 \longrightarrow RCONH_2 + NH_4Cl$
Acid Chloride — Acid Amide

for eg :-



Benzoyl Chloride — + NH_4Cl — Benzamide

Nomenclature of Esters:-

The names of esters are obtained by writing the name of alkyl group or aryl group befor the common or IUPAC name of parent acid and Changing the Suffix -ic to -ate

for eg:-

$HCOOCH_3$ — Esters.

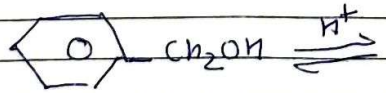
$HCOOH$ — Parent acid

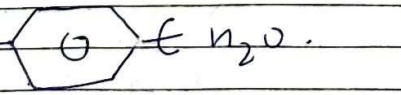
methyl formate — Common name

IUPAC name
methyl Methanoate

Preparation of Esters:-

Esters are generally prepared by direct esterfication of Carboxylic acid with alcohol in the presence of a strong mineral acid or lewis base. This eqn is reversible in nature and is known as esterfication for eg:-

CH_3COOH +  $\xrightleftharpoons{H^+}$

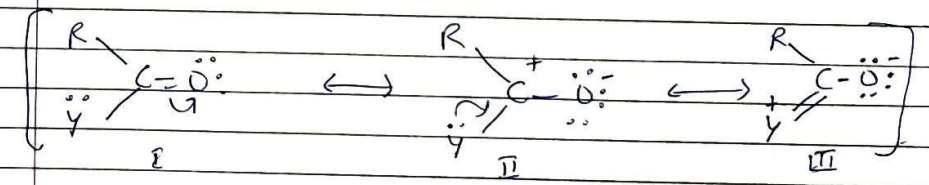
CH_3COOCH_2  $+ H_2O$.

Relative stability of acid derivatives:-

As stated above, acid derivatives readily undergo nucleophilic acyl substitution rxn. However, there is a larger diff. in the reactivity of diff. type of derivatives toward nucleophilic substitution. this can, at least partly, be attributed to the resonance stabilisation of the structure of acid derivatives.

The structure of an acid derivative is

$R-\overset{\overset{O}{\|}}{C}-Y$ is a resonance hybrid of three contributing structures as shown below.



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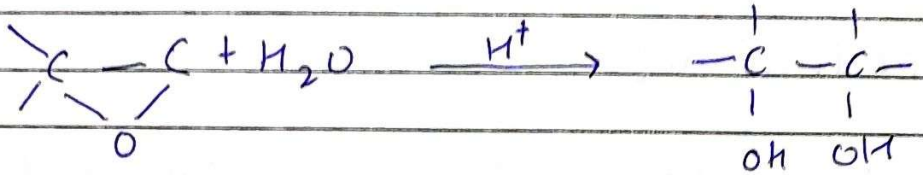
Acid catalysed ring opening :-

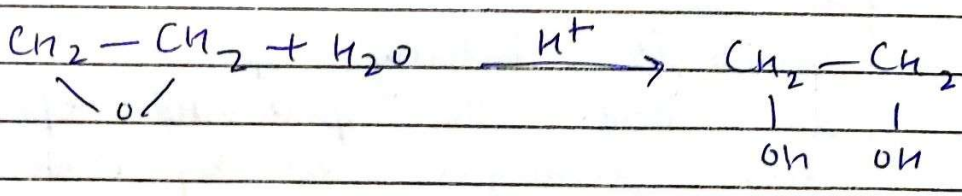
1. Acid catalysed hydrolysis :-

One of the most important cleavage rxn of epoxides is their hydrolysis to form 1,2-glycols.



Epoxide — Glycol

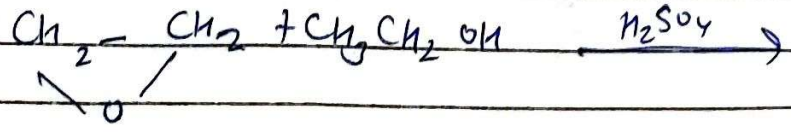
for eg :-



Ethylene oxide — Ethane 1,2-diol

2. Acid catalysed rxn with alcohols :-

for eg :-



$CH_3CH_2OCH_2CH_2OH$

2 ethoxyethanol

3) Rxn with halogen acid:-

Epoxide react with HCl and HBr to form chloro and bromohydrine.

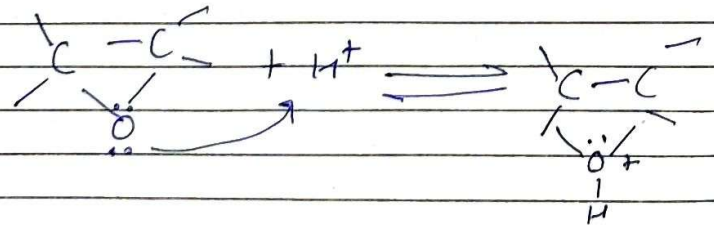
for eg:-

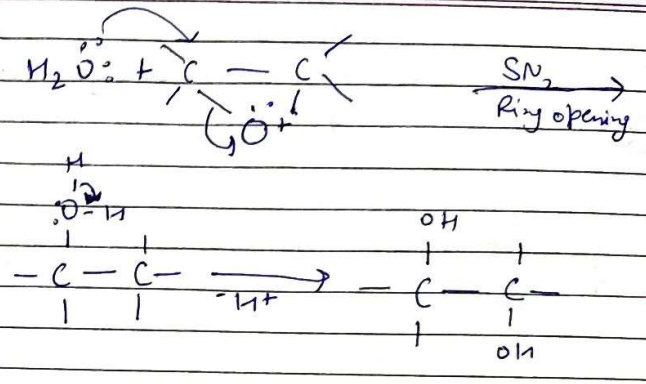
Ethylene Bromohydrin.

mechanism:-

The mechanism of acid catalysed ring cleavage may be illustrated by considering the hydrolysis of epoxides

In this acid catalysed hydrolysis of epoxide is initially protonated by the acid. The protonated epoxide then undergoes S_N2 by water to cause ring opening by the breaking carbon-oxygen bond.

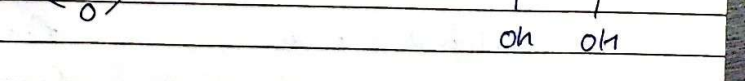




Nucleophilic ring opening:-

Unlike simple ethers which do not undergo ring cleavage by a base or a nucleophile, cleavage epoxide ring takes place even by such agents due to the ring strain in their molecules.

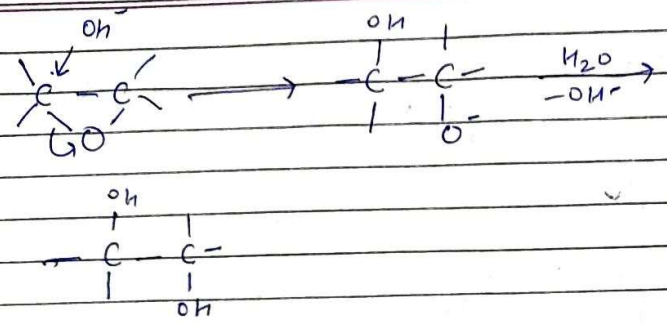
for eg:-



Ethylene Ethane 1-2 diol

Mechanism:-

The mechanism of nucleophilic ring opening is shown below with the help of basic hydrolysis of ethylene epoxide.

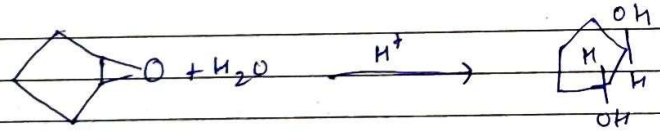


Orientation of ring opening :-

i) Anti-addition :-

The ring opening of epoxide leads to formation of product corresponding to anti-addition to Carbon-Carbon double bond.

for eg :-

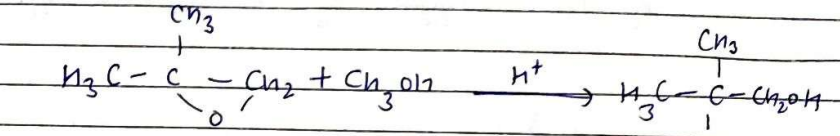


Cyclopentene oxide — Trans-1,2-Cyclopentanediol

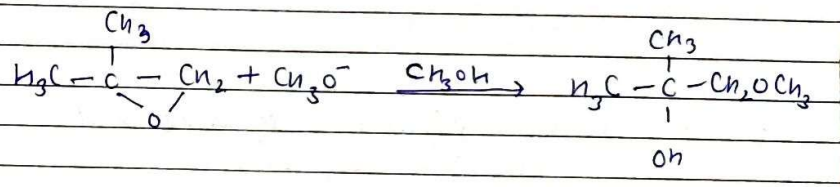
2. In Regioselectivity :-

Unsymmetrical Oxiranes can under go ring opening in two different ways and genrally leads to diff. products in Acidic or basic media.

In Acidic medium, the nucleophile genrally gets attached to more substituted Carbon while in basic medium, the nucleophile becomes attached to the less substituted Carbon.



Isobutylene oxide — Major product (Acidic medium)

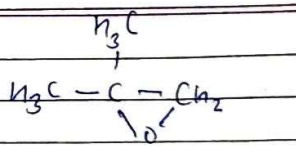


basic medium

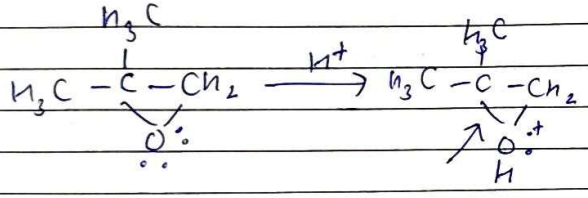
→ Explanation :-

The difference in regioselectivity in Acidic or basic media may be justified as follows.

In basic medium the ring opening is an S_N2 displacement by the unprotonated Oxirane.

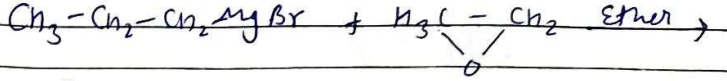


In Acidic medium the protonation of the oxygen of the epoxide ring.

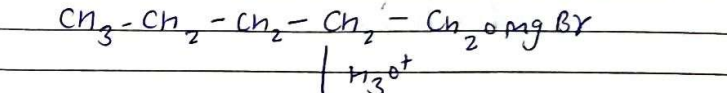


Rxn with Grignard reagents and organolithium reagents :-

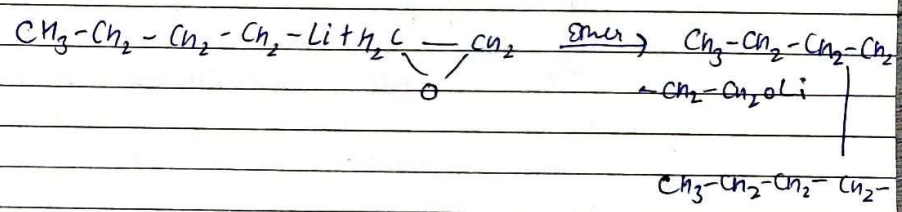
Epoxide also undergo nucleophilic ring opening rxn with Grignard reagents and organolithium reagents. The product initially formed on hydrolysis yields a primary alcohol containg larger no of carbon atoms. The epoxide generally used in this rxn is ethylene oxide and alcohol formed contains two carbon atoms more than in grignard reagents.



n-Propylmagnesium Bromide



1 Pentanol



1-Hexanol.

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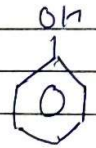
Unit :- 2

Phenols.

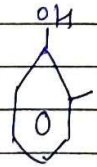
Nomenclature of Phenols :-

The Simplest no of phenols is always known by its popular name phenol although its IUPAC name is benzenol. All substituted monohydric phenols are named as derivative of the smallest no of series. i.e. Phenol and common names. The position of substituent w.r.t. -OH group carring the no. 1.

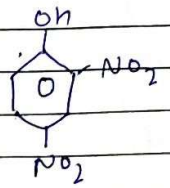
for eg :-



Phenol



2, Chlorophenol
or
O chlorophenol

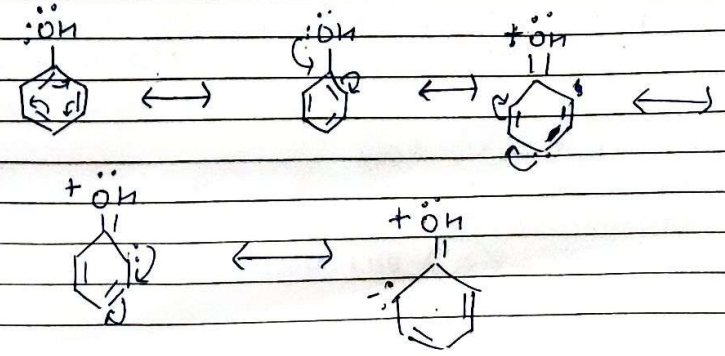


2,4 Dinitrophenol

Structure and bonding :-

Phenols are compound having a hydroxyl group directly bonded to benzene ring. While the oxygen of hydroxyl group is in sp^3 hyberelised state. the carbon of the benzene ring to which oxygen is bonded is in sp^2 hyberdised state.

Resonance interaction takes place b/w a lone pair of e^- on oxygen and the benzene ring so that phenol exist as resonance hybrids of resonating structure.



Due to resonance the C-O bond acquires double bond character and become shorter and stronger than the C-O bond in alcohol.

Method of formation :-

1) Alkali fusion of sulphonates :-

In this method, phenols are obtained by fusion of sodium salts of aromatic sulphonic acid with sodium hydroxide followed by acidification.

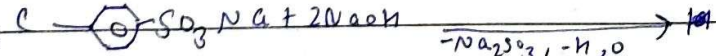
$$ArSO_3Na + 2NaOH \xrightarrow[Na_2SO_3, -H_2O]{Fuse} Ar-ONa$$

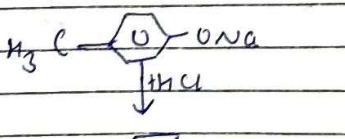
Sodium sulphonate

$$\xrightarrow{HCl} Ar-OH + NaCl$$

Phenol

for eg :-



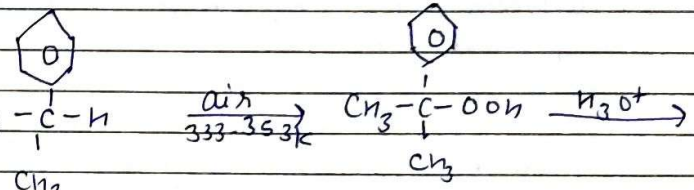


p-Cresol.

2. From Cumene :-

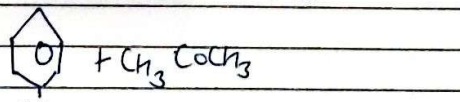
This method is used particularly for the large scale preparation of phenol from isopropylbenzene popularly known as cumene.

Cumene is readily oxidised by air to form cumenehydroperoxide which is converted into phenol and acetone by treatment with an aqueous acid.



Cumene

Cumene hydroperoxide.

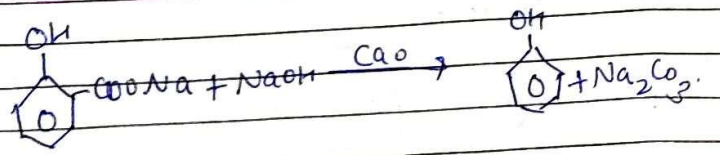


Phenol

3. From phenolic acid :-

Distillation of sodium salt of phenolic acid with soda lime yields phenols.

for eg :-



Sodium Salicylate

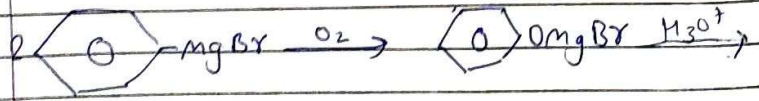
4. From Grignard reagents :-

Phenols may be prepared by treating aryl magnesium bromide with oxygen followed by hydrolysis of the product.

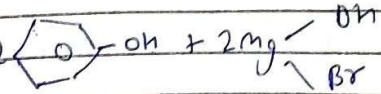
$$2ArMgBr \xrightarrow{O_2} 2ArOMgBr \xrightarrow{H_3O^+}$$

$$2ArOH + 2Mg(OH)(Br)$$

for eg :-



Phenyl mag. Bromide



Phenol

Physical properties :-

1. Physical state :-

Pure Phenols are generally colourless liquids or solid But they usually appear slightly coloured as they readily get oxidised even in air and the oxidation product are coloured compounds.

2. Boiling point :-

B.P. of phenols are higher than hydrocarbons and aryl halides due to formation of intermolecular hydrogen bonding.

Acidic Character :-

Phenols are weakly acidic compound. They react with aqueous alkali metal hydroxide to form salts known as phenorides.

$$ArOH + NaOH \longrightarrow ArO^- Na^+ + H_2O$$

Phenol — Sodium phenoxide

However, phenols do not react with aqueous carbonates or bicarbonates, moreover, the salts of phenols are converted into phenols by aqueous mineral acid, Carboxylic acid or even carbonic acid.

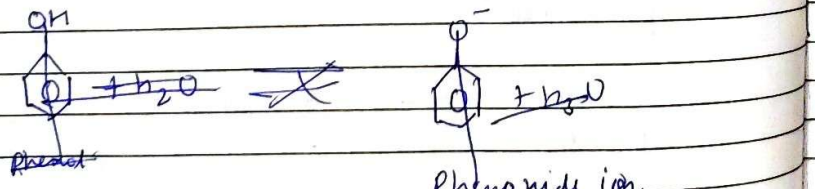
$ArO^- Na^+ \xrightarrow{H_2O + CO_2} ArOH + NaHCO_3$

Carbonic acid (stronger acid) → Phenol (weaker acid)

These observation indicate that phenols are very weak acids.

Comparison with alcohols :-

In case of alcohols, the equilibrium rxn involving alcohol and alkoxide ion does not favor the formation of alkoxide ion hydronium ion. This is because there is no resonance stabilisation of alkoxide ion relative to alcohol since neither the alcohol nor their alkoxide ion exhibits resonance.



$R-OH + H_2O \rightleftharpoons R-O^- + H_3O$

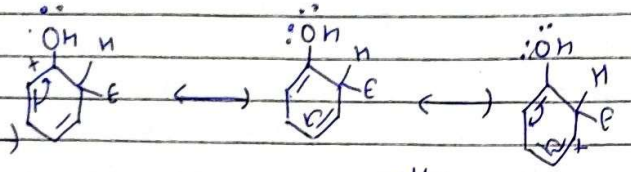
Alcohol — Alkoxide ion.

Resonance stabilization of phenoxide ion :-

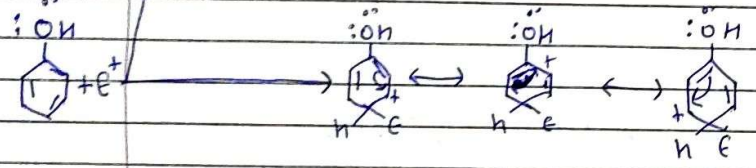
In case of phenoxide ion non of the contributing structures involves charge separation and their structure are almost equally stable. As such phenoxide ion is resonance stabilized to a greater extent than phenol therefor, the equilibrium b/w phenol and phenoxide ion favours the formation of phenoxide ion and hydronium ions.

Electrophile aromatic Substitution :-

The -OH group linked to an aromatic ring activates the ring to electrophilic substitution and direct the incoming group to ortho, para position.



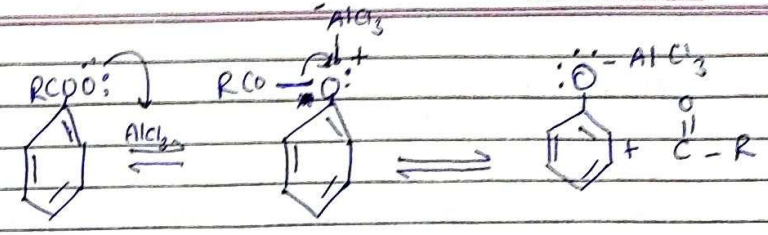
Ortho Attack



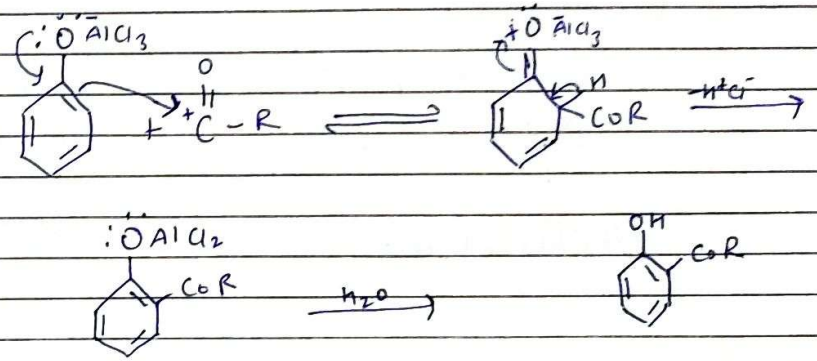
Para attack.

Mechanism of Eries rearrangement :-

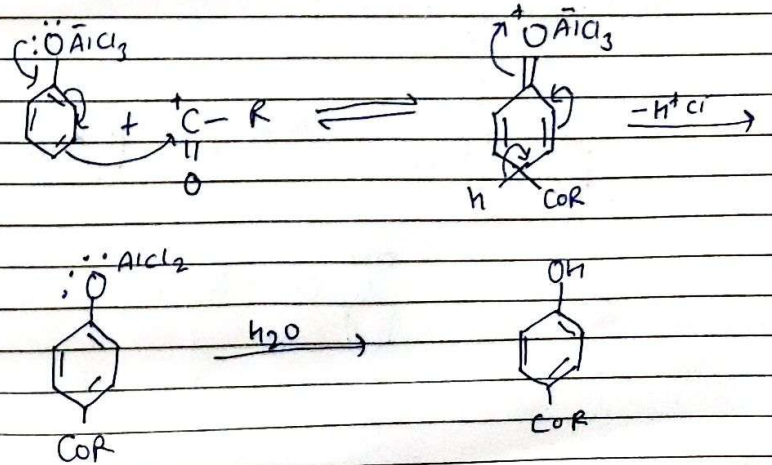
The rearrangement probably involves the formation of an acylium ion which then attack the aromatic ring as in Friedel craft acylation. The complete mechanism may be summed up as follows:



Ortho Attack :-



Para Attack :-



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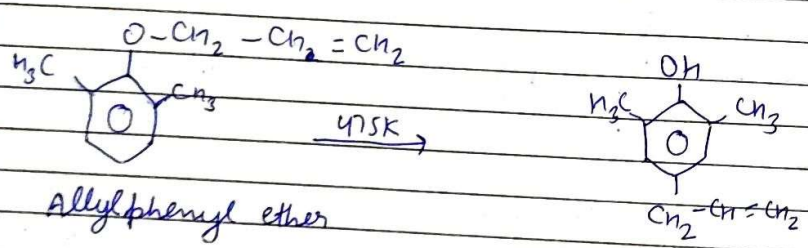
Claisen rearrangement :-

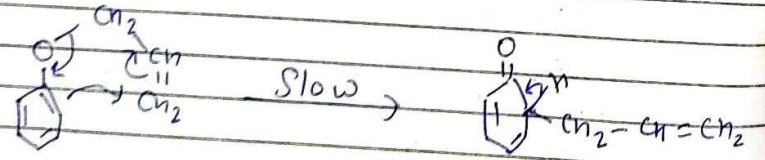
This is an interesting rearrangement rxn involving aryl allyl ethers. When heated to 475K, the allyl group of the ether migrates from ether oxygen to the ring carbon at ortho position & para position for. eg :-

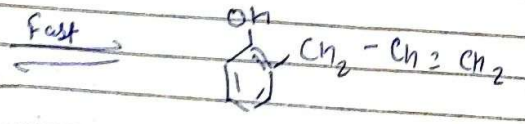


Allyl phenyl ether

4-Allyl-2,6-dimethyl phenol

Mechanism of ortho :-





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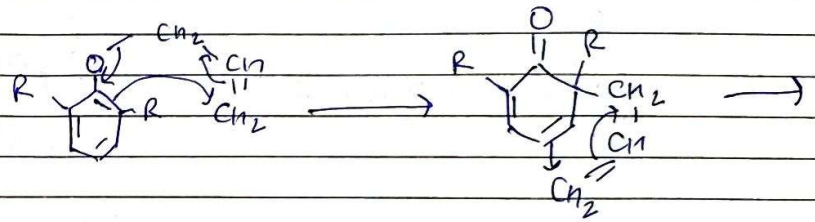
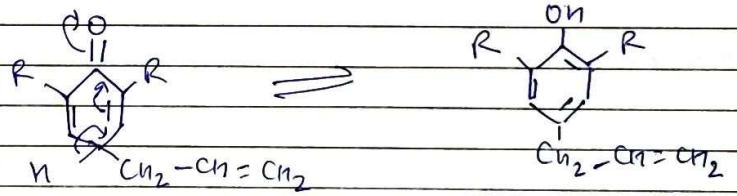
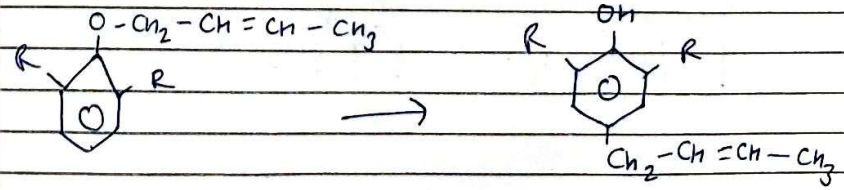
Para's mechanism :-

It has two stages first is ortho migration and other is another migration.





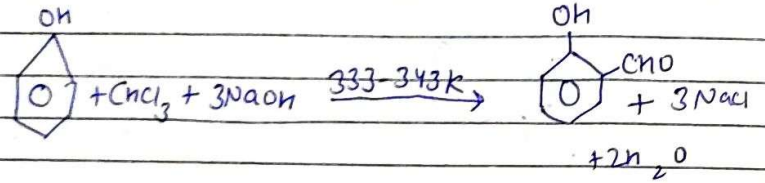


Reime-Tiemann rxn :-

On heating with chloroform and an alkali, phenols are converted into phenolic aldehydes, an aldehyde group

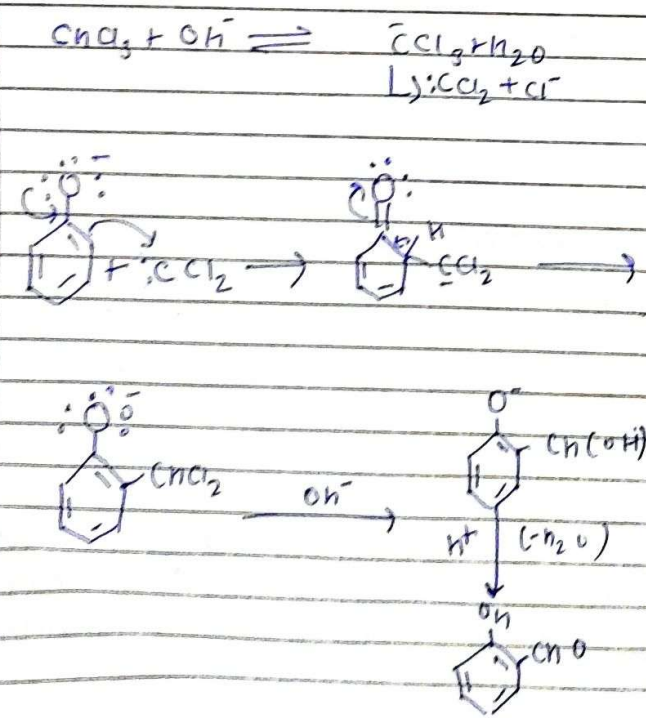
being introduced on the aromatic ring generally in ortho position to the -OH group.

for eg:-



Salicylaldehyde.

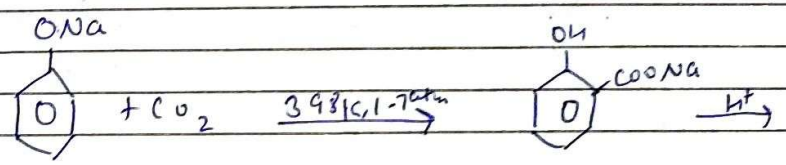
Mechanism:-



Kolbe rxn:-

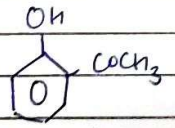
When heated with ~~diazonium salts in~~ Carbon di-oxide under pressure. Sodium salts of phenol undergo Carbonylation to form salts of phenolic acids. the ortho isomers being the main product.

for eg:-



Sodium Phenoxide

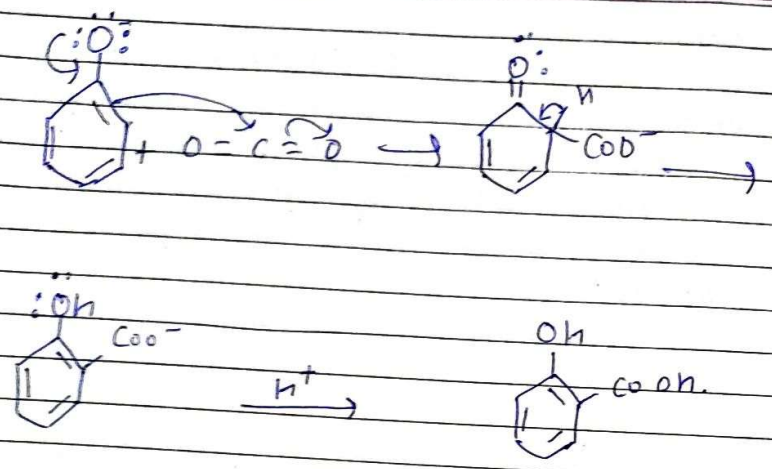
Sodium Salicylate (main product)



Salicylic acid.

Mechanism:-

The mechanism of Kolbe's rxn is believed to involve the electrophilic attack by CO_2 on the phenoxide ion.



Unit :- 3

U.V Absorption Spectroscopy

Absorption Law :-

Beer-Lambert law :-

The laws stated above can be combined to get a genral absorption law, termed as Beer-Lambert law. It may be stated as, The absorption of light by a substance at a particular wavelength is proportional to the no of molecules of the substance in the path of light.

In Mathematically :-

$$\log \frac{I_0}{I} \propto C \qquad \text{(Beer's law)}$$

$$\log \frac{I_0}{I} \propto l \qquad \text{(Lambert's law)}$$

$\therefore$ Beer Lamberts law may be expressed as

$$\log \frac{I_0}{I} \propto cl$$

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$$\log \frac{I_0}{I} = \varepsilon . Cl$$

ε. is constant.

where

I_0 = Intensity of incident light.
I = Int. of transmitted light.
C = Concentration of the absorption substance in $mol\,l^{-1}$
l = Path length
ε = Prop. constant.

The expression of ~~Beer-Lam~~ $\log \frac{I_0}{I}$ is termed optical density or absorbance (A).

→ Limitations :-

i) It is obeyed when dealing with the UV Spectra of single species

2) It is not obeyed the solute sample and solvent interact with each other to form complex.

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Molar absorptivity (ε)

It is a proportionality constant which relates the observed absorbance (A) at a particular wave length (λ) to the molar concentration of the absorbing substance and the length (l) of the path of light in cm. It may be expressed as.

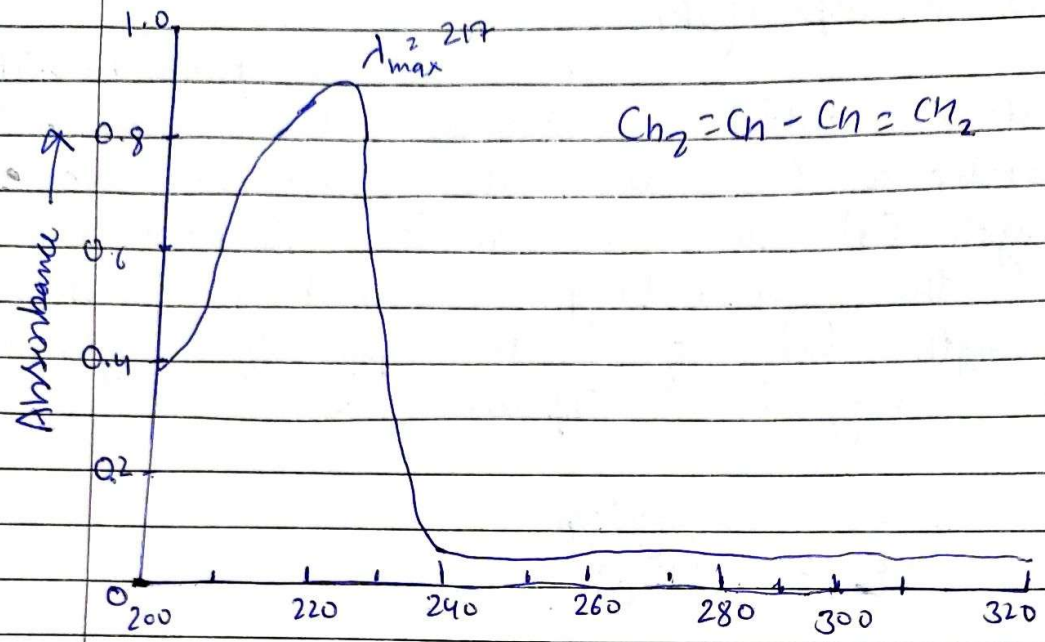
$$\varepsilon = \frac{\log I_0/I}{Cl}$$

$$= \frac{A}{Cl} \quad [\because \log I_0/I = A.$$

Molar absorptivity is measure of the intensity of absorption at a particular wavelength and has the dimensions of $cm^2\ mol^{-1}$ but these units are seldom used.

Presentation of Spectrum :-

The U.V Spectrum of 1,3-butadiene in hexane. It may be seen that absorption of U.V radition by 1,3-butadiene being at wavelength below 200nm and continues upto about 260nm. The absorption is maximum at 217nm.



The spectrum is reported as a single absorption peak using the notation λ_{max} = 217 nm

Electronic transitions :-

Electronic transition involves the promotion of an electron from one orbital to another of higher energy

It has ~~three~~ four types :-

1. $\sigma - \sigma^*$:-

Transition in which a σ bonding electron is excited to an antibonding σ^* orbital are called $\sigma \rightarrow \sigma^*$ transition.